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# Magnetic Properties of NN'-Propylenebis-(salicylaldiminato)oxovanadium(IV)

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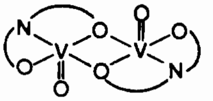
*The title compound, which contains vanadyl oxo-bridges, has a magnetic moment of 1.78 BM at 295°K and obeys the Curie-Weiss law ($\theta = -7°$) over the range 95-295°K. The implications of this observation for possible mechanisms of spin-spin coupling in magnetically anomalous oxovanadium(IV) compounds are discussed.*

## Introduction

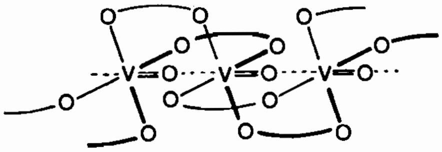
The phenomenon of magnetic coupling in polynuclear or chain polymeric metal complexes continues to attract attention,[1] with the twin objectives of providing more accurate quantitative parameters describing the extent of spin-spin interaction and of determining the mechanism of that interaction, *i.e.* superexchange or direct metal-metal bonding, or their relative contribution if both are possible. One factor which all too frequently limits the interpretation of magnetically anomalous systems is the absence of complete structural information. This is the situation for the various antiferromagnetic oxovanadium(IV) compounds which have been described.[2-7] The structures of these complexes have usually been inferred from their magnetic properties, supplemented in some cases[5] by molecular weight studies, and by analogy with the corresponding copper(II) compounds.

The majority of the magnetically anomalous oxovanadium(IV) complexes reported so far have the stoichiometries [VO(TSB)$H_2O$] or [VO(TSB)] where TSB is a tridentate Schiff base. These compounds have generally been regarded as being dimeric, although association between dimers has been suggested in some cases.[4,5] Zelentsov postulated[2] that the antiferromagnetic coupling observed for these compounds had its origin in a δ-bond between the metal ions. Subsequent workers[4,5] have attributed the exchange coupling to direct σ-overlap between the $3d_{xy}$ orbitals of the vanadium atoms in dimers of type I (with a water molecule occupying the sixth coordination position in the case of the hydrates).



I

Vanadyl acetate also displays pronounced antiferromagnetic coupling.[6,7] In this case, however, the observation[6,7] of a V=O stretching band close to 900 cm$^{-1}$ was taken as evidence for vanadyl oxygen bridges, and the application of both Heisenberg and Ising models to the experimental magnetic susceptibilities led to the suggestion of a chain structure, II, involving both V=O....V and carboxylate bridges. In particular, it has been proposed[6] that the exchange pathway involves the z-component of the spin but not the x- and y-components. This raises the question as to whether the bridging oxygen atoms are significantly involved in the spin-coupling process. Moreover, intermolecular vanadium-vanadium «interactions» via the vanadyl oxygen atoms have also been cited[4] as a possible cause of a higher J value in the oxovanadium (IV) complex with 5-nitro-N-(2-hydroxyphenyl)salicylideneimine, as compared with closely-related complexes, by altering the relative effective charges of the vanadium atoms within each dimer.



II

Recent X-ray work[8] has shown that NN′-propylenebis(salicylaldiminato)oxovanadium(IV), VO(salpn), contains vanadyl oxygen bridges and this provides a good example for checking the possibility of spin-coupling by this pathway.

## Results and Discussion

Orange yellow VO(salpn) was obtained essentially as described by Pfeiffer *et al.*,[9] but using vanadyl sul-

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(1) R.L. Martin, «*New Pathways in Inorganic Chemistry*», Cambridge Univ. Press, 1968, p« 175.

(2) V V. Zelentsov, *Russ. J. Inorg. Chem.*, *7*, 670 (1962).

(3) V.V. Zelentsov, V.T. Kalinnikov, and M.N. Volkov, *Zhur. Strukt. Khim.*, 6, 647 (1965).

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(5) L.J Theriot, G.O. Carlisle, and H.J. Hu, *J. Inorg. Nucl. Chem.*, *31*, 3303 (1969).

(6) A.T. Casey and J.R. Thackeray, *Aus. J. Chem.*, *22*, 2549 (1969).

