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Note

Spectral and Thermal Studies of 1,10-Phenanthroline *N,N'*-Dioxide Chelates of Oxovanadium(IV)

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A new series of penta-coordinated oxovanadium(IV) chelates of 1,10-phenanthroline *N,N'*-dioxide (PhenO₂) have been synthesized and characterized by conductance, magnetic moments, infrared, electronic spectra and TG-data.

INTRODUCTION

The coordination chemistry of aromatic amine *N*-oxides has been reviewed in recent years¹. Of the heterocyclic *N*-oxides studied by far the largest amount of work has been carried out with pyridine *N*-oxide and 2,2'-bipyridyl *N,N'*-dioxide¹. But the study of coordinating ability of a similar ligand, i. e. 1,10-phenanthroline *N,N'*-dioxide, with metal ions is comparatively less^{2,3}. Thus, it is worthwhile to study the ligational behaviour of 1,10-phenanthroline *N,N'*-dioxide (PhenO₂) with oxovanadium(IV).

EXPERIMENTAL

The ligand PhenO₂ was prepared from 1,10-phenanthroline by the method described for 2,2'-bipyridyl *N,N'*-dioxide,³ while the Lewis acids were obtained as reported in ref. 4.

The complexes were prepared by mixing warm acetone solutions of oxovanadium(IV) salts with PhenO₂ in the same solvent. In some cases, the precipitation of the complexes occurred on mixing the solutions while in the others, the precipitates were obtained on keeping the mixtures on water bath for 5 minutes under stirring. The solid products were collected, washed with ether and dried in vacuo over P₂O₅.

Analytical procedure

Vanadium metal in all the complexes was estimated by EDTA titrations using Erichrome Black-T as indicator and was confirmed by igniting the complexes in air and estimating the metal as V₂O₅. The halides in the complexes were estimated by Volhard's method. The perchlorate was determined by the method of Kurz et al.⁵ All other physico-chemical studies of the complexes were made as reported earlier.⁶

RESULTS AND DISCUSSION

The interaction of oxovanadium(IV) salts with PhenO₂ results in the formation of compounds of the general composition VOX₂ · PhenO₂ (X = Cl, Br, I, NCS, NO₃ or C₂O₄) and VO(ClO₄)₂ · 2PhenO₂. The analytical data are given in Table I. The compounds are quite stable and can be stored for a long

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TABLE I
Analytical, Conductivity and Partial IR Data (cm⁻¹) for VO⁺ Chelates of PhenO₂

Compound	Found (Calcd.)/%		$\frac{\Omega_m}{\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}}$	Average Mol. Wt. (Formula Wt.)	ν (N=O)	δ (N—O)	ν (M—O)
	V	N					
PhenO ₂	—	—	—	—	1310s 1280s	855s	—
VOCl ₂ · PhenO ₂	14.39 (14.57)	7.81 (8.00)	20.02 (20.28)	342 (350)	1280s 1265m	845m	420m
VOBr ₂ · PhenO ₂	11.42 (11.61)	6.12 (6.37)	35.87 (36.44)	431 (439)	1290m 1270m	850m	425m
VOI ₂ · PhenO ₂	9.41 (9.56)	5.06 (5.25)	46.82 (47.65)	528 (533)	1290m 1280sh	845w	430m
VOCl ₂ · PhenO ₂	13.73 (13.89)	7.44 (7.62)	—	358 (367)	1280s 1270sh	850m	427w
VO(ClO ₄) ₂ · 2PhenO ₂	7.21 (7.39)	3.87 (4.05)	28.05 (28.84)	233 (690)	1270s 1240m	850m	430m
VO(NO ₃) ₂ · PhenO ₂	12.43 (12.65)	13.69 (13.89)	—	397 (403)	1280m 1270sh	852m	425m
VO(NCS) ₂ · PhenO ₂	12.72 (12.91)	14.02 (14.17)	28.82 (29.36)	387 (395)	1290m 1275w	860m	420m

time. The compounds are fairly soluble in common organic solvents. The electrical conductances measured in nitrobenzene at room temperature (32 °C) are consistent with the non-electrolytic nature of halo, pseudohalo, oxalato and nitrate complexes, while the perchlorate complex is 1:2 electrolyte.

