Magnetic and Spectroscopic Studies of some Oxovanadium(IV) Complexes having O = V(O)$_4$ Chromophore

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Three oxovanadium(IV) complexes with bidentate ligands having only oxygen donor atoms, benzohydroxamic acid (Hben), 8-hydroxyquinoline-N-oxide(Hhqno) and picolinic acid-N-oxide(Hpicn) are prepared and magnetic and spectroscopic properties are investigated for the complexes VO(ben)$_2$, VO(hqno)$_2$ and VO(picn)$_2$. Magnetic data together with IR results strongly indicate that dimeric intermolecular interaction is significant in VO(ben)$_2$ while the presence of polymeric V-O··V-O interaction is suggestive in VO(picn)$_2$. For all three complexes, three electronic *d-d* transitions were observed; extremely strong optical absorption of these bands of VO(ben)$_2$ in DMSO are supposed to be arised from a great metal-ligand covalency. Some fundamental vibration modes of oxovanadium(IV) complexes were empirically assigned from the differences in the spectrum of metal complexes with free ligand.

Introduction

A wide variety of oxovanadium(IV), vanadyl complexes have been prepared and characterized.[1,2] Square pyramidal (C_4v) geometry has been well established or, more frequently assumed for the vanadyl compounds. These square-pyramidal complexes generally exhibit strong tendency to remain five coordinate.[3-6] However, X-ray crystallographic data have revealed that N,N-bis(salicylidene)propane-1,3-diamino)oxovanadium(IV), VO(sal)$_2$tn, exhibits a structure containing an infinite chain of square pyramidal molecules connected by V-O-V bonds.[7]

Other polymeric[8] and dimeric interaction[9] in the type of VOL$_2$ complexes are found in some mono thio-diketone complexes of oxovanadium, achieving hexacoordination in the solid state. Vibrational spectroscopy is an effective tool for the study of the nature of metal-ligand interactions and especially, the stretching frequency of V = O double bond is very sensitive both to the intermolecular interaction and to the achievement of hexacoordination.[7-9] The magnetic properties of oxovanadium(IV) complexes have been intensively studied and most oxovanadium(IV) complexes have magnetic moment close to the spin only value of 1.73 B.M.[10,11] However, some oxovanadium(IV) complexes have unusual magnetic properties due to the dimerization or polymerization in the solid states.[12] In this work, we prepared three oxovanadium(IV) complexes having a O = V(O)$_4$ moiety and carried out magnetic and spectroscopic investigation on these compounds to discover the mode of complexation of vanadyl ion with ligands having oxygen donor atoms, and to elucidate the type of intermolecular interaction if it exists.

Experimental

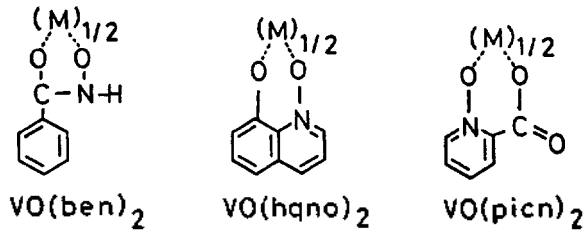
Preparation of Complexes. Benzohydroxamic acid, picolinic acid-N-oxide, and 8-hydroxyquinoline-N-oxide were obtained from Aldrich Chemical Co., and were used without further purification. VOSO$_4$·3H$_2$O was also purchased from Aldrich Co. All other chemical used in the preparation of oxovanadium(IV) complexes were of the best available reagent or spectroscopic grades. Water was triply distilled and deionized before use.

Bis(benzohydroxamato)oxovanadium(IV), VO(ben)$_2$. Potassium benzohydroxamate was prepared as precribed by C. R. *Hauser et al.*[13] Ca. 1.0 gram of potassium benzohydroxamate was dissolved in Ca. 25 m*l* of distilled water in a milk dilution bottle and deoxygenated by bubbling through nitrogen. To this solution, 0.01 M VOSO$_4$ solution was added dropwise with a syringe while the solution was being warmed and stirred. The mixture was digested in a boiling water bath for several minutes. The violet colored crystals precipitated and they were isolated by filtration and washed successively with warm water, and ethanol. The crystals were dried in a vacuum oven. Anal. Calcd; C, 49.2; H, 4.13; N, 8.19. Found; C, 49.1; H, 4.69; N, 8.26.

