A Novel Salt Formed by Mixed-Valence Vanadium(IV, V) $[(VO)_2O(bpy)_2(C_2O_4)_2]$ Anions and Ferromagnetic $[Cu_2(bpy)_4(C_2O_4)]$ Cations: Structure, Spectroscopic Characterization and Magnetic Properties

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Keywords: Vanadium / Copper / Oxalate ligands / Magnetic properties

The new heterometallic, mixed-valence compound $[Cu_2(bpy)_4(C_2O_4)][(VO)_2O(bpy)_2(C_2O_4)_2]_2 \cdot 10H_2O$ has been synthesized, its crystal structure determined and its spectroscopic characterization accomplished by means of solid-state vibrational (far and mid FTIR) spectroscopy. The title compound crystallises in the triclinic system, space group $P\bar{1}$ (No. 2) [a = 13.488(5) Å, b = 14.160(6) Å, c = 15.829(9) Å, α = 87.22(2)°, β = 66.33(2)°, γ = 64.49(2)°, V = 2471(2) Å^3, Z = 1]. The compound consists of the cationic binuclear copper(II) complex $[Cu_2(bpy)_4(C_2O_4)]^{2+}$, two anionic binuclear mixed valence vanadium(IV)–vanadium(V) complexes $[(VO)_2O(bpy)_2(C_2O_4)_2]^-$, and ten uncoordinated water molecules. The copper atom exhibits a Jahn–Teller-distorted octahedral coordination. The vanadium atoms adopt a strongly distorted octahedral coordination and form a characteristic O=V–O–V=O moiety with a significantly bent V–O–V link. The temperature dependence of the magnetic susceptibilities has been investigated in the temperature range 2–300 K and explained in terms of the ferromagnetic interaction between Cu^{II} ions giving J = 22.7 yJ (1.14 cm^{-1}) and g = 2.014.

Introduction

Homo- and heterometallic systems involving oxalate ions (ox) as bridging ligands have been intensively studied since these ligands are very effective in transmitting exchange interactions.[1−3] Homopolynuclear copper(II) complexes consisting of both dinuclear and chain structures[4−6] have been studied, and in order to tune the dimension of spin coupling, complexes with terminal ligands such as tetramethyl-1,2-ethanediamine,[7] 1,2-ethanediamine,[8] 1,10-phenanthroline[9] or 2,2′-bipyridine[10] (bpy) have been synthesized so far. Complexes of VO^{3+} or VO^{2+} containing the oxalate ion as a bidentate ligand are also known, but they have not been studied that extensively.[11−13] Heterodimetallic copper(II)−oxovanadium(IV) oxalates, $[(terpy)Cu(ox)VO(ox)(H_2O)]\cdot H_2O$ and $[(terpy)_2Cu_2(ox)_2VO(H_2O)](ClO_4)_2\cdot H_2O$ (terpy = 2,2′:6′,2′′-terpyridine), have been the subject of recent studies[14] with the aim of elucidating the mechanism of spin coupling between paramagnetic ions through the bridging oxalate ligand. Bimetallic oxalate complexes in the copper(II)−oxovanadium(IV) system have been synthesized[15] and their ability to act as catalysts for the autoxidation of aliphatic aldehydes has been proved. As part of our continuing work in this field[16] this paper presents the structural and spectroscopic characterisation of a new heterometallic, mixed-valence compound obtained in the system vanadium/copper/oxalate which turned out to be $[Cu_2(bpy)_4(C_2O_4)][(VO)_2O(bpy)_2(C_2O_4)_2]_2\cdot 10H_2O$.

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Results and Discussion

Synthesis

The synthesis of the title compound was performed in a basic aqueous solution of Na_2S. Some experimental parameters, including the Cu:V molar ratio, were varied, but the resulting products remained the same. Finally, a copper/vanadium ratio of 1:2 was used. Although the crystals formed from an aqueous solution, their solubility in pure water was low. The crystals are insoluble in common organic solvents (i.e. DMSO, DMF, C_1-C_5 alcohols, acetone, acetonitrile, and chloroform).

