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THE LUMINESCENCE OF OXINES AND METAL OXINATES*

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INTRODUCTION

The 8-quinolinols (oxines) and their sulfur and selenium analogs are useful molecules for the evaluation of the dependence of luminescence efficiency upon structure. A wide variety of molecules can be studied as neutral species, anions and cations. Stable metal complexes with diverse central ions may be prepared. Several studies involving these molecules have been reported [1, 2]. In the previous work an increase in the quantum yield of luminescence was observed with a reduction in temperature but quantitative results at low temperature were not obtained. In the present study, the yields were measured at 80°K where dissipative processes with appreciable activation energies were absent. In this way the effect of structure on the radiationless processes from the low vibrational levels of the excited states may be evaluated.

EXPERIMENTAL

The luminescence quantum yields were measured with a spectrofluorometer previously described [3]. The wave length dependence of the monochromator-photomultiplier response was determined by means of a Xenon

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lamp and Bausch and Lomb 250 mm. monochromator combination calibrated by means of a Rhodamine B quantum counter [4] from 3000-5200 Å and a thermopile from 5000-9000 Å. The emission spectra are very broad and the peak maxima quite sensitive to this calibration. Agreement with published data is generally rather good [1], but discrepancies of 8 mμ would not be unexpected.

All quantum yields were measured with 3660 Å excitation and are computed relative to quinine bisulfate in 0.1 N H₂SO₄ ($\Phi = 0.55$). Samples were dissolved in 95% ethanol and the emission spectra determined as a function of temperature. At least three determinations at different concentrations were made for each compound. The removal of air from solutions of 8-quinolinol and the aluminum chelate is without effect upon the quantum yield. Non-degassed samples were used in the remainder of the work.

The free ligands were obtained commercially and recrystallized from ethanol. The purification of the metal chelates is often rather difficult and we obtained quite pure materials from the research group of Drs. H. Freiser and Q. Fernando. Except where noted the bis complexes were thermogravimetrically analyzed and particular care was taken to remove water and "extra" moles of ligand (free or coordinated). The tris chelates were analyzed for nitrogen content.

RESULTS - FREE LIGANDS

Neutral Ligands

The emission spectrum of an 8-quinolinol solution at several temperatures is shown in Fig. 1. At room temperature the very weak fluorescence emission occurs at longer wave lengths than anticipated from the absorption spectrum. As the temperature is reduced this weak

band is somewhat intensified but a band at shorter wave lengths appears. Finally, this higher energy transition, which mirrors the absorption spectrum and resembles the expected fluorescence band, dominates the spectrum. The spectra indicate the presence of two species, one being the "normal" neutral molecule. Absorption bands in the 400-500 m μ region of the spectra of 8-quinolinol, quinoline-8-thiol (thioxine), and quinoline-8-selenol (selenoxine) have been ascribed to zwitter-ions. Support for this interpretation comes from temperature dependence of the O-methyl-8-quinolinol emission spectrum. No zwitter-ions can be formed in this case and the spectrum consists of only one band at all temperatures.

The luminescence yields are listed in Table I. In all cases reported in this paper, when the quantum yield exceeds 0.05 the low temperature limiting yield is reached above 80°K. When the quantum yield is less than 0.05 this limiting yield is not obtained and these smaller yields may be low by as much as 25%.

Typical absorption and emission spectra are shown in Fig. 2.

Anions and Cations

Zwitter-ion formation is not possible in the cationic and anionic species derived from the neutral ligands by proton addition or removal. The fluorescence spectra are more intense at lower temperature but no long wave length band is observed. The band maxima are blue shifted as the temperature is decreased, a phenomenon which may be related to the formation of a rigid glass [6]. In any event the observed behavior is consistent with the presence of only one species in solutions of these ions and is consistent with zwitter-ion interpretation discussed above.

In all cases attempts to observe phosphorescence were unsuccessful.

Comparison of the quantum yields of the neutral molecules with those of the anions and cations (Tables II and III) reveals no apparent pattern. In some cases protonation reduces the yield while in others an increase is observed. In only one case, 2-methyl-8-quinoline, does removal of a proton reduce the quantum yield.

RESULTS - METAL COMPLEXES

The results obtained for a number of metal complexes with various 8-quinolinols are shown in Table IV. The chelation of the oxinate anions with Zn(II) produces only small changes in quantum yields. Thus, the effect of charge is rather small. A pronounced reduction in the thio-oxinate yield accompanies chelation with zinc. The chelation of a transition metal ion results in a very marked diminution of the luminescence yield.

With Pb(oxinate)_2 a second band appears which may be due to ligand phosphorescence.

An interesting phenomenon is observed with the Cr(III) complexes. In Cr(oxinate)_3 only the ${}^2\text{E} \rightarrow {}^4\text{A}_2$ Cr(III) luminescence is present, but in $\text{Cr(5,7-dibromooxinate)}_3$ only ligand fluorescence occurs.

The substitution of sulfur and selenium for the oxygen in oxinate results in a progressive reduction in the luminescence yield.

A surprising dependence of the emission spectrum with excitation wave length (365 and 313 m μ) has been reported for the oxinates of Cu(II), Pb(II), Mg(II), and Cd(II) [1]. We have found no comparable behavior in the carefully purified Cu(oxinate)_2 but a similar wave length effect is observed in the less pure Pb(II), Hg(II) and Cd(II) complexes. However, the relative emission intensities are not the same as those previously observed. The coordination of extra moles of ligand has been observed [7] and this

coordination may perturb the ligand sufficiently to shift the emission maximum from the free ligand position. It is quite clear that the wavelength effect is due to impurities and does not indicate emission from higher excited states.

