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Synthesis and Spectroscopic Properties of [VO(aspa/gluta)H_2O] and [VO(aspa/gluta)ImH]

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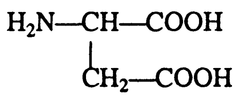
Reaction of the tridentate amino acids, *viz.*, aspartic acid and glutamic acid with VO^{2+} ion in 1 : 1 molar ratio in aqueous solution yields [VO(aspa/gluta)H_2O], (dimeric), while reaction with VO^{2+} ion, amino acid and imidazole in 1 : 1 : 1 molar ratio in aqueous solution yields [VO(aspa/gluta)ImH], (monomer). In addition to synthesis, we report the magnetic IR, EPR and optical absorption data of these compounds.

Key Words: Oxovanadium(IV), Aspartic acid, Glutamic acid, Imidazole, IR, EPR.

INTRODUCTION

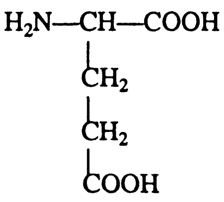
Oxovanadium(IV) forms complexes with polydentate ligands with NO donors, resulting in complexes of varied geometry depending on ligand design. The amino acids are expected to form the oxovanadium(IV) complex for which polymeric structures must be supposed. In case of complexes formed with VO^{2+}, aspartic acid/glutamic acid and imidazole (ImH) the polymeric structure is not necessary.

Recently Patel *et al.*[1–3] reported copper(II) complexes with amino acids and imidazoles and studied their stereochemical properties and reactions. Transition metal complexes of groups IVb, Vb and VIb are well known for their ability to catalyze oxygen transfer reactions. With this view in mind, oxovanadium(IV) complexes using aspartic acid (I), glutamic acid (II) and imidazole (III) have been synthesized. In this paper synthesis, magnetic, IR, EPR and optical absorption data are being reported.



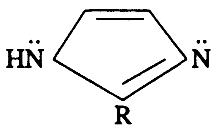
$H_2N{-}CH(CH_2{-}COOH){-}COOH$

(I)



$H_2N{-}CH(CH_2{-}CH_2{-}COOH){-}COOH$

(II)



(III)

(a) R = H; (b) R = $-CH_3$; R = $-CH_2CH_3$

EXPERIMENTAL

Oxovanadium(IV) complexes of aspartic acid and glutamic acid were obtained by adding equimolar aqueous solution of $VO(SO_4)$ and aspartic acid/glutamic acid. The mixed solution was stirred well and refluxed for 20 min. After cooling the pH of the solution was adjusted to 7 by adding a few drops of NaOH and left overnight; a green-coloured complex was obtained which was washed with diethyl ether. The obtained complexes were desiccated in calcium chloride desiccator at room temperature.

These mixed ligand complexes, e.g., VO(Aspa)(ImH) or VO(Gluta)(ImH) were obtained by similar method as described above for [VO/aspa/gluta)H_2O] by taking equimolar amount of each constituent.

Analyses were carried out by the microanalytical laboratory CDRI Lucknow. Magnetic susceptibility measurements were carried out at room temperature using Gouy balance and diamagnetic corrections was corrected with Pascal constants. The IR spectra were recorded on Perkin-almer instrument-137. Epr spectra were recorded at both room and liquid nitrogen temperature using E-line century series epr spectrometer.

RESULTS AND DISCUSSION

All the compounds synthesized hereby give satisfactory elemental analyses (Table-1). At room temperature magnetic moments in the solid state are in the range 0.95–1.00 B.M. for the [VO(aspa/gluta)H_2O] compounds derived from tridentate amino acids for which dimeric structure must be supposed in order to reach penta-coordination of the vanadium atom; such a dimeric structure is in the plane of the tridentate ligand thus creating a favourable geometry for an antiferromagnetic exchange interaction. The magnetic moment values for [VO(aspa/gluta)ImH] compounds are 1.65–1.71 B.M. We suggest that these compounds are five coordinated monomers in which a molecule of imidazole occupies one of the coordination sites.

