Synthesis and characterisation of oxovanadium(IV) complexes with tridentate ONO donor azo ligands

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Reaction of $VOSO_4$ with three tridentate dibasic ONO donor azo ligands (H_2L^{1-3}, 1) separately in aqueous alcoholic medium produces complexes 2–4 of the type $[VO(L)(H_2O)_x]_y$, where $x = 1$, $y = 1$ for H_2L^1 : complex 2; $x = 0$, $y = 2$ for H_2L^2 and H_2L^3 : complexes 3 and 4 respectively. Complex 2 shows normal magnetic moment for a d^1 system while 3 and 4 show subnormal behaviour. This behaviour is explained in terms of metal-metal bonding, and the magnetic moment order, 2 > 3 > 4 is correlated with the basicity of the donor atoms. One bonded water molecule is present only in complex 2. Among the three complexes only 2 shows two ligand field transitions. All the three complexes exhibit one LMCT transition and two intraligand transitions characteristic for azo group. They display either irreversible or quasireversible one-electron oxidation peaks in DMF. The electrochemical behaviour has been rationalised on the basis of basicity of the coordinating atoms.

The good affinity of oxovanadium(IV) ion towards tridentate dibasic ONO donor ligands is the principal cause for its rich chemistry with such donor atoms. The complexes with such donor atoms, either in simple[1-10] or in mixed-ligand[3,11,12] systems are mainly with Schiff bases. There are also examples with simple molecules containing this type of donor moieties[13,14], but such type of complexes with azo ligands have received little attention[15]. Though a significant amount of work has been done by Chakravorty *et al*[15] either in mixed-ligand or simple oxovanadium(V) system with H_2L^{1-2} type of ligands but to our knowledge no systematic study has been done with oxovanadium(IV) ion so far. With this idea in mind, we carried out a systematic study of such complexes with three tridentate dibasic ONO donor azo ligands (H_2L^{1-3}, 1) as a part of our programme on oxovanadium(IV/V) chemistry[11,16]. The main reason for utilising such types of ligands is to know how the magnetic moment and redox potential values of the complexes vary with the basicity of the third donor site, the other two remaining invariant of a tridentate dibasic ligand. The complexes are of the type $[VO(L)(H_2O)_x]_y$ (for $L^1 : x = 1, y = 1$, complex 2; for L^2 and $L^3 : x = 0$ and $y = 2$, complexes 3 and 4 respectively). Their redox behaviour is also discussed. Trends in the VO^{2+}–VO^{3+} oxidation potentials and the magnetic moment values are correlated with the basicity of the donor sites of the ligand. Studies of such complexes are important because of their chemical and biochemical significance[17,18]

Results and Discussion

Three tridentate ONO donor azo ligands, H_2L^1–H_2L^3
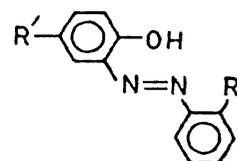
	R	R′
H_2L^1	COOH	CH_3
H_2L^2	OH	H
H_2L^3	CH_2OH	5,6-benzo

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(general abbreviation H_2L, 1) have been used. Treatment of equimolar mixture of VO^{2+} with the respective H_2L inaqueous ethanolic solution, produced complex $[VOL(H_2O)_x]_y$ in nearly quantitative yield. The H_2L ligands bind to VO^{2+} in a dinegative tridentate fashion. The compositions of the complexes have been confirmed by elemental analysis and infrared spectra. The room temperature magnetic moment values also support it.

The magnetically dilute oxovanadium(IV) complexes (d^1 system) should exhibit magnetic moment very close to the spin-only moment and so complex 2 (1.88 B.M.) belongs to this category. The room temperature magnetic moment values of complexes 3 and 4 (1.23 and 1.16 B.M. respectively) are significantly less than the spin-only moment, which indicates that antiferromagnetic exchange process is operating in these two complexes. As the ligands are tridentate in nature, so these 1 : 1 metal : ligand com-

plexes must either take up one or more solvent molecules (for the formation of mononuclear complex) or must be involved in the formation of bridges (forming dinuclear species), so that the metal can satisfy its usual coordination number. An analysis of ir spectra of the complexes reveals that H_2O molecule is present only in complex 2. The thermal analysis of 2 indicates that a weight-loss occurs endothermally (DTA curve) at 190° and TGA data confirm the mass-loss of only one water molecule (Fig. 1). The loss of water molecule at this temperature is also confirmed from the ir spectrum of 2 after heating it at ca 200°, which shows no band for water but for carboxylate group (vide infra). The high temperature required for water-loss indicates that water molecule is strongly bonded to vanadium and also H-
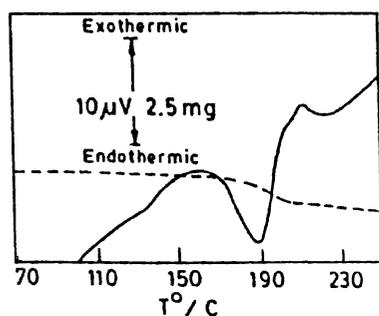
Fig. 1. TGA (----) and DTA (—) curves for complex 2.

