OXOVANADIUM(IV) COMPLEXES OF SUBSTITUTED N-(2-THIOPHENYL)SALICYLIDENEIMINE

APPROVED:

L. J. Theriot

Major Professor

Benny R. Russell

Minor Professor

C. G. Skinner

Chairman of the Department of Chemistry

Robert B. Toulouse

Dean of the Graduate School

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THESIS

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

For the Degree of

MASTER OF SCIENCE

BY

Cheng Chang Lee, B. S.
Denton, Texas
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CHAPTER I

INTRODUCTION

Metal complexes of Schiff Bases have occupied a central role in the development of coordination chemistry[1]. A tremendous variety of stable chemical species have been synthesized containing both transition and non-transition metals and numerous ligand systems. Schiff bases are condensed from a primary amine and an active carbonyl group. They always have the azomethine group (-RHC=N-). Usually the stable complexes are formed by coordinating the donating atom, such as -O, N, S of the Schiff bases. This forms a five or six membered chelate ring. As the detailed structure of ligands often influences the properties of the metal complex, many stereochemical, spectral, and magnetic changes in the salicylaldimine complexes may be due to the structural change of the ligands.

The most common structures of metal complexes of salicylaldimines are either (I) or (II). There is another cate-

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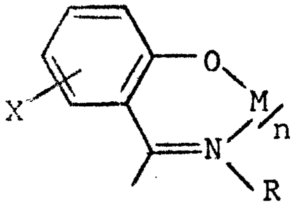
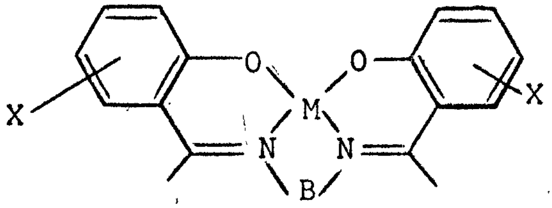
[1] F. A. Cotton, Ed., "Progress in Inorganic Chemistry," Vol. 7, Interscience Publishers, New York, N. Y., 1966, pp. 83-214.



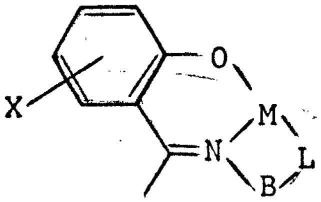
(I)



(II)

X = ring or substituents.
B = bridging group.
R = alkyl or aryl.

gory of complexes with the structure (III). Complexes of the type (III) have not been investigated thoroughly. The vacant



(III)

coordination position of complexes (III) can be filled by a solvent molecule or by bridging donor atoms in binuclear complexes. In most cases L is O, N, or S.

The salicylaldimines complexes of most first row transition elements, especially copper, have received significant attention. Co(II) and Co(III) complexes with salicylaldimines are well established. Copper (II) complexes of salicylaldimines with the structures (I), (II), and (III) have been reported.[1] The complexes of types of (I) and (II) are usually planar and have a magnetic moment from 1.7 to 2.2 BM. (BM is a unit of magnetic moments, and defined in terms of fundamental constants as $1\text{BM} = \frac{eh}{4\pi mc.}$) Copper (II) is a d^9 system and has one unpaired 3d electron. The spin magnetic moment of electrons is calculated by using

$$\mu_S = g[S(S+1)]^{1/2}$$

where μ_S is the spin only magnetic moment, S is the total spin angular moment and g is the gyromagnetic ratio. For the free electron, g has the value 2.00023, which may be taken as 2.00 for most purposes. The spin only magnetic moment for one unpaired electron is 1.73 BM. However in the case of copper, there is some spin-orbital interaction. The effective magnetic moments of copper complexes are almost always higher than the spin only value. If monomeric copper complexes of type (III) are formed with a solvent molecule occupying the fourth coordinating position the magnetic moment corresponding to one unpaired electron is expected. However in many cases, the copper complexes of type (III) undergo dimerization to form binuclear structures of type (IV)[2,3] giving subnormal magnetic moments. The actual moment will

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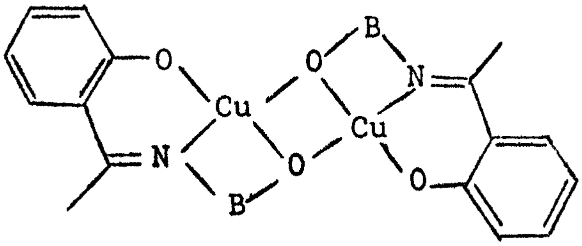
[2] M. Kishita, Y. Muto, and M. Kubo, Australian J. Chem., 10, 386 (1957).

[3] G. Barcley, C. M. Harris, B. F. Hoskins, and E. Kokot, Prac. Chem. Soc., 264 (1961).

will depend on the nature of B.



(IV)

In the majority of coordination compounds, the bulky diamagnetic ligands surrounding the transition metal ion keep the paramagnetic centers well separated and provide magnetic dilution and therefore there is no interaction between central metal paramagnetic centers. However, in some complexes such as the complexes of type (IV), the paramagnetic centers in the molecule interact directly or by means through the donating atom and lead to ferromagnetism and antiferromagnetism. In ferromagnetism the energy level corresponding to parallel spins lies lowest. In antiferromagnetism, which is of concern in a later chapter, the energy level corresponding to the singlet state lies lowest.[4]

Tetravalent vanadium has the ground state configuration, Ar[$3d^1$] and therefore resembles Cu(II) ion magnetically in that each contains one unpaired 3d electron; however, they differ in the degree of orbital contribution to the magnetic

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[4] J. Lewis and R. G. Wilkins, Eds., "Modern Coordination Chemistry," Interscience Publishers, New York, N. Y., 1960.

moment. There is no significant spin-orbital interaction in the tetravalent vanadium and the orbital component of the magnetic moment of tetravalent vanadium is almost completely absent.

Vanadium (IV), an important oxidation state of vanadium, is the most stable one under ordinary conditions. Aside from a few halo-compounds, the chemistry of V(IV) is mostly that of oxovanadium (IV).[5]

The chemistry of oxovanadium (IV) species, VO^{2+}, has become interesting recently. This is because the VO^{2+} ion is perhaps the most stable and persistent diatomic cation available for research. It forms hundreds of stable anionic, cationic, or neutral complexes. The VO^{2+} entity maintains a discrete discernable existence in each complex and in each phase. X-ray diffraction studies of the solid compounds of $VOSO_4 \cdot 5H_2O$[6] and $VO(acac)_2$[7] clearly support the existance of the VO^{2+} entity in these solid complexes. Faltham[8] found that the vanadium (IV) ion in aqueous solutions is $VO^{2+} \cdot nH_2O$ based on its visible and electron spin resonance spectra

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[5] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, New York, N. Y., 1966, p. 815.

[6] G. Lundgren, Rec. Trav. Chim., 75, 585 (1956).

[7] R. P. Dodge, D. H. Templeton, and A. Zalkin, J. Chem. Phys., 35, 55 (1961).

[8] R. D. Feltham, Thesis, University of California, UCRL-3867 (1957).

which are very similar to those of the solid five coordinated vanadyl complexes and quite different from those of the more symmetric VCl_4 and six coordinated chelates. The complexes may, depending on the ligand, be either penta- or hexa-coordinate.[9] From a theoretical point of view the stable VO^{2+} having a single electron outside of a closed shell is a very good model for study. On the contrary, the other d^1 systems: (Ti, Zr, Hf, Th) (III), (Nb, Ta, Pa) (IV), (Cr, Mo, W, U) (V), (Mn, Tc, Re) (VI) and (Ru, Os) (VII), are all much less stable and less common species and, except for Ti(III) and Mo(V), form very few compounds amenable to detailed and facile investigation.[10]

One of the very significant features of vanadyl, oxovanadium (IV) complexes is that the VO bond can be regarded as multiple bonds, the π component arising from flow of electron density $O_{(p\pi)} \rightarrow V_{(d\pi)}$[5]. The penta-coordinate complexes have been shown to take up a sixth ligand quite readily,[11] becoming octahedral, with donors such as pyridine or triphenylphosphine. The metal-oxygen multiple bonds can be studied by infrared bands. $(VO)^{2+}$ has very strong and sharp

---

[9] J. Selbin and L. H. Holmes, J. Inorg. Nucl. Chem., 24, 1111 (1962).

[10] J. Selbin, Coord. Chem. Rev., 1 (1966) pp. 293-314.

[11] R. L. Carlin and F. A. Walker, J. Amer. Chem. Soc., 87, 2128 (1965).

I. R. bands, generally in the range 960±50 cm^{-1}.[12] These bands are quite sensitive to the nature of the trans ligand, which will determine the electron density on the metal, and in turn affect the acceptor properties of metal toward the ligand. Therefore, it will cause the change of the V-O multiple bond character and the stretching frequency.

