

Crystal Structure and Magnetic Properties of a Copper(II)–Vanadium(IV) Complex of an ‘Open-Ended’ Dinucleating Ligand

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The heterodinuclear copper(II)/vanadium(IV) complex, [bpmpCu(Cl)VO(H₂O)](ClO₄)₂, where bpmp[−] is the ligand 2,6-bis[(bis(2-pyridylmethyl)amino)methyl]-4-methylphenolate(1[−]), has been prepared in a one-pot reaction from Hbpmp, VCl₃ and Cu(ClO₄)₂ in air. The X-ray structure shows the complex to be monoclinic, space group C2/c with eight cations in a cell of dimensions $a = 23.445(3)$, $b = 16.392(3)$, $c = 20.612(3)$ Å and $\beta = 106.955(7)^\circ$. The structure refined to a final R -value of 0.064 for 3379 reflections and 504 variables. The copper and vanadium atoms are bridged by the phenolic oxygen atom of bpmp[−] with $V-O_{\text{phenolate}} = 1.958(6)$ Å and $Cu-O_{\text{phenolate}} = 2.361(5)$ Å. Two dinuclear units are associated via chloride bridging between the Cu atoms with $Cu-Cl = 2.280(3)$ and $3.226(2)$ Å. The vanadium is incorporated as a vanadyl ion and also has a water molecule coordinated. Magnetic susceptibility measurements indicate a very weak ferromagnetic coupling ($J = 0.43 \text{ cm}^{-1}$); this probably originates from a Cu...Cu interaction in the tetranuclear units. The ESR spectrum of [bpmpCu(Cl)VO(H₂O)](ClO₄)₂ confirms the very weak coupling.

The study of heterometallic complexes is interesting due to their potential for unique physiochemical and catalytic properties. However, the syntheses of mixed metal systems is not trivial, and strategies based on providing non-symmetrical ligand environments for the different metal ions have been predominant in attempts to access these types of complexes.^{1–10} In most cases the syntheses have involved step-by-step procedures, i.e. the mononuclear complex of one of the metal ions is first prepared and this is treated with an equivalent of the second metal ion.^{1–4}

Complexes containing a copper(II) and vanadium(IV) ion in close proximity have been of interest due to the possibility of the ferromagnetic coupling of the single unpaired electrons on these d⁹ and d¹ ions, respectively. Only few examples of heterodimetallic copper–vanadium complexes have been reported.^{7–11} One of the complexes, CuVO(fsa)₂en · CH₃OH reported by Kahn *et al.*, was shown to be strongly ferromagnetic.⁷ In this particular complex the vanadium atom has a square-pyramidal geometry and the copper a square-planar geometry, an edge of the two square planes is shared, with two phenolate oxygen atoms bridging

between the metal ions. This particular arrangement led to an orthogonal orientation of the magnetic orbitals on the neighboring paramagnetic metal ions. An ‘open-ended’ compartmental ligand derived from heptane-2,4,6-trione was used to prepare another Cu/V complex.⁸ The magnetic behaviour of this complex was, however, not reported. In contrast to the ligand system we have used in the work described below, the ligand systems used in the two complexes mentioned above are unsymmetrical: chemically different ‘compartments’ are provided for the Cu and V ions.

The phenolate-based ligand, 2,6-bis[(bis(2-pyridylmethyl)amino)methyl]-4-methylphenolate(1[−]), bpmp[−], has been previously reported^{12,13} as capable of giving heterodinuclear complexes of the type [bpmpMM'(RCO₂)]²⁺ despite the fact that the ligands two metal binding compartments are chemically identical. These earlier complexes all differ from the present complex in the type and charge of the metal ions used: all contained one tripositively charged ion (Fe³⁺ or Ga³⁺) and one dipositively charged ion (Zn²⁺, Ni²⁺ or Fe²⁺).^{12,13} Significantly they contain also two supporting exogenous carboxylate bridging groups between the metal ions, in contrast to the system here, in which the phenolate oxygen atom is the only bridge between the copper and vanadium ion.

