METAL COMPLEXES OF 2,3-QUINOXALINEDITHIOL

APPROVED:

Graduate Committee:

Major Professor

Committee Member

Committee Member

Director of the Department of Chemistry

Dean of the Graduate School
METAL COMPLEXES OF 2,3-QUINOXALINEDITHIOL

DISSENTATION

Presented to the Graduate Council of the
North Texas State University in Partial
Fulfillment of the Requirements

For the Degree of

DOCTOR OF PHILOSOPHY

By

Kalyan Kumar Ganguli, B.S., M.S.
Denton, Texas
May, 1969
ACKNOWLEDGMENT

The financial support of this investigation by the North Texas State University Faculty Research Fund and The Robert A. Welch Foundation is gratefully acknowledged.
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CHAPTER I

INTRODUCTION

During the last few years a remarkable series of compounds of transition metals has been reported in which the central metal ions have been coordinated by sulfur donor atoms. Recent papers\textsuperscript{1,2,3} summarize what is known to date about the electronic and structural properties of the species.

The interest can be classified into the following areas of development.

(a) The extension of planar complexes to many transition metals of varying spin multiplicities heretofore unknown. For example, the first paramagnetic planar complexes of Ni, Pd, and Rh\textsuperscript{4,5} have been prepared with sulfur donors.

\begin{enumerate}
\end{enumerate}
(b) The recognition that the complexes could be oxidized by electron transfer reactions without a change in structure by Davison et al. In many inorganic reactions oxidation is accompanied by a change of structure. These complexes were the first examples of planar complexes being oxidized without a change in structure.

(c) The startling x-ray results which showed that the six coordinate triis complexes with Re were trigonal prismatic in structure. All metal complexes have heretofore been octahedral in structure, even though hexagonal and trigonal prismatic are distinct possibilities. These results have intensified interest in the structural aspects of these metal complexes. It is important to determine the factors which determine whether a given complex will adopt an octahedral or a trigonal prismatic structure.

(d) There has been an intense effort in understanding the electronic structure of these complexes. A controversy has existed over the oxidation states of the metal in NiL₂⁻ and NiL₂. It is

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possible to attribute the oxidation process entirely to the metal and thus describe NiL₂ as Ni⁴⁺. Another view is that the oxidation takes place entirely by removal of electrons from the ligand and NiL₂ can be considered as a Ni²⁺ complex.

(e) The recognition that for a given complex a dimeric structure is possible. It has been recognized only recently that a metal complex like cobalt can exist not only as a planar and octahedral complex but also as a dimeric unit.

An investigation of complexes of 2, 3-quinoxalinedithiol (QDT-H₂) was initiated in order to prepare new complexes for the purpose of correlating the existing data with other ligand systems. 2, 3-quinoxalinedithiol

![Figure 1 2,3-Quinoxalinedithiol](image-url)
is known from various studies to exist in the tautomeric forms\(^7\) (Figure 1).

The thione form is the most stable in the solid state and the ability of the ligand to perform as a coordinating agent was one of the aims of the work. It was important also to see if under these unfavorable conditions the metal ions would be coordinated by S and N donor atoms rather than S donor atoms alone.

Stable planar complexes of many transition metals with unusual stability have been observed in complexes with the dianions of maleonitriledithiol\(^8\)(MNT) and toluene-3, 4-dithiol\(^9\)(TDT). It is a well-established fact that most square planar transition metal complexes are changed to octahedral coordination when treated with donor solvents. It has been found that in [Ni(MNT)\(_2\)]\(^{-2}\), ligands provide a stable planar matrix. The electronic spectrum of this complex does not change in solvents with a wide range of coordinating ability. The spectrum


of $[\text{Ni} (\text{MNT})_2]^{-2}$ is essentially the same in acetone, acetonitrile, dimethylformamide (DMF), dimethylsulfoxide (DMSO), ethanol and pyridine. It was found that coordination number of $[\text{Ni} (\text{MNT})_2]^{-2}$ does not change even in a concentrated ethanolic solution of a powerful ligand such as o-phenanthroline.

The cause of this unusual stability has been rationalized through the involvement of the metal $p_z$ valence orbital in an extensive $\pi$-orbital network, such that the total $\pi$-stabilization overcomes the extra stability gained when the $p_z$ orbital is used to form extra $\sigma$-bonds with axial groups. All the bidentate sulfur-chelates chosen until now form five-membered rings with the central metal.

The bis complexes of Ni, Pd, Pt, and Cu dithiolene are truly square planar and they retain this geometry even after electron transfer reactions. The Zn dithiolates are bis with a tetrahedral stereochemistry and since no polarographic waves were found for these complexes it will be concluded that zinc dithiolates do not undergo electron transfer reactions.

No bis complexes of Cr or V has yet been made, but a bis complex of $\text{VO}^{2+}$ is reported in the literature by

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McCleverty et al.\textsuperscript{11} Attempts to make a bis complex with vanadium as the central metal instead of vanadyl ($\text{VO}^{2+}$) have resulted in formation of tris complexes.

The chemistry of cobalt dithiolenes need special mention from that of the corresponding Ni, Pd, Pt, Cu, and Zn complexes because of the complexity and hence the intense interesting properties arising out of these investigations. The electronic spectra of cobalt (II) in its tetrahedral and octahedral sterochemistry are now quite well known. Several generalizations can readily be made. Briefly, with relatively simple ligands, the spectrum of tetrahedral cobalt\textsuperscript{12, 13} is more intense than that of octahedral cobalt and is characterized by a more strongly structured peak in the visible region (Figure 2).

Few compounds have been shown definitively to contain square planar cobalt. The only complete crystal structure analysis of cobalt (II) reported in this environment is that of an organometallic compound\textsuperscript{14},

\textsuperscript{11}N. M. Atherton, J. Locke and J. A. McCleverty, \textit{Chem. Ind.}, 1300 (1965).


The visible spectra of \([\text{Co(H}_2\text{O)}_6]^{2+}\) (curve A) and \([\text{CoCl}_4]^{2-}\) (curve B).
trans-[Co(mesityl)₂(P₄Et₂Ph)₂] before results of planar cobalt dithiolene complexes began to appear. It has been shown by Cotton and Holm from simple ligand field theory for d⁷ systems that Co (II) can exist in a square planar matrix either as a spin-doublet or a spin-quartet ground state depending upon the strength of the in-plane field. Experimentally a spin-quartet ground state in square geometry has never been observed. There has been no doubt about the existence of spin-doublet Co (II) planar complexes and the existence of high spin planar Co (II) complexes has been open to genuine question.

In 1962 Gray et al. prepared the first planar cobalt (II) complex R₂[Co(MNT)₂]. This compound was claimed to have a spin-quartet ground state from the evidence of the magnetic properties, electron spin resonance results, and the compatibility of the electronic spectra with that conclusion. The compound was reported to be the first example of a planar cobalt (II) complex with a spin-quartet ground state.

It has been shown conclusively\(^{16}\) that these results are incorrect and the compound is actually a spin-doublet with a magnetic moment of 2.16 B.M. instead of the 3.92 B.M. reported.

It has been shown in the case of the isoelectronic \([\text{Ni}(\text{MNT})_2]^-\) complex that there is a substantial exchange demagnetization resulting in a moment of 1.02 B.M. in the solid state. The question arises whether the \(\text{Co}(\text{MNT})_2^-\) is (1) a spin-doublet or (2) a spin-quartet with appreciable exchange demagnetization or (3) an effective spin-doublet with a thermally accessible spin-quartet state. Situation (2) can not be a fact because magnetic moment of \([\text{n-Bu}_4\text{N}]_2[\text{Co}(\text{MNT})_2]\) does not change upon magnetic dilution. Although it has been shown\(^ {17}\) conclusively that the complex is a spin-doublet in a wide range of solvents, very little is known about the solid state.

It is very interesting that all the spin-doublet dithiolenes with similar electronic structures, i.e., \(\text{M}(\text{MNT})_2^-\), \(\text{M}(\text{TDT})_2^-\), \(\text{M}(\text{S}_2\text{C}_2\text{Ph}_2)_2^-\), \(\text{M} = \text{Ni}, \text{Pd}, \text{Pt}, \text{and} \text{Rh}(\text{MNT})_2^=\), have \(g\) values 2.08 ± 0.06. The only high \(\langle g\rangle\) value is in the spin-doublet \(\text{Co}(\text{MNT})_2^-\).

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complex, where the value is 2.255. This may indicate that this complex has a different ground-state electronic structure.

Evidences bearing on the occurrence and generality of another important stereochemistry pattern in dithiolene chemistry is the elegant discovery of the bis-chelate dimers \([\text{M-S}_4]^2\). The first indication of interionic intermolecular interaction\(^{18}\) was found in the reduced magnetic moments of some crystalline salts of \([\text{MS}_4]^-\) where \(\text{M}=\text{Ni, Pd, Pt}\). In solution these complexes gave moments expected for a doublet ground state. The neutral \([\text{Co(S}_4\text{C}_4(\text{CF}_3)_4])\] has been found to be diamagnetic and dimeric in carbon tetrachloride solutions.\(^{18}\) These reduced magnetic moments of the crystalline salts of \([\text{M(MNT)}_2]^-\), where \(\text{M}=\text{Ni, Pd and Pt}\), have been investigated by Weiher, Melby and Benson.\(^{19}\) They interpreted these results in terms of pairwise interaction of doublet-state anions.

The crystal structure of \([\text{Ni(MNT)}_2]^-\) in the methyl triphenyl phosphonium salt has been investigated by

Fritchie. The results show that the complex is not a true dimer. The apical Ni-S distance indicate a nearly limiting case of weak yet discernible dimerization (Figure 3).

Six-coordinate 1, 2-dithiolenes of some transition metals are now known. At this time no tris complexes of Ni, Pd, Pt, Cu, and Zn are known with a dithiolene ligand.

At the beginning of the study of six-coordinate complexes, attention was largely focused only on vanadium and chromium metals, though at present tris-dithiolenes of other metals, for example, iron, cobalt, and rhenium, are very well known. The study of crystal structure of $[\text{ReS}_6\text{C}_6\text{Ph}_6]^0$ by Eisenberg and Ibers resulted in the first example of a trigonal prismatic stereochemistry. Previous to this report, six coordinate

\begin{footnotesize}
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\end{footnotesize}
Figure 3

Monoanion orientation in methyltriphenyl phosphonium bis (1,2-dicyanoethylene-1,2-dithiolato) nickel (III).
complexes have been known either in octahedral or distorted octahedral geometry, though hexagonal and trigonal prismatic are distinct possibilities. An interesting part of this study is that this geometry does not change even in solution. It has been shown by X-ray diffraction that the highly oxidized tris-dithiolenes of vanadium \(^{26}\) and chromium \(^{27}\) are also trigonal prismatic in structure. Until very recently \(^{28}\), very little has been reported about the structures of charged species except that of \([\text{VS}_6\text{C}_6\text{Ph}_6]^−\). The ion is isoelectronic with \([\text{CrS}_6\text{C}_6\text{Ph}_6]^0\), and on the basis of comparative electronic spectra it has been concluded that the structure is trigonal prismatic.

A very recent study of the crystal structure of \([\text{Me}_4\text{N}]_2[\text{V(MNT)}_3]\) by Stiefel, Dori, and Gray \(^{28}\) has shown that \([\text{V(MNT)}_3]^{−2}\) has a geometry intermediate between a trigonal prismatic and trigonally distorted octahedral arrangement.

It would be very interesting and important to investigate the following point, where (1) the bis- to tris-structured rearrangement takes place in first row

transition metals, (2) whether both bis- and tris-
complexes could coexist for the same metal with the
same ligand, and (3) where in the series of the tris-
complexes the geometry changes from trigonal prismatic
to octahedral and whether the charges on the complexes
are the governing factors of determining the geometry
or not.

Little work has been done on the dithiolene chem-
istry of the transition metals and more investigations
are needed to give a satisfactory answer to these
questions.

The tris complexes of dithiolenes with Ni, Pd, Pt,
Cu and Zn have not been observed and so the question of
trigonal prismatic\textright octahedral does not arise here. As
one moves from right to the left in the first row
transition metals to Co, Fe, Mn, both bis- and tris-
complexes are possible.