Bis(8-hydroxyquinolinolato-N-oxo)oxovanadium(IV), VO(quin)$_2$. Ca. 0.70 gram of 8-hydroxyquinoline-N-oxide was dissolved in Ca 20 m*l* of sodium hydroxide solution (50% ethanol solution) and Ca. 0.40 gram of vanadyl sulfate was added very slowly to form green colored precipitate. The crystals were isolated and washed successively with water, ethanol and ether, and dried in a vacuum oven. Anal. Calcd; C, 55.5; H, 3.65; N, 7.20. Found; C, 54.3; H, 3.55; N, 7.12.

Bis(picolinato-N-oxo)oxovanadium(IV), VO(picn)$_2$. Sodium salt of the ligand was prepared by adding stoichiometric amount of sodium hydroxide to the solution of picolinic acid-N-oxide. The complex was prepared by adding aqueous solution of sodium salt dropwise to a stoichiometric amount of vanadyl sulfate dissolved in warm water. A precipitate formed immediately was collected, and washed sucessively with water, ethanol and ether, and vacuum dried. Anal. Calcd; C, 41.8; H, 2.92; N, 8.12. Found; C, 42.1; H, 3.24; N, 8.17.

The results of element analysis (C, H, and N) were obtained from analytical laboratory of Korean Institute of Chemical Research.



Magnetic and Spectroscopic measurements. Magnetic susceptibility measurements were made on a powdered sample over the temperature range of 77K to 300K using a vibrating sample magnetometer of the Foner type[14] with a

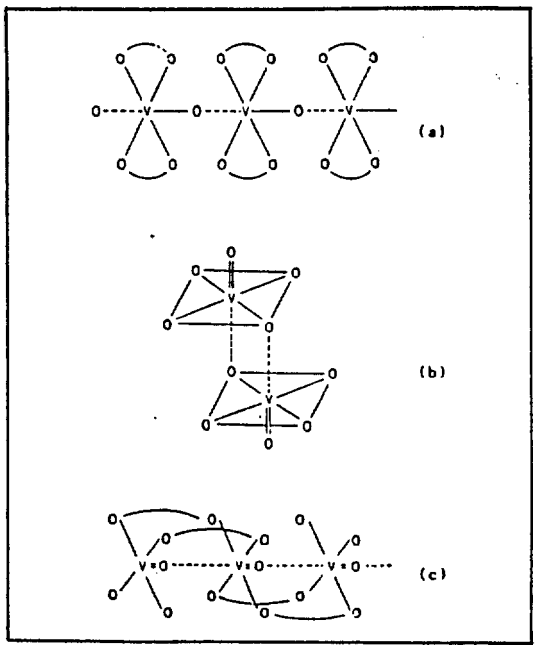


Figure 1. Intermolecular O—V—O polymeric interaction (a), dimeric interaction (b), and carboxylate bridges (c) in the type of VOL_2 complexes.

field calibrated at 10,000G using magnetic susceptibility standard $HgCo(NCS)_4$.[15] The data was corrected for the diamagnetism of the constituent atoms using Pascals constants, and for the temperature paramagnetism of the vanadyl(IV) ion, 148×10^{-6} cgs.[17] EPR spectral measurements were made on a powder sample at 77.3 K and at room temperature (9370GHz, 100KHz modulation) using a Varian E-3 X-band spectrometer with the field strength calibrated using magnetic resonance techniques. Infrared spectra ($2000cm^{-1}$-$200cm^{-1}$) were obtained using Nujol mull on cesium iodide plate and potassium bromide pellet with a Perkin Elmer model 621 recording spectrometer. Spectra were calibrated with polyethylene film. Before the IR measurement, all the complexes were vacuum dried until IR absorption bands attributed to water modes disappeared. Optical spectra were measured with Simadzu model UV-240 and Cary 14 UV-Visible spectrophotometer.