TABLE-1
ANALYTICAL AND PHYSICAL DATA FOR OXOVANADIUM(IV) COMPLEXES

S.No	Complex	Colour	M.P. (0°C)	Yield (%)	Found (Calcd.) %				μ_{eff} (B.M.)
					C	H	N	VO	
1.	VO(Aspa) (H_2O)	Green	120*	65	22.24 (22.21)	3.19 (3.24)	6.50 (6.48)	23.55 (23.57)	0.95
2.	VO(Aspa) (ImH)	Green	180*	70	31.58 (31.56)	3.35 (3.38)	15.76 (15.78)	19.18 (19.14)	1.00
3.	VO(Gluta) (H_2O)	Grey	>265*	60	26.05 (26.07)	3.95 (3.91)	6.10 (6.08)	22.18 (22.14)	1.65
4.	VO(Gluta) (ImH)	Green	260	55	34.24 (34.26)	3.73 (3.92)	15.01 (14.99)	18.20 (18.18)	1.71

*Decomposition temperature

Assignments of some main bands are presented in Table-2. The compounds [VO(aspa/gluta)H_2O] exhibit a band in the range 3400–3100 cm^{-1}, which is assigned to the ν(OH) of coordinated water molecule[4]. The broadness of the bands is indicative of hydrogen bonding. The ν(V—N) stretching frequency lies in the range *ca.* 505 cm^{-1} and ν(COO) frequency ranges from 1512–1398 cm^{-1}. The vanadium oxo ν(V=O) stretching frequencies have normally intense absorption[5, 6] between 900 and 1000 cm^{-1}. The corresponding bands for our compounds lie in the range 1026–951 cm^{-1}.

The solid state epr spectra at LNT exhibit a signal at $g \approx 2.0$ which is characteristic of isotropic spectra. We have also recorded the epr spectra in aqueous solutions at room temperature and at liquid nitrogen temperature. Some representative spectra are shown in Figs. 1 and 2. The derived epr parameters are given in Table-3.

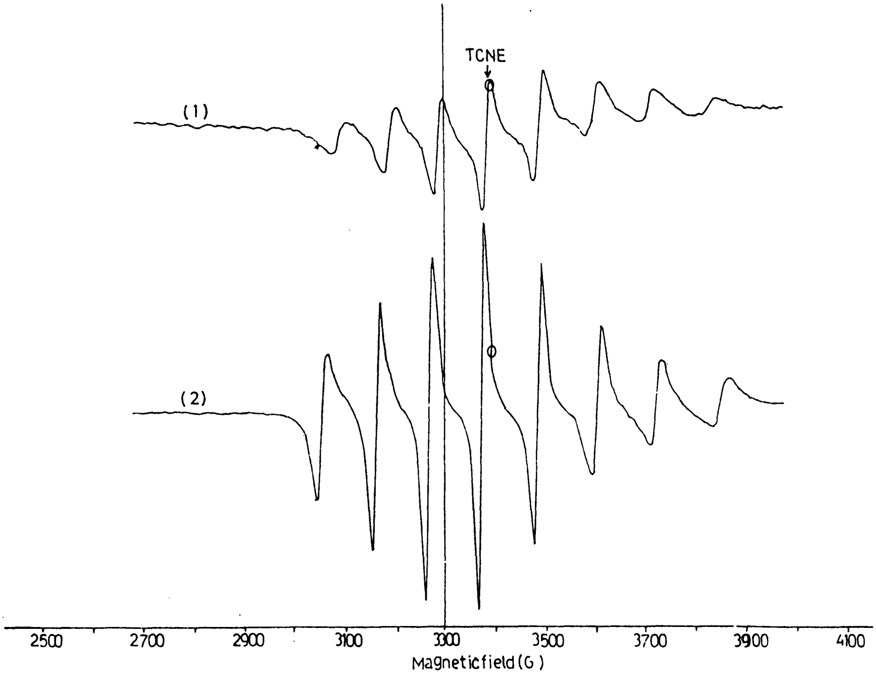


Fig. 1. X-band epr spectra (RT) of (1) [VO(Gluta)H_2O] and (2) [VO(Gluta)ImH].

For solutions at room temperature, all complexes show eight line isotropic epr spectra (Fig. 1). The eight line epr spectra are owing to the coupling of unpaired electron with the large moment of nearly 100% abundant 5'V nucleus (I = 7/2). In frozen solution, spectra are anisotropic and two sets of resonance components, one each due to parallel and perpendicular features, are observed for all the complexes. The frozen solution epr spectra of [VO(aspa/gluta) H_2O] show $g_{||}$ signals as doublets (Fig. 2). This is indicative of presence of two species. Similar work was reported by Casella *et al*[7]. They have suggested that the two species may be either isomers with different structures or solvated and unsolvated species formed at the time of glass formation, or monomer and dimer in equilibrium. The remaining two complexes show the spectra for a typical of mononuclear oxovanadium(IV) complexes.

