

Spectral and magnetic investigations on some binuclear oxovanadium compounds

P S ZACHARIAS*, M ATHAR MASOOD and
J MARY ELIZABATHE

School of Chemistry, University of Hyderabad, Hyderabad 500 134, India

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Abstract. Several binuclear oxovanadium compounds of binucleating ligands are synthesised and investigated by magnetic, spectral and esr methods. The experimental results show that there is weak exchange interaction mediated by the bridging organic molecules between the vanadium centres. The magnitude of this interaction is more than that observed in the corresponding copper(II) dimers. The possible reason for this is discussed.

Keywords. Oxovanadium compounds; weak exchange interaction; bridging organic molecules.

1. Introduction

Complexes of oxovanadium(IV) cations with d^1 configuration are expected to have spectral and magnetic properties similar to the complexes of copper(II) with d^9 configuration. A number of oxovanadium(IV) complexes of various ligands have been synthesised and investigated to verify this (Selbin 1965, 1966; Ginsberg *et al* 1966; Wood 1972; Hasty *et al* 1973; Syamal 1975; Felthouse and Hendrickson 1978). Magnetically coupled copper(II) complexes have been studied extensively. A relatively less number of oxovanadium(IV) systems are known (Carlisle *et al* 1973; Rastogi *et al* 1979; Pasquali *et al* 1980; Casellato *et al* 1982; Hahs *et al* 1982) which show magnetic interactions between metal centres in dimers. As part of our investigations on the magnetic and spectral characteristics of binuclear complexes of binucleating ligands, several binuclear oxovanadium(IV) complexes have been synthesised and investigated. These results will be discussed and compared with those of the corresponding copper(II) complexes in the following sections.

2. Experimental

Triazene-1-oxide binucleating ligands were synthesised by a modified procedure reported earlier (Zacharias and Ramachandraiah 1985). It involves the tetrasotisation of the diamine followed by coupling with *n*-alkyl hydroxylamine hydrochloride,

* For correspondence

prepared by the reduction of the corresponding nitro alkane with zinc dust and ammonium chloride. The yellow solids were recrystallised from acetone or methanol.

All the complexes were prepared by a similar procedure. To a hot solution of the ligand (2 mmoles) in acetone (150 ml), an aqueous ethanolic solution of oxovanadium(IV) sulphate monohydrate (2 m moles) was added slowly with stirring. On complete addition of the metal salt solution, the colour of the reaction mixture changed to dull green. It was then concentrated on a water bath to 50 ml. On cooling a grey green solid precipitated. This was filtered, washed repeatedly with water, ethanol and dried. These complexes were purified by recrystallisation from a mixture of dichloromethane and pentane.

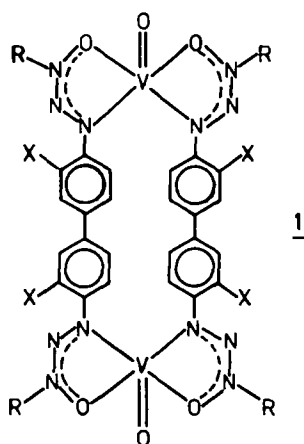
Infrared spectra were recorded in the region $4000\text{--}600\text{ cm}^{-1}$ on a Perkin-Elmer 297 spectrometer and in the region $600\text{--}200\text{ cm}^{-1}$ region on a Perkin-Elmer 283 spectrometer as KBr pellets. C, H, N analyses were done on a Perkin-Elmer 240 V elemental analyser and the vanadium content was estimated to be V_2O_5 after treating with conc. HNO_3 . Room temperature magnetic susceptibility measurements were done on a Bruker MB-6 magnetic susceptibility set up by the Gouy method with copper(II) sulphate penta hydrate as calibrant and diamagnetic corrections were made using Pascal's constants. Solution electronic spectral measurements were carried out using either a Shimadzu 200 S Spectrometer (800–200 nm) or Cary 17 D Spectrometer (1600–300 nm). Solid spectra were recorded on a PARC 6001 photoacoustic spectrometer with carbon black as reference and magnesium oxide as diluent. A JEOL FE-3X esr spectrometer was used for recording the electron spin resonance spectra in the solid, solution and frozen states. DPPH was used as internal standard in these measurements.

3. Results and discussion

The structure of the binuclear complexes based on ligand structure, coordination sites and compatible with experimental data is shown (1). The C, H, N, V analytical data presented in table 1 are in agreement with this formulation. The dull green complexes have melting points $> 250^\circ\text{C}$ and are only partially soluble in organic solvents. These compounds, for convenience, will be represented as $[\text{VO}(\text{R-triaz-bp-X})]_2$.