Results and Discussion. Analytical results show a 1:2 metal to ligand stoichiometry in all cases. The complexes are insoluble in water and their magnetic moments have been found to be in the range of 2.0-1.4 B.M. at room temperature. The effective magnetic moment of these complexes did not vary appreciably in the range of experimental temperature and the complexes studied in this work exhibit a straight line when the inverse value of susceptibility is plotted against temperature, satisfying Curie-Weiss equation. The effective magnetic moments of $VO(ben)_2$ and $VO(hqno)_2$ are found to be 1.42, and 1.53 B.M. respectively which are abnormally lower than the spin-only value (1.73 B.M.) for a d^1 configuration. These subnormal values may be due to the presence of exchange couple antiferromagnetism in this complex. Zelentsov[18] suggested for the magnetic abnormality of oxovanadium(IV) complexes of substituted N-(2-hydroxyphenyl)salicylidenmine a dimeric oxygen bridged structure, which provides an appropriate symmetry for the 3d orbitals of vanadium(IV) to overlap with each other and form strong metal-

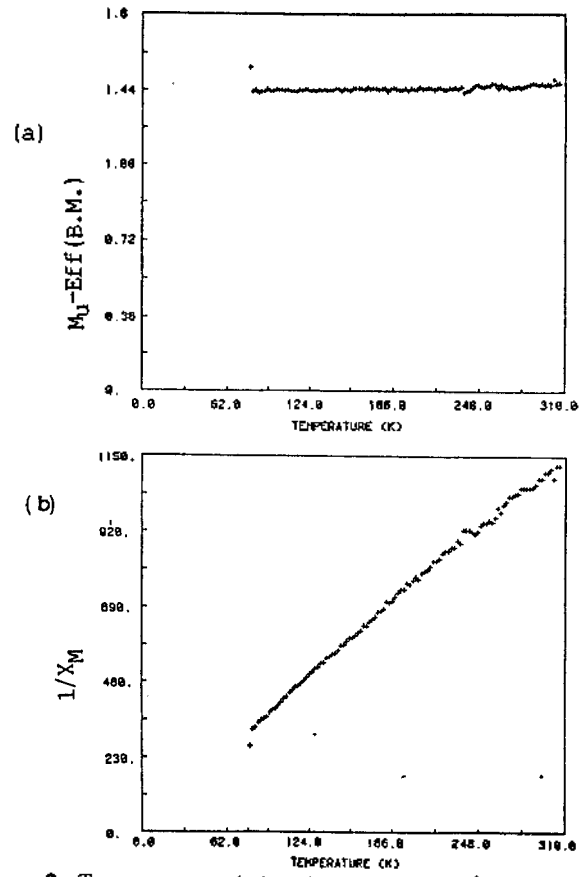


Figure 2. Temperature variation of (a) μ_{eff} and (b) X_M^{-1} for $VO(ben)_2$.

ligand bond.