DISCUSSION

The most striking regularity in the results is the effect of transition metal ions. Thus, the effect of metal ion on the luminescence yield may be small as in the case of Zn(II) or large, e.g., transition metal ions. One characteristic shared by the transition metal ions employed in this work, Mn(II), Cu(II), Ni(II) and Cr(III) is the presence of metal ion energy levels (d-d transitions) below the lowest singlet and triplet levels of the ligands. These provide a pathway for non-radiative removal of the excitation energy.

The absence of Cr(III) ${}^2E \rightarrow {}^4A_2$ emission from Cr(5,7-dibromooxinate)₂ is the one observation that does not fit this explanation. The ${}^2E \rightarrow {}^4A_2$ emission is very weak in Cr(oxinate)₃. The bromination of chromium acetylacetonate reduces the luminescence yield [3]. A comparable effect in Cr(5,7-dibromooxinate)₃ would reduce this metal emission below a detectable level.

TABLE I

Emission of Neutral Ligands at 80°K
(95% Ethanol Solution)

<u>Compounds</u>	<u>$\tilde{\nu}_{\max}(\text{cm}^{-1})$</u>		<u>Φ</u>
	<u>Absorption (300°K)</u>	<u>Emission</u>	
oxine	32,250	23,300	0.28
5-chloroxine	30,300	23,300	0.32
5,7-dichloroxine	30,600	21,300	0.12
5,7-dibromoxine	30,853	23,600	0.062
5,7-diiodoxine	29,650	23,200	0.008
2-methyloxine	32,800	22,500	0.54
4-methyloxine	32,050	21,800	0.25
5-isoquinolinol	30,600	22,600	0.13
O-Me-8-quinolinol		21,750	0.55

TABLE II

Emission of Anions at 80°K

<u>Anion</u>	<u>$\tilde{\nu}_{\text{max}}$ (cm⁻¹)</u>		<u>Φ</u>
	<u>Absorption (300°K)</u>	<u>Emission</u>	
oxinate	27,400	20,600	0.28
5-chlorooxinate	26,300	20,000	0.42
5,7-dichlorooxinate	25,650	20,000	0.42
5,7-dibromooxinate	26,000	20,300	0.39
5,7-diiodooxinate	26,000	20,000	0.034
2-methyloxinate	28,200	20,800	0.36
4-methyloxinate	27,400	21,100	0.50
5-isoquinolinolate	20,400	22,600	0.57
thiooxinate	26,000	18,900	0.023

TABLE III

Emission of Cations at 80°K

$\tilde{\nu}_{\text{max}}$ (cm⁻¹)

<u>Cation</u>	<u>Absorption (300°K)</u>	<u>Emission</u>	<u>Φ</u>
8-quinolinium	27,800	20,800	0.043
5-chloroquinolinium	26,300	19,800	0.026
5,7-dichloroquinolinium	27,050	17,900	0.054
5,7-dibromoquinolinium	26,950	19,500	0.015
5,7-diiodoquinolinium	29,700	20,200	0.008
2-methylquinolinium	29,400	20,800	0.13
4-methylquinolinium	27,600	21,300	0.33
5-isoquinolinium	27,400	22,400	0.54

TABLE IV

Emission of Metal Complexes at 80°K

<u>Chelate</u>	<u>$\bar{\nu}_{\text{max}}$ (cm⁻¹)</u>		<u>Φ</u>
	<u>Absorption (300°K)</u>	<u>Emission</u>	
Zn(oxinate) ₂	26,650	19,900	0.32
Mn(oxinate) ₂	26,050	20,200	0.015
Cu(oxinate) ₂	25,800	21,000	0.012
Cd(oxinate) ₂ ^a	26,650	19,700	0.21
Pb(oxinate) ₂ ^a	26,000	19,900 16,200	0.013 0.005
Hg(oxinate) ₂ ^a	27,050	19,600	0.11
Ni(oxinate) ₂ ^a	26,110	not detected	0.001
Al(oxinate) ₃	26,810	20,490	0.30
Cr(oxinate) ₃	24,690	13,230	0.0033
Zn(5,7-dibromooxinate) ₂	25,000	19,600	0.25
Mn(5,7-dibromooxinate) ₂	25,150	20,500	0.010
Cr(5,7-dibromooxinate) ₃	25,310	20,750	.021
Zn(5,7-diiodooxinate) ₂	24,500	19,500	0.025
Mn(5,7-diiodooxinate) ₂	24,700	21,400	0.005
Zn(2-methyloxinate) ₂	26,450	20,000	0.35
Mn(2-methyloxinate) ₂	26,000	20,100	0.020
Zn(4-methyloxinate) ₂	24,300	20,000	0.45
Mn(4-methyloxinate) ₂	26,000	20,500	0.035
Zn(thiooxinate) ₂	25,300	19,500	0.007
Zn(selenooxinate) ₂	24,700	20,200	0.003

a. May contain some free ligand.

b. $^2E \rightarrow ^4A_2$ Cr(III) emission.

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LEGENDS

Fig. 1 Spectra of 8-quinolinol
(a) 80°K, (b) 180°K, (c) 300°K.

The spectra are not corrected for wave length variation of instrument sensitivity. The relative intensities in different spectra are not meaningful.

Fig. 2 Absorption (300°K) and emission spectra (80°K, corrected) of 8-quinolinol and ions: a and a'-8-quinolinol; b and b', 8-quinolinium cation; c and c'-8-quinolate anion. Neither absorption nor emission intensity differences between spectra are meaningful.

Figure 1

Figure 2