# Magnetism of Oxovanadium(IV) Complexes of Binucleating Ligands. Oxidation to and Structure of a Mononuclear Oxovanadium(V) Complex of *N,N'*-(pentan-3-ol)bis(salicylaldimine)

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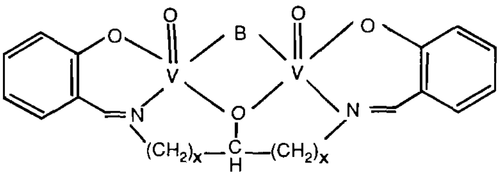
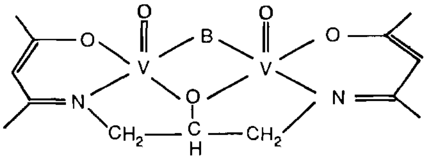
In this communication we report examples of binuclear oxovanadium(IV) moieties complexed to pentadentate binucleating ligands of the types shown in **1** and **2**. Coordination of such ligands to the terminal and endogenous sites of $Cu^{2+}\cdot\cdot Cu^{2+}$ pairs is now well established [1, 2] but there is only one previous report of $VO^{2+}\cdot\cdot VO^{2+}$ pairs and this involved use of a 4-methylphenolate endogenous bridging group [3].



**1**

| Complex | *x* | B |
|---|---|---|
| **1a** | 1 | pyrazolate |
| **1b** | 1 | $OH^-$ |
| **1c** | 2 | $OMe^-$ |
| **1d** | 2 | $OEt^-$ |

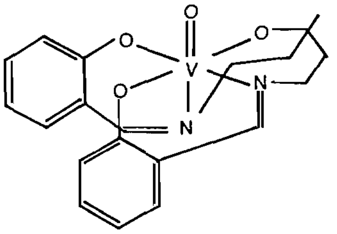


**2**

**2a** B= pyrazolate
**2b** B= acetate

A long time interest in vanadium chemistry [4] has been rekindled in the present work, not only in order to obtain magnetostructural correlations for comparison with other $VO^{2+}\cdot\cdot\cdot VO^{2+}$ ($d^1\cdot\cdot d^1$) dimers, but also because of the recent recognition of the coordination of vanadium to the active sites of various biomolecules [5]. With the bioinorganic point of view in mind we have recently reported the structural, ESR and redox features of {S, N}-chelated oxovanadium(IV) compounds [6] and now turn our attention, once more [7], to {O, N}-bonded systems.

It is clear from the present work, and from other recent related studies [8–10], that oxovanadium(IV) chelates are not as stable to air as is traditionally thought and so, as indicated above, care has to be taken to avoid the formation of the oxovanadium(V) analogues. However, the formation of such $V^V$ species does have the advantage that it allows studies of redox relations between $V^{IV}$ and $V^V$ as a function of the coordination environment and geometry, etc. The structure is described for a mononuclear oxovanadium(V) complex (**3**), a rare example of a six-coordinate $VO^{3+}$ complex [11], obtained as an oxidative by-product in the synthesis of **1c** and **1d**.



**3**

## Experimental

### *Synthesis of binuclear oxovanadium(IV) complexes*

A typical procedure is given in the case of complex **1a**. A solution of *N,N'*-(propan-2-ol)bis(salicylaldimine) (0.045 g, 0.15 mmol) [2] in acetonitrile (5 ml) was mixed with an acetonitrile/chloroform solution (5 ml/3 ml) containing $VO(acac)_2$ (0.08 g, 0.30 mmol) and pyrazole (0.018 g, 0.26 mmol). On standing at room temperature, the resulting red–brown solution first deposited a yellow/orange solid of formula VO(LH) (where $LH_3$ = fully protonated ligand). This solid showed $\nu(OH) = 3480$ cm$^{-1}$ and $\nu(V{=}O) = 875$ cm$^{-1}$. The filtered solution, on slow evaporation, then yielded well-formed violet-coloured crystals of **1a**. *Anal.* Calc. for $C_{20}H_{18}N_4O_5V_2$; C, 48.4; H, 3.7; N, 11.3. Found: C, 47.8; H, 3.4; N, 10.7%. Mass spectrum: $m/e = 496$ ($M^+$). I.R. (Nujol, cm$^{-1}$) 990 cm$^{-1}$ ($\nu(V{=}O)$). UV-Vis (DMF, nm) 510 ($\epsilon = 105$), 378 ($\epsilon = 4507$).