Infrared bands characteristic of $\text{V}=\text{O}$ vibrations appear in the region $960\text{--}980\text{ cm}^{-1}$ and are included in table 1. Electronic spectra of the complexes in solid and solution phases show a broad band at $\sim 590\text{ nm}$ as a shoulder on the low energy side of the steeply rising UV band (figure 1). λ_{max} values of complexes in different solvents are given in table 2. In oxovanadium(IV) complexes of square pyramidal geometry, three transitions are possible (Ballhausen and Gray 1962). They are at $\sim 770\text{ nm}$ ($b_2 \rightarrow e_g^*$, I); $\sim 590\text{ nm}$ ($b_2 \rightarrow b_1^*$, II) and at less than 500 nm ($b_2 \rightarrow a_1^*$, III). The last one is often masked by charge transfer bands.

The position of the 590 nm band agrees with type II transition ($b_2 \rightarrow b_1^*$). There is no other band in the higher wavelength region. It is possible that the two transitions, I and II, are unresolved resulting in the asymmetric nature of the $\sim 590\text{ nm}$ band. Oxovanadium complexes are known where I and II transitions are not resolved (Havinala and Pujar 1981). The λ_{max} values do not show any appreciable deviation in solvents like benzene, tetrahydrofuran or dimethyl formamide, while there is a shift of $\sim 45\text{ nm}$ towards the low energy side in pyridine. Such small shifts are known to result from the difference in the dielectric constant of the solvent (Boucher *et al* 1968).



X = OCH₃, CH₃

R = CH₃, C₂H₅, nC₃H₇, iC₃H₇

Table 1. Elemental analysis, infrared spectral and magnetic moment values of [VO(R-triaz-bp-X)]₂ type complexes.

Complex	Elemental analysis data*(%)				$\nu_{V=O}$ (cm ⁻¹)	Magnetic moment μ_{eff} (BM) at 297 K
	C	H	N	V		
[VO(CH ₃ -triaz-bp-OCH ₃)] ₂	45.34 (45.16)	4.10 (4.26)	19.52 (19.76)	12.28 (11.98)	985	0.80
[VO(CH ₃ -triaz-bp-CH ₃)] ₂	48.62 (48.80)	4.42 (4.61)	21.06 (21.35)	12.68 (12.95)	960	0.99
[VO(C ₂ H ₅ -triaz-bp-OCH ₃)] ₂	47.38 (47.64)	4.61 (4.80)	18.34 (18.52)	11.46 (12.23)	970	0.87
[VO(C ₂ H ₅ -triaz-bp-CH ₃)] ₂	51.06 (51.26)	5.31 (5.62)	19.71 (19.93)	11.46 (12.09)	985	1.30
[VO(n-C ₃ H ₇ -triaz-bp-OCH ₃)] ₂	49.76 (49.85)	5.26 (5.44)	17.10 (17.45)	10.56 (10.58)	980	0.90
[VO(n-C ₃ H ₇ -triaz-bp-CH ₃)] ₂	53.18 (53.10)	5.70 (5.83)	18.54 (18.69)	11.56 (11.33)	970	1.06
[VO(i-C ₃ H ₇ -triaz-bp-OCH ₃)] ₂	49.74 (49.85)	5.12 (5.44)	17.28 (17.45)	10.06 (10.58)	985	1.18
[VO(i-C ₃ H ₇ -triaz-bp-CH ₃)] ₂	53.09 (53.40)	5.68 (5.83)	18.51 (18.69)	11.10 (11.33)	990	1.28

* Values in parentheses are theoretical values

The μ_{eff} values for these complexes fall in the range 0.8–1.3 BM per metal ion and are appreciably lower than the spin only value of 1.73 BM expected for a d^1 system. The range of μ_{eff} values of these complexes are given in table 1. The decrease in μ_{eff} values can arise from any of the following possibilities. Antiferromagnetic interaction in systems where the metal-metal distance is about 3 Å is common resulting in decreased μ_{eff} values (Kuge and Yamada 1970; Carlisle and Crutchfield 1972; Syamal