Syama[19], in a series of Schiff base complexes of the type $VO(ONS)_4 \cdot nH_2O$, proposed a binuclear structure on the basis of their subnormal magnetic moment (1.27-1.52 B.M.). Similarly, Poddar *et al.*[20] and Kuge and Yamada[21] also observed subnormal magnetic moment in the case of oxovanadium (IV) complexes of bidentate Schiff base and suggested the oxygen bridged dimeric structure (see Figure 1). Casey and Thackery[22] suggested that the oxovanadium(IV) acetate complexes have both V=O---V interaction and carboxylate bridges as shown in Figure 1. The effective magnetic moment of $VO(picn)_2$ is larger than the spin-only value. The Weiss constant θ is +5.88 for $VO(picn)_2$. Although Weiss constant is positive, it is plausible to suggest that the high magnetic moment of $VO(picn)_2$ may arise from the ferromagnetic interaction between the molecules through the formation of V=O----V chain. Cavell *et al.*[23] have previously reported that the complexes $VO(S_2PX_2O)_2$ (X = F and CH_3) have abnormally high magnetic moments of 2.25 and 2.13 B.M. with positive Weiss constant (θ = +17 and +10). Other oxovanadium(IV) complexes having high magnetic moment were also reported.[24,25] When the orbital contribution is completely quenched the magnetic moment of the oxovanadium (IV) complexes is 1.73 B.M.. However if the orbital contribution is not completely quenched the magnetically dilute oxovanadium(IV) complexes may exhibit magnetic moments even less than spin only value.[19] Normal oxovanadium(IV) complexes usually have the magnetic moments in the range of 1.65 ~ 1.80 B.M.. The magnetic moment and magnetic susceptibility data for oxovanadium(IV) complexes are summarized in the Table 1, and the effective magnetic moment

Table 1. Magnetic Susceptibility, Magnetic moment[a] and ESR data of Oxovanadium(IV) Complexes

Compounds	Temp.(K)	$X_M(\times 10^{-3})$	μ_{eff}	θ	$<g>^b$
$VO(ben)_2$	278	0.950	1.45	0.0	1.984
$VO(hqno)_2$	277	1.101	1.55	+13.6	1.984
$VO(picn)_2$	278	1.475	1.97	+5.8	1.983

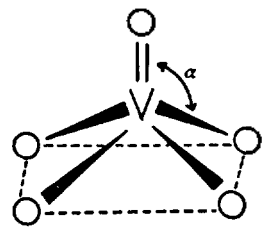
[a]The magnetic moment was calculated from Curie-Weiss equation; $\mu_{eff} = 2.83\{X_M(T-\theta)\}^{1/2}$. [b]Isotropic g-factor, g is obtained from the polycrystalline ESR spectra of compounds at room temperature.

μ_{eff}, magnetic susceptibility, X_M and $1/X_M$ plotted against temperature for $VO(ben)_2$ are shown in Figure 2. EPR powder spectra of the complexes only provide isotropic g values which is well within the characteristic g values for most oxovanadium(IV) complexes.[26] The results are also listed in Table 1.

The assignments in the IR spectra were made empirically by comparing the spectra of free ligand and their complexes and by reference to the literature on the spectra of similar compounds. The characteristic IR frequencies of there oxovanadium(IV) complexes with suggested assignments are listed in Table 2.

IR spectrum of ligands containing carboxylic, N-oxide and hydroxyl functional group are greatly affected by the complexation with the VO^{+2} ion. A broad and strong band appeared in the spectra of picolinic acid -N-oxide at 1030 cm^{-1}. This band disappeared upon complex formation and is assigned to the deformation vibration of hydroxyl group of -COOH. The complexation did not change the C = C double bond stretching frequencies as expected. The C = N double bond stretching frequency of ring skeleton could not be determined since the energy difference between the C = N bond stretching and C = C bond stretching is very small. The N-oxides of pyrimidines have been examined and compared with the pyridine N-oxide by Wieley and Slaymaker[27] and by Katrizky.[28] The N-oxide absorption occurrs in the 1300-1250 cm^{-1} range. A strong band of N-oxide, ν_{NO} appeared at 1254 cm^{-1} for picolinic acid-N-oxide. This band is shifted to 1200 cm^{-1} upon complex formation. Also a strong band of N-oxide, ν_{NO} for 8-hydroxyquinoline-N-oxide appeared at 1275 cm^{-1} is shifted to 1206 cm^{-1} upon complexation. The OH stretching band appeared at 3300 cm^{-1} for benzohydroxamic acid dissappeared upon complex formation.