The complexes are termed "dithiolene" instead of
dithiolate when they are complexed to transition metals.
The use of this terminology avoids the confusion that
may arise out of the formal oxidation states of the
metal. Formal oxidation number is ambiguous in $[\text{NiL}_2]^{-1}$
and meaningless in $[\text{VS}_6\text{Co}_6\text{R}_6]^{0}$. 
It must be emphasized that the use of this terminology in no way represents a criticism, implied or real, of the existing discussion of the ground states of these unusual sulfur complexes.
CHAPTER II

PLANAR METAL COMPLEXES OF 2,3-QUINOXALINEDITHIOL

Experimental and Results

Reagents

Nickel (II) chloride hexahydrate was obtained from Fisher Scientific Company, Fair Lawn, New Jersey; palladium (II) chloride and platinum (II) chloride were obtained from K and K Laboratories Inc., Plainview, New York; thiourea, zinc (II) chloride and anhydrous methanol were obtained from Mallinckrodt Chemical Works, St. Louis, Missouri; ethanol was obtained from U.S. Industrial Chemical Co., New York, N.Y.; n-tetrabutylammonium bromide was obtained from Eastman Organic Chemicals, Rochester, New York, N.Y. These chemicals were used without further purification except for the solvents, which were dehydrated through molecular sieves.

Electrolytic Conductivities

Electrolytic conductivities were measured in nitromethane unless otherwise mentioned, because conductance of most of the other dithiolenes were measured
in this solvent. Spectro grade nitromethane from Eastman Organic Chemicals, Rochester, New York, N.Y. was used without further purification. The conductivity cell was calibrated with an aqueous potassium chloride solution. A concentration of $1 \times 10^{-3}$ mole per liter was used for all measurements. The molar conductances are given in Table-I.

**Magnetic Susceptibilities**

The magnetic susceptibilities were measured by the Gouy method, using an Alpha Model 7500 Electromagnet equipped with power supply and current regulator. The magnetic moments reported in Table-II are the averages of susceptibilities from three different fields roughly


$^{30}$The calculation of molar conductances were made according to the equation given in "Instrumental Methods of Analysis", by H. H. Willard, L. L. Merrit, Jr., and J. A. Dean published by D. Van Nostrand Company, Inc., New York, N. Y., 1958, p. 568-573. The equation used is

$$\Lambda m = \frac{G \cdot K}{C} \cdot 1000$$

where $\Lambda m$ = molar conductance, $G$ is the observed conductance, $K$ is the cell constant, and $C$ is the concentration in mole per liter.

corresponding to field strengths of 6000, 7000, and 8000 gauss. Susceptibilities reported are the average of three different measurements. All measurements were made at room temperature using Hg[Co(SCN)$_4$] as the calibration standard$^{32}$.

The effective magnetic moments were calculated from the equation

$$\mu_{\text{eff}} = 2.84 \left( x_{\text{corr}}^m \right)^{1/2}.$$  

The molar susceptibilities were corrected for metal and ligand diamagnetism. The molar diamagnetic corrections were estimated by using Pascal's constants$^{33}$.

**Analyses**

Carbon, hydrogen, nitrogen, and sulfur analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, Queens, N. Y., Galbraith Laboratories, Knoxville, Tennessee, and North Texas State University Analytical Service.


Melting Point

Melting points of the complexes were determined with a Thomas Hoover Capillary Melting Point Apparatus. They are uncorrected and are given in Table-I.

Infrared Spectra

Infrared spectra were recorded from 4000 cm\(^{-1}\) to 200 cm\(^{-1}\) on a Perkin-Elmer Model 621 Recording Spectrophotometer. Both nujol mull and KBr disc techniques were used. Each spectrum was calibrated with a polystyrene film. Nujol showed no water bands. Potassium bromide was infrared spectroscopic grade and was previously heated to 120\(^\circ\) under vacuum for three hours. Some characteristic absorption frequencies for complexes \([\text{M(QDT)}_2]^2\) are listed in Table-X. The spectrum of the ligand is shown in Figure 20.

Electronic Spectra

A Cary Model 14 Recording Spectrophotometer was used for obtaining the spectra. Both solid state and solution spectra were recorded for each complex. Solid state spectra were obtained by mulling the complexes in nujol as described by Cotton.\(^{34}\) Solution spectra

were recorded from 4800 cm\(^{-1}\) to 33000 cm\(^{-1}\) in spectrograde solvents in one-centimeter, five-centimeter, and ten-centimeter cylindrical cells. The electronic absorption frequencies in solid and solution are given in Tables VII and VIII, respectively. The spectra of \([\text{M}(QDP)_2]^-\) where M= Ni, Pd, Pt are shown in Figures 16, 17, and 18 respectively together with the corresponding MNT complexes for the purpose of comparison.

**Electron Spin Resonance**

Electron spin resonance spectra were recorded on a Varian Model 4502 Spectrometer operating at 9.5 Gc sec\(^{-1}\). Strip chart recordings were calibrated with a Hewlett-Packard counter and a Harvey-Wells 6502 gauss-meter. The frequency of the klystron was determined using a Hewlett-Packard frequency meter. Isotropic spectra were obtained from a 10\(^{-3}\) molar solution of the complex in CHCl\(_3\)-DMF mixture and are shown in Figure 4. Anisotropic spectra were obtained from the same solution frozen (70\(^0\)K) to a glass and is shown in Figure 5.

**Polarographic Measurements**

Polarograms were obtained with a Sargent Model XV Recording Polarograph. Both dropping mercury
electrode (DME) and rotating platinum electrode (RPE) were used as indicator electrode, and a standard calomel electrode (SCE) was used for the reference. A saturated aqueous potassium chloride was used as the supporting electrolyte in the reference compartment. N-tetrabutylammonium perchlorate or tetraethylammonium perchlorate was used as the supporting electrolyte in the sample compartment. The instrument was standardized against a standard resistance before recording each spectrum. A 2-3% aqueous solution of agar was used as salt bridge impregnated with about 10% of the supporting electrolyte dissolved in the solvent used for that particular spectrum. Solutions were 0.05 molar in n-tetrabutylammonium perchlorate (or tetraethylammonium perchlorate) and $10^{-3}$ molar in the complex under study.

**Preparation of the Ligand**

Since the commercially available material is too impure for our purposes, we prepared the compound from 2,3-dihydroxyquinoxaline using a method from the literature\(^{35}\) as follows:

o-Phenylenediamine (0.51 mole) and oxalic acid dihydrate (0.51 mole) were dissolved in 300 ml of 4N HCl and the solution was heated to boiling. The white solid which formed was filtered, washed three times with cold water and dried at 140°C using an oil bath. This material (83g) was ground together with phosphorus pentachloride (210g) and the entire mixture was placed in a one-liter round-bottom flask fitted with a water cooled condenser. The mixture was heated to 160°C with an oil bath and held at this temperature for two hours. At the end of this time, a brown solid had formed. This was allowed to cool and excess phosphorus pentachloride was removed by intimately mixing the solid with 200g of crushed ice. After allowing the mixture to reach room temperature, the product (2,3-dichloroquinoxaline) was filtered, washed with cold water and air dried. It was found convenient to work with 4g portions of the ligand 2,3-quinoxalinedithiol (QDT-H₂). For this purpose, 12g of 2,3-dichloroquinoxaline and 24g of thiourea were refluxed in 300 ml of ethanol for two hours. At the end of this period, the mixture was cooled and 600 ml of water containing 75g of sodium hydroxide were slowly added. The resulting mixture was refluxed for an additional hour, cooled and acidified slowly with glacial
acetic acid. The dark orange product was filtered and washed four times with water. A further treatment with base and acid gave a material which melted at 340-342° (dec.) when dry, in reasonable agreement with the reported value of 345°C (dec.). The compound was not characterized further and was used directly for the preparation of the complexes.

Preparation of \([n-\text{Bu}_4\text{N}]_2[\text{Ni}\text{QDT}_2]_2\).—4.0 g of 2,3-quinoalinedithiol were added to a solution of 4.0 g sodium methoxide dissolved in 500 ml of ethanol. The mixture was stirred until a solution was obtained, and a solution of 2.50 g of NiCl₂·6H₂O in 30 ml of ethanol was slowly added. The intensely purple solution which formed immediately was filtered free of a small amount of yellow material and then added to a solution of tetra-n-butylammonium bromide in 20 ml of ethanol. Water was then slowly added to the point of incipient crystallization (400 ml), and the mixture was allowed to stand for 24 hours. The crude product was filtered, then dissolved in 50 ml of ethanol to which 5 ml of concentrated aqueous ammonia had been added. Water
was again added until incipient crystallization. The mixture was allowed to stand overnight, filtered, and the purple needles which resulted were dried at 80°C in vacuo overnight. The yield was 5.6 g.

Preparation of $\text{[n-Bu}_4\text{N]}_2\text{[Cu(QDT)}_2$]$ \_2$.—2 g of sodium metal were added to 50 ml of ethanol and after the reaction was over, 300 mg of 2,3-quinoxalinedithiol were added and stirred into solution. A solution of 130 mg of CuCl$_2$ • 2H$_2$O dissolved in 10 ml of ethanol was added slowly, resulting in a dark brown solution. 0.9 g of (n-$\text{C}_4\text{H}_9$)$_4$NBr was dissolved in this solution and water was added until incipient crystallization. The mixture was allowed to stand overnight and the crude product was filtered and air-dried. This material was dissolved in 20 ml of ethanol to which 2 ml of concentrated ammonia had been added, followed by sufficient water (300 ml) until the crystals began to appear. The mixture was allowed to stand overnight, filtered, and the product dried in vacuo at 80°C. The yield was 0.80 g of red-brown needles.

Preparation of $\text{[n-Bu}_4\text{N]}\text{[Cu(QDT)}_2$.—0.50 g of $\text{[(n-C}_4\text{H}_9)]_2\text{[Cu(QDT)}_2$]$ \_2$ was dissolved in 180 ml of a
solution of ethanol, ether and tetrahydrofuran, one-third each by volume, and air was passed through until the solvent had been evaporated, leaving a light-brown solid residue. This material was dissolved in 20 ml of ethanol and 10^{-3} molar aqueous ammonia was added until incipient crystallization. The mixture was allowed to stand overnight. The light-brown needles which formed were filtered and dried in vacuo overnight. The yield was 0.31 g m.p. 223-225°.

Preparation of [n-Bu₄N]₂[Pd(QDT)₂]–2,3 quin-oxalinedithiol (1.94 g) was dissolved in 75 ml of methanol containing 0.8 g of metallic sodium and was stirred for 10 minutes. Palladium chloride (0.885 g) suspended in methanol was slowly added to this alkaline solution of the ligand and was stirred for 15 minutes and filtered. To the filtrate 3.22 g of n-Bu₄N⁺Br⁻ was added and stirred for another 15 minutes. Water was slowly added to the solution until orange-colored precipitate started to come out of solution. The preparation was allowed to stand for 6 hours and then filtered. The product was dissolved in methanol containing about 1% ammonia and water was added until precipitation occurred. The product was allowed to
stand for 6 hours and filtered. The product was dried under vacuum at 80°C overnight.

Preparation of \([\text{n-Bu}_4\text{N}]_2[\text{Pt(QDT)}_2]\).—Metallic sodium (0.6 g) was dissolved in 50 ml of methanol and 0.97 g of 2,3-quinoxalinedithiol was added and stirred until a clear solution was obtained. Platinum chloride (0.66 g) in 100 ml of methanol was added slowly over a period of 20 minutes. The solution was stirred for about 15 minutes and then filtered. The filtrate, with a few drops of ammonia, was added to 1.61 g of \(\text{n-Bu}_4\text{N}^+\text{Br}^-\) and stirred for about 10 minutes. Water was added slowly until precipitation started. The resulting product was allowed to stand for 12 hours and then filtered. The resulting red precipitate was dissolved in a minimum quantity of methanol containing about 1% ammonia and water was added until incipient precipitation occurred. The product was left standing overnight. Reprecipitation was repeated three times and the red product was dried under vacuum overnight at 80°C.

Preparation of \([\text{n-Bu}_4\text{N}]_2[\text{Zn(QDT)}_2]\).—Metallic sodium (1.0 g) was dissolved in 100 ml of methanol and
3.88 g of 2,3-quinoxalinedithiol was added with stirring. Zinc chloride (1.36 g) was added to the resulting solution and stirred for 5 minutes. The resulting solution was then filtered. The filtrate was added to 6.44 g of n-Bu$_4$N$^+$Br$^-$ in approximately 30 ml of water. Immediate precipitation was observed. The yellow precipitate was filtered and redissolved in methanol and precipitated with water and left for about 2 hours. The product was filtered and dried under vacuum at 80°C overnight. The analytical results were found to be as follows:

\[[(n-C_4H_9)_4N]_2 \text{Ni(QDT)}_2\] Calculated: C, 62.12; H, 8.69; N, 9.06; S, 13.82. Found: C, 63.00; H, 8.76; N, 9.19; S, 13.66.

\[[(n-C_4H_9)_4N]_2 \text{Cu(QDT)}_2\] Calculated: C, 61.79; H, 8.64; N, 9.01; S, 13.75. Found: C, 62.02; H, 8.65; N, 9.05; S, 13.96.

\[[(n-C_4H_9)_4N] \text{Cu(QDT)}_2\] Calculated: C, 55.66; H, 6.43; N, 10.14; S, 18.57. Found: C, 55.92; H, 6.83; N, 10.24; S, 18.54.

\[[(n-C_4H_9)_4N]_2 \text{Zn(QDT)}_2\] Calculated: C, 61.70; H, 8.57; N, 8.99; S, 13.71. Found: C, 61.41; H, 8.73; N, 8.76; S, 13.97.
([(n-C₄H₉)₄N]₂ Pd(QDT)₂ Calculated: C, 59.13; H, 8.21; N, 8.61; S, 13.14. Found: C, 58.85 H, 8.50; N, 8.48; S, 12.85.