bonded with the ligand molecule otherwise it would be removed at lower temperature[19]. Fig. 1 also reveals that after the endothermic loss of H_2O there is a phase transition (the exotherm at 210° is not accompanied by any weight-loss), indicating possibly a structural change from a discrete five-coordinate to a polymeric entity. The compound decomposes above 250°. The meridional disposition of $(L^1)^{2-}$ ion is well known[15] and assuming one basal position of H_2O, a distorted square-pyramidal geometry (I) with a vacant coordination site trans to the V=O bond is reasonable for complex 2. The meridional disposition of $(L^2)^{2-}$ ion is also well known[15] and extending this nature to $(L^3)^{2-}$ ion, a dinuclear distorted square-pyramidal geometry (II) is proposed for complexes 3 and 4, the bases being constituted of N and O atoms of tridentate ligands and one phenolic oxygen[3] and one alcoholic oxygen[7] atom of neighbouring molecule as bridging atom respectively. The bridging by phenolate and alcoholate oxygen atoms in 3 and 4 respectively, is supported by the ir spectra. It is also known that, for such square-pyramidal VO^{2+} complexes the unpaired electron will be in the $3d_{xy}$ orbital[3,20] and because of appropriate symmetry of $3d_{xy}$ orbitals of metals in these dinuclear complexes for di-

z = p for 3
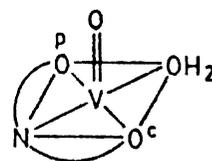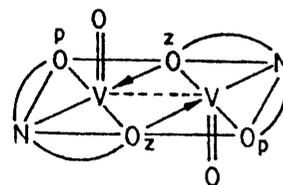
z = a for 4

II

rect overlapping, it is reasonable to assume that a V–V σ-bond will be the most favourable path for lowering the magnetic susceptibility value. The extent of direct overlapping is expected to be inversely proportional to the effective nuclear charge on the metal which in turn depends directly on the basicity of the coordinating sites of the bonded ligand molecule. The ligand donor sites of the three complexes are : $OPN^{az}O^c$ (2) $OPN^{az}O^p$ (3), $OPN^{az}O^a$ (4), where superscripts p, az, c and a stand for phenolic, azo, carboxylic and alcoholic moieties respectively. Among the three donor sites the two are identical (i.e. O^p and N^{az}) in all the three complexes and only the difference in the third oxygen donor sites i.e. O^c, O^p and O^a and their basicity order is $O^c < O^p < O^a$ as is evident from their pK_a values (cf. the pK_a values of PhCOOH, PhOH and EtOH : 4.2, 10.0 and 15.90 respectively[21,22]) and this explains the observed magnetic moment order : 2 > 3 > 4. In the complex 2, due to the presence of very weak O^c ion, the effective nuclear charge on V is so high that no effective metal-metal bonding takes place. So, it is monomeric in nature and assumes distorted square-pyramidal geometry by taking up one water molecule in the coordination zone. Hence, it can be concluded that the third donor site (others remaining invariant) play vital roles in determining the structure and hence in the magnetic moments by affecting the effective nuclear charge of metal atom through their basicity.

Ir and electronic spectra : The complexes display a strong V=O stretch at 995–1000 cm^{-1} which is compatible with pentacoordination[1,3,7,8]. The presence of one symmetric (1320 cm^{-1}) and two asymmetric (1640 and 1620 cm^{-1}) stretching modes in complex 2 characterises

monodentate carboxylate binding[23]. A relatively broad band around 3200 cm^{-1} present only in complex 2, indicates the presence of coordinated water molecule and suggesting its involvement in hydrogen bonding. The expected ν N=N mode of the bonded ligands is observed[24] at 1375–1410 cm^{-1} for all the three complexes. The band at 555–570 cm^{-1} is assigned to V–O (aryl) and 480–490 cm^{-1} to V–N bond. The ν(C–O)Φ band in complex 3 observed at 1565 cm^{-1}, is in the higher energy side by 25 cm^{-1} (*cf* the ν (C–O)Φ band of the ligand 1540 cm^{-1}) indicating its involvement in bridge[25] in the magnetically condensed complex 3. The appearence of ν(C–O) alcoholic band at 1295 cm^{-1} which is in the higher energy side by *ca* 30 cm^{-1}, indicates its involvement in bridge and no significant change in ν(C–O)Φ band rules out the possibility of other alternate bridging medium in complex 4. So the proposed magnetically condensed dinuclear alcoholic oxygen bridge structure of complex 4 is expected to be correct.

