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Notes

A Ferromagnetic Cu^{II}–$V^{IV}O$ μ-Oxalato Complex: Crystallographic Structure and Spectroscopic and Magnetic Properties

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Introduction

Exchange-coupled clusters of transition-metal ions are relevant to many different scientific areas,[1–8] ranging from chemistry to solid-state physics and to biology. There is a clear interest from the bioinorganic community in heterometal polynuclear complexes because an increasing number of active centers in metalloproteins are found to contain more than one metal atom. These kinds of complexes have been the subject of many recent studies with the hope of mimic those active sites of different metal enzymes containing dissimilar metal ions, such as cytocrome oxidase[9] and superoxide dismutase,[10] and elucidating the mechanism of spin coupling between paramagnetic metal ions. In particular, vanadium is receiving considerable attention as a biologically important metal due to the recent discovery of the first two vanadoenzymes (bromoperoxidase from marine algae[11,12] and nitrogenase from *Azotobacter vinelandii*[13]).

The magnetic and ESR data for heteropolynuclear complexes with different paramagnetic centers are still limited today by the small number of known and fully structurally characterized compounds.[5,6] New exchange pathways can be expected for these complexes, where unusual sets of magnetic orbitals can be brought into close proximity. The design of heteropolymetallic complexes has for a long time been a challenging field for coordination chemists because of the relative difficulty of synthesizing new compounds. In general, such a synthesis[14] requires either the use of metal complexes as ligands[15] for a simple metal salt or the use of a stepwise reaction of two different metal ions with polynucleating ligands[16] having dissymmetric coordination sites.

Table 1. Data Collection and Structure Refinement Parameters for $[(terpy)Cu(ox)VO(H_2O)]\cdot H_2O$

$C_{19}H_{15}N_3O_{10}CuVO$	fw 575.83
monoclinic	space group $P2_1/c$ (No. 14)
$a = 11.247(4)$ Å	$T = 25$ °C
$b = 12.690(4)$ Å	$\lambda = 0.710\ 69$ Å
$c = 14.759(5)$ Å	$\rho_{obs} = 1.80(2)$ g cm^{-3}, $\rho_{calc} = 1.83$ g cm^{-3}
$\beta = 97.47(3)°$	$\mu = 12.85$ cm^{-1}
$V = 2088(1)$ Å^3	$R(F_o)^a = 0.048$
$Z = 4$	$R_w(F_o)^b = 0.052$

$^a R = \sum(|F_o| - |F_c|)/(\sum|F_o|)$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

The oxalato group has shown to be an excellent bridging ligand to achieve a strong antiferromagnetic interaction between metal ions far away from each other in homobimetallic complexes.[17,18] The aim of this work is to provide some answers to the question of whether the bridging oxalate would be able to transmit ferromagnetic interactions in a system showing strict orthogonality like the Cu^{II}–$V^{IV}O$ one. With this aim, and considering the understanding of the factors that determine the spin physics of the different metal-containing biomolecules, we have synthesized the $[(terpy)Cu(ox)VO(ox)(H_2O)]\cdot H_2O$ and $[(terpy)_2Cu_2(ox)_2VO(H_2O)](ClO_4)_2\cdot H_2O$ title compounds, hereinafter [CuVO] and [CuVOCu], respectively.

Experimental Section

Synthesis. ***Caution!***. Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts should be prepared and should be handled with caution.

The [CuVO] compound was prepared as follows. A 0.237-g sample (10^{-3} mol) of 2,2′:6′,2″-terpyridine (terpy) was added with continuous stirring to a solution of 0.371 g (10^{-3} mol) of copper perchlorate hexahydrate in 10 mL of water. This solution (containing the $Cu(terpy)(H_2O)(ClO_4)_2$ ([Cu–]) precursor) was then slowly added to a rapidly stirred solution of a 0.315-g (10^{-3} mol) sample of diammonium aquobis(oxalato)oxovanadate(IV) hydrate ([–VO]), previously prepared,[19] in 10 mL of hot water. A blue precipitate of [CuVO] was removed by filtration, and the concentrated solution was allowed to cool slowly to room temperature to obtain well-shaped single crystals of the compound, which were filtered off and dried under vacuum. The compound [CuVOCu] was prepared as a unique phase by the same method used to obtain [CuVO], but employing a 2:1 proportion of the initial copper–terpyridine complex with respect to the vanadium one. The elemental analyses and atomic absorption results were consistent with the formulas $C_{19}H_{15}N_3O_{10}CuVO$ and $C_{34}H_{26}N_6O_{18}Cl_2Cu_2VO$, respectively.

Crystal Structure Determinations. A blue crystal of [CuVO] with dimensions 0.15 × 0.21 × 0.25 mm^3 was mounted on an Enraf-Nonius CAD-4 diffractometer. Graphite-monochromatized Mo Kα radiation ($\lambda = 0.71069$ Å) was used to collect the data. The lattice parameters were obtained at 296 K by a least-squares refinement of the angular settings ($10° < 2\theta < 25°$) of 25 carefully centered reflections. The experimental densities were determined by a flotation method in a bromoform/chloroform mixture. The data are summarized in Table 1.