Crystal Structure

$[Cu_2(bpy)_4(C_2O_4)][(VO)_2O(bpy)_2(C_2O_4)_2]_2\cdot 10H_2O$ crystallises in the triclinic system, space group $P\bar{1}$, with a unit cell content of one formula unit. It consists of a cationic, dinuclear copper(II) complex (Figure 1), an anionic, dinuclear mixed-valence vanadium(IV)−vanadium(V) complex (Figure 2), and water molecules filling large voids of the structure (Figure 3). The $[Cu_2(bpy)_4(C_2O_4)]^{2+}$ complex is centrosymmetric with the centre of inversion halfway between the carbon atoms C(1) and C(1A) of the bridging

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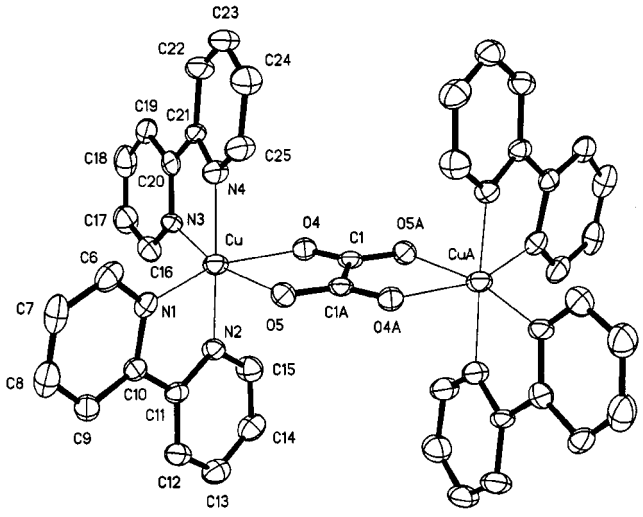


Figure 1. Thermal ellipsoid plot (20% ellipsoids) of the cationic dinuclear copper(II) complex $[Cu_2(bpy)_4(C_2O_4)]^{2+}$

bis-bidentate oxalate anion (Figure 1). The complex, including the bpy moieties, approaches quite well a noncrystallographic 2/*m* symmetry with the twofold axis passing through the two Cu atoms.

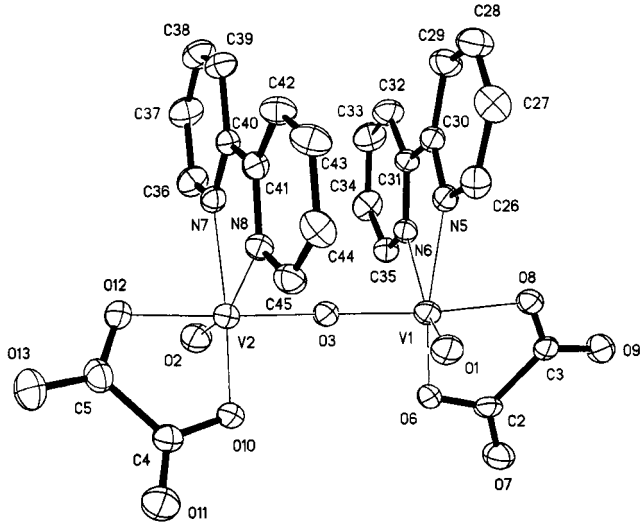


Figure 2. Thermal ellipsoid plot (20% ellipsoids) of the anionic mixed valence vanadium(IV, V) complex $[(VO)_2O(bpy)_2(C_2O_4)_2]^-$

Copper exhibits a moderately distorted octahedral coordination to two O atoms and four N atoms. A relatively weak Jahn–Teller distortion of the CuO_2N_4 polyhedron towards an elongated octahedron with four short equatorial bonds to N(1), N(2), N(4), and O(4) (Cu–N: 1.981– 2.059 Å; Cu–O: 2.141 Å) and two slightly longer axial bonds to N(3) and O(5) (Cu–N: 2.125Å; Cu–O: 2.237 Å) can be noted. The bond angles in the CuO_2N_4 octahedron are clearly controlled by the chelating bidentate ligands oxalate and 2,2′-bipyridine (O–Cu–O: 75.4 °; chelating N–Cu–N