The DMF solutions of these complexes are orange-red to red-violet in colour. Among these three complexes, two ligand-field transitions are observed only in complex 2 at 1025 and 880 nm due to $d_{xy} \rightarrow d_{xz}$, d_{yz} ($\varepsilon = 28$) and $d_{xy} \rightarrow d_{x2-y2}$ ($\varepsilon = 36$) respectively[20]. Strong absorptions at higher energies preclude observation of other possible ($d_{xy} \rightarrow d_{z2}$) ligand-field transition. All the complexes exhibit one intense transition in the region 483–492 nm ($\varepsilon = 5200$) probably due to $p \rightarrow d$ (LMCT) excitation (where p and d represent phenolic oxygen and metal d orbital respectively). The transition characteristics for N=N group were observed at 432 nm ($\varepsilon = 3500$) and at 312–334 nm ($\varepsilon = 10000$) due to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions respectively[26].

Electrochemistry : The electrochemical properties of all the oxovanadium(IV) complexes were examined by cyclic voltammetry in DMF solution at a Pt working electrode and they exhibited a well defined voltammetric response due to V^{IV}–V^V couple. While complex 3 showed quasireversible behaviour ($E_p^a = 0.33$ V and $E_{1/2} = 0.25$ V), complexes 2 and 4 showed irreversible V^{IV}–V^V process ($E_p^a = 0.64$ and 0.22 V respectively; E_p^a being the anodic peak potential value and $E_{1/2}$ the average of anodic and cathodic peak potential values). Representative voltammogram of metal redox process for complex 3 is shown in Fig. 2. From the basicity point of view of the donor atoms, it is expected that the electron density on the vanadium centre will be in the order : 2 < 3 < 4, and hence the expected order of E_p^a values will be 2 > 3 > 4. In fact, this has been observed experimentally. So, from the comparison of E_p^a values, it is evident that this value gradually decreases with the increase in basicity of the third donor atom (the others remaining invari-

ant) and hence, the more basic atoms have tendency to stabilise VO^{3+} motif preferably than VO^{2+} motif and vice-versa. Two other distinct quasireversible reduction peaks were also observed for all the three complexes at high negative potentials, near –0.5 and –1.10 V due to electron transfer at the azo group (eqns. 1 and 2),
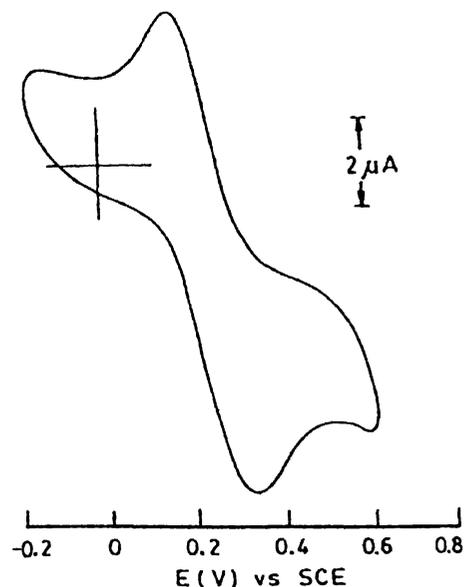
$$[-N=N-] + e \rightarrow [-N\cdots N-]^- \tag{1}$$

$$[-N\cdots N-]^- + e \rightarrow [-N-N-]^{2-} \tag{2}$$
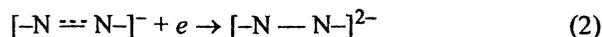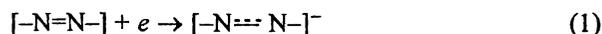
The reduced species does not appear to be stable enough to show the reversibility.