This indicates that the oxygen of hydroxide of free ligand is coordinated to the oxovanadium(IV) ion. The new modes of vibration arises from the formation of $O = V(O)_4$ moiety upon complexation. According to the normal mode analysis of vibration for $O = V(O)_4$ moiety having C_4v symmetry, Γvib reduces to $3A_1 + 2B_1 + 2B_2 + 3E$, where B_1 and B_2 vibration modes are not infrared active. Among six IR active bands, the ν_1 (V = O) represent vanadium-oxygen double bond stretching and its magnitude was initially considered to be directly proportional to the strength of the metal-oxygen interaction. However, the shift of ν_1(V = O) has been shown also to be dependent upon coordination expansion and the type of donor atoms.[29] The x-ray crystallographic data[30] show that the loss of a donor molecule from the sixth position give rise to an increase in O = V-(equatorial donor atom) bond angle which, in turn, increases the V = O stretching frequency.



Intermolecular dimeric interaction where V = O unit does not involve directly, will cause the increase in frequency (see Figure 1). However, if the complexes have an intermolecular O = V----O = V interaction utilizing the V = O unit (see Figure 1), the V = O stretching band will appear at low frequency. In $VO(picn)_2$, the V = O stretching band appears at 892 cm^{-1} and 814 cm^{-1} respectively.

This unusually low frequency compared to the usual value

Table 2. Characteristic Infrared Frequencies of VO^{2+} Complexes with Suggested Assignments

$VO(ben)_2$		$VO(picn)_2$		$VO(hqno)_2$	
Frequency(cm^{-1})	Assignments	Frequency(cm^{-1})	Assignments	Frequency(cm^{-1})	Assignments
1648(s)	$\nu_{C=O}$	1680(vs,br)	$\nu_{C=O}$	1575(vs)	
1601(vs)	$\nu_{C=C}$	1607(s)		1518(m)	$\nu_{C=C}$, $\nu_{C=N}$
1578(vs)					
1508(vs)		1460(vs)	$\nu_{C=C}$, $\nu_{C=N}$	1455(vs)	
1385(vs)	ν_{N-O}	1442(vs)		1381(s)	ν_{C-O}
1085(w)	ν(N-O or OH deformation)				
1050(s)		1380(vs,br)	ν_{C-O}	1299(m)	ν_{N-O}
987(vs)	$\nu_{1V=O}$	1206(m)	ν_{N-O}	971(s)	$\nu_{1V=O(A_1)}$
942(vs)	ν(V-O···V-O)				
720(vs,br)	$\nu_{2VO_4(A_2)}$	892(vs)	$\nu_{1V=O(A_1)}$	643(m)	$\nu_{2VO_4(A_1)}$
643(s)	$\nu_{7VO_4(E)}$	620(w)	$\nu_{2VO_4(A_1)}$	608(m)	$\nu_{7VO_4(E)}$
575(vs)					
315(s)	$\nu_{3VO_4(A_1)}$	590(m)	$\nu_{7VO_4(E)}$	541(m)	$\nu_{7VO_4(E)}$
287(s)	or $\nu_{8VO_4(E)}$	392(m)			
275(sh,m)		315(m)	$\nu_{3VO_4(A_1)}$ or $\nu_{8VO_4(E)}$		
		302(m)			

Table 3. Electronic Spectral data of Oxovanadium(IV) Complexes

Compound	Medium	ν_1kK(logϵ_1)	ν_2kK(logϵ_2)	ν_3kK(logϵ_3)
$VO(ben)_2$	DMSO	10.52	16.29 (3.43)	21.01 (2.25)
	Nujol Mull		16.39	21.74
$VO(hqno)_2$	DMSO	12.66	17.09	25.00
	Nujol Mull		17.24	24.69
$VO(picn)_2$	Nujol Mull	12.20	18.18	15.00