According to the information gathered by Barraclough[13] and Selbin[12], it is apparent that the environment of the VO^{2+} entity has a marked effect upon the stretch frequency, and hence upon the force constant and strength of the V-O bond. It can be concluded that the stretching frequency shifts are directly and primarily caused by the ability of pπ-dπ donation from oxygen to metal, which may be written

$$\Delta\nu = -\sigma(L\rightarrow M)-\pi\ (L\rightarrow M)-\pi\ (L\rightarrow M)$$

where it is assumed that the M→L donation is negligible for the d^1 vanadyl and estimated that the relative importance for term 8 : 2 : 1.

Vanadyl complexes with normal magnetic moments are well established. By comparison with the research on Cu(II) complexes with subnormal magnetic moments[14] only few vanadyl com-

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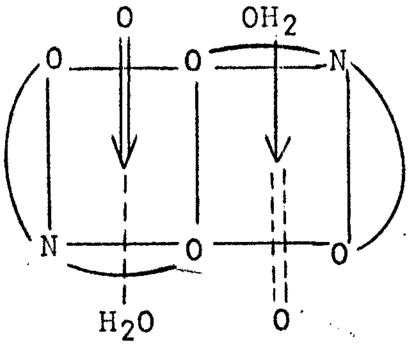
[12] J. Selbin, L. M. Holmes, Jr., and S. P. McGlynn, *J. Inorg. Nucl. Chem.*, *25*, 1359 (1963).

[13] C. G. Barraclough, J. Lewis and R. S. Nyholm, *J. Chem. Soc.*, 3552 (1959).

[14] M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Revs.*, *64*, 99 (1964).

plexes have been reported to have such phenomena. In 1962, Zelentsov synthesized a series of vanadyl complexes with 5-substituted-N-(2-hydroxyphenyl)salicylideneimine having low magnetic moments from 0.77 to 1.55 BM. A structure (V) was suggested to account for the abnormal magnetic moment.[15] Since the unpaired electron in vanadyl complexes is in a d_{xy} orbital,[16,17] the electron has the right symmetry to overlap



(V)

forming a metal-metal bond, which results in a stronger spin coupling and produces antiferromagnetic exchange.

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[15] V. V. Zelentsov, Russ. J. Inorg. Chem., 1, 670 (1962).

[16] C. J. Ballhausen and H. B. Gray, Inorg. Chem., 1, 111 (1962).

[17] D. Kivelson and S. K. Lee, J. Chem. Phys., 41, 1896 (1964).

Recently, Theriot, Carlisle, and Hu[18,19] reported that with N-Salicylideneamino acids (Sal : AA), both paramagnetic complexes with normal magnetic moments, VO(Sal : AA)(H_2O), and a corresponding series of antiferromagnetic complexes, [VO (Sal : AA)(H_2O)] have been synthesized. The dimeric nature of the subnormal magnetic complexes is supported by the demagnetization of the complexes by using pyridine and molecular weight determination of the VO(Sal : L-phenylalanine)(H_2O).

However, this is not the case of square planar Cu(II) complexes, because the unpaired 3d electron is in a d_{x2-y2} orbital.[14] Here the electron does not have the right symmetry for forming a metal-metal bond. A copper (II) complex derived from a Schiff base, acetylacetone-mono(o-hydroxyanil) has been proven by x-ray methods to have an oxygen-bridged dimeric structure. Furthermore a tetrameric structure (VI) was suggested for the acetylacetone-mono(o-hydroxyanil)Cu(II) complex based on magnetic susceptibility data.[20] The structural information suggests that the spin coupling of the Cu(II) complexes must take place through the bridging oxygen

---

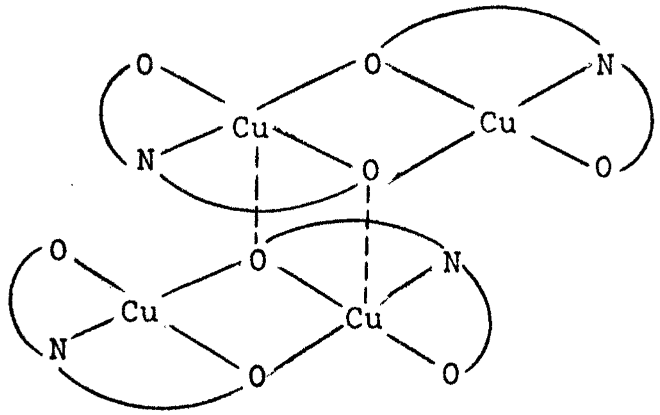
[18] L. J. Theriot, G. O. Carlisle, and H. J. Hu, J. Inorg. Nucl. Chem., 31, 2841 (1969).

[19] L. J. Theriot, G. O. Carlisle, and H. J. Hu, J. Inorg. Nucl. Chem., 31, 3303 (1969).

[20] W. E. Hatfield and G. W. Inman, Jr., Inorg. Chem., 8, 1376 (1969).

atoms, i.e. superchange.[21]

Although metal complexes of Schiff bases derived from



(VI)

substituted salicylaldehyde and o-aminophenol have been studied extensively[2,22,23,24], comparatively little attention has been given to systems in which the Schiff base is derived from substituted salicylaldehyde and 2-aminothiophenol. Muto[23] studied the magnetic susceptibility of tri-coordinated copper (II) with Schiff bases of the N-salicylideneaminothiophenol type and established the interesting fact that the compounds all have effective magnetic moments above 1.73 BM, which are

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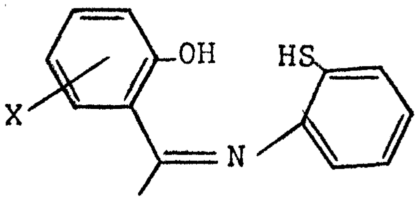
[21] P. W. Anderson, Phys. Rev., 79, 350 (1950).

[22] A. P. Ginsberg, E. Koubek, and H. J. Williams, Inorg. Chem., 4, 1656 (1966).

[23] Y. Muto, Bull. Chem. Soc. Jap., 33, 1242 (1960.

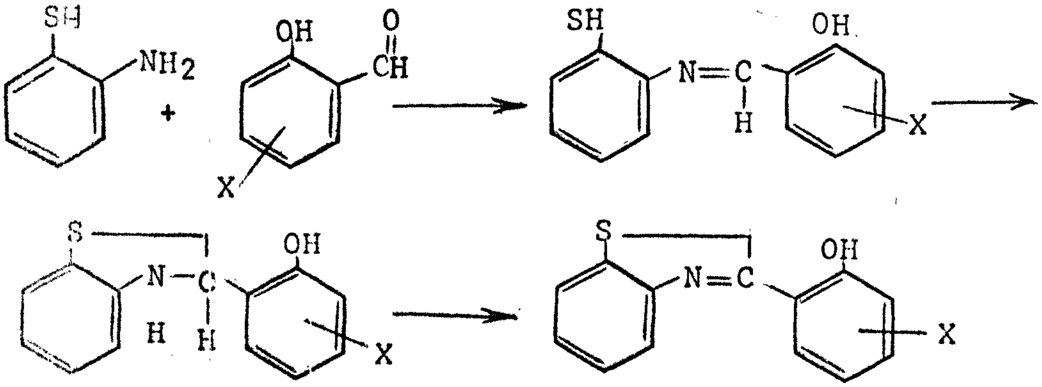
[24] M. Kishita, Y. Muto, and M. Kubo, Austral. J. Chem., 11, 309 (1958).

contrary to those of copper (II) with Schiff bases of the N-(o-hydroxyphenyl)salicylideneimine. The N-salicylideneaminothiophenol Schiff bases are condensed from substituted salicylaldehyde and 2-aminothiophenol. The ligands, abbreviated as (ABC) and shown in figure (VII), are tridentate with ONS donors, which is only one donating atom different from the N-(o-hydroxyphenyl)salicylideneimine type ligands.



(VII)

If the reaction temperature is above 30°C, the ligands (VII) undergo a rearrangement to form thiazoles (VIII). The mechanism of the reaction can be represented as follows:[25]



(VIII)

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[25] M. T. Bogert and A. Stull, J. Am. Chem. Soc., 47, 3078 (1925).

The ligand (VIII) can be used as a monovalent and bidentate chelate ligand coordinating through N and O atoms and is abbreviated as (AB).

In an effort to study the spectral, magnetic, and stereochemical properties of vanadyl complexes, both a new series of vanadyl complexes derived from type (VII) ligands with subnormal magnetic moment and from type (VIII) ligands with normal magnetic moment are synthesized and characterized.