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Experimental

IR spectra were measured as KBr discs using a Hitachi 270-30 IR spectrometer. UV-visible absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer. Electrospray ionization mass spectra were obtained using a Finnigan TSQ 710 instrument with a combined electrospray and atmospheric pressure chemical ionization source, using an acetonitrile solution. Elemental analyses were carried out at the microanalytical laboratory of the H.C. Ørsted Institute, Copenhagen. Electron spin resonance measurements at X-band frequency were obtained using a Bruker ESP-380E FT-EPR spectrometer, operating at 77 K. A neat powdered sample and a frozen acetonitrile solution were investigated. The magnetic susceptibility was measured using a Quantum Design MPMS 5 instrument operating under a field of 1 T, with the powdered sample contained in a gelatine capsule which was held in the center of a soda straw fixed to the end of the sample rod. The instrument was calibrated with a standard palladium sample, supplied by Quantum Design, and powdered CuSO₄·5H₂O. The ligand 2,6-bis[(bis(2-pyridylmethyl)amino)methyl]-4-methylphenol, Hbpmp, was synthesized as reported previously.¹⁴

Caution: The complex was isolated as a perchlorate salt and thus handled as a potential explosive.

[bpmpCu(Cl)VO(H₂O)](ClO₄)₂. Solid VCl₃ (0.1104 g, 0.70 mmol) was added to a mixture of Hbpmp (0.3556 g, 0.67 mmol) and Cu(ClO₄)₂·6H₂O (0.2467 g, 0.67 mmol) in methanol (10 mL) to give a gray-blue colored solution. Turquoise crystals of the product were deposited overnight. These were collected and washed with methanol. Recrystallized from acetonitrile. (0.508 g, 84%) [bpmpCu(Cl)VO(H₂O)](ClO₄)₂, C₃₃H₃₅N₆O₁₁Cl₃CuV requires: C, 43.43; H, 3.87; N, 9.21%. Found: C, 43.35; H, 3.89; N, 8.67%. IR (cm⁻¹): ν_(V=O) 976 cm⁻¹. *m/z*: [bpmpCu(Cl)VO]²⁺, 100%. UV-vis (CH₃CN) λ, nm (ε, M⁻¹ cm⁻¹): 258 (15738); 300sh (6438); 634 (154).

Crystal structure determinations. Cell dimensions were determined from 25 reflections measured at four positions, ±20 and high and low χ. Intensities were measured at room temperature using a Huber diffractometer. The intensities of two standard reflections were measured every 50 reflections. Crystal data for [bpmpCu(Cl)VO(H₂O)](ClO₄)₂ are given in Table 1. Data were corrected for background, Lorentz and polarization effects and for absorption. An empirical absorption correction¹⁵ was made after isotopic refinement. The structure was solved using SIR92¹⁶ and was refined by the least-squares minimization of Σw(|F_o|-|F_c|)² using a modification of ORFLS.¹⁷ All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms of the ligand were kept fixed at calculated positions, with isotropic thermal parameters 20% larger than the equivalent isotropic thermal parameter of the atom to which

Table 1. Crystal data and details of data collection and structure refinement.

FW	918.56
Space group	C2/c
Cell parameters (294 K)	
<i>a</i> /Å	23.445(3)
<i>b</i> /Å	16.392(3)
<i>c</i> /Å	20.612(3)
β/°	106.955(7)
<i>V</i> /Å ³	7577(2)
No. reflections centred	4 × 25
2θ range/°	20.1–26.0
Calculated density (294 K)/g cm ⁻³	1.610
Formula units per cell	8
Crystal size/mm	0.4 × 0.3 × 0.2
λ(Mo Kα)/Å	0.71073
Scan type	ω–2θ
No. steps	50
θ limits/°	1–25
Octants collected	± <i>h</i> + <i>k</i> + <i>l</i>
Standard reflections	8 0 0, 3 –3 –3
Fall-off in intensity (%)	<1
No of unique data	5512
No. of data with <i>I</i> /σ(<i>I</i>) > 3.0	3379
No. of variables	504
Weighting scheme, <i>w</i> ^{-1/2}	[σ _{cs} (<i>F</i> ²) + 1.03 <i>F</i> ²] ^{1/2} – <i>F</i>
Linear absorption coefficient/cm ⁻¹	10.77
Range of transmission factors	0.33–1.44
<i>R</i> = Σ(<i>F</i> _o – <i>F</i> _c)/Σ <i>F</i>	0.064
<i>R</i> _w = [Σw(<i>F</i> _o – <i>F</i> _c) ² /Σw <i>F</i> _o ²] ^{1/2}	0.079
Σ = Σw(<i>F</i> _o – <i>F</i> _c) ² /(<i>N</i> _o – <i>N</i> _v)	1.66
Δ/σ _{max}	0.04
Δρ _{max} /e Å ⁻³	0.54(6)

they were attached. Fractional atomic coordinates for [bpmpCu(Cl)VO(H₂O)](ClO₄)₂ are listed in Table 2. Atomic scattering factors and anomalous dispersion corrections were taken from Ref. 18.