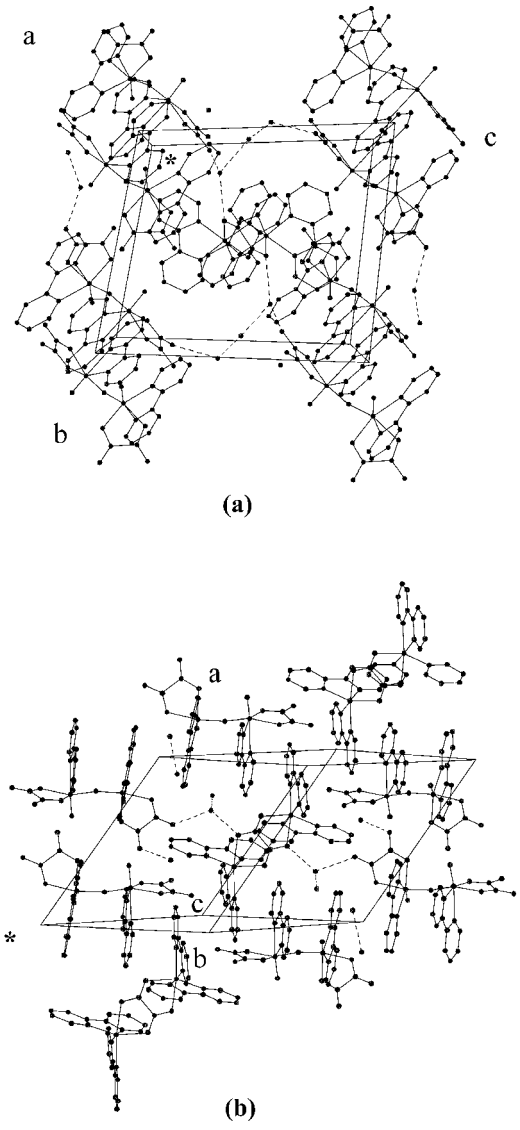


Figure 3. Packing diagram of $[Cu_2(bpy)_4(C_2O_4)][(VO)_2O(bpy)_2(C_2O_4)_2]_2 \cdot 10H_2O$ (a) viewed down the *a* axis; and (b) view approximately perpendicular to $(0\bar{1}1)$ showing the π-stacking most clearly (see text)

angles: 78.8–80.2°) whereas the remaining angles vary in the ranges 83.7–108.0° and 157.4–175.7°. Similar weak Jahn–Teller distortions were found for CuO_2N_4 octahedra in related complexes.[17,18] While the title compound represents the first example of a binuclear oxalato-bridged Cu complex with Cu:bpy = 1:2, such complexes with Cu:bpy in a 1:1 ratio have been observed before in several cases. However, they differ from the title compound by having either a square planar or a square pyramidal coordination for Cu, for example in $[Cu_2(bpy)_2(ox)(H_2O)_2][Cu(bpy)(ox)](BF_4)_2$.[19]

The dinuclear mixed-valence vanadium(IV)–vanadium(V) complex $[(VO)_2O(bpy)_2(C_2O_4)_2]^-$ is built up from two crystallographically independent vanadium atoms in distorted octahedral coordinations, each with four O and two N atoms. Each of the two vanadium atoms forms a typ-

ical vanadyl group (V=O) with a terminal oxo oxygen strongly bonded [V(1)−O(1) = 1.588 Å and V(2)−O(2) = 1.586 Å]. The second shortest V−O bonds are towards the bridging oxo oxygen O(3), with V(1)−O(3) = 1.814 Å, V(2)−O(3) = 1.796 Å and V(1)−O(3)−V(2) = 164.8°. This oxygen O(3), the V-bonded oxygen atoms of the chelating oxalate groups and the nitrogen atoms N(5) and N(7) define, with intermediate bond lengths, the slightly pyramidal equatorial coordination environments around the V(1)−O(1) and V(2)−O(2) groups. The significantly longest bonds are those to the nitrogen atoms N(6) and N(8) *trans* to O(1) and O(2). The mean V−O,N bond lengths of the two VO_4N_2 octahedra are 1.975 Å for V(1) and 1.969 Å for V(2). This, and the similarity in V−O(3) bond lengths, suggests that tetra- and pentavalent vanadium is approximately equally distributed over the two crystallographic metal sites. A further support for this view is that the complex exhibits a clear-cut noncrystallographic twofold pseudosymmetry with the twofold pseudoaxis passing approximately parallel to the V-bonded bpy's and through the bridging O(3) (Figure 2). The dimensions of the V coordination polyhedra in the title compound are in good agreement with many other oxo-bridged vanadium(IV,V) compounds. Of particular interest is the geometry of the O(1)=V(1)−O(3)−V(2)=O(2) fragment with respect to V−O−V bond angle, as well as to the O=V···V=O torsion angle. Whereas in many compounds[20−22] these quantities are exactly, or close to, 180°, in the title compound they are 164.8(3)° and 141.6(2)° and thus are close to the values for the compound of Chakravarty et al.[23] (142.0 and 160.8°) which has vanadium(V) in a square-pyramidal coordination.