([(n-C₄H₉)₄N]₂ Pt(QDT)₂ Calculated: C, 54.18; H, 7.52; N, 7.90; S, 12.05. Found: C, 54.25; H, 7.65; N, 7.80; S, 11.90.

Discussion

Analytical and Conductance Results

The analytical data given to support the formulations used in this work are presented at appropriate points within the Experimental Section, and are considered to be in good agreement with theoretical values. Conductance data obtained on all new complexes are found in Table I. Nitromethane was selected as solvent since the majority of the conductivities of previously characterized metal-dithiolene complexes were measured in this solvent. Comparison of these data with literature values indicates a dissociation behavior in solution expected from the empirical formula of each complex. Thus, RCu(QDT)₂ behaves as a 1:1 electrolyte.

TABLE I

PHYSICAL PROPERTIES

<table>
<thead>
<tr>
<th>Complex a</th>
<th>Color</th>
<th>m.p. °C</th>
<th>( \Lambda^{b} )</th>
<th>( E^{c} 1/2 ) aV</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_2Ni(QDT)_2 )</td>
<td>Purple</td>
<td>204-205</td>
<td>151</td>
<td>+0.22</td>
</tr>
<tr>
<td>( R_2Cu(QDT)_2 )</td>
<td>Red-brown</td>
<td>196-198</td>
<td>154</td>
<td>-0.20</td>
</tr>
<tr>
<td>( RCu(QDT)_2 )</td>
<td>Brown</td>
<td>223-225</td>
<td>71</td>
<td>-----</td>
</tr>
<tr>
<td>( R_2Zn(QDT)_2 )</td>
<td>Yellow</td>
<td>201</td>
<td>125</td>
<td>-----</td>
</tr>
<tr>
<td>( R_2Pd(QDT)_2 )</td>
<td>Orange</td>
<td>212</td>
<td>123</td>
<td>+0.61</td>
</tr>
<tr>
<td>( R_2Pt(QDT)_2 )</td>
<td>Red</td>
<td>203</td>
<td>127</td>
<td>+0.38</td>
</tr>
</tbody>
</table>

a R represents \( n-(C_4H_9)_4N^+ \) throughout

b Obtained at room temperature; results expressed are in cm² ohm⁻¹ mole⁻¹

c Rotating platinum electrode as indicator electrode, DMSO as solvent vs SCE
Magnetic Susceptibility Results

$\text{R}_2\text{Cu(QDT)}_2$ has a measured magnetic moment of 1.84 B.M., a value consistent for copper with a doublet ground state. The complex $\text{RCu(QDT)}_2$ was found to be diamagnetic. This result may be compared with the diamagnetism which has been observed for the similar complexes $\text{RCu(TTF)}_2$ and $\text{RCu(MNT)}_2$. These three complexes are examples of very few square-planar copper complexes displaying this magnetic behavior. $\text{R}_2\text{Ni(QDT)}_2$, $\text{R}_2\text{Pd(QDT)}_2$, $\text{R}_2\text{Pt(QDT)}_2$, and $\text{R}_2\text{Zn(QDT)}_2$ are diamagnetic, the normal magnetic state for these metal (II) complexes.

Oxidation of $\text{R}_2\text{M(QDT)}_2$ Complexes

Polarographic Results

The syntheses described in the Experimental Section yielded dianionic complexes. Polarographic studies of metal-dithiolene complexes have been useful in indicating the existence and relative stability of species involved in a particular metal-ligand series. Each of the $\text{R}_2\text{M(QDT)}_2$ complexes synthesized in this work exhibits one wave of approximately the same diffusion current (Table-III). Half-wave potentials measured for
<table>
<thead>
<tr>
<th>COMPLEXES</th>
<th>$\mu_{\text{eff.}}$ in B. M.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_2[\text{Ni(QDT)}_2]$</td>
<td>Diamagnetic</td>
</tr>
<tr>
<td>$R_2[\text{Cu(QDT)}_2]$</td>
<td>1.84</td>
</tr>
<tr>
<td>$R[\text{Cu(QDT)}_2]$</td>
<td>Diamagnetic</td>
</tr>
<tr>
<td>$R_2[\text{Pd(QDT)}_2]$</td>
<td>Diamagnetic</td>
</tr>
<tr>
<td>$R_2[\text{Pt(QDT)}_2]$</td>
<td>Diamagnetic</td>
</tr>
<tr>
<td>$R_2[\text{Zn(QDT)}_2]$</td>
<td>Diamagnetic</td>
</tr>
</tbody>
</table>

$R = n$-tetrabutylammonium ion.
TABLE III

SOME DATA ON POLAROGRAPHIC HALF-WAVE POTENTIAL AND DIFFUSION CURRENT

<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>$E_{1/2}$</th>
<th>$i_d/C$ (in $\mu$A/mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(QDT)$_2^-$</td>
<td>0.27</td>
<td>9.8</td>
</tr>
<tr>
<td>Pd(QDT)$_2^-$</td>
<td>0.61</td>
<td>11.22</td>
</tr>
<tr>
<td>Pt(QDT)$_2^-$</td>
<td>0.38</td>
<td>10.98</td>
</tr>
<tr>
<td>Ni(MNT)$_2^-$</td>
<td>0.42</td>
<td>9.45</td>
</tr>
</tbody>
</table>

Measurements were taken with RPE as indicator electrode vs SCE as reference and DMSO as solvent.
these processes appear in Table I. As a relative measure of oxidative stability with respect to $R_2Cu(QDT)_2$ half-wave potentials of $R_2Cu(TDT)_2$ and $R_2Cu(MNT)_2$ were obtained using a dropping mercury electrode, DMSO as solvent, and SCE as reference cell. The values obtained for these three complexes are -0.20, -0.56, and +0.30v, respectively, and are shown in Table IV. It is noted that these values appear to follow an order with respect to stability toward oxidation. $R_2Cu(MNT)_2$ is stable in air and requires iodine for conversion to the monoanion, whereas $R_2Cu(TDT)_2$ and $R_2Cu(QDT)_2$ are both air oxidizable.

Information concerning stability of dithiolene complexes as ligand structures are varied with a given metal ion, may be obtained by considering values of half-wave potentials for the couple $ML_2^2 \rightleftharpoons ML_2^- + e^-$. Oxidative stability of the dianion is enhanced by electron withdrawing groups while poor electron withdrawing groups render these species containing the largest number of valence electrons unstable. It appears that the presence of the heterocyclic ring nitrogens in 2,3-quinoxalinedithiol is sufficient to enable the direct isolation of $Ni(QDT)_2^{2-}$ while $Ni(TDT)_2^{1-}$
### TABLE IV

HALF-WAVE POTENTIALS OF PLANAR SPECIES IN SOLUTION vs SCE

<table>
<thead>
<tr>
<th>Couple</th>
<th>Indicator Electrode</th>
<th>Solvent</th>
<th>E&lt;sub&gt;1/2&lt;/sub&gt;, V</th>
<th>Oxidative Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(QDT)&lt;sup&gt;-&lt;/sup&gt; = Ni(QDT)&lt;sup&gt;-&lt;/sup&gt; + e</td>
<td>DME</td>
<td>DMSO</td>
<td>+0.18</td>
<td>Ni &gt; Cu</td>
</tr>
<tr>
<td>Cu(QDT)&lt;sup&gt;-&lt;/sup&gt; = Cu(QDT)&lt;sup&gt;-&lt;/sup&gt; + e</td>
<td>DME</td>
<td>DMSO</td>
<td>-0.20</td>
<td>Ni &gt; Cu</td>
</tr>
<tr>
<td>Ni(QDT)&lt;sup&gt;-&lt;/sup&gt; = Ni(QDT)&lt;sup&gt;-&lt;/sup&gt; + e</td>
<td>DME</td>
<td>DMF</td>
<td>+0.27</td>
<td>Ni &gt; Cu</td>
</tr>
<tr>
<td>Cu(QDT)&lt;sup&gt;-&lt;/sup&gt; = Cu(QDT)&lt;sup&gt;-&lt;/sup&gt; + e</td>
<td>DME</td>
<td>DMF</td>
<td>-0.29</td>
<td>Ni &gt; Cu</td>
</tr>
<tr>
<td>Ni(QDT)&lt;sup&gt;-&lt;/sup&gt; = Ni(QDT)&lt;sup&gt;-&lt;/sup&gt; + e</td>
<td>RPE</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CN</td>
<td>+0.23</td>
<td>Ni &gt; Cu</td>
</tr>
<tr>
<td>Cu(QDT)&lt;sup&gt;-&lt;/sup&gt; = Cu(QDT)&lt;sup&gt;-&lt;/sup&gt; + e</td>
<td>RPE</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CN</td>
<td>-0.36</td>
<td>Ni &gt; Cu</td>
</tr>
<tr>
<td>Couple</td>
<td>Indicator Electrode</td>
<td>Solvent</td>
<td>$E_{1/2}, \text{V}$</td>
<td>Oxidative Stability</td>
</tr>
<tr>
<td>-----------------</td>
<td>---------------------</td>
<td>---------</td>
<td>---------------------</td>
<td>---------------------</td>
</tr>
<tr>
<td>$\text{Cu(MNT)}_2^+ = \text{Cu(MNT)}^2^- + e$</td>
<td>RPE</td>
<td>$\text{CH}_3\text{CN}$</td>
<td>0.41</td>
<td>$\text{Cu} \gg \text{Ni}$</td>
</tr>
<tr>
<td>$\text{Ni(MNT)}_2^+ = \text{Ni(MNT)}^2^- + e$</td>
<td>RPE</td>
<td>$\text{CH}_3\text{CN}$</td>
<td>0.32</td>
<td>$\text{Cu} \gg \text{Ni}$</td>
</tr>
<tr>
<td>$\text{Cu(MNT)}_2^+ = \text{Cu(MNT)}^2^- + e$</td>
<td>RPE</td>
<td>$\text{DMSO}$</td>
<td>0.52</td>
<td>$\text{Cu} \gg \text{Ni}$</td>
</tr>
<tr>
<td>$\text{Ni(MNT)}_2^+ = \text{Ni(MNT)}^2^- + e$</td>
<td>RPE</td>
<td>$\text{DMSO}$</td>
<td>0.42</td>
<td>$\text{Cu} \gg \text{Ni}$</td>
</tr>
<tr>
<td>$\text{Cu(MNT)}_2^+ = \text{Cu(MNT)}^2^- + e$</td>
<td>DME</td>
<td>$\text{DMSO}$</td>
<td>0.30</td>
<td>$\text{MNT} \gg \text{QDT} \gg \text{TDT}$</td>
</tr>
<tr>
<td>$\text{Cu(QDT)}_2^+ = \text{Cu(QDT)}^2^- + e$</td>
<td>DME</td>
<td>$\text{DMSO}$</td>
<td>-0.20</td>
<td>$\text{MNT} \gg \text{QDT} \gg \text{TDT}$</td>
</tr>
<tr>
<td>$\text{Cu(TDT)}_2^+ = \text{Cu(TDT)}^2^- + e$</td>
<td>DME</td>
<td>$\text{DMSO}$</td>
<td>-0.56</td>
<td>$\text{MNT} \gg \text{QDT} \gg \text{TDT}$</td>
</tr>
</tbody>
</table>
### TABLE IV (continued)

**HALF-WAVE POTENTIALS OF PLANAR SPECIES IN SOLUTION vs SCE**

<table>
<thead>
<tr>
<th>Couple</th>
<th>Indicator Electrode</th>
<th>Solvent</th>
<th>$E_{1/2}, \text{V}$</th>
<th>Oxidative Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ni}^{\text{MNT}}<em>{2}^{\text{+}} = \text{Ni}^{\text{MNT}}</em>{2}^{\text{-}} + e$</td>
<td>DME</td>
<td>CH$_3$CN</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td>$\text{Ni}^{\text{QDT}}<em>{2}^{\text{+}} = \text{Ni}^{\text{QDT}}</em>{2}^{\text{-}} + e$</td>
<td>DME</td>
<td>CH$_3$CN</td>
<td>0.18</td>
<td>MNT$\Rightarrow$QDT</td>
</tr>
<tr>
<td>$\text{Ni}^{\text{MNT}}<em>{2}^{\text{+}} = \text{Ni}^{\text{MNT}}</em>{2}^{\text{-}} + e$</td>
<td>RPE</td>
<td>DMSO</td>
<td>0.42</td>
<td></td>
</tr>
<tr>
<td>$\text{Ni}^{\text{QDT}}<em>{2}^{\text{+}} = \text{Ni}^{\text{QDT}}</em>{2}^{\text{-}} + e$</td>
<td>RPE</td>
<td>DMSO</td>
<td>0.27</td>
<td>MNT$\Rightarrow$QDT</td>
</tr>
<tr>
<td>$\text{Ni}^{\text{MNT}}<em>{2}^{\text{+}} = \text{Ni}^{\text{MNT}}</em>{2}^{\text{-}} + e$</td>
<td>RPE</td>
<td>CH$_3$CN</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td>$\text{Ni}^{\text{QDT}}<em>{2}^{\text{+}} = \text{Ni}^{\text{QDT}}</em>{2}^{\text{-}} + e$</td>
<td>RPE</td>
<td>CH$_3$CN</td>
<td>0.23</td>
<td>MNT$\Rightarrow$QDT</td>
</tr>
</tbody>
</table>
is the product with similar synthetic conditions using TDT as the ligand, again implying that the role of an electron-withdrawing group is the determining factor. These complexes closely resemble the related MNT complexes, with one important difference. R₂Ni(QDT)₂ is more stable to oxidation to the monoanion than R₂Cu(QDT)₂. This is the reverse of the trend of the MNT complexes. The trend is also found using a dme in DMSO (+0.18 vs -0.20) and DMF (+0.27 vs -0.29).