CHAPTER II

FIVE-COORDINATE VANADYL COMPLEXES WITH NORMAL MAGNETIC MOMENT: $VO(AB)_2$ AND VANADYL COMPLEXES WITH ANTIFERROMAGNETIC EXCHANGE: VO(ABC)

Experimental and Results

Reagents

Reagent grade salicylaldehyde and purified reagent grade vanadyl sulfate dihydrate obtained from Fisher Scientific Company, Fair Lawn, New Jersey. The electronic spectrum of vanadyl sulfate dihydrate agreed with that reported in the literature.[1] Ethanol was obtained from U. S. Industrial Chemical Co., New York, N. Y. Vanadyl dichloride was obtained from K. & K. Laboratories, Inc., Plainview, N. Y. 2-Aminothiophenol, 5-chlorosalicylaldehyde, 5-bromosalicylaldehyde, 3-nitrosalicylaldehyde, and 5-nitrosalicylaldehyde were purchased from Eastman Organic Chemicals, Rochester, New York. 5-Chloro-2-mercaptoaniline hydrochloride was obtained from Aldrich Chemical Col, Inc., Milwaukee, Wisconsin. These chemicals were checked by taking melting points and infrared

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[1] C. J. Ballhausen and H. B. Gray, Inorg. Chem., 1, 111 (1962).

spectra[2] and used without further purification. Other chemicals used were all of reagent grade quality.

Preparation of Vanadyl Complexes with Antiferromagnetic Exchange

Preparation of [VO(5-chloro-Sal:2-Aminothiophenol)(H_2O)].--
2-Aminothiophenol (0.01 mole) and 5-chlorosalicylaldehyde (0.01 mole) were added to 20 ml of absolute ethanol. The solution was stirred on a magnetic stirrer for 2 hours. An ice-bath was provided to keep the reaction temperature below 25°C. A crude yellow powder precipitated and was filtered, washed with ethanol, and then dried in vacuum desiccator at 25°C. The Schiff base is a yellow powder (70 per cent yield) obtained and melts sharply at 130°C. 0.005 mole of Schiff base was dissolved in 20 ml of ethanol and 0.005 mole vanadyl dichloride in 5 ml ethanol was added. This mixture was refluxed and stirred magnetically for 12 hours. The greenish yellow precipitates were collected on a filter, washed several times with water, ethanol, ethyl ether, and then dried at 80°C overnight in a vacuum desiccator. The yield is about 70 per cent based on vanadyl dichloride. The compound turns green at 200°C and did not melt at 300°C.

Another method of preparation is to make the complex

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[2] "Sadtler Standard Spectra," Sadtler Research Laboratories, Philadelphia, Pennsylvania.

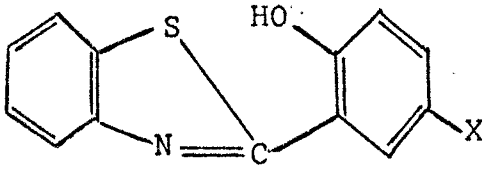
directly without synthesis of a Schiff base. 0.005 mole of 2-aminothiophenol and 0.005 mole of 5-chlorosalicylaldehyde were added to 20 ml ethanol and stirred on a magnetic stirrer for 15 minutes. Then 0.005 mole of vanadyl dichloride in 5 ml ethanol was added dropwise to the solution. After the addition of vanadyl dichloride, the mixture was stirred and refluxed overnight. The resulting product was filtered, washed, and then dried in the same condition as the above.

Vanadyl sulfate dihydrate can be used as a substitute for vanadyl dichloride to react with the Schiff base, or with the 2-aminothiophenol and 5-chlorosalicylaldehyde directly. However, in this case, a weak base such as sodium acetate and an 80 per cent ethanol - 20 per cent water solution is required. The mixture was stirred and refluxed overnight and then the same product could be obtained.

Preparation of [VO(5-bromosal:aminothiophenol)]: -- The Schiff base was made according to the same method described in the above except using 5-bromosalicylaldehyde instead of 5-chlorosalicylaldehyde. 0.01 mole of Schiff base was dissolved in 30 ml anhydrous methanol and filtered. Then 0.01 mole of vanadyl sulfate dihydrate and 0.02 mole of sodium acetate in 5 ml water was added. The mixture was stirred and refluxed overnight. The resulting greenish yellow compound was filtered, washed with water, methanol, and dried. The complex did not melt up to 250°C.

Preparation of Five-coordinated Vanadyl Complexes with Normal Magnetic Moment

The complexes of the series $VO(AB)_2$ were prepared by the following general method: 2-Aminothiophenol (0.01 mole) and 5-substituted salicylaldehyde (0.01 mole) were added to 25 ml absolute ethanol. The solution was stirred on a magnetic stirrer for four hours. In some cases, the solution was heated to 40°C. The crude product was filtered and washed with ethanol to remove unreacted reactants, and then dried in vacuum desiccator at 25°C. These Schiff bases are formed in about 85 per cent yield, are white or pale yellow color. The melting point and analytical data of C, H, and N suggests these Schiff bases are of the following formulation.



Therefore, the compounds serve as monovalent and bidentate ligand. 0.01 mole of Schiff base was dissolved in 25 ml of ethanol and 0.005 mole vanadyl dichloride in 5 ml of ethanol was added. This mixture was refluxed overnight. Finally the greenish yellow powder precipitates were collected on a filter, washed several times with water, ethanol, ethyl ether, and dried at 80°C under vacuum overnight. In some cases, the simple washing process can not remove all the impurities.

Therefore the resulting complexes were boiled with 40:60 per cent water-ethanol solution for several hours. The yield for all the complexes are above 70 per cent.

Vanadyl sulfate dihydrate with a weak base can be used in place of vanadyl dichloride. However, an 80 per cent ethanol - 20 per cent water solution is required.

Analyses of the Complexes

Carbon, hydrogen, and nitrogen analyses were performed by North Texas State University Analytical Services. The analytical results for the five-coordinated complexes with normal magnetic moment are listed in Table I. Table II lists the analytical results of the complexes with antiferromagnetic exchange.

TABLE I

ANALYTICAL DATA FOR $VO(AB)_2$

Complex	Formula	Per cent C		Per cent H		Per cent N	
		Calc.	Found	Calc.	Found	Calc.	Found
VO(Sal:2-Aminothiophenol)$_2$	$C_{26}H_{16}N_2O_3S_2V$	60.1	60.03	3.03	3.05	5.38	5.27
VO(Sal:5-Cl-2-Aminothiophenol)$_2$	$C_{26}H_{14}N_2O_3S_2ClV$	53.1	52.93	2.38	2.39	4.76	4.58
VO(5-Cl-sal:2-Aminothiophenol)$_2$	$C_{26}H_{14}N_2O_3S_2ClV$	53.1	52.66	2.38	2.46	4.77	4.72
VO(5-NO$_2$-sal:2-Aminothiophenol)$_2$	$C_{26}H_{14}N_4O_7S_2V$	51.30	51.40	2.31	2.23	9.20	8.95
VO(3-NO$_2$-sal:2-Aminothiophenol)$_2$	$C_{26}H_{14}N_4O_7S_2V$	51.30	51.28	2.31	2.51	9.20	9.44

TABLE II

ANALYTICAL DATA FOR VO(ABC)

Complex	Formula	Per cent C		Per cent H		Per cent N	
		Calc.	Found	Calc.	Found	Calc.	Found
VO(5-Cl-sal:2-Aminothio-phenyl)(H_2O)	$C_{13}H_{10}NO_3SClV$	45.00	44.38	2.9	2.62	4.05	3.9
VO(5-Br-sal:2-Aminothio-phenyl)	$C_{13}H_8NO_2SBrV$	41.85	41.95	2.16	1.78	3.75	3.58
VO(5-NO_2-sal:2-Aminothio-phenyl)	$C_{13}H_8N_2O_4V$	46.00	45.31	2.35	2.43	8.28	8.78

Carbon, hydrogen, and nitrogen analyses were performed by North Texas State University Analytical Service.

Melting Points

The melting points for the complexes are uncorrected and were determined in sealed tubes using a Thomas Hoover Capillary Melting Point Apparatus. Melting points for all the complexes are above 250°C.

Solubilities of the Complexes

The complexes of the series VO(ABC) and $VO(AB)_2$ are all almost insoluble in water, acetone, ether, chloroform, methanol, ethanol, pyridine, and other common solvents. This prevents the further purification of complexes and makes it very difficult to perform some physical measurements such as electrolytic conductance, molecular weight measurement, and solution spectroscopy.

Electrolytic Conductivities

Electrolytic conductivities were determined in absolute methanol at room temperature on a Model RC 16B2 Conductivity Bridge by Industrial Instruments, Inc. The conductivity cell with platinum electrodes was calibrated with an aqueous potassium chloride solution[3]. There were three complexes soluble enough to an electrolytic conductivity. The concentration of $VO(3\text{-Nitro-sal:2-Aminothiophenol})_2$ was $1 \times 10^{-4}M$, the other

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[3] F. A. Cotton, W. R. Robinson, R. A. Walton, and R. Whyman, Inorg. Chem., 6, 929 (1967).

two were 1 X 10^{-6}M. The molar conductance[4] for the three complexes are given in Table III. For comparison the conductances of 1:1 and 1:2 electrolytes in methanol are also presented in the table.