### *Synthesis of the oxovanadium(V) complex 3*

To a methanolic solution containing *N,N'*-(pentan-3-ol)bis(salicylaldimine) and $VO(acac)_2$ in a 1:2 molar ratio was added a methanolic KOH solution. A grey–green precipitate of the $\mu$-hydroxo-oxovanadium(IV) dimer was deposited from the brown solu-

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tion. Evaporation to dryness, extraction into chloroform, followed by washing of the chloroform layer with water and drying over $MgSO_4$ yielded a red–brown solution from which well-formed crystals of **3** were obtained on addition of absolute ethanol. The crystals were suitable for X-ray analysis. Mass spectrum: $m/e = 390(M^+)$ I.R. 940 $cm^{-1}$ ($\nu$(V=O)).

### *X-ray Crystallography of 3*

Intensity data for 2915 reflections ($\theta_{max}$22.5°) were collected on an Enraf-Nonius CAD4 diffractometer fitted with Mo K$\alpha$ radiation, $\lambda = 0.7107$ Å. The data were corrected for Lorentz and polarization effects and for absorption (max and min transmission factors: 0.911 and 0.840). There were 2683 unique reflections of which 1714 satisfied the $I \geqslant 2.5\sigma(I)$ criterion.

Crystal data for $C_{19}H_{19}N_2O_4V$ are: $M = 390.3$, monoclinic, space group $P2_1/n$, $a = 6.752(1)$, $b = 18.091(2)$, $c = 14.324(1)$ Å; $\beta = 101.93(1)°$, $U = 1711.9$ Å$^3$, $Z = 4$, $D_c = 1.514$ g cm$^{-3}$, $F(000) = 808$, $\mu = 5.55$ cm$^{-1}$. The structure was solved from the Patterson and refined by a full-matrix least-squares procedure based on $F$ [12]. The V, N and O atoms were refined anisotropically and the remaining atoms were refined isotropically; hydrogen atoms were included in their calculated positions. Unit weights were employed throughout the refinement and at convergence final $R = 0.054$.

### *Physical Measurements*

Magnetic and spectral measurements were made as described previously [2].

## Results and Discussion

### *Binuclear oxovanadium(IV) complexes*

A range of conditions have been employed in synthesizing complexes of type **1** and **2**. The salicylaldimine ligands used in **1** were isolated prior to reaction while the acetylacetoneimines in **2** were formed *in situ*. Two mole equivalents per ligand of $VO(acac)_2$ were commonly used as the source of $VO^{2+}$ but it is also possible to employ {$VOCl_2$ + base} or {$VCl_3$ + base (in air)}. Variation in solvent medium can lead to different products being formed and variation in the length of the diamine backbone can also influence the nature of the product. Air sometimes needs to be excluded to prevent oxidation to vanadium(V). Use of the exogenous bridging ligand B = pyrazole led to the formation of well-formed pale violet crystals of the $\mu$-pyrazolate complexes **1a** and **2a**, both of which contain the *N,N′*-propan-2-ol backbone. A combination of good analytical data and observation of the parent ion in the mass spectra confirm the binuclear formulation. It was found in the case of ligand **1** ($x = 1$), in this synthesis and especially in others using alcohol solvents, that an insoluble yellow/orange 'mononuclear' product has to be selectively crystallised from the desired product. A $\nu$(OH) band at 3480 cm$^{-1}$ and $\nu$(V=O) at 875 cm$^{-1}$ were indicative of a non-coordinated (protonated) alcohol group and intermolecular ··V=O··V=O··V=O interactions within a polymeric structure [13].