of ca. 960 cm^{-1} seems to be attributed to the formation of polymeric V-O-V-O chains. In $VO(ben)_2$ complexes, bands appear at high frequencies of 994 cm^{-1} relative to usual value of 960 cm^{-1}. It may be attributed to the dimeric interation as shown as it is expected from magnetic data. In this complex vanadium might achieve hexacoordination in solid state. In the hexacoordination state, one oxygen donor of the ligand is shared by two metal atom. Furthermore, in $VO(ben)_2$ complexes, the new band appears at 814 cm^{-1} and 942 cm^{-1}, respectively. These band may be attributed to the fact that V-O-V-O weak chain is added to the dimeric stucture. In the majority of oxometal complexes, the axial stretching frequency A_1 is much higher than the equatorial stretching frequencies or deformation frequencies (ν_2, ν_3, ν_7, ν_8 and ν_9). In general, the order of the stretching frequencies is $\nu_7 \gg \nu_8 \gg \nu_9$, while the order of deformation frequencies is $\nu_7 \gg \nu_8 \gg \nu_9$.[31,32]

The general frequency ranges for other stretching and deformation modes for oxometal complexes of C_4v symmetry are; for ν_2 and ν_3; 450-700 cm^{-1}, for ν_3 and ν_8, 200-400 cm^{-1} and for ν_9; 120-250 cm^{-1}.[33,35] The ν_2, ν_7, ν_3 and ν_8. Vibrational frequencies of $VO(picn)_2$, $VO(hqno)_2$ and $VO(ben)_2$ are emperically assigned to the bands which come from the differences in the spectrum of complexes and free ligands. The results are summerized in Table 3. For oxovanadium (IV) complexes having C_4v symmetry, there are three potential intra *d* shell electronic transitions, although not all are necessarily allowed.

Ballhausen and Gray,[36] in molecular orbital study of VO $(H_2O)_5^{+2}$ ion, suggested that the *d* orbital energy order might be expected to be; $b_2(xy)<e\ (xz,yz)<b_1(x^2\text{-}y^2)<a_1(z^2)$. In general, three electronic transitions, $\nu_1(d_{xz}, d_{yz} \leftarrow d_{xy})$, $\nu_2(d_{z^2\text{-}y^2} \leftarrow d_{xy})$ and $\nu_3(d_{z^2} \leftarrow d_{xy})$ are observed below 30.0 kK, with intensities of the order of 5 - 100 L $mole^{-1}cm^{-1}$, but their assignments have long been the subject of controversy.[37] The electronic spectra of $VO(ben)_2$ and $VO(hqno)_2$ in DMSO are shown in Figure 3, and spectroscopic data for $VO(ben)_2$ and other complexes are summarized in Table 3. Due to the poor solubility of $VO(picn)_2$ in most solvents, only Nujol mull spectrum of $VO(picn)_2$ was obtained. Very large extinction coefficients for ν_2 and ν_3 of $VO(ben)_2$ compared to other complexes may arise either from a greater metal-ligand bond covalency or a large distortion from C_4v geometery assumed for the complexes. Distortion from C_4v symmetry could occur where LL is a bidentate ligand in common complexes of the type $VO(LL)_2$. But if it is the case, an additional *d-d* transition or splitting of ν_1 band may be seen as the degeneracy of the *e* orbitals is lifted.[38] Then "*d-p*" and "*s-p*" mixing which can be invoked[39,40] to account for the spectral band intensities of noncentrosymmetric complexes can be seen to be of importance by inspection of valence orbitals involved in

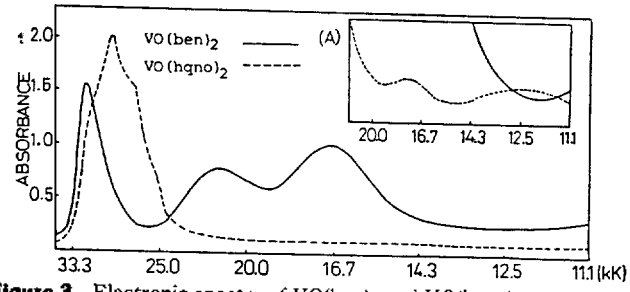


Figure 3. Electronic spectra of $VO(ben)_2$ and $VO(hqno)_2$ in DMSO. (A) This spectral result was obtained at the higher concentration of $VO(ben)_2$, and $VO(hqno)_2$(2.4×10^{-3}M).

the various molecular states even through the actual calculation of spectral intensities must take other things, *e.g.*, charge transfer state, into account. Vanadium electron spin-nuclear spin hyperfine coupling constant is usually a good measure of metal-ligand covalency and provide good information on the nature of metal-ligand bonding. Our attempt to evaluate coupling constants $A_{\parallel}$ and $A_{\perp}$ for $VO(ben)_2$ was unsucessful as strong magnetic dipolar interaction in powder $VO(ben)_2$ obscure the fine structure of EPR spectrum.