Conclusion : The results reveal the important role of third donor site (the other two remaining invariant) in determining the composition, structure, magnetic moment and redox potential values of the complex. A trend in the magnetic moment and redox potential data has also been examined. Due to the insoluble nature of such complexes in common solvents no redox potential data are available for most of the complexes reported so far but because of sufficient solubility of the complexes reported here (the exception is complex 4, which is sparingly soluble) it has been possible to report their redox potential values.

Experimental

VOSO$_4$.5H$_2$O (Loba), *p*-cresol, β-naphthol, anthranilic acid, *o*-nitrophenol and sodium acetate (all S.D. Chemicals) were used as received. *o*-Aminobenzyl alcohol was used. H$_2$L^1 and H$_2$L^3 ligands[27] and H$_2$L^2 ligand[28] were prepared

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by the reported procedures. Electrochemical grade Et_4NClO_4 (TEAP) was prepared[29]. Dimethyl formamide was dried by distillation under reduced pressure over P_4O_{10} and then stored over Linde AW-500 molecular sieves.

Electronic spectra (DMF) were recorded on a Hitachi 330 spectrophotometer and ir spectra (KBr) on a Perkin-Elmer 783 spectrophotometer. Electrochemical measurements were performed on a PAR 370-4 electrochemistry system according to the reported procedure[30]. All potentials reported are uncorrected for junction contributions. A Perkin-Elmer 240C elemental analyser was used for C, H, N analyses. The thermal analyses (TG-DTA) were carried out using a Shimadzu DT-30 instrument in a dynamic atmosphere of nitrogen. Magnetic susceptibility was measured using a PAR 155 magnetometer using $Hg[Co(SCN)_4]$ as the calibrant.

The complexes were prepared by the same general method. All the complexes gave satisfactory C, H and N analyses.

(Aquo)(5-methylazobenzene-2-olato-2'-crboxylato)-oxovanadium(IV), [VO(L¹)(H₂O)] : H_2L^1 (2 mmol) and sodium acetate (4 mmol) were dissolved in aqueous alcohol (25 cm³ of ethanol and 15 cm³ of water) by heating. A solution of $VOSO_4.5H_2O$ (2 mmol) in water (10 cm³) was added to it dropwise with continuous stirring. The reaction mixture was stirred at hot condition (~80°) for 1 h and then cooled. The resulting brown-red complex was washed with water, alcoholic water (1 : 1) and finally with diethyl ether and dried over $CaCl_2$ (fused), (665 mg, 98%).

Acknowledgement

References

1. L. J. Theriot, G. O. Carlisle and H. J. Hu, *J. Inorg. Nucl. Chem.*, 1969, **31**, 2841.

2. A. K. Mukherjee and P. Ray, *J. Indian Chem. Soc.*, 1955, **32**, 505.

3. A. P. Ginsberg, E. Koubek and H. J. Williams, *Inorg. Chem.*, 1966, **5**, 1656.

4. S. A. Fairhurst, D. L. Hughes, G. J. Leigh, J. R. Sanders and J. Weisner, *J. Chem. Soc., Dalton Trans.*, 1994, 2591; S. A.

Fairhurst, D. L. Hughes, U. Kleinkes, G. J. Leigh, J. R. Sanders and J. Weisner, *J. Chem. Soc., Dalton Trans.*, 1995, 321.

5. A. Syamal, *Coord. Chem. Rev.*, 1975, **16**, 309.

6. U. Casellato, P. A. Vigato and M. Vidali, *Coord. Chem. Rev.*, 1977, **23**, 31.

7. A. Syamal and K. S. Kale, *Indian J. Chem., Sect. A*, 1980, **19**, 225.

8. A. Syamal and K. S. Kale, *Inorg. Chem.*, 1979, **18**, 992; *Indian J. Chem., Sect. A*, 1977, **16**, 431; 1980, **19**, 486; A. Syamal, E. F. Carey and L. J. Theriot, *Inorg. Chem.*, 1973, **12**, 245; A. Syamal, S. Ahmed and O. P. Singhal, *Transition Met. Chem.*, 1983, **8**, 156; D. K. Rastogi, S. K. Sahni, V. B. Rana, K. Dua and S. K. Dua, *J. Inorg. Nucl. Chem.*, 1979, **41**, 21.