**1a** and **2a** showed strong bands at 990 cm$^{-1}$, a position generally indicative of five-coordinate $VO^{2+}$ [14]. The more flexible pentane-3-ol backbone ligand ($x = 2$) could not be induced to form a $\mu$-pyrazolate bridged complex presumably because the V–N–N–V exogenous bridge could not be locked into position long enough for the compound to precipitate out.

A variable temperature magnetic study on **1a**, shown in Fig. 1, yields a maximum in susceptibility typical of weakly antiferromagnetically coupled $S = 1/2$ $VO^{2+}$ ions with a sharp rise in $\chi$ at low temperatures due to monomer impurity. Least-squares fitting to the $-2JS_1 \cdot S_2$ Bleaney–Bowers equation [15] gave the $g$ and $J$ values shown in Table 1. As can be seen in Table 1, **1a** and **1c** are some of the first examples of asymmetrically bridged $VO^{2+}\cdots VO^{2+}$ dimers, most of the other examples quoted being symmetrical. The $\mu$-pyrazolate exogenous bridge gives weaker coupling than does the $\mu$-methoxo, as generally expected [2]. The coupling in **1a** is weaker than it is in the $Cu^{II}\cdots Cu^{II}$ analogue, which is in line with the magnetic orbitals being of different symmetry in the two analogues. This, in turn, affects any superexchange mechanism operating via the pyrazolate and alcoholate bridging group [16]. Direct exchange involving the vanadium $d_{xy}$ orbitals might also be a contributing factor in the present system. The $J$ value in **1c** is of similar magnitude to that in the related phenolate-bridged complex [$((VO)_2$-fsalapH)OMe] [3] and to those displayed by the symmetrical O-bridged systems listed in Table 1. A multiatomic bridging ligand, oxalate, in $(VO(acac))_2$-

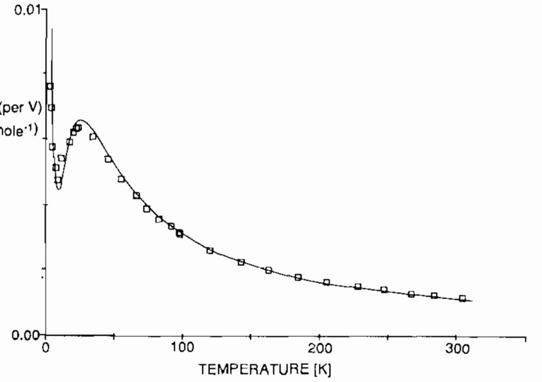

Fig. 1. A plot of susceptibility vs. temperature for complex **1a**. The solid line uses the calculated values of $g$ and $J$ given in Table 1.

TABLE 1. Exchange coupling in **1a**, **1c** and related VO••VO binuclear systems[a]

| Complex | *g* | *J* ($cm^{-1}$) | % monomer | Reference |
|---|---|---|---|---|
| **1a** | 1.93[b] | −16.5 | 8.8 | tw |
| $Cu_2$ analogue of **1a** | 2.00 | −120 | | 2 |
| **1c** | 1.80 | −107 | 5.1 | tw |
| $(VO)_2$(fsalapH)(OMe) | 1.86 | −115 | | 3 |
| $[(VO(acac)OMe)]_2$ | 1.95 | −61 | | 21 |
| $[VO(tpen)(OH)]_2{}^{2+}$ | 1.80 | −150 | | 22 |
| $[VO(L)(OH)]_2{}^{2+}$ | | −177 | | 23 |
| $[VO(L)(OAc)]_2{}^{2+}$ | 2.2 | −114 | | 24 |
| $[[VO(acac)]_2(C_2O_4)]\cdot 4H_2O$ | 1.98 | −5.7 | | 16 |

[a] tw = this work; tpen = tetrakis(2-pyridylmethyl)ethylenediamine; L = 1,4,7-triazacyclononane; fsalapH = 2,6-bis[*N*-(2-hydroxyphenyl)iminomethyl]-4-methylphenol. [b] From ESR (77 K), *g* 1.95.