The room temperature magnetic moments of the complexes are in the range 1.72–1.80 B. M. These values correspond to one unpaired spin per vanadium atom, demonstrating the tetravalency of vanadium in the complexes and also the absence of metal-metal interaction between vanadium atoms.⁷

Infrared Spectra

Table I records important IR bands for the ligand and the complexes. In the IR spectra of the free ligand two (N—O) bands at 1310 and 1280 cm^{-1} have been observed¹⁻³. These bands were shifted to lower frequencies upon complex formation. The decrease in the frequency of the $\nu(\text{N—O})$ vibration is attributed to O—O chelation in PhenO_2 . Absorption of strong intensity at 855 cm^{-1} has been assigned to NO bending mode, and from the tabulated data it appears that this absorption changes only slightly on complexation¹⁻³. This further supports oxygen linkage between metal and ligand. In the far IR region the metal-ligand vibration is tentatively assigned to $\nu(\text{V—O})$ mode.

The bands due to the $\nu(\text{V=O})$ vibration occur in the 980–960 cm^{-1} region. These values are in the range observed for monomeric VO^{++} species in all the PhenO_2 complexes of oxovanadium(IV)⁷. However, it may be pointed out that the lower values of $\nu(\text{V=O})$ normally inferred⁸ the polymeric nature of the complexes. But recent views indicate that solid state effects⁹ and electron-withdrawing groups¹⁰ can also cause a lowering of the $\nu(\text{V=O})$ frequency.

The ionic nature of the perchlorate group may be suggested by the presence of a fairly broad ν_3 band at 1090 cm^{-1} and ν_4 band at 625 cm^{-1} ^{4,11}. The thiocyanato complexes show three bands at 2080 ($\nu \text{C=N}$), 850 cm^{-1} ($\nu \text{C—S}$) and 460 cm^{-1} (δNCS). This may be taken as an evidence of the bonding of the thiocyanate through nitrogen in the VO^{++} complex¹². The bidentate nature of the coordinated oxalate group, bonded covalently to the VO^{++} moiety, is revealed by the presence of ν_7 , ν_1 and ν_2 bands at 1715, 1650 and 1360, respectively¹³. In the IR spectra of $\text{VO}(\text{NO}_3)_2 \cdot \text{PhenNO}_2$, the bands appearing at 1575 (ν_1), 1260 (ν_2), 1030 (ν_3) and 805 (ν_4) indicate the covalent nature of the nitrate groups in the complex¹⁴. The two combination bands appear at 1770 and 1750 cm^{-1} . By applying the 'Lever separation method'¹⁵ the separation of 20 cm^{-1} in this case suggests the monodentate nature of the nitrate groups.

Electronic Spectra

The electronic spectra of the complexes in CH_3CN in the visible range were taken. In all the chelates the bands occur in 12500–12800 cm^{-1} region with a shoulder in 15300–15700 cm^{-1} region. These bands are due to d-d transition spectrum and can be assigned to $d_{xy} \rightarrow d_{xz}$, d_{yz} and $d_{xy} \rightarrow d_{x^2-y^2}$ transitions, respectively. The band due to $d_{xy} \rightarrow d_{z^2}$ seems to have been masked by the intense charge-transfer bands occurring in the UV region¹⁶.

In conclusion, in all these chelates the coordination number of vanadium is five and the penta-coordinated oxovanadium(IV) complexes can have a tetragonal pyramidal structure.