Conclusion

The solid state magnetic moment of 1.42 B.M. for $VO(ben)_2$ being lower than the spin-only value of 1.73 B.M., signifies a spin-coupling interaction. This result, in couple with the enhanced V = O stretching frequency of 996 cm^{-1}, strongly suggest that dimeric interaction in $VO(ben)_2$ is significant. Very large extinction coefficients for *d-d* transition bands for $VO(ben)_2$ might be arised from a greater metal-ligand bond covalency. In contrast to the results of $VO(ben)_2$, the $VO(picn)_2$ has the magnetic moment of 1.98 B.M. and its V = O stretching frequency is observed at 892 cm^{-1}.

The reduction in V = O stretching frequency couple with large value of magnetic moment strongly suggest the presence of polymeric V-O----V-O interaction in this complex. For all three vanadyl complexes studied, three electronic *d-d* transitions were absorved, and high intensities of and bands of $VO(ben)_2$ in DMSO are supposed to be arised from a great metal-ligand covalency.

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References

1. (a) J. Selbin, *Chem. Rev.*, **65**, 153 (1965); (b) Coored. *Chem. Rev.*, **1**, 293 (1966); (c) *Angew. Chem.*, **12**, 692 (1973) and references there in.
2. B. J. McCermick, J. L. Featherstone, H. J. Stokolosa, and J. R. Wasson, *Inorg. Chem.*, **12**, 692 (1973), and reference there in.
3. L. J. Boucher, E. C. Tynan, and T. F. Yen, *Inorg. Chem.*, **7**, 731 (1968).
4. L. J. Boucher, T. F. Yen, *Inorg. Chem.*, **8**, 689 (1969).
5. R. J. Farmer and F. L. Urbach, *Chem. Commun.*, 1515 (1970).
6. R. G. Ciarvey and R. O. Ragsdale, *Inorg. Chem. Acta*, **2**, 191 (1968).
7. M. Mathew, A. J. Carty, and G. J. Plenik, *J. Am. Chem.*