Mode of Coordination in R₂M(QDT)₂ Complexes

Electron Spin Resonance

The purpose of this section is to give evidence that the bonding within metal complexes of 2,3-quin- oxalinedithiol involves the pair of sulfur atoms as donor atoms rather than the alternate possibility of nitrogen and sulfur atoms. The isotropic and the anisotropic spectra are shown in Figures 4 and 5 respectively. Parameters of ESR spectra of R₂Cu(QDT)₂ are of diagnostic value in distinguishing between these two modes of bonding. Hyperfine coupling constants and

Figure 4

Isotropic spectrum of Cu(QDT)$_2$$^{2-}$

100 gauss
Figure 5
Anisotropic spectrum of Cu(QDT)$_2$
g components obtained from these spectra are found in Table V, and VI; along with these are some constants for complexes known to be bonded by sulfur only. These values are virtually alike for each constant, and as a set, differ considerably from those obtained from spectra of Cu(II) complexes where the four coordinating atoms are other than sulfur. The features of the sulfur group are that the spectra exhibit narrow lines separated by relatively small hyperfine splitting constants and $g$ components approaching those of a free electron. Cu (II) complexes coordinated by nitrogen or oxygen exhibit spectra in which the lines are considerably broader, and values of $g_{||}$ and $g_{\perp}$ greater than 2.20 and 2.04, respectively, are found. Clear differences arise also from a consideration of the hyperfine coupling constants $A_{||}$ and $A_{\perp}$.

There are relatively few examples of Cu(II) complexes where the bonding is solely by nitrogen and sulfur. Since this is specifically one of the modes in question, it was thought best to obtain an authentic example and record its ESR spectrum. Because of its relatively simple preparation the complex bis (N-n-butylthiopicolinamidato) copper (II) was chosen.

TABLE V

ISOTROPIC ELECTRON PARAMAGNETIC RESONANCE DATA OF COPPER (II) DITHIOLENES

<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>$\langle \varepsilon \rangle$</th>
<th>$\langle A \rangle$, GAUSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cu(MNT)}_2^{-2}$</td>
<td>$2.045 \pm 0.001$</td>
<td>$76.3$</td>
</tr>
<tr>
<td>$\text{Cu(TDT)}_2^{-2}$</td>
<td>$2.046 \pm 0.002$</td>
<td>$78.9$</td>
</tr>
<tr>
<td>$\text{Cu(QDT)}_2^{-2}$</td>
<td>$2.044 \pm 0.008$</td>
<td>$77.0$</td>
</tr>
</tbody>
</table>

All measurements made in 50% V/V CHCl$_3$-DMF room temperature data.
<table>
<thead>
<tr>
<th>COMPLEXES</th>
<th>$g_u$</th>
<th>$g_\perp$</th>
<th>$A_{uu}$, GAUSS</th>
<th>$A_\perp$, GAUSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(MNT)$_2^{2+}$</td>
<td>2.084 ± 0.001</td>
<td>2.0026 ± 0.003</td>
<td>158.8 ± 0.5</td>
<td>40 ± 2</td>
</tr>
<tr>
<td>Cu(TDT)$_2^{2+}$</td>
<td>2.091 ± 0.002</td>
<td>2.0026 ± 0.002</td>
<td>159 ± 1</td>
<td>43 ± 2</td>
</tr>
<tr>
<td>Cu(QDT)$_2^{2+}$</td>
<td>2.090 ± 0.001</td>
<td>2.023 ± 0.001</td>
<td>156.9 ± 0.5</td>
<td>46 ± 2</td>
</tr>
</tbody>
</table>
Although a good anisotropic spectrum of this compound could not be obtained, the isotropic spectrum furnishes sufficient information to be of great use. The spectrum consists of four broad lines with an average width of 84 gauss. These lines result from interaction with the $^{63}\text{Cu}$ and $^{65}\text{Cu}$ isotopes, both having $I=3/2$. Each of these lines is split further into five peaks which have an intensity ratio of approximately 1:2:3:2:1. Such a pattern can only arise from an unpaired electron interacting with two equivalent nitrogen nuclei ($I=1$) as well as with the nuclear spin of the metal. The parameters obtained from this isotropic spectrum are $\langle g \rangle = 2.078$, $\langle A \rangle = 70.1$ gauss and $\langle A_N \rangle = 15.6$ gauss. All of these characteristics would be expected by the isotropic spectrum of $\text{R}_2\text{Cu(QDT)}_2$ if the bonding were of the mixed mode. However, it is found that none result. The value of $\langle g \rangle$ is 2.044, which is significantly lower and more important, no observable interaction with nitrogen nuclei was detected. This latter fact is of special importance since line-widths of $\text{R}_2\text{Cu(QDT)}_2$ spectra average 58 gauss and, if nitrogen were present in the coordination shell, interactions due to it ought to be easily detected. On this basis, then it is concluded that bonding in this complex is via the pair of sulfur atoms in the ligand.
The structure of the complex\(^{39}\)bis (N-n-butylthiopicolinamidato) copper (II) is shown in Figure 6.

**Electronic Spectra**

The electronic structure of square metal complexes remain a problem of continuing interest in transition metal chemistry. The energy levels are not known with certainty in many cases. The levels may and do vary with different ligands, metals, and the charge on the species. A suitable coordinate system for a consideration of the sigma and pi bonding possibilities is shown in Figure 7.

The ligands are so bonded that the sigma orbitals are directed to the metal and the pi orbitals are parallel and perpendicular to the plane. Each of the ligands so bonded can be considered to have a sigma valence orbital and two equivalent pi valence orbitals. The transition metal is assumed to have nine valence orbitals as the usual case. These are the five \(n\) d orbitals, one (\(n+1\)) s orbital, and three (\(n+1\)) p orbitals.

**Sigma Bonding**

The metal orbitals used in forming the sigma orbitals are the \(n\) \(d_{x^2-y^2}\), (\(n+1\)) \(p_x\), (\(n+1\)) \(p_y\), and a combination of (\(n+1\)) s and \(n\) \(d_{z^2}\). The sigma overlap
Figure 6

Bis (N-n-butyl thiopicolinamidato) copper (II)
Figure 7

Coordinate system for a square planar complex.
Figure 8

Overlap of $\sigma$-metal orbitals with appropriate ligand $\sigma$ functions.
of these metal orbitals with the appropriate ligand sigma functions is shown in Figure 8. The \( n\ d_2 \) orbital is neglected in the sigma overlap consideration because of the relatively little overlap with the ligand system. The bonding can be described then in terms of \( \text{dsp}^2 \) hybrid system.

Pi bonding: The metal orbitals which have the proper symmetry to be involved in the pi molecular orbital system in a square planar complex are the \( nd_{xy}, nd_{yz}, nd_{xz} (n + 1) p_x, (n + 1) p_y, \) and \( (n + 1) p_z \). The most important pi molecular orbitals can be classified conveniently as follows:

1. The "in-plane" pi system: the \( nd_{xy} \) interacts with the four horizontal pi ligand orbitals in an in-plane pi system, as shown in Figure 9.

2. The "trans pi system:" The \( nd_{xz} \) and \( nd_{yz} \) orbitals interact with two trans vertical pi ligand orbitals, as shown in Figure 10.

3. The "ring pi system:"

In addition to these major pi systems, the \( (n + 1) p_x \) and the \( (n + 1) p_y \) orbitals each interacts with two horizontal pi orbitals; thus the \( (n + 1) p_x \) and \( (n + 1) p_y \)
Figure 9

Overlap of $d_{xy}$ with $\pi_h$ functions.
Figure 10
Overlap of $d_{yz}$ with $t_{2g}$ functions.

Figure 11
Overlap of $p_z$ with $t_{2g}$ functions.
p_y orbitals are involved in both the sigma and the pi electronic structures of square planar complexes.

A simple energy level diagram is shown in Figure 12. The most stable levels will no doubt be located mainly on the ligand. At higher energy we expect to find all the pi levels which also are mainly ligand in character. The exact ordering of the next four levels are not known for certainty and are subject to change as the metal, ligand and charge are changed. The most important point is that one level is very unstable relative to the other four levels. If the ligand occupies pi orbitals these should be above the d_x^2-y^2.

In order to obtain a quantitative information regarding the ordering of the orbitals a semiempirical and approximate molecular orbital calculation was carried out by Schrauzer and Mayweg on a model complex of bisdithioglyoxalnickel shown in Figure 13.

In this calculation, mutual overlap as well as non-neighbor interactions were neglected and the off-diagonal elements were simply set directly proportional to the overlap integrals. The starting molecular orbitals of the isolated ligand molecule were calculated using the

\[ 40 \text{G. N. Schrauzer and V. P. Mayweg, J. Am. Chem. Soc., 87, 3585 (1965).} \]
Energy level diagram for a simple square planar system.

Figure 12

Octahedral
Increasing Tetragonal Distortion

Square-planar
Figure 13

Model of the NiS₄C₄H₄ complex used for the calculations.
Pauling-Wheland method with $\Delta_{e} = \Delta_{c} + 0.2\beta_{c}$, neglecting sulfur d-orbitals and putting $\beta_{c} = 0$.

With these approximations Schrauzer and Mayweg obtained a ground state configuration of $(2b_{1u})^{2}(2b_{2g})^{2}$ $(3a_{g})^{2}(2b_{3g})^{2}(4a_{g})^{2}(3b_{2g})^{4}(3b_{1g})^{4}$. With this configuration the lowest unoccupied MO is both the metal and the ligand based $3b_{2g}$ orbital which arises from the antibonding combination of the $3d_{xz}$ orbital with the $1/2 (\Psi_{3} - \Psi'_{3})$ ligand MO set. The energy level diagram, according to this calculation is shown in Figure 14.

According to this scheme of Schrauzer and Mayweg the $B_{1u}$ combination of the lowest unoccupied ligand MO's become stabilized on interaction with the metal $p_{z}$ orbital and is occupied in the neutral complexes. The $B_{2g}$ combination of the same orbitals on the other hand becomes weakly antibonding on interaction with the metal $d_{xz}$ orbital and is filled with one or two electrons during the reduction of the neutral $d^{8}$ transition metal complexes. Both orbitals are delocalized over the whole molecule but consist to a significant extent of the pi MO's of the ligand.

Figure 14
Molecular orbital energy level scheme for NiS₄C₄H₄
The ligand hyperfine structure of the ESR spectrum of the paramagnetic species provides direct information about the nature of the electronic ground state and the extent of electron delocalization over the ligand orbitals. Davison et al. measured the electron paramagnetic resonance spectrum of the low spin \( S = \frac{1}{2} \) planar compound \([\text{Ni(MNT)}_2]^-\) in magnetically dilute single crystal of diamagnetic \([\text{n-Bu}_4\text{N}][\text{Cu(MNT)}_2]\) and from the crystallographic structure known for both of these complexes they obtained the orientation of the principal axis system of \( \Lambda \) and \( g \) with those calculated from various configuration. They concluded that the probable energy level of the \( d \)-orbital in the ground state configuration is \( \left( \ldots a_g^2 b_3^1 \right) \). The same ground state electronic configuration has also been obtained by Schrauzer and Mayweg on \([\text{NiS}_4\text{C}_4\text{Ph}_4]^-\) by molecular orbital calculations. The \( b_{3g} \) (or \( 3b_{2g} \)) orbital has been found to be largely delocalized over the ligands. The molecular orbital calculations by Schrauzer and Mayweg led to 18% \( d_{yz} \) (Figure 15) on the metal atom while analysis of the \( g \) tensor and 61Ni hyperfine tensor on \( \text{Ni(MNT)}_2^- \) yielded 25-50% \( d_{yz} \). In this case, however, the electron density near the sulfur atoms is contained in out-of-plane \( 3p_z \) orbitals (Figure 15).