Magnetic Susceptibilities

The magnetic susceptibilities were measured by using the Gouy method.[5] An Alpha Model 7500 electromagnet equipped with a power supply and current regulator was employed. All magnetic susceptibilities were determined at room temperature at three different field strength roughly corresponding to 6000, 7000, and 8000 gauss. The average results are given in Table IV and V. All the measurements were calibrated by using $HgCo(SCN)_4$ as a standard.[6] The effective magnetic moments

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[4] The calculations of the molar conductances were made according to the equation given in H. H. Willard, L. L. Merritt, Jr., and J. A. Dean, "Instrumental Methods of Analysis," D. Van Nostrand Company, Inc., New York, N. Y., 1958, pp. 568-573. The equation used is $_m = \frac{G \cdot K \cdot 1000}{C}$ where $_m$ is the molar conductance, G is the observed conductance, K is the cell constant, and C is the concentration in moles per liter.

[5] P. W. Selwood, "Magnetochemistry," Interscience Publishers, New York, N. Y., 1956, pp. 3-10.

[6] B. N. Figgis and R. S. Nyholm, J. Chem. Soc., 4190 (1958).

TABLE III

CONDUCTANCE DATA FOR VO(ABC) AND $VO(AB)_2$

	m
Complex	(mho-cm^2, mole^{-1})
VO(5-Br-Sal:2-Aminothiophenol.	0.00
VO(5-Cl-Sal:2-Aminothiophenol)$_2$	0.49
VO(3-NO$_2$-Sal:2-Aminothiophenol)$_2$	0.17
$[(C_2H_5)_4N]Br$	112
$[(C_2H_5)_4N]_2VO(C_4N_2S_2)_2$	165

were calculated by the equation[7]

$$\mu_{eff} = 2.84(\chi_m^{corr} \cdot T)^{1/2}$$

where χ_m^{corr} is the corrected molar susceptibility and T represents the absolute temperature. The molar susceptibilities were corrected for metal and ligand diamagnetisms estimated by using Pascal's constants.[8] The accuracy of these measurements is about 1×10^{-8} cgs units of susceptibility.

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[7] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, New York, N. Y., 1966, p. 640.

[8] B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Eds., Interscience Publishers, New York, N. Y., 1960, p. 403.

TABLE IV

MAGNETIC SUSCEPTIBILITIES AND MAGNETIC MOMENTS FOR VO(ABC)

Complex	Temp. (°K)	X_g	X_m (10^{-6} cgs)	X_m^{corr}	M (BM)
VO(5-Cl-Sal:2-Aminothiophenol)(H_2)	296	1.53	530	698.2	1.28
VO(5-Br-Sal:2-Aminothiophenol)	299.5	1.60	600	750.22	1.34
VO(5-NO_2-Sal:2-Aminothiophenol)	297	1.60	543	675	1.26

The susceptibility and the magnetic moment are per gram-atom of vanadium.

TABLE V

MAGNETIC SUSCEPTIBILITIES AND MAGNETIC MOMENTS FOR $VO(AB)_2$

Complex	Temp. (°K)	X_g	X_m^{uncorr} (10^{-6} cgs)	X_m^{corr}	μ (BM)
$VO(Sal{:}2\text{-Aminothiophenol})_2$	296	2.38	1,230	1,464	1.87
$VO(5\text{-Cl-Sal}{:}2\text{-Aminothiophenol})_2$	297	1.68	931.5	1,266	1.72
$VO(5\text{-}NO_2\text{-Sal}{:}2\text{-Aminothiophenol})_2$	298.5	1.71	1,040	1,298	1.76
$VO(3\text{-}NO_2\text{-Sal}{:}2\text{-Aminothiophenol})_2$	298	1.52	926	1,184	1.69
$VO(Sal{:}2\text{-Amino-4-chlorothiophenol})_2$	297	1.79	1,050	1,335	1.79

The susceptibility and the magnetic moment are per gram-atom of vanadium.

Infrared Spectra

Perkin-Elmer Model 621 was used for recording the infrared spectra from 4000 cm^{-1} to 500 cm^{-1}. Nujol mull and KBr disk techniques were employed. Nujol showed no water bands. The potassium bromide was infrared spectroscopy grade and was dried under vacuum at 120°C for four hours before use. Each spectrum was calibrated with a polystyrene film. The spectrum of VO(5-Cl-Sal:2-Aminothiophenol)(H_2O) in KBr disk is shown in Figure 1. The spectra of the other complexes are very similar and have no water absorption bands.

Electronic Spectra

A Cary Model 14 Recording Spectrophotometer was used to obtain the spectra. As these complexes are almost insoluble, solid spectra were obtained by mulling complexes in nujol as described by Cotton.[9] The spectra were recorded from 4,800 cm^{-1} to 33,300 cm^{-1}. The electronic absorption frequencies for the complexes are listed in Table VI and VII. The mull spectra of VO(5-Cl-Sal:2-Aminothiophenol)(H_2O) and VO(4-Cl-Sal:2-Aminothiophenol)$_2$ are shown in Figure 2.

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[9] F. A. Cotton, J. Amer. Chem. Soc., 83, 4157 (1961).

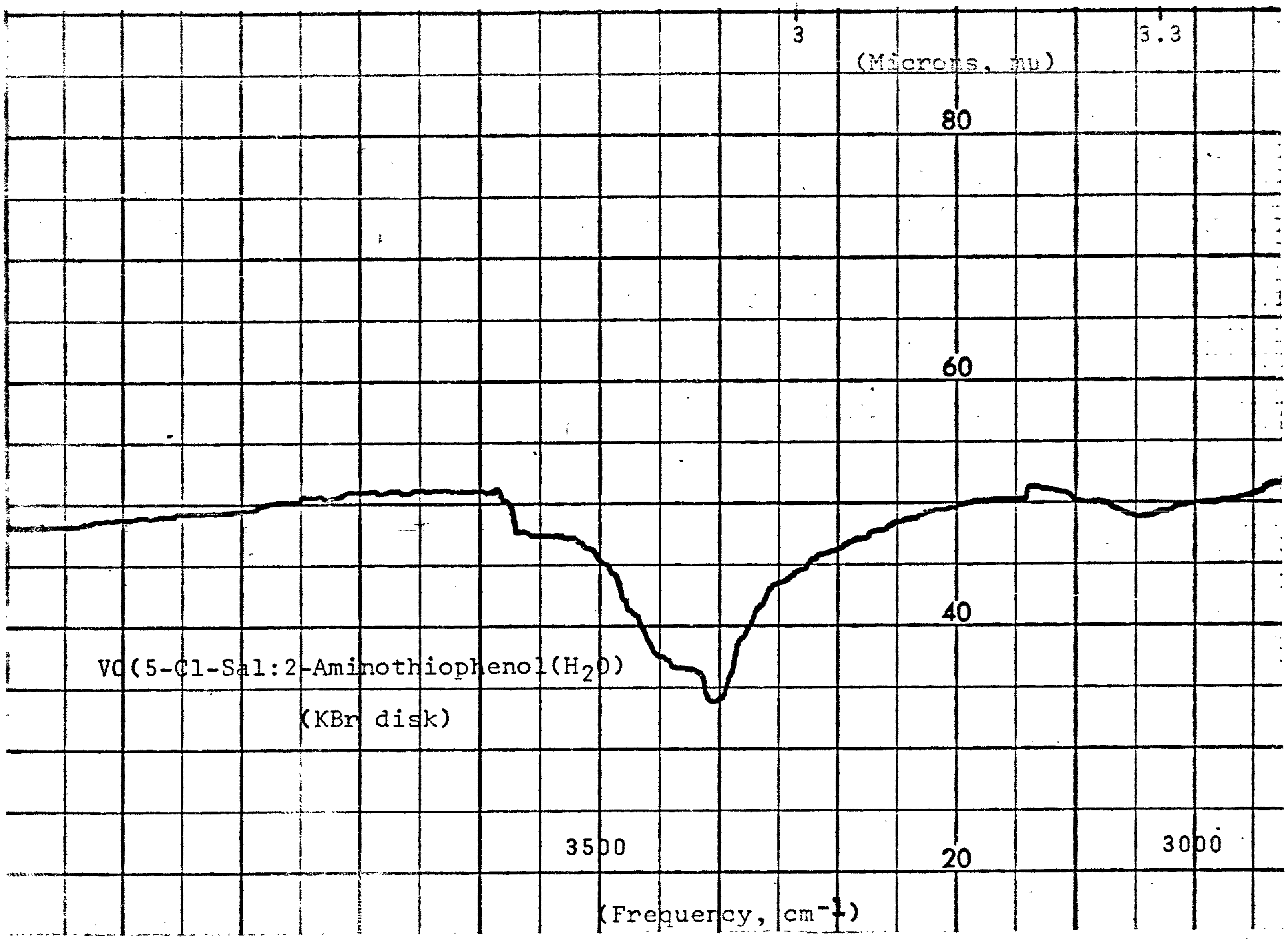


Fig. 1 -- Infrared Spectrum of VO(5-Cl-Sal:2-Aminothiophenol)(H_2O)