Soc., **92**, 3197 (1970).
8. R. L. Farmer and F. L. Urbach, *Inorg. Chem.*, **13**, 587 (1974).
9. R. L. Farmer and F. L. Urbach, *Inorg. Chem.*, **9**, 2562 (1970).
10. A. P. Ginsberg, E. Koubeck and H. J. Williams, *Inorg. Chem.*, **5**, 1656 (1966).
11. Y. Kuge and S. Yamada, *Bull. Chem. Soc.* (Japan), **43**, 3972 (1970).
12. B. J. McCormick and R. A. Bozis, *Inorg. Chem.*, **10**, 2806 (1971).
13. C. R. Houser and W. B. Renfrow, *Jr, J. Org. Chem.*, **34**, 730 (1960).
14. S. Foner, Rev. *Scient. Instrum.*, **30**, 548 (1959).
15. (a) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958); (b) H-st. Rade, *J. Phys. Chem.*, **77**, 424 (1973).
16. P. Selwood, Magnetochemistry, 2nd Edn. Interscience, New York (1956).
17. G. D. Simpson and G. O. Carlisle, *Inorg. Nucl. Chem. Lett.*, **9**, 815 (1973).
18. V. V. Zelentsov, *Russ. J. Inorg. Chem.*, **7**, 670 (1962).
19. A. Symal, *Coord. Chem. Rev.*, **16**, 309 (1975).
20. S. N. Poddar, K. Dey, J. Haldar and S. C. Nathsarkar, *J. Indian Chem. Soc.*, **47**, 743 (1970).
21. Y. Kuge and S. Yamada, *Bull. Chem. Soc.* (Japn), **45**, 799 (1972).
22. A. T. Casey and J. R. Thackeray, *Aust. J. Chem.*, **22**, 2549 (1969).
23. R. G. Cavell, E. D. Day, W. Byers and P. M. Watkins, *Inorg. Chem.*, **11**, 1951 (1972).
24. R. L. Dutta and S. Lahiry, *J. Indian Chem. Soc.*, **40**, 857 (1963).
25. S. N. Poddar, K. Dey and S. C. Nathsarkar, *J. Indian Chem. Soc.*, **40**, 489 (1963).
26. E. A. Boudreaux and L. N. Mulay, "Theory and Applications of Molecular Paramagernatism". John-Wiley and Son, 1976.
27. Wiley and Slaymaker, *J. Am. Chem. Soc.*, **79**, 2233 (1957).
28. Katritzky and Ambler, Katritzty and Taylor, "Physical Methods in Hetrocyclic Chemistry", Vol. 2 and 4, Academic Press, New York (1963) and (1971).
29. R. L. Farmer and F. L. Urbach, *Inorg. Chem.*, **13**, 587 (1974).
30. M. Mattew, A. J. Carty and G. J. Palenik, *J. Am. Chem. Soc.*, **92**, 3197 (1970).
31. J. B. Milne and Moffett, *Inorg. Chem.*, **12**, 2240 (1973).
32. K. O. Kriste and E. C. Carties, *Inorg. Chem.* **11**, 2209 (1972).
33. G. M. Begun, W. H. Fletcher and D. F. Smith, *J. Chem. Phys.*, **42**, 2236 (1965).
34. R. T. Paine and R. S. DcDowell, *Inorg. Chem.*, **13**, 2366 (1974).
35. R. J. Collins, W. P. Griffith and D. Dawson, *J. Mol. Struc.*, **19**, 531 (1973).
36. C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).
37. H. A. Kuska and P. H. Yang, *Inorg. Chem.*, **13**, 1090 (1974).
38. M. H. Valek, W. A. Yeranos, G. Basu, P. K. Hon and R. L. Belford, *J. Mol. Spectry.*, **37**, 228 (1971).
39. A.B.P. Lever, "*Inorganic Electronic Spectroscopy*", 2nd Edn. Elsevier (1984).
40. H. J. Stokolsa and J. R. Wasson, *J. Inorg. Nucl. Chem.*, **36**, 227 (1974).
41. Z. Jaeger and R. Englman, *Chem. Phys. Letts.*, **19**, 242 (1973).

Fluorescence Enhancement of Ethidium Bromide by DNA Bases and Nucleosides

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Fluorescence enhancements of ethidium bromide (EB) by solution species of low molecular weights such as DNA base molecules and nucleosides in water are reported. The degree of enhancements was determined by intensity as well as lifetime measurements for EB fluorescence. Experiments including solvent effects on absorbance and fluorescence spectra of EB, effects of protonation on the EB absorbance spectrum, and determination of equilibrium constants for EB-DNA bases have been performed to help explain the fluorescence enhancement. The results suggest that the excited state stabilization in the hydrophobic environment, the loss of torsional/vibrational energy of amino groups, and the change in the electronic transition characteristics are all responsible for the fluorescence enhancement.

Introduction

Ethidium bromide (3,8-diamino-5-ethyl-6-phenylphenanthridium bromide; EB) is one of the most studied of the intercalating compounds. A great deal of interest in EB might be due to its biological reactivities and unique spectroscopic properties. Biologically, it is trypanocidal[1] and antiviral and inhibits DNA and/or RNA biosynthesis *in vivo*.[2-4] Spectroscopically, the red shifts shown in the absorption and fluorescence bands as well as fluorescence enhancement upon inter-