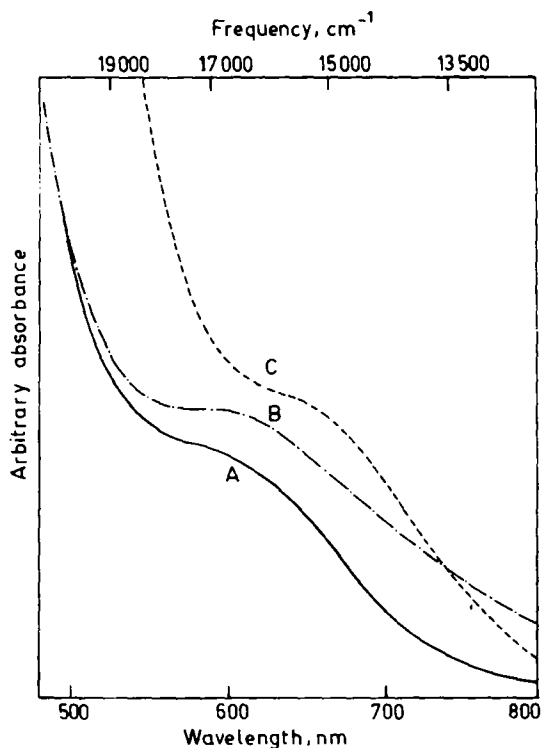


Figure 1. Electronic spectra of $[\text{VO}(\text{C}_2\text{H}_5\text{-triaz-bp-CH}_3)]_2$. (A) in dichloromethane; (B) in benzene; (C) in pyridine.

Table 2. Electronic and esr spectral data of $[\text{VO}(\text{R-triaz-bp-X})]_2$ complexes.

Complex	Electronic spectral data (λ) in solvents (nm)					ESR spectral data				
	CH_2Cl_2	C_6H_6	THF	DMF	Pyridine	g_{iso}	A_{iso}	A_{\parallel}	A_{\perp}	A_0^c
$[\text{VO}(\text{CH}_3\text{-triaz-bp-OCH}_3)]_2$	a	a	a	b	650	2.008	40.0	64.3	11.8	29.3
$[\text{VO}(\text{CH}_3\text{-triaz-bp-CH}_3)]_2$	a	580	590	b	640	2.005	36.8	69.3	10.0	29.6
$[\text{VO}(\text{C}_2\text{H}_5\text{-triaz-bp-CH}_3)]_2$	580	580	580	600	625	2.000	40.0			
$[\text{VO}(n\text{-C}_3\text{H}_7\text{-triaz-bp-OCH}_3)]_2$	580	590	590	b	b	2.010	40.5	71.1	12.1	31.8
$[\text{VO}(n\text{-C}_3\text{H}_7\text{-triaz-bp-CH}_3)]_2$	580	590	590	600	630	2.009	38.6	71.4	11.1	31.2
$[\text{VO}(i\text{-C}_3\text{H}_7\text{-triaz-bp-OCH}_3)]_2$	580	590	580	b	620	2.003	36.4	67.1	11.1	29.8
$[\text{VO}(i\text{-C}_3\text{H}_7\text{-triaz-bp-CH}_3)]_2$	580	590	580	590	b	2.009	36.8	68.5	11.4	30.5

a Insoluble; b Not done; $c A_0 = 1/3 (A_{\parallel} + 2A_{\perp})$.

et al 1973; Okawa *et al* 1974; Havinale and Pujar 1981). In the case of the present complexes this possibility is excluded because of the expected large metal-metal separation of $\sim 12 \text{ \AA}$ (Hodgson 1983). Another alternative is the possible oxidation of the bridging biphenyl unit leaving an unpaired electron on the unit which could be paired with one of the two electrons of the oxovanadium(IV) unit to leave only one unpaired electron per binuclear complex thereby providing a μ_{eff} value of 1.22 BM per

compound (Felthouse and Hendrickson 1978; Hasty *et al* 1978). Such a possibility is excluded because of the range of ω_{eff} values (0.8–1.3 BM) observed for the compounds. Antiferromagnetic interaction mediated through a delocalising ligand system is another possibility. Because of the possible p orbital overlap of the coordinating nitrogen and oxygen with the metal d_{xy} orbital containing the unpaired electron, it can be delocalised from one centre to the other through the conjugated ligand framework. The analogous binuclear copper(II) compounds show such electron delocalisations resulting in reduced μ_{eff} values (Zacharias and Ramachandriah 1985). Exchange interaction through the bridging conjugated ligand system appears to be the predominant mechanism for the reduction of μ_{eff} values.

The X-band esr spectra were recorded for the crystalline, solution and frozen samples. The polycrystalline samples gave strong absorption with a g_{\perp} value of ~ 2.01 . The parallel component is hyperfine split and has been found to spread over a region of 600 G ($g_{\parallel} \sim g_{\perp}$). Solution spectral measurements in dichloro methane gave well-resolved fifteen line patterns in most cases with hyperfine splitting constants (A_{iso}) of ~ 35 G. A representative esr solution spectrum and frozen solution spectrum in dichloro methane are given in figure 2. A fifteen-line pattern is observable in the parallel region. The corresponding monomeric complexes show an eight-line pattern in solution (figure 2) and the relevant esr data are given in table 2.