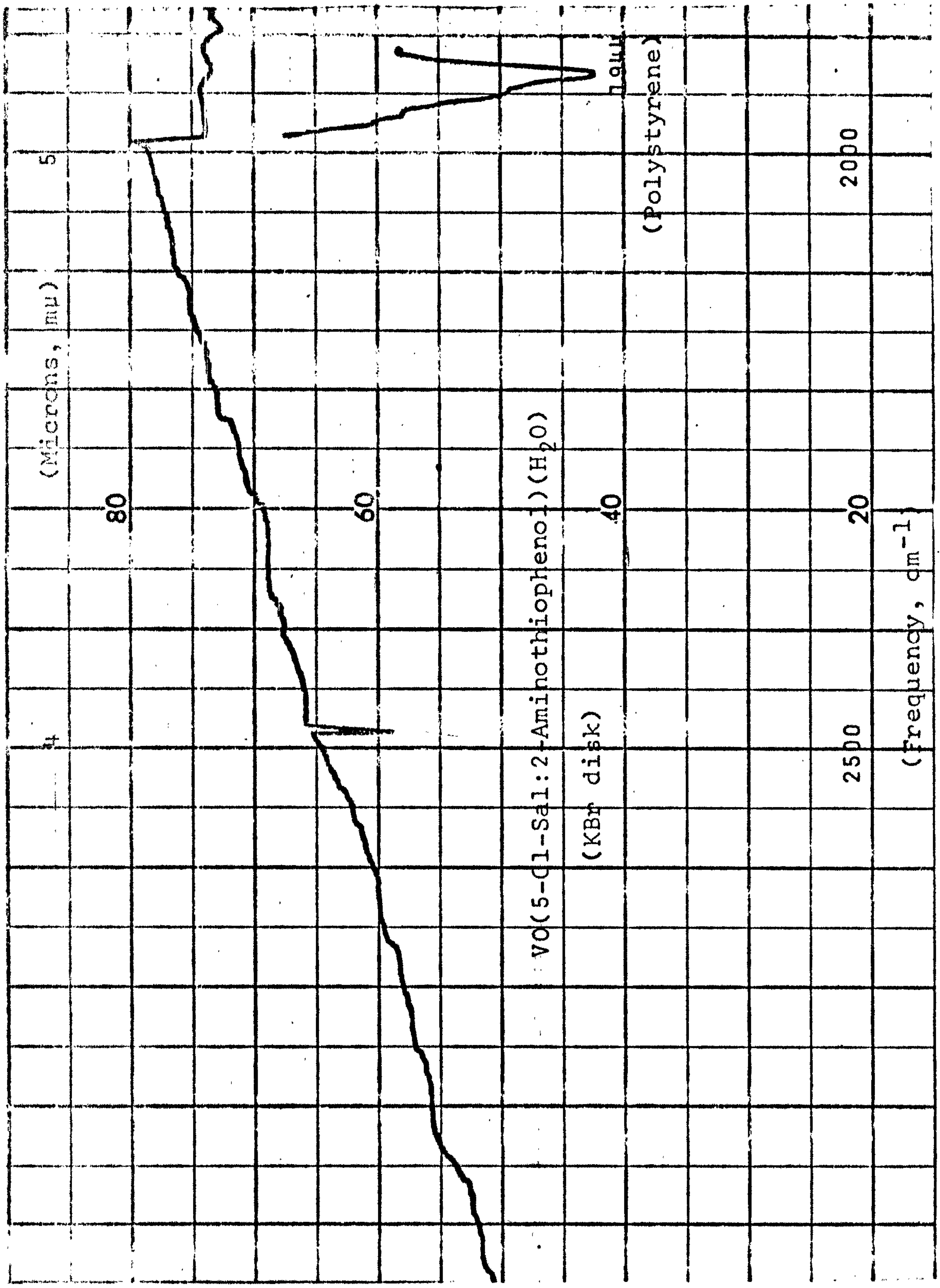


Fig.1 (continued)

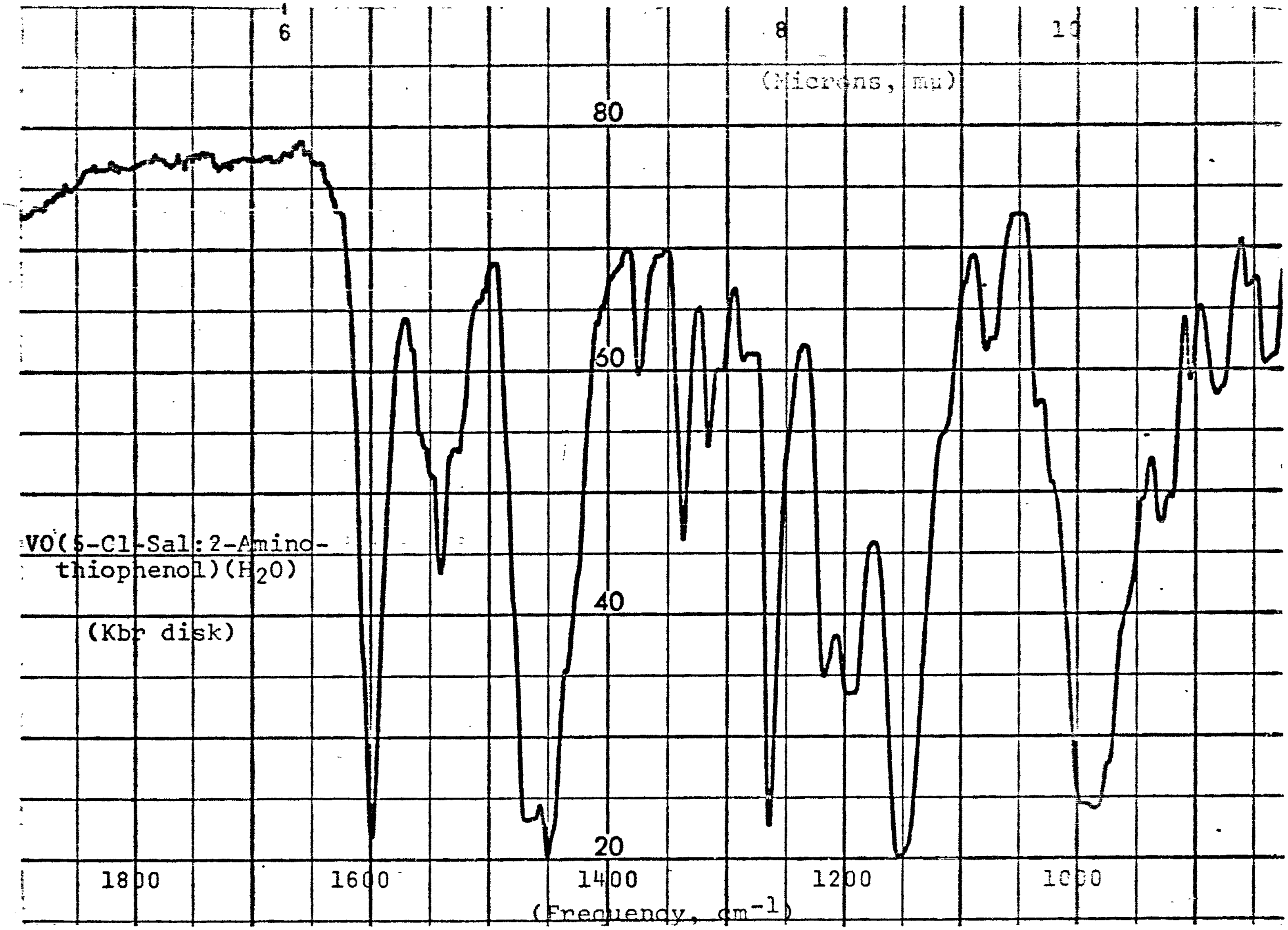


Fig. 1 (continued)