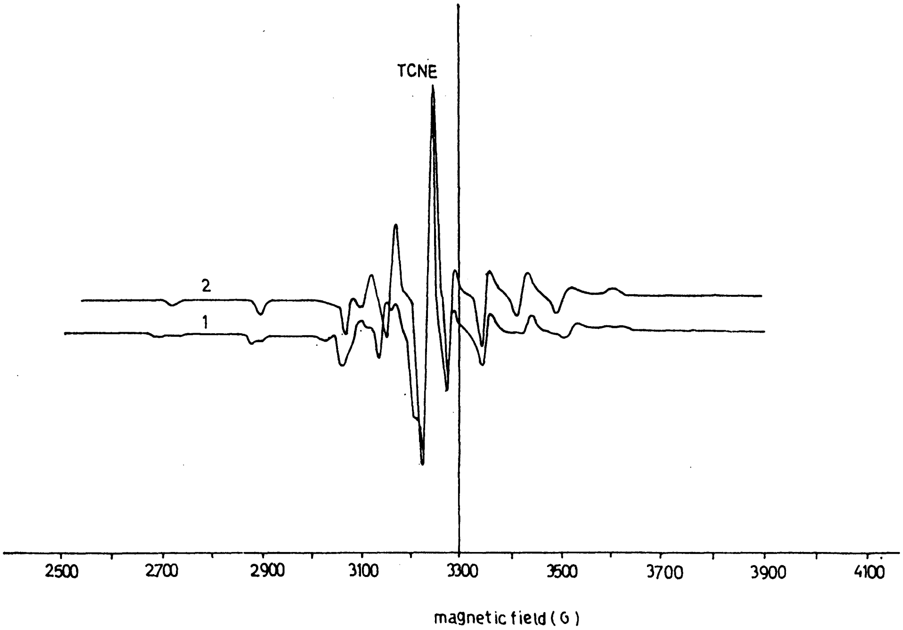


Fig. 2. X-band spectra (LNT) of (1) [VO(Aspa)H_2O] and (2) [VO(Aspa)ImH].

TABLE-2
KEY IR-BAND (cm^{-1}) FOR OXOVANADIUM(IV) COMPLEXES

S.No.	Complex	ν(V═O)	ν(COO)	ν(NH_2)	ν(OH)	ν(V—N)
1.	VO(Aspa) (H_2O)	1026	1398	764	3400	–
2.	VO(Aspa) (ImH)	950	1510	765	3005	508
3.	VO(Gluta) (H_2O)	1000	1404	742	3111	–
4.	VO(Gluta) (ImH)	951	1512	767	3010	505

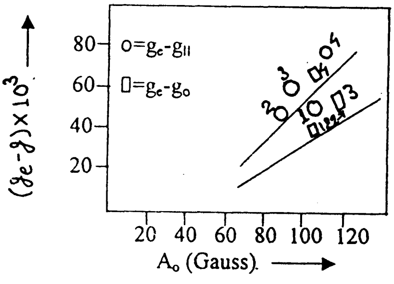


Fig. 3. A correlation plot in between A_o and ge-g(g=$g_{\|}$ or g_o).

The correlation plot in between A_0 and $g_e - g_0$ or $g_e - g_{||}$ is given in Fig. 3. As A_0 increases, both $(g_e - g_0)$ and $(g_e - g_{||})$ increase[8]. Our data points are in fair agreement to this empirical relationship. It may be observed that data points are in present complexes roughly lie at one domain with higher A_0 values.

Dickson *et al.*[9, 10], have made a correlation between g_0 and A_0 oxovanadium(IV) complexes (Fig. 4) having equatorial donor atoms of the type $VO(N_4)$, $VO(N_2O_2)$ and $VO(O_4)$. The parameters cluster in domains according to the ligand environments. This kind of correlation has been used to speciate VO^{2+} compounds in petroleum and protein[8–11]. A correlation[12] in between $A_{||}$ and $g_{||}$ (Fig. 5) was also made. However, in these plots our data points deviate from reference data points. Obvoiusly this deviation may be due to different mechanisms which is involved in the present complexes.