Additional material available from the Cambridge Crystallographic Data Center comprises H-atom coordinates, and remaining bond lengths and angles.

Results and discussion

Syntheses. Reaction of Hbpmp with one equivalent each of VCl₃ and Cu(ClO₄)₂ in air gives spontaneously the mixed metal complex [bpmpCu(Cl)VO(H₂O)](ClO₄)₂. The vanadium(III) is oxidized to vanadyl with a ν_(V=O) stretch at 976 cm⁻¹ evident in the IR spectrum. The mass spectrum shows that the base peak at *m/z* 347.1 is due to the doubly charged cation minus the coordinated water, [bpmpCu(Cl)VO]²⁺. There is no evidence in the mass spectrum that samples of [bpmpCu(Cl)VO(H₂O)](ClO₄)₂ are contaminated with even trace amounts of either of the corresponding homodinuclear complexes.

Crystal and molecular structure of [bpmpCu(Cl)VO(H₂O)](ClO₄)₂. The structure of the dinuclear cation is depicted in Fig. 1. Selected bond distances and angles are presented in Table 3. The ligand Hbpmp is deprotonated, and the phenolic oxygen atom bridges the Cu^{II}

Table 2. Fractional atomic coordinates and U_{eq}^a (in Å²).

Atom	x	y	z	U_{eq}
Cu	0.92461(4)	0.18902(6)	0.77699(5)	0.0359(5)
V	0.76323(5)	0.12042(9)	0.67742(7)	0.0355(7)
Cl(1)	0.9332(1)	0.2185(2)	0.6722(1)	0.048(1)
O(1)	0.8194(2)	0.1880(3)	0.7452(3)	0.034(3)
O(2)	0.7887(2)	0.0300(4)	0.6866(3)	0.053(3)
O(3)	0.8021(3)	0.1700(4)	0.6085(4)	0.050(3)
C(1)	0.8002(3)	0.2320(5)	0.7902(4)	0.034(4)
C(2)	0.8235(3)	0.2153(5)	0.8583(4)	0.037(4)
C(3)	0.8012(4)	0.2571(6)	0.9052(5)	0.049(5)
C(4)	0.7557(4)	0.3149(6)	0.8839(5)	0.050(5)
C(5)	0.7353(4)	0.3313(6)	0.8151(5)	0.048(5)
C(6)	0.7567(3)	0.2921(5)	0.7679(4)	0.040(4)
C(7)	0.8671(3)	0.1479(6)	0.8823(4)	0.043(4)
C(8)	0.7268(5)	0.3539(7)	0.9335(6)	0.077(7)
C(9)	0.7318(4)	0.3055(5)	0.6927(4)	0.043(5)
N(1)	0.9283(3)	0.1639(5)	0.8746(3)	0.041(3)
C(11)	0.9569(3)	0.2319(7)	0.9173(4)	0.051(5)
C(12)	0.9450(3)	0.3104(6)	0.8785(5)	0.044(4)
C(13)	0.9507(4)	0.3853(8)	0.9092(6)	0.065(6)
C(14)	0.9444(5)	0.4534(8)	0.8714(8)	0.082(8)
C(15)	0.9300(5)	0.4492(7)	0.8019(7)	0.075(7)
C(16)	0.9224(4)	0.3718(6)	0.7731(5)	0.054(6)
N(17)	0.9308(3)	0.3040(5)	0.8105(4)	0.047(3)
C(21)	0.9633(4)	0.0851(6)	0.8905(5)	0.056(5)
C(22)	0.9465(3)	0.0292(7)	0.8299(6)	0.052(4)
C(23)	0.9498(4)	−0.0553(8)	0.8358(7)	0.068(6)
C(24)	0.9383(5)	−0.0994(7)	0.7776(10)	0.084(6)
C(25)	0.9225(4)	−0.0613(7)	0.7167(8)	0.073(5)
C(26)	0.9194(3)	0.0230(6)	0.7135(5)	0.054(4)
N(27)	0.9315(3)	0.0676(5)	0.7715(4)	0.042(3)
N(2)	0.7001(3)	0.2306(4)	0.6591(3)	0.041(4)
C(31)	0.6768(4)	0.2412(6)	0.5857(5)	0.051(5)
C(32)	0.6620(4)	0.1587(6)	0.5526(5)	0.049(5)
C(33)	0.6212(4)	0.1475(8)	0.4899(5)	0.068(6)
C(34)	0.6094(4)	0.0698(10)	0.4655(6)	0.082(6)
C(35)	0.6368(5)	0.0035(8)	0.5034(6)	0.071(6)
C(36)	0.6773(4)	0.0199(7)	0.5647(5)	0.058(5)
N(37)	0.6912(3)	0.0953(5)	0.5890(4)	0.044(4)
C(41)	0.6500(3)	0.2104(6)	0.6878(5)	0.048(4)
C(42)	0.6680(3)	0.1515(6)	0.7461(5)	0.042(4)
C(43)	0.6393(4)	0.1487(7)	0.7964(5)	0.063(6)
C(44)	0.6581(5)	0.0927(8)	0.8475(6)	0.079(8)
C(45)	0.7026(5)	0.0386(7)	0.8466(5)	0.070(7)
C(46)	0.7292(4)	0.0435(6)	0.7967(5)	0.050(5)
N(47)	0.7123(3)	0.1004(4)	0.7456(3)	0.038(3)
C(12)	0.8548(1)	0.0513(2)	0.4931(1)	0.057(2)
O(4)	0.8464(3)	0.0456(5)	0.4226(4)	0.082(5)
O(5)	0.7977(3)	0.0674(6)	0.5031(4)	0.108(5)
O(6)	0.8925(3)	0.1184(5)	0.5202(4)	0.098(5)
O(7)	0.8808(5)	−0.0206(6)	0.5262(5)	0.137(11)
Cl(3)	0.9779(1)	−0.2998(2)	0.6051(1)	0.077(2)
O(8)	0.9905(7)	−0.2803(11)	0.6671(7)	0.244(17)
O(9)	0.9234(4)	−0.2984(11)	0.5650(6)	0.208(6)
O(10)	1.0185(4)	−0.2699(13)	0.5765(5)	0.245(6)
O(11)	0.9847(10)	−0.3764(11)	0.6152(17)	0.392(26)