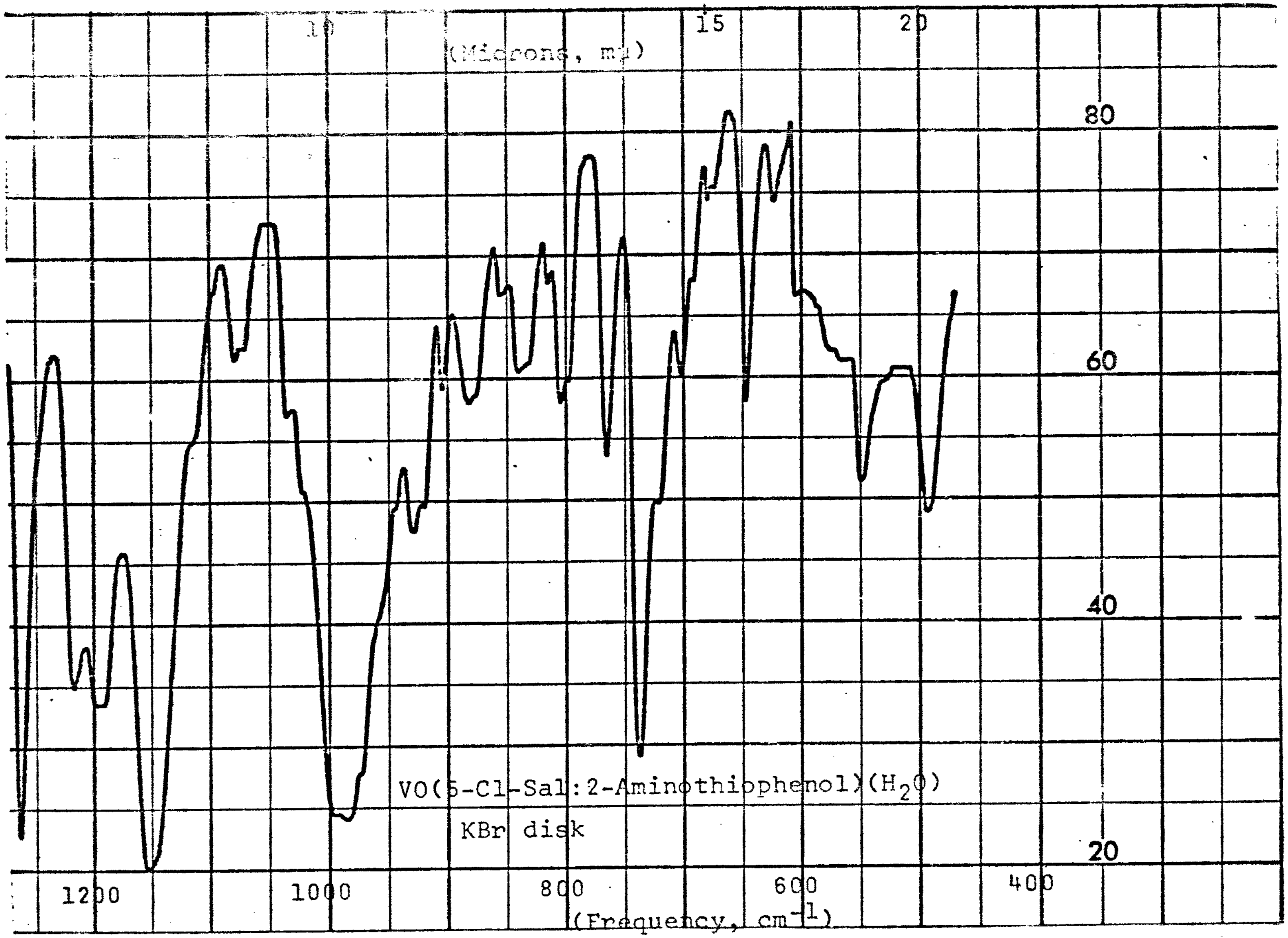


Fig. 1 (continued)

TABLE VI

ELECTRONIC ABSORPTION FREQUENCIES FOR VO(ABC) COMPLEXES

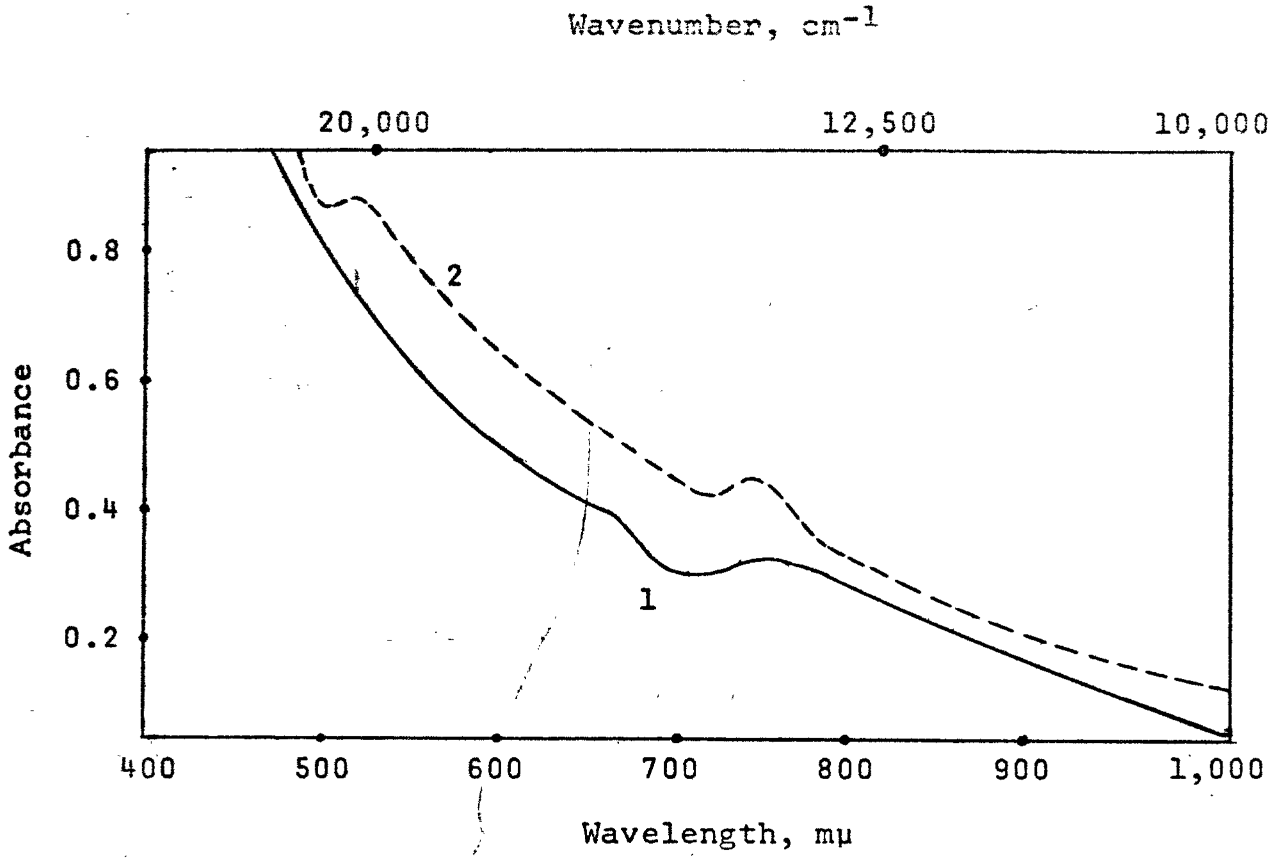
Complex	State	Nujol Mull	
		max (cm^{-1})	max (mμ)
VO(5-Cl-Sal:2-Aminothiophenol)(H_2O)		13300	750
VO(5-NO_2-Sal:2-Aminothiophenol)		14900	670
VO(5-Br-Sal:2-Aminothiophenol)		18200	550

TABLE VII

ELECTRONIC ABSORPTION FREQUENCIES FOR $VO(AB)_2$ COMPLEXES*

Complex	State		Nujol Mull		
		max (cm^{-1})	max (mμ)	max (cm-1)	max (mμ)
$VO(5\text{-}Cl\text{-}Sal{:}2\text{-}Aminothiophenol)_2$		13700	730	18900	530
$VO(5\text{-}NO_2\text{-}Sal{:}2\text{-}Aminothiophenol)_2$		13300	750	17100	585
$VO(3\text{-}NO_2\text{-}Sal{:}2\text{-}Aminothiophenol)_2$		12750	785	17000	590
$VO(Sal{:}2\text{-}Amino\text{-}4\text{-}chlorothiophenol)_2$		13300	750	18500	540
$VO(Sal{:}2\text{-}Aminothiophenol)_2$		14700	680	18200	550

*The charge transfer bands are not included



1--VO(5-Cl-Sal:2-Aminothiophenol)(H_2O) (solid line)

2--VO(5-Cl-Sal:2-Aminothiophenol)$_2$ (dashed line)

Fig. 2--Electronic Spectra in Concentrated nujol mull

Discussion

Magnetic Moments

The magnetic moments and magnetic susceptibilities for the series $VO(AB)_2$ are given in Table V. The value of VO(Sal: 2-Amino-4-chlorothiophenol)$_2$, VO(3-NO_2-Sal:2-Aminothiophenol)$_2$, VO(5-Cl-Sal:Aminothiophenol)$_2$, and VO(5-NO_2-Sal:2-Aminothiophenol)$_2$ are close to the spin-only moment of 1.73 BM for one unpaired electron. This indicates that the orbital contributions in these four complexes are almost quenched as expected because the complexes are in a low ligand field symmetry.[10] The magnetic moment for VO(Sal:2-Aminothiophenol)$_2$ is 1.87 BM, which means that the complex has some orbital contributions.

Magnetic moments and magnetic susceptibilities for the complexes of the series [VO(ABC)] are listed in Table IV. The magnetic moments are from 1.26 to 1.34 BM, which are lower than the normal magnetic moment of one unpaired electron. The corresponding molar susceptibilities are corrected for metal and ligand diamagnetisms, and have values from 675 X 10^{-6} cgs to 750.22 X 10^{-6} cgs per gram vanadium. A small amount of the observed susceptibility can be attributed to temperature independent paramagnetism. The majority of the susceptibility may result from populations of the triplet state.