The spatial arrangement of the Cu and V complexes in the title compound is shown in a view down the *a*-axis (Figure 3, a). Layer-like arrangements of the Cu and V complexes parallel to the $(0\bar{1}1)$ plane can be clearly seen in this view. Between the layers there are large open channels extending parallel to *a* which are occupied by the 10 water molecules per formula unit (5 independent molecules per asymmetric unit). These molecules are anchored in the structure mainly through hydrogen bonds to oxalate oxygen atoms with five independent O(w)···O(ox) distances to four different O(w) below 3.0 Å. Further hydrogen bonds appear to exist between the water molecules themselves, as indicated by the eight independent O(w)···O(w) distances below 3.0 Å. Among them O(3w) stands out in having only three contacts to O(w) but none to oxalate oxygen atoms. Figure 3 (b) shows another view of the structure approximately perpendicular to $(0\bar{1}1)$. This view is interesting because it indicates that the crystal structure owes much of its stability to π-stacking of the bpy molecules, in particular the molecules 2 (Cu-bonded), and 3 and 4 (V-bonded), which have their main planes all aligned approximately in the view direction and exhibit mean plane-separations of about 3.5−3.7 Å. These interactions may be considered to stabilize a structure that suffers from a destabilizing effect due to the large number of noncoordinated water molecules.

The question may arise as to whether the title compound might be a stoichiometrically H^+-bearing vanadium(IV) dimer rather than a mixed valence vanadium(IV, V) compound without additional H^+ as described above. This hypothesis was rejected for the following reasons:

(1) Bond valence calculations according to Brese and O'Keefe[24] show that the assignments of O(1), O(2) and O(3) to oxide oxygen atoms is beyond doubt (bond valence sums between 1.7 and 2.0 indicating that no OH group is present).

(2) H^+ atoms in the hydrate structure or at terminal oxalate oxygen atoms have to be accompanied by outstandingly short hydrogen bond O···O distances (2.4−2.6 Å). Since all O···O distances outside the cation coordination polyhedra are longer than 2.73 Å this possibility can be ruled out as well.

Vibrational Spectroscopy

The solid-state far- and mid-FTIR spectra are given in Figure 4 and 5. The spectra were checked with respect to reproducibility and several measurements of different samples yielded identical results.

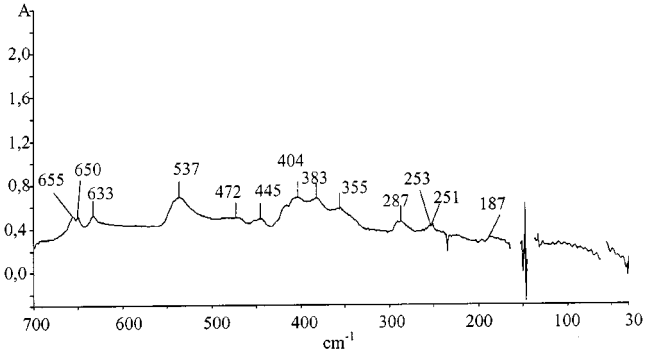


Figure 4. Solid-state far-IR spectrum of $[Cu_2(bpy)_4(C_2O_4)][(VO)_2O(bpy)_2(C_2O_4)_2]_2{\cdot}10H_2O$

