

Spontaneous Self Assembly of the $\{M_2(\mu-O)(\mu-MeCO_2)_2\}^{2+}$ Core. Synthesis, Structure, and Properties of the Binuclear Vanadium(III) Complex

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The green complex $[L_2V_2(\mu-O)(\mu-MeCO_2)_2] \cdot 2H_2O$, where L represents *N,N',N''*-trimethyl-1,4,7-triazacyclononane, is formed spontaneously on hydrolysis of $LVCl_3 \cdot dmf$ (*dmf* = dimethylformamide) in water in the presence of sodium acetate; characterization by X-ray crystallography showed the presence of the μ -oxo-di- μ -acetato-divanadium(III) core.

Recently a number of low-molecular-weight, binuclear complexes containing the $\{M_2(\mu-O)(\mu-MeCO_2)_2\}^{2+}$ core ($M = Fe^{III}$ or Mn^{III}) have been synthesized *via* spontaneous self-assembly¹ indicating the inherent stability of this moiety.² The iron(III) compounds serve as accurate models for the spin-coupled di-iron centres in the metalloproteins hemerythrin³ and possibly in ribonucleotide reductase.⁴ The manganese(III) complexes,⁵ which are electrochemically reversibly oxidized to yield Mn^{III} - Mn^{IV} mixed valence complexes, serve as models for the water oxidizing metalloprotein photosystem II.⁶

Here we report the synthesis, structure, and properties of a similar binuclear complex of vanadium(III). Our knowledge of the co-ordination chemistry of vanadium(III) with O,N-donor ligands and carboxylates is still fragmentary.⁷ Vanadium is an essential element in life and its biochemistry is currently being

studied intensively.⁸ We have prepared the mononuclear violet complex *N,N',N''*-trimethyl-1,4,7-triazacyclononanetrichlorovanadium(III), $LVCl_3 \cdot dmf$, from VCl_3 (0.3 g) dissolved in dry dimethylformamide (*dmf*; 30 ml) at 100 °C under an argon atmosphere followed by addition of the cyclic amine L (0.35 g). The red solution was refluxed for 1 h and then cooled to room temperature. Crystals of $LVCl_3 \cdot dmf$ † were filtered off, washed with ethanol and ether, and dried under argon (yield 60%). When an aqueous solution (50 ml) of $LVCl_3 \cdot dmf$ (0.5 g), which contained sodium acetate (2 g), was heated at 95 °C for 10 min., a clear, dark green solution

† Satisfactory elemental analyses were obtained; i.r. data for $[L_2V_2(\mu-O)(\mu-MeCO_2)_2] \cdot 2H_2O$ (KBr disk): $\nu_{as}(\text{CO})$ 1590 and 1550; $\nu_s(\text{CO})$ 1468 and 1430; $\nu_{as}(V-O-V)$ 670 cm^{-1} .

Table 1. Comparison of crystallographic data for $[L_2M_2(\mu-O)(\mu-MeCO_2)_2]^{2+}$ complexes ($L = N,N',N''$ -trimethyl-1,4,7-triazacyclononane).

	V	Mn	Fe
M-O/Å	1.792(4)	1.810(4)	1.800(3)
M-O-M ^o	130.2(2)	120.9(1)	119.7(1)
M-N/Å ^a	2.219(5), 2.158(5)	2.232(5), 2.131(7)	2.268(6), 2.198(4)
M-O _{ax} /Å	2.055(5)	2.047(4)	2.034(3)
M...M/Å	3.250(2)	3.084(3)	3.12(1)

^a The first value corresponds to the M-N distances *trans* to the μ -oxo bridge.

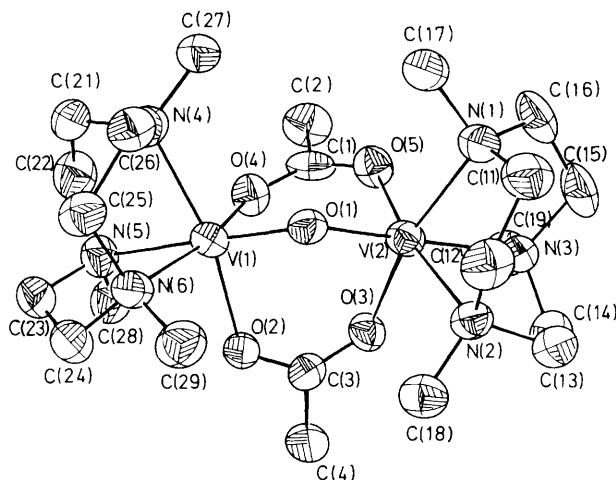


Figure 1. Structure of the cation $[L_2V_2(\mu-O)(\mu-MeCO_2)_2]^{2+}$ with 40% probability thermal ellipsoids and showing the atom labelling scheme. For clarity, hydrogen atoms are omitted. Selected interatomic distances (Å) and angles ($^\circ$) are as follows: V(1)-O(1) 1.794(4); V(2)-O(1) 1.789(4); V(1)-O(2) 2.039(4); V(2)-O(3) 2.052(4); V(1)-O(4) 2.039(5); V(2)-O(5) 2.062(4); V(1)-N(4) 2.166(5); V(2)-N(1) 2.152(5); V(1)-N(5) 2.219(5); V(2)-N(2) 2.155(5); V(1)-N(6) 2.158(5); V(2)-N(3) 2.238(5); V(1) ... V(2) 3.250(2); V(1)-O(1)-V(2) 130.2(2), N-V-N 80.3(2)-81.8(3); O(1)-V(1)-N(5) 177.8(5); O(1)-V(2)-N(3) 180.0(6).

resulted from which, upon addition of sodium iodide (2 g), green crystals of $[L_2V_2(\mu-O)(\mu-MeCO_2)_2]I_2 \cdot 2H_2O^+$ precipitated at 0 $^\circ$ C within 2 weeks. The material is stable towards air oxidation in the solid state but decomposes slowly in solution in the presence of air. Crystals of $[L_2V_2(\mu-O)(\mu-MeCO_2)_2]I_2 \cdot 2H_2O$ suitable for X-ray diffraction studies and elemental analysis were obtained by this method.