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[10] J. Selbin, Chem. Revs., 65, 153 (1965).

The temperature independent paramagnetism arises from a coupling of the ground state of a system with the excited states of higher energy under the influence of the applied magnetic field. Temperature independent paramagnetism exists in systems containing unpaired electrons as well as in systems containing no unpaired electrons.[11,12] Temperature independent paramagnetism resembles diamagnetism in the order of 0 to 100 X 10^{-6} cgs per mole for oxovanadium(IV)[13] and is a weak effect.

Subnormal magnetic moment of vanadyl complexes with tridentate ligand have been recently studied. Theriot[14] and Zelentsov[15] have proposed a dimeric structure to interpret the strong antiferromagnetic exchange in the complexes. VO(Sal-L-phenylalanine)(H_2O) has been shown to have a dimeric structure with concentration dependence in benzene.[14] The unpaired electron in vanadyl complexes is in a vanadium d_{xy} orbital.[2,16]

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[11] J. H. van Vleck, "Theory of Electronic and Magnetic Susceptibilities," Oxford University Press, London, 1959, p. 302.

[12] S. Freed and C. Kasper, *J. Amer. Chem. Soc.*, *52*, 4671 (1930).

[13] A. P. Ginsberg, E. Koubek, and H. F. Williams, *Inorg. Chem.*, *5*, 1656 (1966).

[14] L. J. Theriot, G. O. Carlisle, and H. J. Hu, *J. Inorg. Nucl. Chem.*, *31*, 3303 (1969).

[15] V. V. Zelentsov, *Russ. J. Inorg. Chem.*, *7*, 670 (1962).

[16] D. Kivelson and S. K. Lee, *J. Chem. Phys.*, *41*, 1896 (1964).

In the dimeric structure the d_{xy} orbitals have the correct symmetry for sigma overlap with each other and this can result in a strong metal-metal interaction. However in many cases if the separation energy between the excited triplet state and the spin paired singlet state is just a few hundred cm^{-1}, the thermal energy available to the system at room temperature is sufficient to propulate the upper triplet state. This effect results in subnormal magnetic moment.

The distance between two vanadium atoms in the dimeric structure is directly related to the degree of the overlap between the two d_{xy} orbitals. Large V-V distances result in weaker exchange coupling and higher magnetic susceptibility.

Infrared Spectra

The infrared spectra of the complexes of the series VO(ABC) and $VO(AB)_2$ have a very similar pattern except for the absorptions of the different substituents to the phenyl ring and VO(5-Cl-Sal:2-Aminothiophenol)(H_2O) which has a broad water band. The spectrum of the complex VO(5-Cl-Sal:2-Aminothiophenol)(H_2O) is shown in Figure 1. The results from the study of VO(5-Cl-Sal:2-Aminothiophenol)(H_2O) complex also hold for other complexes of the series.

The complex VO(5-Cl-Sal:2-Aminothiophenol)(H_2O) has a broad band with medium intensity at about 3400 cm^{-1}. This band, as well as the analytical data in Table II suggests the existance of a water molecule. Based on a theoretical calculation, Van Vleck and Cross[17] have shown that free water has two stretching modes occurring at 3560 cm^{-1} and 3520 cm^{-1}, whereas coordinated water in aqua complexes absorbs at 3095 cm^{-1} and 3059 cm^{-1}.[18] The lowering of the water stretching modes for VO(5-Cl:Sal:2-Aminothiophenol)(H_2O) to 3400 cm^{-1} suggests that the water exists as coordinated molecules and not simply water of hydration. This is also indicated by drying the complex at 150°C under vacuum for 12 hours. The coordinated water in the complex can not be removed.

VO(5-Cl-Sal:2-Aminothiophenol)(H_2O) has four strong absorption bands in the region 1450 cm^{-1} to 1650 cm^{-1}. These are at 1610 cm^{-1}, 1550 cm^{-1}, 1480 cm^{-1}, and 1460 cm^{-1}. Assignments of these four bands have been a matter of controversy because the skeletal vibrations of benzene ring and the stretching frequency of C=N are in the region 1400 cm^{-1} to 1700 cm^{-1}. According to recent work the band at 1610 cm^{-1} can be assigned to C=N stretching frequency and the bands at 1550 cm^{-1}, 1480 cm^{-1}, and 1460 cm^{-1} can be assigned to the benzene

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[17] J. H. van Vleck and P. C. Cross, J. Chem. Phys., 1, 357 (1933).

[18] G. Sartori, C. Furlani, and A. Damiani, J. Inorg. Nucl. Chem., 8, 119 (1958).

ring skeletal vibrations.[19,20,21]

The C=N stretching frequency of the complexes of the series VO(ABC) and $VO(AB)_2$ are shown in Table VIII. The absorption bands are from 1614 cm^{-1} to 1590 cm^{-1}.

The intensity of the bands at 1275 cm^{-1}, 1230 cm^{-1}, and 1205 cm^{-1} are very strong. This corresponds to the in plane bending absorption bands of the benzene ring.[22]

Generally, aryl chlorides absorb in the 1096-1089 cm^{-1} region.[22] Comparing the infrared spectrum of VO(5-Cl-Sal:2-Aminothiophenol)(H_2O) to that of VO(Sal:L-phenylalanine)(H_2O),[20] it is reasonable to assign the strong absorption at 1160 cm^{-1} to the stretching frequency of C-Cl of VO(5-Cl-Sal:2-Aminothiophenol)(H_2O). The aryl nitro group in the VO(NO_2-Sal:2-Aminothiophenol) and VO(5-NO_2-Sal:2-Aminothiophenol)$_2$ absorbs at 1500 cm^{-1}, 1330 cm^{-1}, and 870 cm^{-1}. However, the aryl nitro group has one more absorption at 730 cm^{-1} in VO(3-NO_2-Sal:2-Aminothiophenol)$_2$ complex. The aryl bromide group in the VO(5-Br-Sal;2-Aminothiophenol)$_2$ complexes has an absorption band around 810 cm^{-1}.

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[19] Teyssie and J. J. Charette, Spectrochim. Acta, 19, 1407 (1963).

[20] H. J. Hu, Ph.D. Dissertation, North Texas State University, Denton, Texas, 1968.

[21] G. O. Carlisle, Ph.D. Dissertation, North Texas State University, Denton, Texas, 1969.

[22] R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds", John Wiley & Sons, Inc., New York, 1968, pp. 82-83.

TABLE VIII

INFRARED ABSORPTION OF C=N FOR THE COMPLEXES OF THE SERIES VO(ABC) AND VO(AB)$_2$

Complex	Frequency (cm^{-1})
VO(5-Cl-Sal:2-Aminothiophenol)(H_2O)	1610
VO(5-Br-Sal:2-Aminothiophenol)	1590
VO(5-NO_2-Sal:2-Aminothiophenol)	1614
VO(Sal:2-Aminothiophenol)$_2$	1600
VO(Sal:2-Amino-4-chlorothiophenol)$_2$	1605
VO(5-Cl-Sal:2-Aminothiophenol)$_2$	1600
VO(5-NO_2-Sal:2-Aminothiophenol)$_2$	1600
VO(3-NO_2-Sal:2-Aminothiophenol)$_2$	1602

The vanadyl complexes have a diagnostic V=O stretching frequency, which is generally found at 960±50 cm^{-1}. The bands are usually very strong and sharp.[23] The strong absorptions at 995 cm^{-1} and 1005 cm^{-1} are the V=O stretching frequency. A list of V=O absorption frequencies for the complexes of the series VO(ABC) and VO)AB)$_2$ is given in Table IX.

A strong band at 750 cm^{-1} and a medium band at 660 cm^{-1} were attributed to out of plane ring bending of the phenyl ring.[22]

A summary of the assignments of the characteristic absorptions for the complexes of the series VO(ABC) and VO(AB)$_2$ is given in Table X.

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[23] J. Selbin, Coord. Chem. Rev., 1, 293 (1966).