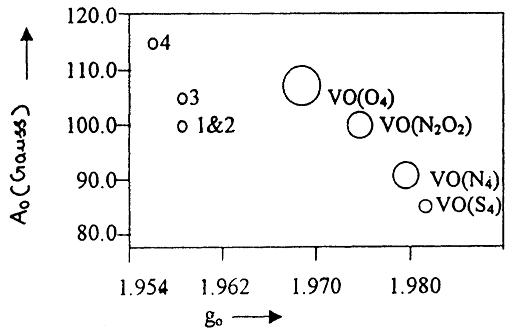


Fig. 4. A correlation plot in between g_0 and A_0.

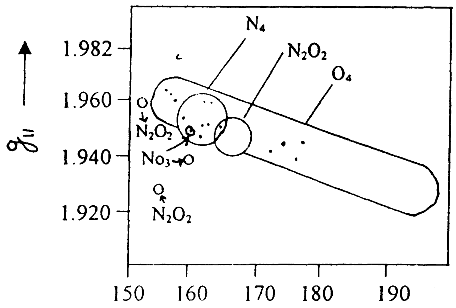


Fig. 5. A correlation plot in between $g_{||}$ and $A_{||}$ values.

On application of additivity relationship[13] for the present complexes the $A_{z,i}$ values for the different involved equatorial binding groups were estimated and it is observed that these estimated $A_{z,i}$ values tally well (Table-3) with the literature values[13].

Pessoa *et al.*[14] have also studied VO^{2+} -peptide binary systems only in aqueous medium and observed similar data.

TABLE-3
X-BAND EPR PARAMETERS OF SOME OXOVANADIUM(IV) COMPLEXES

Complex	g_0	A_0 (G)	$g_\perp$	$g_\parallel$	$A_\perp$ (G)	$A_\parallel$ (G)	Involved equatorial functional groups	$A_{z,i}$	
								Calculated value	Literature[13] value
VO(Aspa) (H_2O)	1.959	102	1.974	1.948	62	172	H_2O	46.5	45.7
							R—NH_2	40.9	40.1
							2R—COO^-	43.5	42.7
VO(Aspa) (ImH)	1.959	102	1.969	1.957	57	164	=N—	38.5	38.3
							2R—COO^-	42.9	42.7
							R—NH_2	40.3	40.1
VO(Gluta) (H_2O)	1.959	105	1.966	1.942	55	171	H_2O	45.5	45.7
							R—NH_2	39.9	40.1
							2R—COO^-	42.5	42.7
VO(Gluta) (ImH)	1.955	115	1.978	1.929	60	164	2R—COO^-	42.9	42.7
							=N—	38.5	38.3
							R—NH_2	40.3	40.1

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REFERENCES

1. K.B. Pandeya and R.N. Patel, *Indian J. Chem.*, **30A**, 193 (1991).
2. R.N. Patel, H.C. Pandeya and K.B. Pandeya, *Indian J. Pure Appl. Phys.*, **35**, 649 (1997).
3. R.N. Patel, H.C. Pandeya, K.B. Pandeya and G.N. Mukherjee, *Indian J. Chem.*, **38A**, 850 (1999).
4. K. Nakamoto, *Infrared and Raman spectra of Inorganic and Coordination Compounds*, 4th Edn., Wiley, New York, (1986).
5. J. Selbin, *J. Coord. Chem. Rev.*, **1**, 293 (1966).
6. J. Selbin, L.H. Holmes(Jr.) and S.P. McGlynn, *J. Inorg. Nucl. Chem.*, **25**, 1359 (1963).
7. L. Casella, M. Gulloti, A. Pintar, S. Colona and A. Manfredi, *Inorg. Chim. Acta*, **144**, 95 (1988).
8. L.J. Boucher, E.C. Tynan and T.F. Yen, in: T.F. Yen (Ed.), Electron Paramagnetic Resonance Spectra of Metal Complexes, Plenum Press, New York, p. 111 (1969).
9. F.E. Dickson, C.H. Kunech, E.H. McGinnis and L. Petrakis, *Anal. Chem.*, **44**, 978 (1972).
10. F.E. Dickson and L. Petrakis, *Anal. Chem.*, **46**, 1129 (1974).
11. L.K. White and N.D. Chasteen, *J. Phys. Chem.*, **79**, 279 (1972).
12. N.H. Holyk, M.S. Thesis, University of New Hampshire, Durham, New Hampshire (1979).
13. N.D. Chasteen, in: L. Berliner and J. Rueben (Eds.), Biological Magnetic Resonance, Plenum Press, New York, Vol. 3, P. 53 (1981).
14. J.C. Pessoa, S.M. Luz and R.D. Gillard, *J. Chem. Soc. Dalton Trans.*, 569 (1997).

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