9. C. J. Carrano, C. M. Nunn, R. Quan, J. A. Bonadies and V. L. Pecoraro, *Inorg. Chem.*, 1990, **29**, 944.

10. V. V. Zelentsov, *Russ. J. Inorg. Chem.*, 1962, **7**, 670.

11. S. P. Rath, S. Mondal and T. Ghosh, *Indian J. Chem., Sect. A*, 1996, **35**, 527.

12. S. Dutta, S. Mondal and A. Chakravorty, *Polyhedron*, 1995, **14**, 1163; J. Chakravarty, S. Dutta, A. Dey and A. Chakravorty, *J. Chem. Soc., Dalton Trans.*, 1994, 557; I. Cavaco, J. C. Pessoa, D. Costa, M. T. Duarte, R.-D. Gillard and P. Matias, *J. Chem. Soc., Dalton Trans.*, 1994, 194; B. J. Pandya and P. K. Bhattacharya, *Transition Met. Chem.*, 1987, **12**, 347.

13. R. L. Dutta and S. Ghosh, *J. Indian Chem. Soc.*, 1967, **44**, 296; H. L. Hoof and R. A. Walton, *Inorg. Chim. Acta*, 1975, **12**, 71; B. H. Bersted, R. L. Belford and I. C. Paul, *Inorg. Chem.*, 1968, **7**, 1557.

14. M. A. Nawi and T. L. Richel, *Inorg. Chim. Acta*, 1984, **93**, 131; R. L. Dutta and S. Ghosh, *J. Inorg. Nucl. Chem.*, 1966, **28**, 247.

15. J. Chakravarty, S. Dutta and A. Chakravorty, *J. Chem. Soc., Chem. Commun.*, 1993, 1091; *J. Chem. Soc., Dalton Trans.*, 1993, 2857; J. Chakravarty, S. Dutta, S. K. Chandra, P. Basu and A. Chakravorty, *Inorg. Chem.*, 1993, **32**, 4249; S. Dutta, P. Basu and A. Chakravorty, *Inorg. Chem.*, 1993, **32**, 5343.

16. S. P. Rath, S. Mondal and T. Ghosh, *Transition Met. Chem.*, 1996, **21**, 309; *Polyhedron*, 1997, **16**, 4179; S. Bhattacharya and T. Ghosh, *Indian J. Chem., Sect. A*, 1998, **37**, 730; 1999, **38**, 000.

17. J. M. Arber, E. de Boer, C. D. Garner, S. S. Hasnain and R. Wever, *Biochemistry*, 1989, **28**, 7968; R. Wever and K. Kustin, *Adv. Inorg. Chem.*, 1990, **35**, 81; A. Butler and C. J. Carrano, *Coord. Chem. Rev.*, 1991, **109**, 61.

18. D. Rehder, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 148; H. Vitler and D. Rehder, *Inorg. Chim. Acta*, 1987, **136**, L7; D. Rehder, H. Vitler, A. Duch, W. Priebsch and C. Widemann, *Recl. Trav. Chim., Pyas-Bas*, 1987, **106**, 408.

19. J. C. Pessoa, J. A. J. Silva, A. L. Vieira, L. Vilas-Boas, P. O. Brien and P. Thornton, *J. Chem. Soc., Dalton Trans.*, 1992, 1745.

20. C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, 1962, **1**, 111.

21. D. D. Perrin, B. Dempsey and E. P. Serjeant, "pka Prediction for Organic Acids and Bases", Chapman and Hall, London, 1981.

22. H. H. Jaffe, *Chem. Rev.*, 1953, **53**, 191.

23. B. Kavanagh, J. W. Steed and D. A. Tocher, *J. Chem. Soc., Dalton Trans.*, 1993, 327; S. Mondal, S. P. Rath, S. Dutta and A. Chakravorty, *J. Chem. Soc., Dalton Trans.*, 1996, 99.

24. S. Chattopadhyay, C. Sinha, S. B. Chowdhury and A. Chakravorty, *J. Organomet. Chem.*, 1992, **427**, 111.

25. E. Sinn and C. M. Harris, *Coord. Chem. Rev.*, 1969, **4**, 351; T. Tokii, Y. Muto, M. Kato and H. B. Jonassen, *J. Inorg. Nucl. Chem.*, 1972, **34**, 3377.

26. K. C. Kalia and A. Chakravorty, *J. Org. Chem.*, 1970, **35**, 2231.

27. A. I. Vogel, "Textbook of Practical Organic Chemistry", 5th. ed., ELBS, London, 1994.

28. H. D. K. Drew and J. K. Landquist, *J. Chem. Soc.*, 1938, 292.

29. D. Datta, P. K. Maschark and A. Chakravorty, *Inorg. Chem.*, 1981, **20**, 1673.

30. S. K. Chandra, P. Basu, D. Ray, S. Pal and A. Chakravorty, *Inorg. Chem.*, 1990, **29**, 2423.