Figure 15

Coordinate system for Ni$_2$S$_2$(CN)$_4$ ion. $Z = Z'$ molecular plane and going into the paper.
Schmitt and Maki\textsuperscript{43} now estimate the extent of electron
delocalization in the half-filled molecular orbital
\((v_{3g})\) using the properties of \(^{33}\text{S}\) hyperfine tensor
\((I=3/2)\) and showed that it agrees only with the \(^2B_{3g}\)
ground state.

Molecular orbital calculation have also been done
by Gray et al.\textsuperscript{10, 37} on Ni(MNT)\textsubscript{2} in which the highest
occupied orbital has the symmetry \(a_g\) and the ground
state configuration is \((4b_{2g})^2(4a_g)^1\). The half
filled \(4a_g\) molecular orbital was calculated to be a
linear combination of \(d_x^2-y^2\) on the metal and in-plane
3\(p_y\), orbitals on the four sulfur atoms. Schrauzer and
Nayweg criticized this orbital scheme calculation based
on the input parameters for the isolated system. The
important feature: to be noted about this configuration
is that near the sulfur atom the electron density is
contained in a \(p\)-type orbital directed in the molecular
plane. Actually, in \(D_{2h}\) symmetry \(3p_y\) and \(3p_x\), as well
as \(3s\) orbitals can mix. However, Gray et al. did not
indicate any such mixing in the MO eigenvectors of
Ni(MNT)\textsubscript{2}\textsuperscript{−}. A small admixture of \(3p_x\), into the \(4a_g\)
orbital would merely rotate the principal axis of the

\textsuperscript{43}R. D. Schmitt and A. H. Maki, \textit{J. Am. Chem. Soc.},
\textbf{90}, 2288 (1968).
local spin distribution slightly away from $y'$, but would remain in the plane of the molecule. This is no longer considered a valid description even by the originators themselves.\textsuperscript{44}

Recently Schrauzer has made a calculation of the ground state configuration of $\text{NiS}_{4}\text{C}_{4}\text{H}_{4}^-$ ion using the extended $\omega$-technique developed by Nakajima,\textsuperscript{45} which produces self consistent molecular orbitals. This treatment produces a singly occupied $3b_{2g}$ MO having 51\% metal and 49\% ligand character, a significant increase in metal character over the original calculation. This distribution is in excellent agreement with Schmitt and Maki's estimate of this molecular orbital from $^{33}S$ hyperfine tensor. Recent molecular orbital calculations by Baker-Hawkes\textsuperscript{46} on square planar nickel dithiolene anion complexes now predict that the half filled molecular orbital is of $b_{2g}$ symmetry rather than the previously obtained $a_g$ symmetry.


The spectra of the dianions of Ni, Pd, and Pt, are shown in Figures 16, 17, and 18 respectively. The occupation of the \(3b_{2g}\) orbital by two electrons in the neutral one should cause all intense low energy transition to vanish; the first allowed \(\pi-\pi\)-transition would be expected at fairly high energy. Absence of strong bands in the low energy part of the spectrum is the most interesting and characteristic feature of the spectra of all the dianions of nickel. This gives room to detect the weak ligand field bands appearing in-between 7000-13,000 cm\(^{-1}\). Though these bands are not very well resolved it is notable that they appear within the calculated range. That these weak bands are \(d-d\) transitions are supported by comparison with spectra of corresponding dianion of Pd and Pt; the general increase of the \(d-d\) splitting in the sequence Ni, Pd, Pt, is in accord with expectation and order of magnitude. The first absorption band in the case of Pd and Pt have a rather small energy with very low extinction coefficients. The solution spectra in dichloromethane and acetonitrile are similar and agree with the mull spectra. A singlet-triplet transition has been suggested for \([\text{Pt}(\text{MNT})_2]^-\), which also absorbs at low energy.
Absorption spectra of (a) Ni(Quin)_2 in CH_3NO_2 and (b) Ni(MNT)_2 in CH_3CN

Figure 16

x 10^3 cm^{-1}  
2000  1800  1600  1400  1200  1000  800  600  400  0
Absorption spectra of (a) Pd(QDT)²⁺ in CH₃NO₂ and (b) Pd(MNT)²⁺ in CH₃CN
Absorption spectra of (a) Pt(QDT)$_2^-$ in CH$_3$NO$_2$ and (b) Pt(MNT)$_2^-$ in CH$_3$CN.
Further evidence that these dithiols provide a stable square planar matrix for the nickel is from the fact that nickel compounds of all these dithiols known up to date exhibit similar electronic spectrum in solvents of wide range of coordinating ability. The spectrum of Ni(QDT)₂⁻ is essentially the same in a wide range of solvents. The lack of axial perturbation is also found in the constancy of the ESR spectrum of Cu(QDT)₂⁻ in the same range of solvents.

Based on the same experimental results of the study of electron spin resonance spectrum of the paramagnetic species, Davison, et al. showed that the probable ground state electronic configuration for Cu(MNT)₂⁻ is \((\Pi_1^*)^2 (\Pi_2^*)^2 (\sigma^*)^1\) and that of Cu(MNT)₂⁻ is naturally \((\Pi_1^*)^2 (\Pi_2^*)^2\). Considering only the three higher molecular orbitals, it was said earlier that the ordering of the molecular orbitals was based on the metal d-orbitals in \(D_{2h}\) symmetry as follows:

\[
\begin{align*}
\sigma^*(b_{1g}) & \quad \Pi_2^*(b_{3g} \text{ or } b_{2g}) & \quad \Pi_1^*(b_{2g} \text{ or } b_{3g}) & \quad \Pi^*(a_g) & \quad \sigma(a_g)
\end{align*}
\]

So, we assign the observed absorptions at 11,299 cm⁻¹ from Table VIII as \(\Pi_2^* \rightarrow \sigma^*\) and the one at 23,585 cm⁻¹ as \(\Pi_1^* \rightarrow \sigma^*\) for Cu(QDT)₂⁻ and 11,300 cm⁻¹ as \(\Pi_2^* \rightarrow \sigma^*\) and the one at 17,650 cm⁻¹ as \(\Pi_1^* \rightarrow \sigma^*\) for Cu(QDT)₂⁻.
As shown in Table VIII, assignment of exact energy of transition for \( \text{Cu(QDT)}_2^- \) will be premature. It has been found impossible to measure the electronic spectrum of the dianion accurately because of the oxidative instability of the complex. From polarographic experiments with the solution after electronic spectrum we have evidence that the dianion is oxidized to the monocation to a quite appreciable amount under the circumstance of the study. We have been unable to prevent the oxidation of this species completely.

It is interesting to consider whether the complex \([\text{Cu(QDT)}_2^-]^-\) is to be regarded as containing Cu(I) with two QDT\(^-\) ligands whose spins are paired or whether it is a Cu(III) with two QDT\(^-\) ligands. Evidences that it is not a copper (I) and rather that it is copper (III) are gathered from the studies of the absorption spectrum and polarography as well as chemical study.

Most of the copper (I) compounds in solution are very unstable and are oxidized to copper (II) complexes. \( \text{Cu(QDT)}_2^- \) can be kept in solution for weeks and yet it does not change to any other species.

If the complex is a Cu (I) with two spin-paired QDT\(^-\) ligands then the central metal should have a d\(^{10}\)
### Table VII

**Transitions in Electronic Spectra in Nujol Mulls in cm\(^{-1}\)**

<table>
<thead>
<tr>
<th>( R_2[\text{Ni(QDT)}_2] )</th>
<th>( R[\text{Cu(QDT)}_2] )</th>
<th>( R_2[\text{Cu(QDT)}_2] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>11300 (sh)</td>
<td>11230</td>
<td>11299</td>
</tr>
<tr>
<td>16950 (sh)</td>
<td>17540 (sh)</td>
<td>17500 (sh)</td>
</tr>
<tr>
<td>18000</td>
<td>24370</td>
<td>24250</td>
</tr>
<tr>
<td>10000</td>
<td>25640</td>
<td>38400</td>
</tr>
<tr>
<td>27000</td>
<td>38000</td>
<td>41660</td>
</tr>
<tr>
<td>31250</td>
<td>42500</td>
<td></td>
</tr>
<tr>
<td>38450</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( R_2[\text{Pd(QDT)}_2] )</th>
<th>( R_2[\text{Pt(QDT)}_2] )</th>
<th>( R_2[\text{Zn(QDT)}_2] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>11000</td>
<td>10870</td>
<td>23600</td>
</tr>
<tr>
<td>19610</td>
<td>17240</td>
<td>25000</td>
</tr>
<tr>
<td>20920</td>
<td>19000</td>
<td>26000</td>
</tr>
<tr>
<td>22470</td>
<td>20410</td>
<td>38500</td>
</tr>
<tr>
<td>23860</td>
<td>23000</td>
<td>42500</td>
</tr>
</tbody>
</table>

2,3-Quinoxalinedithiol

| 20000 (sh)                  | 21800 (sh)                  | 23200                       |
|                            |                            | 35800                       |
|                            |                            | 38500                       |

\( R = n-\text{Bu}_4\text{N}^+ \) ion.

sh = shoulder.
<table>
<thead>
<tr>
<th>( R_2\text{Ni(QDT)}_2 )</th>
<th>( R\text{Cu(QDT)}_2 )</th>
<th>( R_2\text{Cu(QDT)}_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_3\text{NO}_2 )</td>
<td>( \text{CH}_3\text{CN} )</td>
<td>( \text{CH}_3\text{CN} )</td>
</tr>
<tr>
<td>11,300 (44)</td>
<td>11,230 (450)</td>
<td>11,299 ??</td>
</tr>
<tr>
<td>16,900 sh (2,000)</td>
<td>17,650 (670)</td>
<td>23,585 (32,000)</td>
</tr>
<tr>
<td>18,500 (17,200)</td>
<td>24,500 (9,700)</td>
<td>24,752 (77,000)</td>
</tr>
<tr>
<td>19,230 sh (16,500)</td>
<td>26,000 (68,000)</td>
<td>25,800 (54,500)</td>
</tr>
<tr>
<td>27,230 sh (16,500)</td>
<td>38,500 (61,000)</td>
<td>38,462 (57,000)</td>
</tr>
<tr>
<td></td>
<td>41,000 (57,000)</td>
<td>42,553 (56,500)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( R_2\text{Zn(QDT)}_2 )</th>
<th>( R_2\text{Pd(QDT)}_2 )</th>
<th>( R_2\text{Pt(QDT)}_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_3\text{CN} )</td>
<td>( \text{CH}_3\text{NO}_2 )</td>
<td>( \text{CH}_3\text{NO}_2 )</td>
</tr>
<tr>
<td>24,400 (43,000)</td>
<td>12,659 (43)</td>
<td>10,810 (9)</td>
</tr>
<tr>
<td>25,420 (51,000)</td>
<td>18,349 (10,375)</td>
<td>18,727 (14,750)</td>
</tr>
<tr>
<td>26,500 (36,500)</td>
<td>20,492 (21,750)</td>
<td>19,802 (16,190)</td>
</tr>
<tr>
<td>36,600 (44,000)</td>
<td>21,978 (20,750)</td>
<td>21,053 (11,400)</td>
</tr>
<tr>
<td>39,450 (72,000)</td>
<td>23,256 (15,750)</td>
<td>23,530 (14,750)</td>
</tr>
</tbody>
</table>

\( a \) = intensities in \( \text{l} \cdot \text{mole}^{-1} \cdot \text{cm}^{-1} \) are given in parenthesis
Figure 19

Absorption spectra of (a) Cu (QDT)$_2$ and (b) Ni(QDT)$_2$
electronic configuration and the absorption spectrum should have no d-d transition. The spectrum should be comparable to the spectrum of Zn(QDT)$_2^-$ which is a d$^{10}$ system. The two weak ligand field absorptions at 11,230 cm$^{-1}$ (450) and 17,650 (670) transitions preclude the possibility and support a non-d$^{10}$ system. On the other hand a Cu(III) complex is a d$^8$ system and isoelectronic with Ni(II) complexes and the increase in molar extinction coefficient for RCuL$_2$ has been pointed out. The first two absorptions of Ni(QDT)$_2^-$ and Cu(QDT)$_2^-$ are comparable in energy and is shown in Figure 19.