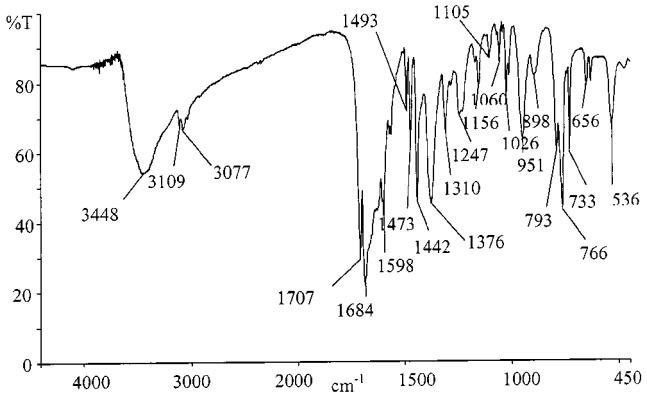


Figure 5. Solid-state mid-IR spectrum of $[Cu_2(bpy)_4(C_2O_4)][(VO)_2O(bpy)_2(C_2O_4)_2]_2{\cdot}10H_2O$

In the far IR the prominent absorption at 537 cm^{-1} is attributable to combinations of V−O(oxalate) with oxalate C−C stretching vibrations.[25] The equal prominent peak at 383 cm^{-1} is assigned to the V−N(bpy) stretching vibrations.[26] The weaker peak at 355 cm^{-1} is considered as being due to combinations of V−O(oxalate) stretching vibra-

tions with V-oxalate chelate ring deformation vibrations.[27] The rather weak absorption at 287 cm^{-1} is due to the symmetric stretching mode ν_{Cu-N} of the Cu−N(bpy) moieties.[28]

The sharp and strong absorption at 1707 cm^{-1} can be assigned to the asymmetric in-phase stretching vibration $\nu_{C=O}$ of the four terminal carbonyl groups C2−O7, C3−O9 and C4−O11, C5−O13 of the two vanadium-bonded oxalate groups. In accordance with literature data the broad and strong absorption at 1685 cm^{-1} is considered as a superposition of two asymmetric out-of-phase stretching vibrations of the carbonyl groups of the same oxalates. The strong absorption at 1376 cm^{-1} is attributed to a mode coupling of the symmetric stretching vibrations of the bridging carbonyls C2−O6, C3−O8 and C4−O10, C5−O12 with the C−C stretching vibrations of the C2−C3 and the C4−C5 bonds, respectively. The slightly weaker peak at 1247 cm^{-1} is due to a combination of the symmetric stretching vibration of the binding carbonyls C2−O6, C3−O8 and C4−O10, C5−O12, with the out-of-plane bending vibrations $\delta_{O-C=O}$ of the oxalates bound to the vanadium atoms. The very prominent absorption at 952 cm^{-1} is characteristic for the vanadyl stretching mode $\nu_{V=O}$ of the V1−O1 and V2−O2 bonds.[29] The fact that only one sharp peak is observed supports the explanation that the two vanadyl groups are indistinguishable, and is consistent with the almost identical V−O bond lengths (see Table 1). The V=O(vanadyl) stretching vibration in mixed-valence vanadium(IV, V) is detected within the range of 947 cm^{-1} (see Nishizawa et al.[30]), 980 cm^{-1} (see Pessoa et al.[31]) and 995 cm^{-1} (see Chakravarty et al.[23]), whereas the V=O(vanadyl) stretching vibration of vanadium(IV) compounds is observed at 975 cm^{-1} and at 890−920 cm^{-1} for vanadium(V) compounds (see Nishizawa et al.[30]). The strong peak at 794 cm^{-1} represents the combination mode consisting of the bending vibration $\delta_{O-C=O}$ and the stretching vibration ν_{V-O}. The rather weak absorption at 898 cm^{-1} could be the stretching vibration of V−O−V. Thus, according to the classification of Robin and Day,[32] the mixed valence vanadium(IV, V) complex of the title compound should belong to type II, where the two metal ions are in inequivalent positions with the unpaired electron shared equally between them.