TABLE IX

INFRARED ABSORPTION OF V=O FOR THE COMPLEXES OF THE SERIES VO(ABC) AND $VO(AB)_2$

Complex	Frequency (cm^{-1})
VO(5-Cl-Sal:2-Aminothiophenol)(H_2O)	1005, 995
VO(5-Br-Sal:2-Aminothiophenol)	900
VO(5-NO_2-Sal:2-Aminothiophenol)	914, 902
VO(Sal:2-Aminothiophenol)$_2$	914
VO(Sal:2-Amino-4-chlorothiophenol)$_2$	895
VO(5-Cl-Sal:2-Aminothiophenol)$_2$	970, 900
VO(5-NO_2-Sal:2-Aminothiophenol)$_2$	970, 897
VO(3-NO_2-Sal:2-Aminothiophenol)$_2$	920

TABLE X

SUMMARY OF ASSIGNMENTS OF CHARACTERISTIC INFRARED ABSORPTIONS FOR THE COMPLEXES OF THE SERIES VO(ABC) AND $VO(AB)_2$

Assignment	Frequency (cm^{-1})
C=N Stretching	1614-1590 s
phenyl ring, skeletal vibration	1560-1550 s,m
phenyl ring	1500-1480 s
phenyl ring, skeletal vibration	1460-1440 s
phenyl ring, in plane bending	1290-1275 s,m
phenyl ring, in plane bending	1200-1120 s,m
V=O Stretching	1005- 895 s
Aromatic C-H bending	750- 730 s
Aromatic C-H bending	600- 630 m
Metal-chelate ring	550- 400 m

s = strong

m = medium

Electronic Spectra

Several energy level schemes have been proposed for the vanadyl complexes.[2,24,25] A molecular orbital energy diagram derived by Ballhausen and Gray from $VO(H_2O)_5^{2+}$ has been widely accepted and used for interpretation of the electronic spectra of vanadyl complexes. Recently, Vanquickenborne and McGlynn[26] reported a new molecular orbital study by adopting some modifications on the B.G. (Ballhausen and Gray) energy diagram. Five 3d orbitals of oxovanadium(IV) were arranged in VM (Vanquickenborne and McGlynn) energy level diagram as

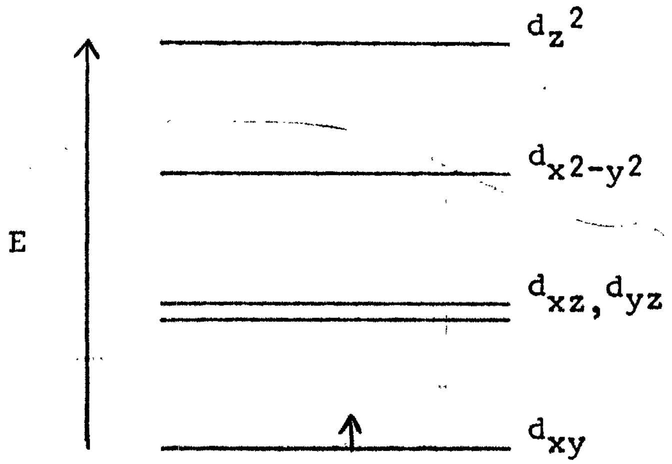

Fig. 3-- VM energy level diagram for 3d orbitals of oxovanadium (IV) in C_{2v} symmetry.

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[24] C. K. Jorgenson, Acta Chem. Scand., 11, 73 (1957).

[25] T. R. Ortolano, J. Selbin, and S. P. McGlynn, J. Chem. Phys., 41, 262 (1964).

[26] L. G. Vanquickenborne and S. P. McGlynn, Theor. Chem. Acta, 9, 390 (1968).

The unpaired 3d electron in $VO(H_2O)_5^{2+}$ is in the d_{xy} orbital. Therefore, three d-d transitions ($d_{xy} \rightarrow d_{xz}, d_{yz}$, $d_{xy} \rightarrow d_{x^2-y^2}$, and $d_{xy} \rightarrow d_{z^2}$) are expected. However, the spectra of $VO(H_2O)_5^{2+}$ shows only two ligand field bands, which were assigned to the first two d-d transitions. The last d-d transition, $d_{xy} \rightarrow d_{z^2}$, was assumed to be buried beneath high intensity charge transfer and ligand bands in the ultraviolet region.[2] This is also the case for most vanadyl complexes.[24]

The electronic absorption frequences for VO(ABC) and $VO(AB)_2$ complexes are summarized in Table VI and Table VII. All complexes follow a similar pattern for their electronic spectra. Figure 2 is the electronic spectra for VO(5-Cl-Sal: 2-Aminothiophenol)(H_2O) and VO(5-Cl-Sal:2-Aminothiophenol)$_2$. These complexes are insoluble in common solvent, only electronic spectra in concentrated nujol mull were taken.

VO(5-Cl-Sal:2-Aminothiophenol)$_2$ complex and its series have two bands at frequencies lower than 20,000 cm^{-1}. These two bands are not well developed and are observed as shoulders. Based on the VM energy level diagram, the bands can be assigned to the $d_{xy} \rightarrow d_{xz}, d_{yz}$ and $d_{xy} \rightarrow d_{x^2-y^2}$ transitions. The last transition, $d_{xy} \rightarrow d_{z^2}$, is assumed to be covered underneath charge transfer bands.

The subnormal magnetic moment VO(5-Cl-Sal:2-Aminothiophenol)(H_2O) complex and its series have only one broad absorption in the middle of the visible region. This spectrum is very similar to that of VO(Sal:Amino acid)(H_2O) complexes[21] and of the diamagnetic copper(II) complex with 1,3-diphenyltriazen.[27]

The VO(ABC) Complexes are insoluble in common solvents, only nujol mull spectra were taken. The only absorption band observed for the complexes of the series VO(ABC) is in the region from 18,200 cm^{-1} to 13,700 cm^{-1}. The band is not well developed and observed as shoulder. The band is lower in energy than that of VO(Sal:Amino acid)(H_2O) complexes. This is expected because the ligand of VO(ABC) complexes is a ONS donor system, which is weaker than the ONO donor system of VO(Sal:Amino acid)(H_2O) complexes.

Composition and Configuration

(A) VO(ABC) Complexes:

The analytical data shown in Table II agree with this formulation. The conductance data indicates that the complexes are nonelectrolytes. Infrared absorptions show the presence of the Schiff base ligand and the VO entity in the complexes. The infrared spectrum showing an absorption at about 3400 cm^{-1} for VO(5-Cl-Sal:2-Aminothiophenol)(H_2O) indicates the existance of coordination water, but the spectra of VO(5-Br-Sal:2-Aminothiophenol) and VO(5-NO_2-Sal:2-Aminothio-

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[27] C. M. Harris, B. F. Hoskins, and R. L. Martin, J. Chem. Soc., 3728 (1959).

phenol) indicate no water in the complexes. All the complexes of the series VO(ABC) have magnetic moments from 1.26 to 1.34 BM, which are less than the magnetic moment of one unpaired electron. This information suggests that there are antiferromagnetic interactions between VO entities. The dimeric structure such as that proposed by Zelentsov[15] for the vanadyl complexes with 5-substituted N-(2-hydroxyphenyl)salicylideneimines and by Hu[21] for the VO(Sal:Amino acid)(H_2O) is favorable. However, the possibility of having a tetrameric or polymeric structure can not be excluded.

(B) VO(AB)$_2$ Complexes:

The analytical data in Table I are in accordance with a five coordinate formula of VO(AB)$_2$. Conductance data tell that the complexes are nonelectrolytes. Infrared spectra also indicate the existance of the Schiff base ligand and VO entity, but no water in the complexes. The magnetic and electronic data agree the complexes to be of oxovanadium (IV) and no antiferromagnetic exchange between this series of complexes.

CHAPTER III

CONCLUSION

Vanadyl complexes of Schiff bases derived from substituted salicylaldehyde and various amines have been studied extensively. Comparatively little work has been done to a system in which the same Schiff base can be coordinating as a tridentate ligand and a bidentate ligand. The complexes with tridentate ligands have subnormal magnetic moments and with bidentate ligands have normal magnetic moment. Two cases of vanadyl complexes with subnormal magnetic moments are known with tridentate ligands. The structures, magnetic exchange mechanism, and spectroscopic properties are still not well understood. Further work in this area is required.

The ligand derived from substitute salicylaldehyde and 2-aminothiophenol have a novelty. They can coordinate as bivalent tridentate ligands, or as monovalent bidentate ligands. The tridentate ligands bond through O, N, and S. The bidentate ligands coordinate through O and N.

Two series of new vanadyl complexes with N-Substituted-salicylideneaminothiophenol have been prepared. The complexes of the series VO(ABC) were prepared with tridentate ligands having subnormal magnetic moments from 1.26 BM to 1.34 BM. The unpaired electron of oxovanadium (IV) is in the d_{xy}-

orbital, so the lowering of the moment is believed to be the overlap between two d_{xy} orbitals from two adjacent VO centers. This magnetic exchange mechanism is different from the case of copper (II) complexes. The complexes have been characterized from the study of their analyses, magnetic susceptibilities, infrared spectra, electrolytic conductivities, and electronic spectra. A dimeric structure providing the correct symmetry for d_{xy}-d_{xy} overlapping is preferable for this series complexes. However, a possibility of having a tetrameric, or a polymeric structure can not be excluded.

VO^{2+} reacts with the bidentate ligands giving a series of five coordinate complexes with a formula as $VO(AB)_2$. They have magnetic moments equal to that of one unpaired electron. The antiferromagnetic exchange does not exist in this series of complexes. From the study of their analyses, magnetic susceptibilities, infrared spectra, conductance, and electronic spectra, a tetragonal pyramidal structure is preferable for $VO(AB)_2$ complexes.

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