($C_2O_4$) yields a similar sized *J* value to that in **1a** [16]. More detailed structure/magnetism correlations must await crystal structure determinations on complexes **1** and **2**.

### *Formation and Structure of the Six-coordinate Oxovanadium(IV) Monomer 3*

It was found that the mother liquors left behind after precipitation of the grey–green-coloured binuclear $VO^{2+}$ complexes **1c** and **1d**, as well as those left from attempts to make corresponding μ-pyrazolate dimers, yielded orange/red diamagnetic crystals on standing in air. The mass spectra of these crystals show peaks due to the monometallic fragment [VO(ligand)], while the IR spectra show a strong peak at 940 $cm^{-1}$ indicative of a terminal V=O group perhaps within a six-coordinate geometry. A crystal structure determination confirmed these findings and, as can be seen in Fig. 2, the trinegatively charged pentadentate *N,N′*-pentane-3-ol-based ligand has wound itself around five of the coordination sites of the $[VO]^{3+}$ moiety. The other vanadyl group has been lost during oxidation. Similar oxidations of other Schiff base [9, 10] hydrazone [8] or oxine [17] chelates of $VO^{2+}$ have recently been reported and the structures of a few five-coordinate [8, 9, 18] and six-coordinate [19, 20] $VO^{3+}$ products have been solved in which the coligands have usually been bidentate, tridentate or tetradentate chelates. Interestingly, and in contrast to **3**, a recently reported dioxovanadium(V) dimer [10], prepared in basic solution, contains a protonated and non-bonded $-CH_2CH_2OH$ fragment attached to a bonded salicylaldimine group.

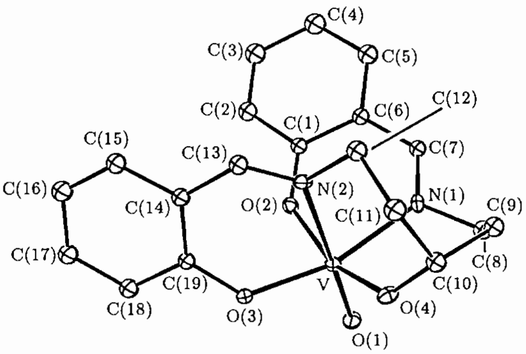

Fig. 2. Molecular structure and numbering scheme for the oxovanadium(V) complex 3. Selected interatomic parameters: V–O(1), 1.614(4); V–O(2), 1.909(5); V–O(3), 1.886(4); V–O(4), 1.819(5); V–N(1), 2.105(5); V–N(2), 2.329(5) Å; O(1)–V–N(2), 178.3(2); O(2)–V–O(4), 159.6(2); O(2)–V–N(1), 83.0(2); O(3)–V–N(1), 163.2(2); O(4)–V–N(1), 82.8(2); O(4)–V–N(2), 81.6(2)°.

The vanadium atom in **3** exists in a distorted octahedral geometry comprised of the oxo function and three oxygen and two nitrogen donor atoms of the multidentate ligand which results in the formation of four six-membered rings. The greatest deviation from the ideal octahedral geometry is manifested in the O(2)–V–O(4) angle of 159.6(2)° reflecting the steric constraints of the ligand. The V–N(2) bond *trans* to the oxo group is significantly longer at 2.329(5) Å than the V–N(1) bond distance of 2.105(5) Å which is *trans* to the O(3) atom. This *trans* effect has also recently been noted in other six-coordinate $VO^{3+}$ structures [19, 20].

## Supplementary Material

Tables of fractional atomic coordinates, thermal parameters, interatomic bond distances and angles are available on request from the authors (E.R.T.T.).

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