The structure (Figure 1) consists of binuclear cations $[L_2V_2(\mu-O)(\mu-MeCO_2)_2]^{2+}$, nonco-ordinated iodide, and water of crystallization.[‡] The vanadium(III) centres are in a distorted octahedral environment of three amine nitrogen atoms and three oxygen atoms of one μ -oxo bridge and of two symmetrical μ -acetato groups, respectively. Very similar structures have been found in the complexes $[L_2M_2(\mu-O)(\mu-$

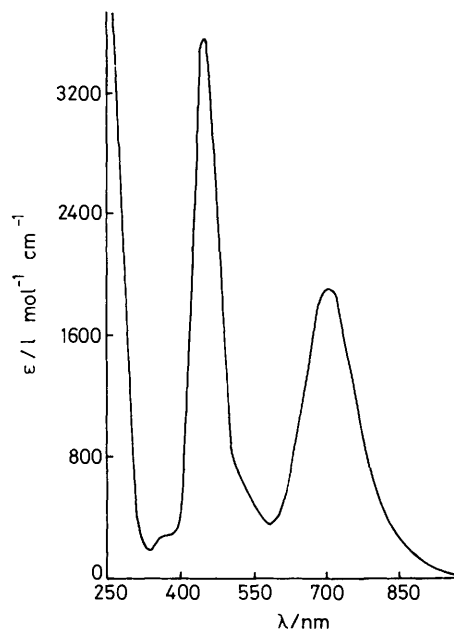


Figure 2. Electronic spectrum of $[L_2V_2(\mu-O)(\mu-MeCO_2)_2]I_2 \cdot 2H_2O$ in acetonitrile.

$MeCO_2)_2]^{2+}$ ($M = Mn^{III}$ or Fe^{III}). The V-O_{oxo} distances are short and comparable to those in the Mn^{III} and Fe^{III} complexes (Table 1) and agree well with those reported for $(thf)_3Cl_2VOVCl_2(thf)_3$ [V-O_{oxo} 1.769(5) Å] ($thf =$ tetrahydrofuran) which is a linearly oxo-bridged dimer of vanadium(III).⁹ Lengthening of V-N distances *trans* to the bridging oxo atoms is a feature also observed in the structures of the Fe^{III} analogues.² In the i.r. spectrum the ν_{as} (V-O-V) band has been identified at 670 cm^{-1} .

Figure 2 shows the electronic spectrum of $[L_2V_2(\mu-O)(\mu-MeCO_2)_2]^{2+}$ measured in acetonitrile. The intense band at 449 nm (ϵ 3550 $l\ mol^{-1}\ cm^{-1}$ per dimer) is characteristic for the (V-O-V)⁴⁺ moiety,^{9,10} and is probably due to an internal charge transfer transition within the V-O-V moiety. The band at 706 nm (ϵ 1.9×10^3 per dimer) is also a charge transfer band.

Magnetic susceptibility measurements for a powdered sample of $[L_2V_2(O)(MeCO_2)_2]I_2 \cdot 2H_2O$ were made by using a Faraday balance in the range 100-300 K. The magnetic moment of 4.95 μ_B per dimer was found to be independent of temperature and indicates four unpaired electrons per dimer with no or negligible intramolecular exchange coupling. An effective magnetic moment of 4.95 μ_B per dimer at 298 K was also measured in acetonitrile solution using an n.m.r. method. This magnetic behaviour of the vanadium(III) oxo-bridged dimer (d^2-d^2) is in contrast to that reported for its iron(III)

[‡] Crystal data: $C_{22}H_{52}I_2N_6O_7V_2$, monoclinic, space group $P2_1/c$, $a = 8.836(5)$, $b = 21.637(6)$, $c = 18.560(7)$ Å, $\beta = 103.09(5)^\circ$, $U = 3456.3$ Å³, $Z = 4$, $R = 0.049$ for 4190 observed [$I \geq 1.5 \sigma(I)$] diffractometer-collected reflections (Mo- K_{α} -radiation, 295 K). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

analogue, where strong intradimer exchange coupling (d^5-d^5 ; $J -115 \text{ cm}^{-1}$) is observed,² and for its manganese(III) analogue which exhibits weak ferromagnetic coupling (d^4-d^4 ; $J +18 \text{ cm}^{-1}$).^{5,11}

In conclusion, we have shown that the $\{M_2(\mu-O)(\mu-MeCO_2)_2\}^{2+}$ core is a very stable entity, which readily is formed in solution *via* spontaneous self-assembly from mononuclear species of various first-row transition metals (V^{III}, Mn^{III}, or Fe^{III}). In addition, the same core has recently been identified in a titanium(IV) dimer.¹²

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