^a $U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j a_i$.

and V^{IV} atoms. The three nitrogen donor atoms of the two bis(2-picoly)amine side arms of the ligand are bound to the respective metal ions. The coordination geometries of the copper atom and of the vanadium atom are approximately octahedral. The phenolic oxygen atom occupies an apical position in the coordination

sphere of the Cu ion, and the coordination sphere is completed by two chloride ions, one in an equatorial position, the second (with a Cu–Cl bond distance 0.946 Å longer) in an apical position. The geometry around the vanadium is octahedral, with the two exogenous sites being filled by the vanadyl oxo group and a water

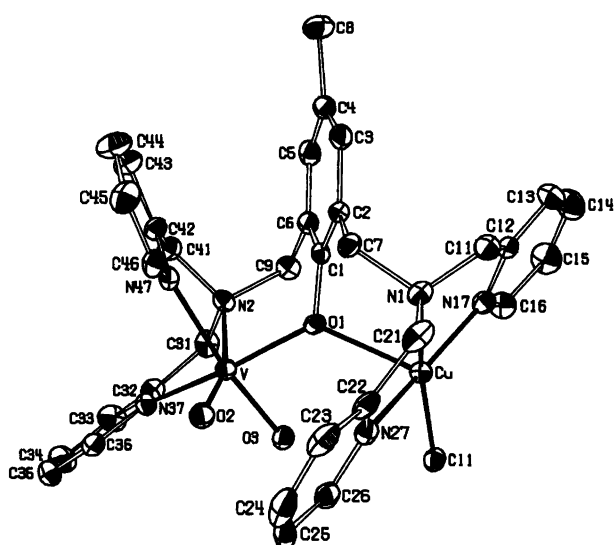


Fig. 1. An ORTEP¹⁹ drawing of [bpmcCu(Cl)VO(H₂O)]²⁺ showing the atomic numbering, (brackets have been omitted for clarity). Thermal ellipsoids are drawn at the 50% probability level.