TABLE II
Thermoanalytical Results Obtained for the VO⁺ Chelates of PhenO₂

Compound	Sample Wt. mg	Residual mass mg	Mass loss (%)						Residue %	
			140—220 °C		280—375 °C		530 °C		Theor. ^c	Exp.
			Theor. ^a	Exp.	Theor. ^b	Exp.	Theor. ^c	Exp.		
VOCl ₂ · PhenO ₂	28.72	7.07	30.28	32.16	60.57	62.15	26.00	24.65		
VOBr ₂ · PhenO ₂	30.16	5.76	24.14	25.95	48.29	50.06	20.72	19.12		
VO(NCS) ₂ · PhenO ₂	27.32	6.17	26.83	28.16	53.67	55.02	23.03	22.59		
VO(NO ₃) ₂ · PhenO ₂	26.92	5.66	26.30	27.92	52.60	54.06	22.58	21.06		
VOC ₂ O ₄ · PhenO ₂	29.12	6.75	28.88	30.06	57.76	59.06	24.79	23.19		

^a Calculated for loss of 0.5 mole of ligand.

^b Calculated for total loss of ligand.

^c Calculated as V₂O₅.

Thermal Studies

The results of thermal analysis of VO(IV) complexes are presented in Table II. The t. g. and d. t. curves of VO(IV) chelates of PhenO₂ do not show the presence of water molecules, either in or out of the coordination sphere. The t. g. curves show that all the chelates complete their decomposition process according to the following schemes:



REFERENCES

1. N. M. Karayannis, A. N. Speca, D. E. Chasan, and L. L. Pytlewski, *Coord. Chem. Rev.* **20** (1976) 37.
2. A. K. Srivastava, Shashi Sharma, and R. K. Agarwal, *Inorg. Chim. Acta* **61** (1982) 235.
3. R. K. Agarwal, Gyanendra Singh, M. Srivastava, and A. K. Srivastava, *Thermochim. Acta* **73** (1984) 243.
4. R. K. Agarwal and Gyanendra Singh, *Thermochim. Acta* (In Press).
5. E. Kurz, G. Kober, and M. Berl, *Analyst Chem.* **30** (1958) 1983.
6. R. K. Agarwal, A. K. Srivastava, and T. N. Srivastava, *Transition Met. Chem.* **5** (1980) 95.
7. J. Selbin, *Chem. Rev.* **65** (1965) 153.
8. R. L. Farmer and F. L. Urbach, *Inorg. Chem.* **13** (1974) 587.
9. M. Pasquate, F. Marchetti, C. J. Floriani, and S. Merlino, *J. Chem. Soc., Dalton Trans.* (1977) 139.
10. H. A. Kuska and P. H. Yang, *Inorg. Chem.* **16** (1977) 1938.
11. S. K. Madan and A. M. Donohue, *J. Inorg. Nucl. Chem.* **28** (1966) 1303.
12. J. L. Burmeister, *Coord. Chem. Rev.* **1** (1968) 205; **3** (1966) 225.
13. G. Durga Prasad and C. C. Patel, *Indian J. Chem.* **11** (1973) 1300.
14. S. K. Sahni and S. K. Sangal, *Synth. React. Inorg. Met.-Org. Chem.* **8** (1978) 291.
15. A. B. P. Lever, E. Montovani, and B. S. Ramaswamy, *Can. J. Chem.* **49** (1971) 1957.
16. D. N. Sathyanarayana and C. C. Patel, *Indian J. Chem.* **5** (1967) 360.

SAŽETAK

Spektrometrijsko i termometrijsko istraživanje kelatnih kompleksa vanadil-iona s 1,10-fenantrolin N,N'-dioksidom

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Interakcijom vanadil-iona s 1,10-fenantrolin-N,N'-dioksidom (PhenO₂) nastaju spojevi opće formule VOX₂ · PhenO₂ (X = Cl, Br, I, NCS, NO₃ ili C₂O₄) i VO(ClO₄)₂ · 2PhenO₂. Nastalim kompleksima snimljeni su IR i UV/VIS spektri, te je određen magnetski moment i molarna provodnost. Kompleksi su također podvrgnuti termičkoj (TG i DT) analizi, koja je pokazala odsutnost molekula vode unutar koordinacijske sfere centralnog iona i izvan nje.