The possibility that Cu(QDT)$_2^-$ contains a Cu(II) ion with one QDT$^-$ (spin-paired ligand) and one QDT$^+$ ligand can be ignored since Cu(II) is a d$^9$ paramagnetic system and the complex is diamagnetic.

From Table IX it is noticed that like the MNT series, the energy of the lowest allowed band in the QDT planar complexes follow the same relationship, i.e.

$$\gamma[Ni(MNT)_2]^- > \gamma[Cu(MNT)_2]^- > \gamma[Cu(MNT)_2]^-,$$

likewise

$$\gamma[Ni(QDT)_2]^- > \gamma[Cu(QDT)_2]^- > \gamma[Cu(QDT)_2]^-$$
TABLE IX

LOWEST ENERGY ALLOWED BANDS IN SOME PLANAR COMPLEXES

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\nu$ $\text{Cm}^{-1}$</th>
<th>$\epsilon$</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Ni(QDT)}_2]^+$</td>
<td>11,300</td>
<td>44</td>
<td>$\text{CH}_3\text{NO}_2$</td>
</tr>
<tr>
<td>$[\text{Cu(QDT)}_2]^+$</td>
<td>11,299</td>
<td>118</td>
<td>$\text{CH}_3\text{CN}$</td>
</tr>
<tr>
<td>$[\text{Cu(QDT)}_2]^-$</td>
<td>11,230</td>
<td>450</td>
<td>$\text{CH}_3\text{CN}$</td>
</tr>
<tr>
<td>$[\text{Ni(MNT)}_2]^+$</td>
<td>11,690</td>
<td>30</td>
<td>$\text{CH}_3\text{CN}$</td>
</tr>
<tr>
<td>$[\text{Cu(MNT)}_2]^+$</td>
<td>8,340</td>
<td>71</td>
<td>$\text{CH}_3\text{CN}$</td>
</tr>
<tr>
<td>$[\text{Cu(MNT)}_2]^-$</td>
<td>6,400</td>
<td>337</td>
<td>$\text{CH}_3\text{CN}$</td>
</tr>
</tbody>
</table>
Infrared Spectra

The infrared spectra of the complexes are given in Table X. The IR spectra of 2,3-quinoxalinedithiol (shown in Figure 20) and related compounds are not always conclusive. For example, the absence of S-H and N-H stretching bands has consistently been observed. Hannan et al. studied a number of quinoline thiols and hoped that the thiols would exhibit an absorption in the region of 2400-2600 cm\(^{-1}\). None of the compounds studied showed any absorption in this region. If the compounds were to be considered in the thione form, then absorptions at 3400 cm\(^{-1}\) showing the N-H stretching band should appear. Unfortunately none of these compounds showed either S-H or N-H stretches. Thiones could also be expected to show a band due to the C=S stretch at 1400-1800 cm\(^{-1}\). However the inherent weakness of this band did not provide any help in the considerations and their conclusion was that infrared spectra does not offer a solution to this problem. Some assignments are possible; e.g., the band at 3040-3050 cm\(^{-1}\) can be

---


assigned to the C-H stretch. The band at 2870-2790 cm\(^{-1}\) can be assigned to the heterocyclic ring. The absorption at 700-600 cm\(^{-1}\) can be assigned due to the aromatic ring. The dependence of the structure of the complexes is shown by the spectra of the zinc analogs being different from the spectra of the planar species. Zinc complexes have tetrahedral stereochemistry.
### TABLE X

PRINCIPAL INFRARED BANDS OBSERVED FOR COMPLEXES PREPARED IN THIS WORK ON KBr WAFER

| [n-Bu₄N]₂[Ni(QDT)₂] | 3040 (m), 2945 (s), 2920 (s), 2860 (m), 1555 (w), 1475 (s), 1420 (w), 1385 (w), 1365 (s), 1265 (s), 1170 (s), 1125 (s), 1070 (w), 1025 (w), 940 (w), 890 (w), 800 (m), 760 (s), 600 (s), 425 (m), 320 (w). |
| [n-Bu₄N]₂[Cu(QDT)₂] | 3040 (m), 2945 (s), 2920 (s), 2865 (m), 1550 (w), 1470 (s), 1410 (w), 1400 (w), 1365 (s), 1255 (s), 1155 (s), 1110 (s), 1070 (w), 1020 (w), 940 (w), 880 (w), 800 (m), 750 (s), 600 (s), 400 (m), 320 (w). |
| [n-Bu₄N]₂[Cu(QDT)₂] | 3040 (m), 2950 (s), 2920 (s), 2860 (m), 1540 (w), 1460 (s), 1420 (w), 1385 (w), 1360 (s), 1240 (s), 1150 (s), 1090 (s), 1050 (w), 1000 (w), 940 (w), 850 (m), 765 (w), 740 (s), 590 (s), 400 (s), 325 (m). |
| [n-Bu₄N]₂[Pd(QDT)₂] | 3040 (m), 2950 (s), 2925 (s), 2865 (s), 1550 (s), 1475 (s), 1365 (s), 1365 (s), 1265 (s), 1175 (s), 1125 (s), 1060 (w), 1025 (m), 988 (m), 790 (s), 750 (s), 590 (s), 400 (m). |
| [n-Bu₄N]₂[Pt(QDT)₂] | 3050 (m), 2950 (s), 2940 (s), 2860 (s), 1550 (s), 1475 (s), 1380 (w), 1385 (s), 1260 (s), 1165 (s), 1120 (s), 1060 (w), 1010 (s), 888 (m), 790 (s), 740 (s), 585 (s), 400 (m). |
| [n-Bu₄N]₂[Zn(QDT)₂] | 3050 (m), 2950 (s), 2940 (s), 2850 (s), 1725 (s), 1450 (s), 1355 (s), 1245 (s), 1145 (s), 1120 (s), 1090 (s), 1010 (s), 865 (s), 775 (s), 735 (s), 560 (s), 420 (m), 385 (s). |
### TABLE X—Continued

2,3-Quinoxalinedithiol

<table>
<thead>
<tr>
<th>Frequency</th>
<th>Mode</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3055 (m), 2950 (s), 2880 (s), 2780 (m), 2675 (w), 1925 (w), 1620 (m), 1600 (s), 1550 (m), 1490 (m), 1470 (s), 1350 (s), 1315 (s), 1240 (m), 1180 (w), 1145 (s), 1135 (s), 1050 (m), 1020 (w), 920 (w), 890 (w), 830 (m), 735 (s), 630 (w), 610 (s), 580 (s), 510 (s), 440 (m), 390 (m), 360 (m).</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* s = strong; m = medium; w = weak
CHAPTER III

COBALT DITHIOLENE COMPLEXES

Experimental and Results

Reagents

Cobalt (II) chloride hexahydrate was obtained from J. T. Baker Chemical Company, Phillipsburg, New Jersey. Tetraphenyl arsonium chloride hydrate was obtained from Aldrich Chemical Company, Inc., Milwaukee, Wisconsin. Other reagents are described in Chapter II.

Measurements

The measurements were performed as described in Chapter II.

Preparation of \([nBu_4N]^+2[Co(QDT)_2]^-\). One gram of metallic sodium was dissolved in about 100 ml of methanol and 3.88 grams of 2,3-quinoxalinedithiol was added to the solution. To the clear solution, 1.19 g of CoCl$_2$.6H$_2$O dissolved in 30 ml of ethanol, was added slowly. The solution was stirred for 10 minutes under a nitrogen atmosphere. About 1 ml of hydrazine hydrate was added after the metal halide to prevent any oxidation. The solution was then filtered under nitrogen. To the filtrate 6.44 g of n-Bu$_4$N$^+$Br$^-$ was added and stirred for 5 minutes. Water containing about 1% of
NH₃ was added slowly until precipitation started. The resulting solution was left under nitrogen for 15 minutes and filtered. The black precipitate obtained was dissolved in methanol under nitrogen. Water, containing 3% NH₃, was added slowly until precipitation started. The black precipitate obtained was filtered and washed with water several times. A final washing was performed with 10 ml of ethanol. The compound was then dried under vacuum at about 40°C. The analytical results were found to be as follows.

Calculated: C, 62.14; H, 8.63; N, 9.06; S 13.81.
Found: C, 61.50; H, 8.78; N, 9.61; S 14.88.

Preparation of [n-Bu₄N]₂[Co(QDT)₂]₂. Metallic sodium (1.52 g) was dissolved in 150 ml of anhydrous methanol. 2,3-quinoxalinedithiol (6.20 g) was added with stirring until a clear solution was obtained. To this solution 2.38 g of CoCl₂. 6H₂O dissolved in 50 ml of water, was added slowly. The solution was stirred for about 15 minutes and filtered. To the filtrate 9.66 g of n-Bu₄N⁺ Br⁻ was added and stirred for 15 minutes. After cooling inside a refrigerator for about 90 minutes the solution was filtered. To the filtrate, water, containing about 2% NH₃, was added until precipitation started. The solution was left for about 30 minutes
and filtered. The resulting brown precipitate was washed with water, ether, and dried at 80°C under vacuum. The analytical results are as follows:

Calculated: C, 56.06; H, 6.42; N, 10.22; S, 18.70.
Found: C, 54.75; H, 5.85; N, 10.75; S, 18.49.

Preparation of [(Ph₄As)]₂[Co(QDT)₂]. The same procedure mentioned above was followed with the exception that tetraphenyl arsonium chloride was used instead of n-tetrabutylammonium bromide. The analytical results are as follows:

<table>
<thead>
<tr>
<th></th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calc.:</td>
<td>58.11</td>
<td>3.39</td>
<td>6.78</td>
</tr>
<tr>
<td>Found:</td>
<td>58.00</td>
<td>3.37</td>
<td>5.96</td>
</tr>
</tbody>
</table>

Preparation of [n-Bu₄N]₃[Co(QDT)₃]. 2, 3-quinoxalinedithiol (4.85 g) was added to a solution of sodium methoxide obtained from 2 g metallic sodium in 150 ml of methanol. To the solution 3.02 g of Na₃[Co(CO₃)₃]. 3H₂O was added slowly over a period of 30 minutes with constant stirring. The reaction was run under a nitrogen atmosphere at room temperature. Na₃[Co(CO₃)₃]. 3H₂O was prepared as described in the literature. The solution was filtered and 8.06 g of n-Bu₄N⁺Br⁻ was added to the solution. Water, containing about 1% NH₃, was added slowly and left over night. The orange colored crystalline precipitate was

---

recrystallized from methanol and water under nitrogen. The product was filtered and dried at 60°C under vacuum for 12 hours. The analytical results are as follows:

Calculated: C, 63.48; H, 8.82; N, 9.26; S, 14.11.

Found: C, 62.40; H, 8.97; N, 9.63; S, 14.84.

Preparation of $[\text{Ph}_4\text{As}]_2[\text{Co}(\text{ODT})_3]$. 2,3-quinoxalinedithiol (2.88g) was added to a solution containing 1.5 g of metallic sodium and 200 ml of ethanol. To a clean filtrate of the above solution 1.20 g of Na$_3$[Co(CO$_3$)$_3$]. 3H$_2$O was added slowly over a period of 30 minutes in air with stirring at 50°C. The resulting solution was filtered and 6.0 g of Ph$_4$As$^+$Cl$^-$ was added. The solution was concentrated by heating over a steam bath and cooled to 0°C. The tar-like product dissolved in ethanol-methanol mixture (1:1 by volume). The solution was concentrated on the steam bath. About 100 ml of water was added slowly which precipitated a green crystalline substance. The product was left for about an hour at 0°C and then filtered. The product was recrystallized from ethanol-methanol-water mixture and dried under vacuum at 60°C overnight. The analytical results are as follows:

Calculated: C, 61.67; H, 3.71; N, 6.00; S, 13.70.

Found: C, 61.70; H, 3.76; N, 5.73; S, 12.99.
Discussion

Analytical and Conductance Data. Carbon, hydrogen, nitrogen and sulfur analysis of the complexes and the conductance data given in Table XI suggest the above formulations for the compounds. It might appear at the first glance that the conductances are lower than expected. The data agree with the conductances of large cations where the mobility has been decreased. The conductance of a salt depends on the number, the charges and the sizes of the ions.