The esr spectral results can be discussed on the basis of two models. In the first, a system with two interacting oxovanadium(IV) centres is considered. The fifteen-line esr pattern with hyperfine splitting constant approximately half that of the corresponding monomer complexes ($A_{\text{iso}} \sim 70$ G for monomers) and the low magnetic

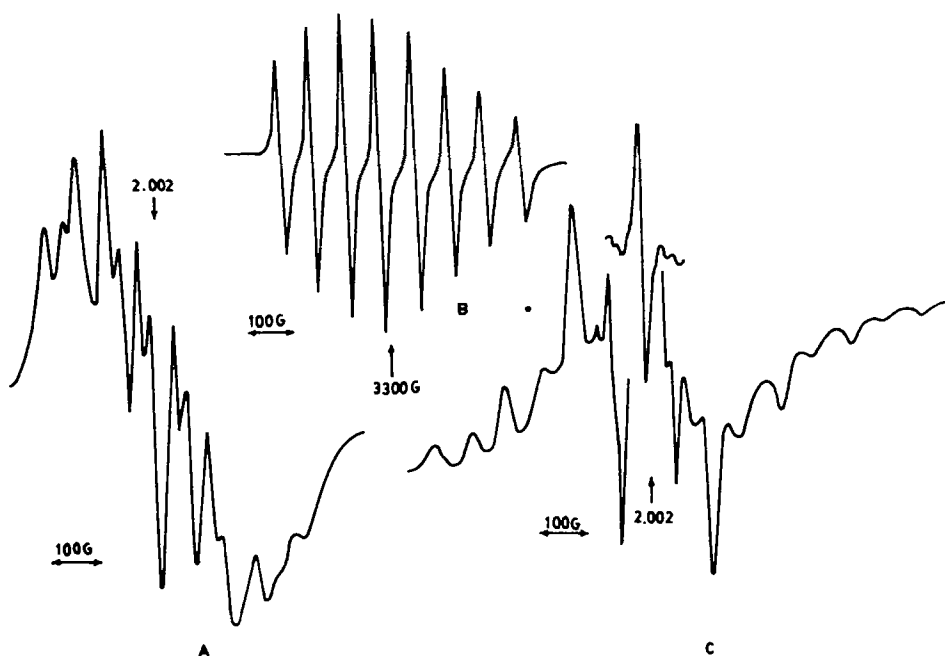


Figure 2. (A) solution esr spectrum of $[\text{VO}(\text{C}_2\text{H}_5\text{-triaz-bp-CH}_3)_2]$ at 297 K in dichloromethane; (B) $[\text{VO}(\text{C}_2\text{H}_5\text{-triaz-bp-CH}_3)_2]$, monomer at 297 K in dichloromethane; (C) frozen esr spectrum of $[\text{VO}(\text{CH}_3\text{-triaz-bp-CH}_3)_2]$ at 115 K.

moments observed for the complexes can be explained by this model. The possible pathway for this interaction has been discussed above. In the second model, a system with two non-interacting oxovanadium centres is considered. The occurrence of the fifteen-line pattern can then be the result of the splitting of the eight-line pattern of the isolated vanadium centre by the two nitrogens coordinated to the metal centre. This possibility has been discounted by the fact that the nitrogen hyperfine splitting constant is very low compared to the values observed here. Also the number of lines expected from this model far exceeds the fifteen-line pattern. This model cannot explain the low magnetic moment.

It may be pointed out that the analogous binuclear copper(II) complexes whose structures have been determined by the X-ray method show esr spectra (seven-line pattern) and low μ_{eff} values characteristic of interacting metal centres. The magnitude of exchange interaction is greater in oxovanadium complexes as evidenced by the larger deviation of μ_{eff} values. This may be due to the difference in the d orbital which contains the unpaired electron. In the binuclear oxovanadium system the unpaired electron is in the d_{xy} orbital while in the binuclear copper(II) system it is in the $d_{x^2-y^2}$ orbital.

4. Conclusions

It can be concluded from these experimental data that binuclear complexes of the type $[\text{VO}(\text{R-triaz-bp-X})_2]$ show magnetic properties which can be explained on the basis of an interacting dimer. The enhanced magnitude of interaction in these complexes as compared to analogous copper(II) complexes is attributed to the difference in the d orbitals which contain the unpaired electron. The esr spectral data support the presence of interacting oxovanadium(IV) centres.

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