Table 1. Selected geometric data for $[Cu_2(bpy)_4(C_2O_4)][(VO)_2O(bpy)_2(C_2O_4)_2]_2 \cdot 10H_2O$

N(2)−Cu−N(4)	175.7(2)	Cu−N(2)	1.981(5)
N(2)−Cu−N(1)	80.2(2)	Cu−N(4)	2.025(6)
N(2)−Cu−N(3)	96.9(2)	Cu−N(1)	2.059(5)
N(2)−Cu−O(4)	91.5(2)	Cu−N(3)	2.125(6)
N(2)−Cu−O(5)	91.0(2)	Cu−O(4)	2.141(4)
N(4)−Cu−N(1)	101.6(2)	Cu−O(5)	2.237(5)
N(4)−Cu−N(3)	78.8(3)		
N(4)−Cu−O(4)	88.3(2)	V(1)−O(1)	1.588(4)
N(4)−Cu−O(5)	93.1(2)	V(1)−O(3)	1.814(4)
N(1)−Cu−N(3)	108.0(2)	V(1)−O(6)	1.972(4)
N(1)−Cu−O(4)	157.4(2)	V(1)−O(8)	2.018(4)
N(1)−Cu−O(5)	83.7(2)	V(1)−N(5)	2.156(5)
N(3)−Cu−O(4)	93.8(2)	V(1)−N(6)	2.301(4)
N(3)−Cu−O(5)	166.8(2)		
O(4)−Cu−O(5)	75.4(2)	V(2)−O(2)	1.586(4)
O(1)−V(1)−O(3)	102.2(2)	V(2)−O(3)	1.796(4)
O(1)−V(1)−O(6)	104.5(2)	V(2)−O(10)	1.976(4)
O(1)−V(1)−O(8)	100.2(2)	V(2)−O(12)	2.051(4)
O(1)−V(1)−N(5)	89.5(2)	V(2)−N(7)	2.128(4)
O(1)−V(1)−N(6)	161.5(2)	V(2)−N(8)	2.279(5)
O(3)−V(1)−O(6)	90.6(2)		
O(3)−V(1)−O(8)	157.2(2)		
O(3)−V(1)−N(5)	98.9(2)		
O(3)−V(1)−N(6)	79.9(2)		
O(6)−V(1)−O(8)	79.9(2)		
O(6)−V(1)−N(5)	161.1(2)		
O(6)−V(1)−N(6)	93.8(2)		
O(8)−V(1)−N(5)	85.3(2)		
O(8)−V(1)−N(6)	80.2(2)		
N(5)−V(1)−N(6)	72.1(2)		
O(2)−V(2)−O(3)	103.0(2)		
O(2)−V(2)−O(10)	106.0(2)		
O(2)−V(2)−O(12)	94.9(2)		
O(2)−V(2)−N(7)	91.9(2)		
O(2)−V(2)−N(8)	163.7(2)		
O(3)−V(2)−O(10)	93.0(2)		
O(3)−V(2)−O(12)	161.9(2)		
O(3)−V(2)−N(7)	93.9(2)		
O(3)−V(2)−N(8)	82.8(2)		
O(10)−V(2)−O(12)	79.3(2)		
O(10)−V(2)−N(7)	158.8(2)		
O(10)−V(2)−N(8)	88.7(2)		
O(12)−V(2)−N(7)	88.1(2)		
O(12)−V(2)−N(8)	80.7(2)		
N(7)−V(2)−N(8)	72.3(2)		

Magnetochemical Investigations

The magnetic properties of $[Cu_2(bpy)_4(C_2O_4)][(VO)_2O(bpy)_2(C_2O_4)_2]_2 \cdot 10H_2O$ (SQUID, 2−100 K) are depicted in Figure 6. At 100 K, $\chi_M T$ is equal to 19.2 10^{-6} m^3 mol^{-1} K (1.53 cm^3 mol^{-1} K). This value is equal to that expected for two vanadyl ions and two noninteracting copper centres. The expected behaviour for the two mixed-valence vanadium dimers is a Curie law for two uncoupled $S = 1/2$. Therefore, all the variation of the $\chi_M T$ value with temperature is due to the $[Cu_2(bpy)_4(C_2O_4)]$ entity. Upon cooling, $\chi_M T$ increases smoothly showing that the dominant interaction between the Cu^{II} ions is ferromagnetic. The best fit is obtained using the following parameters $J = 22.7$ yJ (1.14 cm^{-1}) and an average g value for the copper and vanadyl ions of $g = 2.014$. The individual g factor for the copper and the vanadium cannot be determined from the magnetic data nor from EPR spectrum. The agreement factor R is then equal to $3.4 \cdot 10^{-6}$. Many binuclear Cu^{II} complexes with an oxalato bridging ligand have been structurally and magnetically characterized. Most of them are antiferromagnetically coupled, but the coupling constants depend strongly on the coordination sphere around the copper ions. The experimental coupling constants are in the −7950 to 22.8 yJ (−400 to +1.2 cm^{-1}). The largest interaction is observed for the so-called coplanar arrangement **1a**,[33] intermediate interactions are measured in the case of the perpendicular geometry **1b**,[34] and finally rare cases of ferromagnetic interactions are observed for the parallel geometry **1c**.[34,35] All these behaviours have recently been rationalized by theoretical DFT calculations.[36]