The \([\text{C}_6\text{H}_5\text{As}]_2\text{[Co(QDT)_3]}\) complex is the first example of a tris-dianion complex of cobalt dithiolenes. The existence of this species was reported by McCleverty et. al., mainly from their polarographic data of the tris-trianion cobalt maleonitrile dithiolene complex. Attempted isolation of the corresponding dianion by oxidizing the tri-anion led to the dimeric dianion.\(^2\) The tris-cobalt MNT complex is fairly stable in certain solvents like DME or dichloromethane. Dilute solutions, particularly, in acetone were very unstable and only salts of \([\text{Co(MNT)}_2]^-\) could be isolated from these solutions.\(^2\)

The tris-dianion complex isolated here is characterized mainly from the analytical, conductance and magnetic properties. For the purpose of comparison, the calculated

TABLE XI

PHYSICAL PROPERTIES OF COBALT DITHIOLENES

<table>
<thead>
<tr>
<th>Complex&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Color</th>
<th>Melting Point</th>
<th>Ω&lt;sup&gt;b&lt;/sup&gt;</th>
<th>E&lt;sub&gt;1/2&lt;/sub&gt;&lt;sup&gt;V&lt;/sup&gt;</th>
<th>µ&lt;sub&gt;eff&lt;/sub&gt;, B.M.</th>
</tr>
</thead>
<tbody>
<tr>
<td>R&lt;sub&gt;2&lt;/sub&gt;[Co(QDT)&lt;sub&gt;2&lt;/sub&gt;]</td>
<td>Black</td>
<td>115 (dec)</td>
<td>127</td>
<td>-0.33(DMSO)</td>
<td>2.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>+0.125(CH&lt;sub&gt;3&lt;/sub&gt;CN)</td>
<td></td>
</tr>
<tr>
<td>R'&lt;sub&gt;2&lt;/sub&gt;[Co(QDT)&lt;sub&gt;2&lt;/sub&gt;]&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Brown</td>
<td>145 (dec)</td>
<td>89</td>
<td>----</td>
<td>2.02/Co</td>
</tr>
<tr>
<td>R&lt;sub&gt;2&lt;/sub&gt;[Co(QDT)&lt;sub&gt;2&lt;/sub&gt;]&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Brown</td>
<td>162 (dec)</td>
<td>91&lt;sup&gt;c&lt;/sup&gt;</td>
<td>+0.40(CH&lt;sub&gt;3&lt;/sub&gt;CN)</td>
<td>1.96/Co</td>
</tr>
<tr>
<td>R&lt;sub&gt;3&lt;/sub&gt;[Co(QDT)&lt;sub&gt;3&lt;/sub&gt;]</td>
<td>Orange</td>
<td>198-9</td>
<td>159</td>
<td>+0.56(DMSO)</td>
<td>Diamagnetic</td>
</tr>
<tr>
<td>R'&lt;sub&gt;2&lt;/sub&gt;[Co(QDT)&lt;sub&gt;3&lt;/sub&gt;]</td>
<td>Green</td>
<td>250</td>
<td>89&lt;sup&gt;c&lt;/sup&gt;</td>
<td>----</td>
<td>2.15</td>
</tr>
</tbody>
</table>

<sup>a</sup> R represents [n-C<sub>4</sub>H<sub>9</sub>]<sup>4</sup>N<sup>+</sup> in all cases and R' represents [Ph<sub>4</sub>As]<sup>+</sup>

<sup>b</sup> Obtained at room temperature in nitromethane and the results expressed as cm<sup>2</sup>-ohm<sup>-1</sup>-mole<sup>-1</sup>

<sup>c</sup> Results in DMSF
analytical data are shown in Table XII together with the data found.

TABLE XII

ANALYTICAL DATA OF SOME COBALT DITHIOLENES

<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>FORMULA WEIGHT</th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
<th>%S</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R'_2[Co(QDT)_2]$</td>
<td>1209</td>
<td>63.52</td>
<td>3.97</td>
<td>4.63</td>
<td>10.58</td>
</tr>
<tr>
<td>$R'_2[Co(QDT)_2]_2$</td>
<td>1652</td>
<td>58.11</td>
<td>3.39</td>
<td>6.78</td>
<td>15.49</td>
</tr>
<tr>
<td>$R'_3[Co(QDT)_3]$</td>
<td>1784</td>
<td>64.57</td>
<td>4.04</td>
<td>4.71</td>
<td>10.76</td>
</tr>
<tr>
<td>$R'_2[Co(QDT)_3]$</td>
<td>1401</td>
<td>61.67</td>
<td>3.71</td>
<td>6.00</td>
<td>13.70</td>
</tr>
<tr>
<td>FOUND</td>
<td>....</td>
<td>61.70</td>
<td>3.74</td>
<td>5.73</td>
<td>12.44</td>
</tr>
</tbody>
</table>

$R' = [C_6H_{14}As]^+$

Magnetic Moments. The magnetic properties are shown in Table XIII. The magnetic moment (2.40 B.M.) for the tetrabutyl ammonium salt of $Co(QDT)_2^-$ suggest that the complex has a low spin-doublet ground state with one unpaired electron. This agrees with the results found for other dithiolene complexes in a planar matrix. No authentic planar cobalt complex has ever been prepared with a spin-quartet ground state.$^3$

The compound \([n-\text{Bu}_4\text{N}]_3[\text{Co(QDT)}_3]\) is diamagnetic like all other tris cobalt (III) dithiolene complexes and is in agreement with the expectation for a \(d^6\) low-spin system. McCleverty et al.\(^2\) have also found \([\text{Ph}_4\text{P}]_3[\text{Co(MNT)}_3]\) to be diamagnetic in the solid state.

The most unusual magnetic moment observed is that of \([n-\text{Bu}_4\text{N}]_2[\text{Co(QDT)}_2]\). Five independent room temperature measurements gave individual values in the range of 1.96 to 2.00 B.M. per cobalt atom. This could be the first example of a bis cobalt dithiolene compound with this unusual magnetic moment. The previous examples show that only two kinds of magnetic properties are possible\(^4\) for the complexes of the empirical formula \(R[\text{CoI}_2]\)—either a diamagnetic dimeric solid or a monomer with a spin-triplet ground state. No paramagnetism was observed with dimeric species in the solid state and the paramagnetism associated with the monomer corresponds to two unpaired electrons. Davison et al.\(^5\) first reported the diamagnetism of \(R[\text{Co(MNT)}_2]\) and later found the compound to be a dimeric. The x-ray

\[\text{\textsuperscript{4}A. L. Belch, I. G. Dance, and R. H. Holm, J. Am. Soc., 90, 1139 (1968).}\]

\[\text{\textsuperscript{5}A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, Inorg. Chem., 2, 1227 (1963).}\]
TABLE XIII

MAGNETIC PROPERTIES OF CORBAIT DITHIOLENES

<table>
<thead>
<tr>
<th>Complexes</th>
<th>$\chi^M_{\text{Corr}} \times 10^6$ cgs units $^b$</th>
<th>$\mu_{\text{eff; B.M.}} , ^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[n-Bu$_4$N]$_2$[Co(TM$_2$)]$_2$</td>
<td>2440</td>
<td>2.40</td>
</tr>
<tr>
<td>[n-Bu$_4$N]$_2$[Co(NT$_2$)]$_2$</td>
<td>1590$^d$</td>
<td>1.96/Co</td>
</tr>
<tr>
<td>[Ph$_4$As]$_2$[Co(NT$_2$)]$_2$</td>
<td>1755$^d$</td>
<td>2.02/Co</td>
</tr>
<tr>
<td>[n-Bu$_4$N]$_3$[Co(NT$_3$)]$_3$</td>
<td>Diamagnetic</td>
<td></td>
</tr>
<tr>
<td>[Ph$_4$As]$_2$[Co(NT$_3$)]$_3$</td>
<td>1943$^c$</td>
<td>2.15</td>
</tr>
</tbody>
</table>

a. Calculated from the Curie Law $\mu_{\text{eff}} = 2.84(\chi^M_{\text{Corr}} T)^{1/2}$ at room temperature on solids by the Gouy method standardized against Hg[Co(SCN)$_4$]  


c. Accurate susceptibilities measurements were not possible.

d. Based on monomeric unit.
diffraction study of Co(S₄C₆(CF₃)₄ by Enemark and Lipscomb first showed that cobalt complexes of this type could exist in a dimeric form explaining the magnetic properties. Figure 21 may be taken as the prototype for all bisdithiolene dimers based on the availability of all the structural data up to date. The structural data are summarized in the following table, which reveals the close similarity of the coordination polyhedra supporting our structural assumption (Figure 21).

**TABLE XIV**

**STRUCTURAL DATA OF DIMERIC DITHIOLENE COMPLEXES**

<table>
<thead>
<tr>
<th>Distance (Å)</th>
<th>[CoS₄(CF₃)₄]₂⁻</th>
<th>[Co(o-S₂C₆Cl₄)₂]⁻²</th>
<th>[Ni(MNT)₂]⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basal M-S' (av.)</td>
<td>2.16</td>
<td>2.18</td>
<td>2.15</td>
</tr>
<tr>
<td>Apical M-S</td>
<td>2.38</td>
<td>2.40</td>
<td>3.59</td>
</tr>
<tr>
<td>M-S₄ Plane</td>
<td>0.37</td>
<td>0.26</td>
<td>...</td>
</tr>
<tr>
<td>M...M</td>
<td>2.78</td>
<td>3.10</td>
<td>4.40</td>
</tr>
</tbody>
</table>

a. Data from ref. 5
b. Ref. 9
d. Vertical distance of M from S₄ Plane.

---

Figure 21

Idealized structure for the dimeric dithiolenes based on the structures of $[\text{CoS}_4C_4(\text{CF}_3)_4]_2$ and $(\text{n-Bu}_4\text{N})_2[\text{Co}(\text{o-S}_2\text{C}_6\text{Cl}_4)]_2$. 
The first high-spin planar cobalt dithiolene complex was reported by Gray et al.\(^7\) with TDT as the ligand and it was found that this compound \(R[\text{Co}(\text{TDT})_2]\) has a room temperature magnetic moment of 3.18 B.M. with tetrabutylammonium as the cation. This is the only example of a planar cobalt complex with a spin-triplet ground state. The compound obeys the Curie-Weiss relationship with a \(\Theta\) value of 14°. This agrees with the spin-triplet ground state.

Both \([\text{Co(MNT)}_2]^-\) and \([\text{Co}_4\text{S}_4\text{C}_4(\text{CF}_3)_4]^-\) ions are diamagnetic in different salts. This behavior does not prove their dimeric formulation. Diamagnetic monomers \([\text{CoS}_4]^-\) are in principle possible.

The complex \([\text{n-Bu}_4\text{N}]_2[\text{Co}(\text{o-S}_2\text{C}_6\text{Cl}_4)]_2\) is diamagnetic\(^8\) in the solid state. The complex is paramagnetic in cyclohexanone solution (3.14 B.M.) and in THF (3.18 B.M.). This suggests that this dimeric species is broken into monomeric unit in solution.

The monomeric units have spin-triplet ground state, as does the [Co(TDT)₂]⁻ ion.⁹

An x-ray study of cobalt complexes of MMT reported in progress by Davison et al.¹⁰ should further clarify the structure-magnetic relationship of these diamagnetic cobalt species.

The magnetic moment of these cobalt complexes should not drop so much below the spin-only values for the various spin states. The small spin-orbit coupling in the first transition series and the considerable covalency in the metal-ligand bonding should not allow a lowered magnetic moment of this magnitude. Spin-doublet, triplet, and quartet dimers using the formula $\mu_s = \frac{[4(S + 1) S]}{2}$ are then expected to have moments equal to or in excess of 1.73, 2.83, and 3.88 B.M. In terms of monomeric units the values would be 1.23, 2.00, and 2.74 B.M. respectively.

The room temperature moment of 1.96-2.00 B.M. per monomeric unit for solid salt of [Co(QDT)₂]⁻² agrees with the spin-only formula for a spin-triplet dimer state. The complex [n-Bu₄PF₆][Co(TDT)₂] has a magnetic moment of 3.18 B.M. This indicates that there is no magnetic exchange in the TDT complex. On the other

---


hand, the diamagnetism of the corresponding MNT complex indicates that this exchange is strong enough to cause complete demagnetization. In the case of the $[\text{Co} (\text{QDT})_2]^{-2}$ ion, the moment is in between these two extremes. This suggests that the properties of 2,3-quinoxalinedithiol is intermediate to that of MNT and TDT.

The $[\text{Co} (\text{QDT})_3]^{-3}$ ion is a $d^6$ system and is diamagnetic. One-electron oxidation of this species would be expected to lead a product with one unpaired electron. This would be the case whether the oxidation has taken place entirely from the metal or the ligand. The magnetic moment of $[\text{Ph}_4\text{As}]_2[\text{Co} (\text{QDT})_3]$ has been found to be 2.15 B.M. This is in good agreement for a complex with one unpaired electron.

**Electronic Spectra**

The electronic transitions are given in Table XV. There is no detail report of the electronic spectrum of the square-planar Co (II) complexes in the literature. Only a preliminary report has been given by Figgis and Nyholm\textsuperscript{11} concerning the ordering of the energy level of square-planar Co (II) complexes. A simple point charge model was assumed for the ligand systems.