molecule. The latter appears to be hydrogen bonded to one of the perchlorate counter anions with O(3)···O(5)=2.726(11) Å. The bond lengths between the metal atoms and the bridging phenolic oxygen atom are very different, with V–O(1), 1.958(6) Å and Cu–O(1), 2.361(5) Å. Two dinuclear units are associated via chloride bridging between the Cu atoms as depicted in Fig. 2. The interatomic distances in the two Cu–Cl–Cu moieties are different, with each chloride atom formally bonded to one of the copper atoms with Cu–Cl(1),

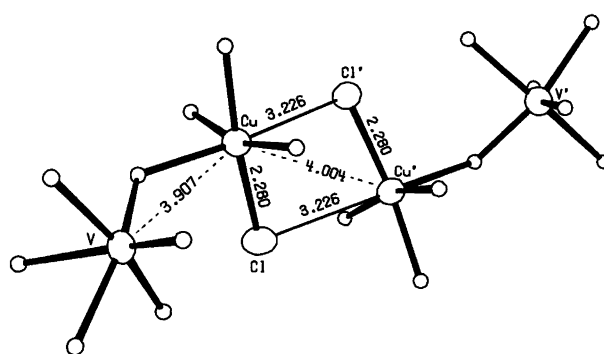


Fig. 2. An ORTEP drawing showing the weak bonding between the cations across a two-fold axis. Symmetry code '2-x, y, 1/2-z'.

2.280(3) Å and the same chloride atom closely associated to the second copper atom with Cu'–Cl(1'), 3.226(2) Å. The distance between the copper atoms of the tetranuclear units is 4.004(2) Å.

Magnetic susceptibility and ESR spectra. A plot of $1/\chi$ versus temperature, in the range 300–4.2 K, is Curie-like with $\chi T = 0.72 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$. The corresponding magnetic moment per dinuclear Cu–VO molecule remains constant at 2.40 BM between 300 and 20 K. It then increases gradually, reaching 2.47 BM at 4.2 K, without levelling off. Figure 3 shows the μ and $1/\chi$ behavior per half molecule. Such behavior is indicative of very weak ferromagnetic coupling of spins. The ESR spectra of the neat powder (Fig. 4) and of a frozen acetonitrile solution show a similar, broad, symmetrical resonance at $g \approx 2$, with no hyperfine splitting evident. A weak 'half-field'

Table 3. Selected distances (in Å) and angles (in °).

Cu···V	3.907(2)	V–O(1)	1.958(6)
Cu–Cu ⁱ	4.004(2)	V–N(2)	2.296(7)
Cu–Cl(1)	2.280(3)	V–O(2)	1.588(6)
Cu–Cl(1 ⁱ)	3.226(2)	V–N(37)	2.132(7)
Cu–N(1)	2.031(7)	V–O(3)	2.065(7)
Cu–N(17)	1.998(8)	V–N(47)	2.118(7)
Cu–N(27)	2.003(8)	O(3)–O(5)	2.726(11)
Cu–O(1)	2.361(5)		
Cl(1)–Cu–O(1)	96.5(1)	O(2)–V–N(2)	162.9(3)
Cl(1)–Cu–N(1)	172.8(2)	O(2)–V–N(37)	95.6(3)
Cl(1)–Cu–N(17)	96.3(3)	O(2)–V–N(47)	92.4(3)
Cl(1)–Cu–N(27)	97.3(2)	O(3)–V–N(2)	88.3(3)
O(1)–Cu–N(17)	93.9(2)	O(3)–V–N(37)	83.5(3)
O(1)–Cu–N(27)	94.1(2)	O(3)–V–N(47)	164.7(3)
O(1)–Cu–N(1)	90.7(2)	N(2)–V–N(37)	72.5(3)
N(1)–Cu–N(17)	82.6(3)	N(2)–V–N(47)	76.7(3)
N(1)–Cu–N(27)	82.7(3)	N(37)–V–N(47)	94.5(3)
N(17)–Cu–N(27)	163.3(3)	Cu–O(1)–V	129.3(3)
O(1)–V–O(2)	107.0(3)	Cl(1)–Cu–Cl(1 ⁱ)	84.7(1)
O(1)–V–O(3)	85.9(3)	O(1)–Cu–Cl(1 ⁱ)	171.3(2)
O(1)–V–N(2)	86.5(2)	N(1)–Cu–Cl(1 ⁱ)	88.1(2)
O(1)–V–N(37)	156.7(3)	N(17)–Cu–Cl(1 ⁱ)	77.4(2)
O(1)–V–N(47)	90.3(2)	N(27)–Cu–Cl(1 ⁱ)	94.3(2)
O(2)–V–O(3)	102.9(3)		

Symmetry code: 2-x, y, 1/2-z.