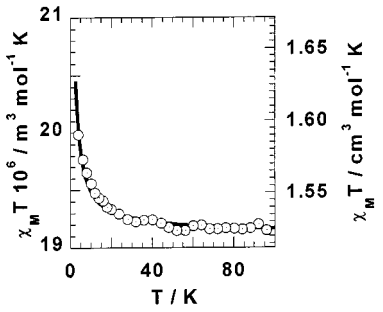
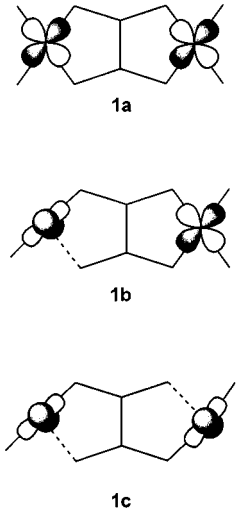


Figure 6. Plot of $\chi_M T$ vs. T for $[Cu_2(bpy)_4(C_2O_4)][(VO)_2O(bpy)_2(C_2O_4)_2]_2 \cdot 10H_2O$

The binuclear copper unit in $[Cu_2(bpy)_4(C_2O_4)][(VO)_2O(bpy)_2(C_2O_4)_2]_2 \cdot 10H_2O$ belongs to the **1c** family (see Scheme 1) with the equatorial planes of elongated octahedra perpendicular to the oxalato bridge. It is therefore not surprising to find a ferromagnetic interaction. Furthermore, the magnitude of the coupling observed for $[Cu_2(bpy)_4(C_2O_4)][(VO)_2O(bpy)_2(C_2O_4)_2]_2 \cdot 10H_2O$ is in the same range as the previous examples.



Scheme 1

Conclusion

The heterodimetallic compound $[Cu_2(bpy)_4(C_2O_4)][(VO)_2O(bpy)_2(C_2O_4)_2]_2 \cdot 10H_2O$ was synthesized and the structure was determined by crystallographic analysis. The anions consist of binuclear mixed-valence vanadium(IV)−vanadium(V) complexes in which: (*i*) the metal centres lie at almost equal distance to the bridging oxo oxygen, (*ii*) the unpaired electron is equally shared, and (*iii*) no magnetic interactions occur between the paramagnetic centres. Ferromagnetic interactions occur at low temperature between the copper(II) centres as a result of the orthogonality of the neighbouring magnetic orbitals on the oxalato bridge.

Experimental Section

General: All reagents were purchased from commercial sources (Fluka).

$[Cu_2(bpy)_4(C_2O_4)][(VO)_2O(bpy)_2(C_2O_4)_2]_2 \cdot 10H_2O$: $Cu(CH_3COO)_2 \cdot H_2O$ (0.5 g, 2.5 mmol) was mixed with 2,2′-bipyridine (0.78 g, 5 mmol) in 20 cm^3 water and the blue solution thus obtained was poured into 60 cm^3 of a solution containing 5 mmol $VO(C_2O_4)$ (stock solution) with vigorous stirring. The suspension formed was treated after a few minutes with a solution of Na_2S (0.08 g, 2.5 mmol) in 5 mL water. The obtained mixture was heated to 80 °C for one hour. After cooling to room temperature the solution was filtered. While keeping the clear solution in darkness at 5 °C (refrigerator) for a period of 2−3 weeks green crystals of the novel compound formed as a by-product, as our intention was to obtain copper-vanadium compounds with sulfide as ligand. − $C_{90}H_{84}Cu_2N_{16}O_{36}V_4$ (2296.6): calcd. C 47.07, H 3.69, N 9.76, Cu 5.53, V 8.87; found C 46.98, H 3.72, N 9.68, Cu 5.58, V 8.94.