(7) D.R. Dakternieks, C.M. Harris, P.J. Milham, B.S. Morris, and E. Sinn, *Inorg. Nucl. Chem. Lett.*, *5*, 97 (1969).

(8) M. Mathew, A.J. Carty, and G.J. Palenik, *J. Am. Chem. Soc.*, *92*, 3197 (1970).

phate instead of vanadyl acetate. The $V=O$ stretching frequency of 857 cm$^{-1}$ for our sample is in good agreement with the literature[8] value. The X-band e.p.r. spectrum of a polycrystalline sample at 117°K showed a single, relatively sharp band at $g = 1.964$.

The magnetic moment of the complex was found to be 1.78 BM at 295°K, and variable temperature studies (Table I) showed that it obeyed the Curie-Weiss law over the range 95-295°K with only a small Weiss constant (–7°). The magnetic susceptibilities were not field dependent.

**Table I.** Temperature dependence of the magnetic susceptibilities of VO(Salpn)

| T(°K) | $10^6\chi'_m$ | $\mu_{eff}$(BM)[a] |
|---|---|---|
| 295 | 1325 | 1.78 |
| 266 | 1460 | 1.77 |
| 231 | 1560 | 1.76 |
| 196 | 1990 | 1.77 |
| 162 | 2310 | 1.73 |
| 130 | 2910 | 1.75 |
| 97 | 3890 | 1.75 |

[a] Calc. from Curie law.

The lack of significant spin coupling between the metal ions in this compound suggests that the unpaired electron on each vanadium atom is in the $d_{xy}$ orbital, and that the vanadyl oxygen bridges provide little or no antiferromagnetic coupling due to intra-ionic exchange[1] via $\sigma$ ($Op_z$–$Vd_{z^2}$) or $\pi$ ($Op_x$, $p_y$–$Vd_{xz}$, $d_{yz}$) pathways. This fact and the observation[7] that vanadyl sulphate, which also contains oxovanadium bridges,[10] has a normal magnetic moment at room temperature, imply that in vanadyl acetate the vanadyl oxygen atoms do not contribute significantly to the antiferromagnetic coupling.

Bridging acetate groups could, however, provide a very effective pathway for the spin exchange by $\pi$-overlap of the singly occupied $d_{xy}$ orbital of each vanadium atom with the $\pi$-symmetry molecular orbitals of the carboxylate groups. Intra-ionic exchange arising from carboxylate→vanadium $\pi$-bonding ($\pi \rightarrow d_{xy}$ and $\pi_{n.b.} \rightarrow d_{xy}$) and also from mutual overlap of the half-filled $d_{xy}$ orbitals on each vanadium with empty $\pi^*$-carboxylate orbitals would in each case lead to spin-coupling of antiferromagnetic sign.

## Experimental Section

*Preparations.* *NN'–Propylenebis–salicylaldimine.* Concentrated ethanolic solutions of salicylaldehyde and propane-1,3-diamine (slight excess over 2:1 molar ratio) were mixed at room temperature. On cooling the solution, yellow crystals of the Schiff's base separated. The crystals were filtered, washed with small quantities of cold ethanol and dried in vacuo.

*Anal.* Found: C, 72.08; H, 6.52; N, 9.69. Calcd. C, 72.40; H, 6.38; N, 9.93%.

*NN'–Propylenebis(salicylaldiminato)oxovanadium* (IV). The ligand (1.4 g, 5 m*M*) and hydrated vanadyl sulphate (Hopkins and Williams) (0.8 g, 5 m*M*) were warmed together in methanol (100 ml). The orange-yellow complex precipitated as a fine powder. The complex was filtered off, washed with methanol and dried in vacuo. Recrystallisation of the complex proved impossible due to its low solubility in most solvents.

*Anal.* Found: C, 58.78; H, 4.72; N, 7.82. Calcd. C, 58.80; H, 4.61; N, 8.06%.

*Physical Measurements.* The i.r. spectrum was obtained using a nujol mull and a Perkin Elmer Model 257 instrument. The other measurements were carried out as described previously.[11]

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(10) P. Kierkegaard and J.M. Longo, *Acta Chem. Scand.*, *19*, 1906 (1965).

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