Information about the electronic spectra of cobalt dithiolenes is almost nil. Contradictory data of planar

Co (II) dithiolenes were given by Gray et al. The first two absorptions for the planar complex $[\text{Co(TDT)}_2]^{-1}$ were reported at 9,300 and 11,300 cm$^{-1}$. In a later communication the lowest energy transition for the same species was reported at 15,200 cm$^{-1}$.

For $[\text{Co(TDT)}_2]^{-1}$ the band at 9,300 cm$^{-1}$ ($\varepsilon=58$) and the shoulder at 11,300 cm$^{-1}$ ($\varepsilon=100$) are assigned as d-d transitions. In the compound $[\text{Co(QDT)}_2]^{-2}$ the first absorption occurs at 9,900 cm$^{-1}$ ($\varepsilon=56$). The second band is very well resolved and is found at 11,970 cm$^{-1}$ ($\varepsilon=260$).

From the polarographic evidence it is known that the compound $[\text{Co(QDT)}_2]^{-2}$ ($E_p=-0.33$) is very susceptible to oxidation. Complexes of the type CoL$^2$ undergo oxidation to form CoL$^-$. This species may dimerize to form $[\text{CoL}_2]^2$. Table XV shows that the spectrum of $[\text{Co(QDT)}_2]^{-2}$ is almost identical with that of $[\text{Co(QDT)}_2]^{-2}$. Thus, it is believed that the species $[\text{Co(QDT)}_2]^{-2}$ has been oxidized to $[\text{Co(QDT)}_2]^{-2}$ in the solution and it has been impossible to prevent the oxidation.

Jørgensen$^{13}$ has observed that the first spin-allowed


transition in low-spin square planar Ni (II) complex occurs at about the same energy as the first spin-allowed band in the corresponding low-spin Co(III) complex. This idea holds well with dithiocarbamates$^{14}$, 1,1-dicyanoethylene 2,2-dithiolates (i-MNT complexes) and dithiocxalates$^{15,16}$. Because of the lack of pi-electron delocalization, as shown below, the unusual spectral properties of the dithiolenes are not seen when the ligand is a 1,1-dithiol instead of a 1,2-dithiol, where there is pi-electron delocalization.

However, this prediction does not work$^2$ in the maleonitriledithiol system where the first spin-allowed band in $[\text{Ni(MNT)}_2]^{-2}$ occurs at 11,690 cm$^{-1}$ and $[\text{Co(MNT)}_3]^{-3}$ at 14,930 cm$^{-1}$. The same prediction was made by Fackler


and Coucouvanis for the position of the bands in the spectra of octahedral \((D_3)\) Cr(III) complexes based on the transitions of the Ni (II) complexes. But it also did not work for \([\text{Cr}(\text{MNT})_3]^-\) complexes, where the predicted absorptions were at 12,000 and 16,000 cm\(^{-1}\) but were actually observed at 14,100 and 17,700 cm\(^{-1}\).

The first absorption band observed for \([\text{Co}(\text{QDT})_3]^-\) is a shoulder at 16,800 cm\(^{-1}\) \((\varepsilon=70)\) and the second band is well resolved at 20,000 cm\(^{-1}\) \((\varepsilon=863)\). The only two absorptions reported for \([\text{Co}(\text{MNT})_3]^-\) were at 14,900 cm\(^{-1}\) \((\varepsilon=1,100)\) and 21,500 cm\(^{-1}\) \((\varepsilon=6800)\).

**Infrared Spectra**

The infrared spectra of the complexes are given in Table XVI. The infrared spectra of the dithiol derivatives of quinoline and quinoxaline types of compounds are very complicated, and have been discussed in Chapter II. The infrared spectra of these complexes do not help very much in coming to any conclusions.

---

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Wavelengths (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{n-Bu}_4\text{N})_2[\text{Co(QDT)}_2])_a</td>
<td>9850(40)</td>
</tr>
<tr>
<td></td>
<td>11,970(295)</td>
</tr>
<tr>
<td></td>
<td>14,970(18,500)</td>
</tr>
<tr>
<td></td>
<td>20,400(28000)</td>
</tr>
<tr>
<td></td>
<td>21,740(28,000)</td>
</tr>
<tr>
<td></td>
<td>27,020(68,000)</td>
</tr>
<tr>
<td></td>
<td>37,040(55,000)</td>
</tr>
</tbody>
</table>

\[n\text{-Bu}_4\text{N}]_3[\text{Co(QDT)}_3]_b
- 16,800(70) sh.
- 20,000(863)
- 24,690(72,500)
- 26,310(53,750)

\[\text{Ph}_4\text{As}]_2[\text{Co(QDT)}_2]\_]a
- 9,900(56)
- 11,970(260)
- 14,970(4,250)
- 20,490(13,625)
- 21,740(7,500)
- 27,020(33,750)
- 37,040(58,750)

\[\text{Ph}_4\text{PMe}]_3[\text{Co(MNT)}_3]c
- 14,900 (1,100)
- 21,500 (6,800)

---

a. run in DMF.
b. run in acetonitrile.
c. data taken from ref. 2.
TABLE XVI
PRINCIPAL INFRARED BANDS OBSERVED FOR COMPLEXES PREPARED IN THIS WORK ON KBr WAFERS

<table>
<thead>
<tr>
<th>Complex</th>
<th>Bands</th>
</tr>
</thead>
<tbody>
<tr>
<td>((n\text{-Bu}_4\text{N})_2\text{[Co(QDT)_2]})</td>
<td>2955(s), 2865(s), 1600(b), 1545(w), 1470(s), 1355(s), 1250(s), 1160(s), 1115(s), 1050(w), 1005(w), 870(w), 785(w), 745(s), 590(s), 420(w), 340(m).</td>
</tr>
<tr>
<td>((n\text{-Bu}_4\text{N})_2\text{[Co(QDT)_2]}_2)</td>
<td>2955(m), 2865(s), 1600(m), 1580(m), 1540(w), 1470(s), 1440(m), 1400(s), 1355(s), 1250(s), 1155(s), 1120(s), 585(s), 420(w), 340(m).</td>
</tr>
<tr>
<td>((n\text{-Bu}_4\text{N})_3\text{[Co(QDT)_3]})</td>
<td>2955(s), 2870(s), 1600(b), 1475(s), 1355(s), 1250(s), 1220(m), 1155(s), 1100(s), 1005(s), 870(w), 785(w), 750(s), 650(m), 590(m), 410(m), 385(s), 370(m), 340(s), 320(m), 305(m), 290(m), 255(m), 230(m).</td>
</tr>
<tr>
<td>((\text{Ph}_4\text{As})_2\text{[Co(QDT)_3]})</td>
<td>1950(w), 1970(w), 1600(b), 1560(w), 1465(m), 1450(w), 1425(s), 1370(w), 1380(w), 1340(s), 1240(s), 1165(w), 1145(s), 1120(m), 1100(s), 1065(m), 980(s), 770(m), 740(s), 730(s), 670(s), 635(w), 580(s), 460(s), 445(s), 395(m), 375(m), 330(s), 275(m), 240(m).</td>
</tr>
</tbody>
</table>

s = strong; m = medium; w = weak; b = broad.
CHAPTER IV

CONCLUSION

A series of new planar complexes with the dianion of 2,3-quinoxalinedithiol ligand (QDT) has been prepared. The complexes have the general formula \( [M(\text{QDT})_2]^{-2} \), where \( M = \text{Ni, Cu, Zn, Pd and Pt} \), and \( z = 2 \) and \( M = \text{Cu} \) where \( z = 1 \). The complexes have been characterized from the study of their analyses, magnetic moment, conductance, polarograms, electron spin resonance spectra, and electronic spectra, and compared with the available data on the corresponding maleonitriledithiolene (MNT) and toluene-3,4-dithiolene (TDT) complexes.

The oxidative stability of \( [M(\text{MNT})_2]^{-2} \) where \( M = \text{Ni, Pd and Pt} \) was found as follows: \( \text{Ni}(\text{MNT})_2^{-2} < \text{Pd}(\text{MNT})_2^{-2} < \text{Pt}(\text{MNT})_2^{-2} \). The same trend is observed in the corresponding QDT complexes, i.e., \( \text{Ni}(\text{QDT})_2^{-2} < \text{Pd}(\text{QDT})_2^{-2} < \text{Pt}(\text{QDT})_2^{-2} \). The trend in oxidative stability with these two ligands is found opposite in going from Ni to Cu. For example, the stability of \( \text{Cu}(\text{MNT})_2^{-2} \) was found greater than \( \text{Ni}(\text{MNT})_2^{-2} \), but the stability of \( \text{Ni}(\text{QDT})_2^{-2} \) is greater than \( \text{Cu}(\text{QDT})_2^{-2} \).

Also, in the series \( \text{NiL}_2^{-2} \) where \( L = \text{MNT, QDT or TDT} \) the order of stability is found as follows:

\[
\text{Ni}(\text{MNT})_2^{-2} > \text{Ni}(\text{QDT})_2^{-2} > \text{Ni}(\text{TDT})_2^{-2}.
\]
From polarographic experiments it is found that these complexes undergo electron transfer reactions. One of these electron transfer products, $\text{Cu(QDT)}_2^{-1}$, was isolated in an analytically pure form and characterized. Indications of electron transfer reactions in the series $\text{M(QDT)}_2^{-2}$, where $\text{M} = \text{Ni, Pd and Pt}$, were obtained polarographically but analytically pure compounds could not be isolated.

The energy of the first d-d transition in the electronic spectra of the group $\text{M(QDT)}_2^{-2}$ follows the same order as that of $\text{M(MNT)}_2^{-2}$ where $\text{M} = \text{Ni, Pd and Pt}$, i.e., $\text{NiL}_2^{-2} \langle \text{PdL}_2^{-2} \rangle \text{PtL}_2^{-2}$.

The singlet diamagnetic species $\text{Cu(QDT)}_2^{-1}$, isolated in this investigation, is one of the very few examples of planar copper complexes in this unusual magnetic state.

The electron spin resonance spectra of $\text{Cu(QDT)}_2^{-2}$ demonstrates that the bonding is through sulfur and not mixed mode.

Another series of 2,3-quinoxalinedithiolene complexes studied in this investigation is with cobalt. These are $\text{R}_2[\text{Co(QDT)}_2]$, $\text{R}_2[\text{Co(QDT)}_2]_2$, $\text{R}_2'[\text{Co(QDT)}_2]_2$, $\text{R}_3[\text{Co(QDT)}_3]$ and $\text{R}_2'[\text{Co(QDT)}_3]$ where $\text{R} = \text{n-Bu}_4\text{N}^+$ and $\text{R}' = \text{Ph}_4\text{As}^+$ ions.
The magnetic behavior of \( \text{Co(QDT)}_2^{-2} \) ion shows once again the lack of an authentic spin-quartet \( d^7 \) planar system. A spin-quartet \( d^7 \) planar system was theoretically predicted by Cotton and Holm to be possible with a ligand of very low ligand field strength.

The order of oxidative stability of \( \text{CoL}_2^{-2} \) follows the same order as the corresponding Ni complexes, i.e., \( \text{Co(MNT)}_2^{-2} > \text{Co(QDT)}_2^{-2} > \text{Co(TDT)}_2^{-2} \).

The complex claimed to be \( \text{K}_2[\text{Co(QDT)}_2] \) in this investigation has solid state magnetic moment of 1.96-200 B.M. at room temperature. Extensive study of the magnetic properties of this complex needs to be done before definite conclusion of its ground state configuration.

The electronic spectra of this complex shows absorption comparable to the corresponding TDT complex.

The complex \( \text{R}_2[\text{Co(QDT)}_3] \) is found to be diamagnetic. This is what one expects to be for a \( d^6 \) low-spin compound. The major spectral bands of this complex is comparable to the corresponding MNT complex.

The complex \( \text{R}_2[\text{Co(QDT)}_3] \) is the first example of a tris dianion complex of cobalt dithiolenes. Existence of this species was reported by McCleverty et. al. from polarographic experiment on the tris cobalt MNT complex, \( \text{Co(MNT)}_3^{-3} \).
The magnetic moment of 2.15 B.M. on solids of $R_2[Co(QDT)_3]$ is in agreement with one unpaired electron.

A summary of the chemical reactions of this ligand with metal ions is shown in Figure 22, together with some other possibilities.

The results of this investigation show that the ligands are playing a vital role in the electronic properties of these dithiolene complexes. From all the evidences it seems that the properties of 2,3-quinoxaline-dithiol is in-between MNT and TDT.
Figure 22

Summary and possibility of some chemical reactions of 2,3-quinoxalinedithiolenes.
BIBLIOGRAPHY

Books


Articles