Vibrational Spectroscopy: The dark-green powdered sample was characterised by far and mid-range FTIR spectroscopy. The solid state far-IR measurements were performed on a Perkin−Elmer System 2000 FT spectrometer with polyethylene as the matrix. To accomplish a good signal-to-noise ratio 1000 cycles, each cycle consisting of one reference scan (pure polyethylene), four sample scans and again one reference scan, were summed. During the measurement the spectrometer (optical bench including the sample chamber and the detector) was purged with nitrogen gas of purity >99.99%. The mid-range FTIR was recorded on a Perkin−Elmer 16 PC spectrometer. For good signal-to-noise ratio 64 scans in KBr as matrix were summed. During the measurement the spectrometer was also purged with nitrogen gas (>99.99%).

Magnetochemical Investigations: Magnetic measurements were performed on a Quantum Design SQUID MPMS5 magnetometer. The data were collected in the range 2−300 K for powered microcrystalline samples of $[Cu_2(bpy)_4(C_2O_4)][(VO)_2O(bpy)_2(C_2O_4)_2]_2 \cdot 10H_2O$ at 0.5 T. Diamagnetic corrections were applied based on Pascal's constant. This paper uses the SI units. The molar magnetic susceptibility χM is expressed in $m^3 \cdot mol^{-1}$. The conversion factor to the irrational emu quantity χM(ir) is $106/4\pi$. The energies are expressed in 10^{-24} Joule. The submultiple prefix for 10^{-24} is yocto, its symbol is y. Therefore 1 yJ means 10^{-24} Joule. The conversion factor to cm^{-1} is $5.034 \cdot 10^{-2}$ (1 $cm^{-1} \approx 20$ yJ).

X-ray Crystallographic Study

Crystal Data: formula $C_{90}H_{84}Cu_2N_{16}O_{36}V_4$, molecular mass 2296.58 amu, triclinic, $P\bar{1}$ (No. 2), a = 13.488(5), b = 14.160(6), c = 15.829(9) Å, α = 87.22(2)°, β = 66.33(2)°, γ = 64.49(2)°, V = 2471(2) $Å^3$, Z = 1, d = 1.544 $g \cdot cm^{-3}$, μ = 0.88 mm^{-1}, T = 301 K.

Data Collection: All available crystals were of relatively small size, poor quality and gave only low X-ray intensities. Data collection was therefore restricted to θ_{max} = 23°. X-ray data were harvested with a Siemens/Bruker SMART 3-circle diffractometer with a CCD area detector (sealed X-ray tube, Mo-K_α radiation, graphite monochromator) using ω-scan frames with Δω = 0.3° and 20 seconds per frame to cover a complete sphere of the reciprocal space by 4 × 606 frames. Absorption and crystal decay were corrected semi-empirically by equivalents.[37] Measured reflections 27550, unique reflections 6859, completeness of data 99.6%.

Structure Analysis and Refinement: The structure was solved by direct methods.[38] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the bpy moieties were introduced in calculated positions and refined using a riding model. The hydro-

gen atoms of the water molecules could not be located with acceptable reliability and were therefore left out. The structure was refined against F^2 with the program SHELXL-97.[39] Final agreement indices were $R1 = 0.058$ [4094 $F_o > 4\sigma(F_o)$] and 0.106 for all 6859 data, $wR2 = 0.172$, $GOF = 0.98$, 667 parameters.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-154154. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

Thanks for financial support are due to the Austrian Science Foundation ("Fonds zur Förderung der Wissenschaftlichen Forschung in Österreich") project P-5048 CHE, the Training and Mobility of Researchers Network (TMR) project "Thermal and Optical Spin-State Switching" (TOSS) supported by the European Union under the contract number ERB-FMRX-CT98-0199 and to the European Science Foundation under the project "Molecular Magnets". This work was supported by an exchange convention between the Romanian Academy and CNRS.

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Received December 13, 2000
[I00470]