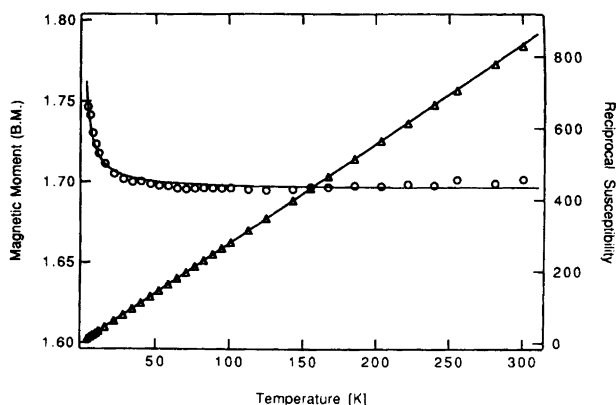


Fig. 3. Plots of μ (per half molecule) and $1/\chi$ versus temperature for $[\text{bpmpCu}(\text{Cl})\text{VO}(\text{H}_2\text{O})](\text{ClO}_4)_2$. The solid lines are those calculated using a $S=1/2; S=1/2$ model with $g=1.96$ and $J=0.43 \text{ cm}^{-1}$.

line was evident in the powder spectrum indicative of nearest-neighbor interactions, perhaps of the dipolar coupling type.²⁰ This half-field line is not apparent in the frozen solution spectrum, suggesting an inter- rather than intramolecular origin. The line shape of the $\bar{g} \approx 2$ signal and the magnetic moment behavior are very similar to those reported for the complex $(\text{tmen})\text{Cu}(\mu\text{-C}_2\text{O}_4)\text{VO}(\text{C}_2\text{O}_4) \cdot 3\text{H}_2\text{O}$, the structure of which was not known with certainty,⁹ and to those of its recently reported apparent analogue, $[(\text{terpy})\text{Cu}(\mu\text{-C}_2\text{O}_4)\text{VO}(\text{C}_2\text{O}_4)\text{H}_2\text{O}] \cdot \text{H}_2\text{O}$, for which X-ray structural data are available.¹¹ For $(\text{tmen})\text{Cu}(\mu\text{-C}_2\text{O}_4)\text{VO}(\text{C}_2\text{O}_4) \cdot 3\text{H}_2\text{O}$ a $|J|$ value of $0.15\text{--}0.5 \text{ cm}^{-1}$ and $\bar{g}=2.04$ were estimated, and the coupling was assumed to be intramolecular in origin, with an even weaker intermolecular interaction responsible for μ decreasing a little at temperatures below 20 K.⁹

The magnetic susceptibility data were fitted to the Bleaney–Bowers $-2JS_1S_2$ equation²¹ assuming one average \bar{g} -value. The parameters $\bar{g}=1.96 \pm 0.02$ and $J=0.43 \pm 0.02 \text{ cm}^{-1}$ were obtained. These parameters reproduced both the 300–20 K plateau in μ and the small increase below 20 K. It is, however, unlikely that this

weak coupling is intramolecular in origin, since the crystal structure of $[\text{bpmpCu}(\text{Cl})\text{VO}(\text{H}_2\text{O})](\text{ClO}_4)_2$ shows that $\text{Cu}\text{--}\text{O}(1)$ is axial whilst $\text{V}\text{--}\text{O}(1)$ is equatorial, suggesting that the magnetic orbitals for $\text{Cu}^{\text{II}}(d_x^2-d_y^2)$ and $\text{V}^{\text{IV}}(d_{xy})$ are far from coplanar and are oriented at close to 90° to each other.

The overlap of these orbitals, via $\text{O}(1)$, is therefore vanishing. This situation can be contrasted to that in the ferromagnetic complex $(\text{CuVO}(\text{fsa})_2\text{en} \cdot \text{MeOH})$,⁷ the structure of which shows that the bridging phenolate oxygens are located in the equatorial planes of both metal ions; thus in this case the magnetic orbitals are coplanar and orientated orthogonally. Indeed it is more likely that the very weak ferromagnetic coupling in $[\text{bpmpCu}(\text{Cl})\text{VO}(\text{H}_2\text{O})](\text{ClO}_4)_2$ originates from intermolecular coupling via the $\text{CuCl}(1) \cdots \text{Cu}'\text{Cl}'(1)$ bridging interaction. A linear (zig-zag) tetranuclear model,²² with two J -values would probably be more appropriate to use in the analysis of the present magnetic data. However, the μ/T data are so featureless that this was not pursued. In any case $J_{\text{Cu-V}}$ and $J_{\text{V-V}}$ are expected to be zero, and one J -value would result.

Perusal of dinuclear μ -chloro copper(II) systems, much studied by Willett,²² Hatfield²⁴ and Hodgson²⁵ have shown that J -values correlate with $\text{Cu}\text{--}\text{Cl}\text{--}\text{Cu}$ bridge angles and with $\text{Cu}\text{--}\text{Cl}$ bond lengths, the latter being very asymmetrical in the present case. $\text{Cu}\text{--}\text{Cl}(1)$ lies in the equatorial plane of $\text{Cu}(1)$, whilst $\text{Cl}'(1)$ is in the axial direction. The $\text{Cu}(1)\text{--}\text{Cl}(1)\text{--}\text{Cu}'(1)$ angle is $91.66(7)^\circ$ and the $\text{Cu} \cdots \text{Cu}$ distance is $4.004(2) \text{ \AA}$. Rather similar bridge geometries have been cited in Hodgson's review²⁵ for compounds of type $[\text{Cu}(2\text{-picoline})\text{Cl}_2]_2$ and $[\text{Cu}(\text{DMG})\text{Cl}_2]_2$, the latter displaying weak ferromagnetism ($J=3.1 \text{ cm}^{-1}$), the former displaying weak antiferromagnetism ($J=-3.7 \text{ cm}^{-1}$). Subtle differences in the $\text{Cu}\text{--}\text{Cl}$ distances and $\text{Cu}\text{--}\text{Cl}\text{--}\text{Cu}$ angles being thought responsible for the change in sign of J .

In summary, we have successfully prepared a mixed metal $\text{Cu}^{\text{II}}/\text{V}^{\text{IV}}$ complex with an intermetallic distance of $3.907(2) \text{ \AA}$; however, in contrast to the diphenolate-

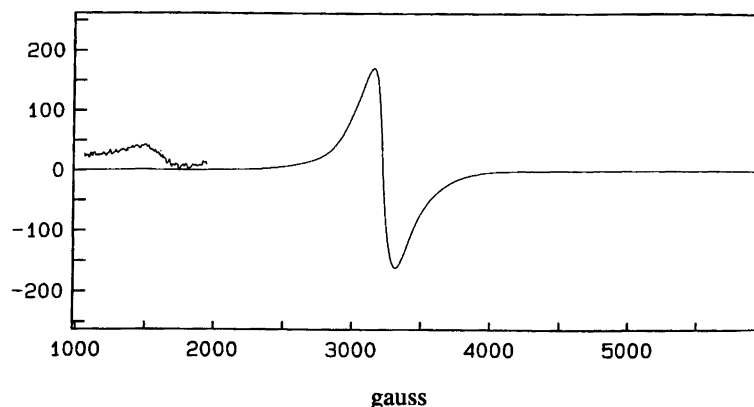


Fig. 4. X-band ESR spectrum of a neat powdered sample of $[\text{bpmpCu}(\text{Cl})\text{VO}(\text{H}_2\text{O})](\text{ClO}_4)_2$ at 77 K. The gain setting was increased in the ca. 1500 G region.

hinged complex CuVO(fsa)₂en·CH₃OH,⁷ our mono-phenolate-hinged [bpmpCu(Cl)VO(H₂O)](ClO₄)₂ shows only very weak ferromagnetism, which is presumably not associated with a Cu···V interaction but rather a Cu···Cu interaction. Interestingly, [bpmpCu(Cl)VO(H₂O)](ClO₄)₂ is the first mixed metal system of an open-ended dinucleating ligand in which the exogenous bridging site is not occupied by a bidentate bridging group. The fact that exogenous terminal ligands are bound to the metal ions in [bpmpCu(Cl)VO(H₂O)](ClO₄)₂ has interesting perspectives with respect to our long term aims of catalysis by dinuclear metal sites, i.e. if separate and different species can be bound at each metal ion they may then have the possibility of reaction with each other by virtue of their close proximity. The combination of Cu and V is interesting with respect to the design of mixed metal homogenous oxidation catalysts. Future work will be aimed at the investigation of this chemistry.

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