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Table 2. Fractional Atomic Coordinates (×10^4; ×10^5 for Cu and V) and Equivalent Temperature Factors (Å^2) for [(terpy)Cu(ox)VO(ox)(H_2O)]·H_2O

atom	*x*	*y*	*z*	B_{eq}[a]
Cu	60511(6)	10710(6)	54426(4)	3.23(02)
V	21698(9)	33784(8)	40211(6)	3.32(03)
N1	6225(4)	814(4)	6802(3)	3.50(13)
N2	7770(4)	1019(4)	5693(3)	2.26(11)
N3	6481(4)	1331(4)	4165(3)	3.38(12)
C1	5349(6)	791(5)	7329(4)	4.16(18)
C2	5564(7)	643(6)	8251(5)	5.05(21)
C3	6717(8)	524(6)	8650(5)	5.82(25)
C4	7649(7)	571(6)	8122(4)	4.80(20)
C5	7381(6)	717(5)	7194(4)	3.75(18)
C6	8268(5)	825(4)	6556(4)	3.46(17)
C7	9521(6)	782(6)	6744(5)	4.57(19)
C8	10197(6)	981(5)	6068(6)	5.22(24)
C9	9661(6)	1209(5)	5179(5)	4.55(20)
C10	8425(5)	1186(4)	5017(4)	3.47(15)
C11	7672(5)	1351(4)	4121(4)	3.55(15)
C12	8122(7)	1493(5)	3311(5)	4.86(20)
C13	7322(8)	1601(6)	2515(5)	5.58(24)
C14	6121(7)	1617(6)	2563(4)	4.70(20)
C15	5737(6)	1456(5)	3396(4)	3.97(17)
O1	5404(4)	2787(3)	5457(2)	3.60(11)
O2	4309(3)	886(3)	5142(3)	3.40(09)
C16	4370(5)	2776(4)	5100(3)	2.90(14)
C17	3705(5)	1729(4)	4929(3)	2.83(14)
O3	3741(3)	3590(3)	4808(2)	3.42(10)
O4	2645(3)	1751(3)	4584(3)	3.70(11)
O5	848(3)	2576(3)	3313(3)	3.95(12)
O6	3040(4)	2874(3)	3016(3)	3.86(11)
C18	1110(6)	2146(5)	2583(4)	3.67(16)
C19	2398(5)	2383(5)	2378(4)	3.53(16)
O7	452(4)	1556(4)	2086(3)	5.18(14)
O8	2721(4)	2129(4)	1654(3)	5.30(14)
O9	1896(5)	4551(4)	3686(3)	2.78(15)
Ow1	1327(4)	3466(5)	5144(3)	5.20(14)
Ow2	–0947(5)	3754(6)	5404(5)	7.72(21)

[a] $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\cdot\mathbf{a}_i\mathbf{a}_j$.

Three standard reflections were collected every 2 h as a monitor for crystal deterioration and/or misalignment, neither of which was observed. The data were corrected for Lorentz and polarization effect, but not for absorption. The scattering factors[20] for neutral non-hydrogen atoms were corrected for both the real and the imaginary components of the anomalous dispersion. A total of 4189 reflections were collected, yielding 2427 significant independent reflections with the selection criterion $I \geq 2.5\sigma(I)$.

The structure was solved by direct methods (MULTAN 88)[21] and refined with SHELX76.[22] All non-hydrogen atoms were refined anisotropically. The positions of H atoms were obtained by Fourier difference syntheses, being included in the refinement cycle with isotropic thermal parameters. The final refinement of this model led to convergence at $R = 0.048$ and $R_w = 0.052$. Final positional parameters are presented in Table 2, while selected interatomic distances and angles are given in Table 3.

Physical Measurements. Fourier transform infrared spectroscopy on KBr pellets was performed on a Perkin-Elmer 1720X FT-IR instrument in the 4000–400-cm^{-1} region. Magnetic susceptibilities of powdered samples were measured using a SQUID SHE magnetometer. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms and for temperature-independent paramagnetism. ESR spectra were recorded on powdered samples at Q-band frequency with a Bruker ESP 300 spectrometer, equipped with a standard Oxford low-temperature device and calibrated by an NMR probe for the magnetic field; the frequency was measured by a Hewlett Packard 5352B microwave frequency counter.

Table 3. Selected Bond Distances (Å) and Angles (deg) for [(terpy)Cu(ox)VO(ox)(H_2O)]·H_2O

	Copper Coordination Sphere		
Cu–N1	2.017(5)	Cu–O1	2.297(4)
Cu–N2	1.921(5)	Cu–O2	1.966(4)
Cu–N3	2.034(5)		
N1–Cu–N2	80.7(2)	N2–Cu–O1	110.0(2)
N1–Cu–N3	160.8(2)	N2–Cu–O2	171.0(2)
N1–Cu–O1	97.7(2)	N3–Cu–O1	88.2(2)
N1–Cu–O2	99.8(2)	N3–Cu–O2	99.2(2)
N2–Cu–N3	80.2(2)	O1–Cu–O2	78.9(2)
	Vanadium Coordination Sphere		
V–O3	2.002(4)	V–O6	1.986(4)
V–O4	2.264(4)	V–Ow1	2.016(5)
V–O5	1.983(4)	V–O9	1.586(5)
O3–V–O4	76.2(2)	O4–V–O9	176.0(2)
O3–V–O5	156.7(2)	O5–V–O6	81.3(2)
O3–V–O6	89.6(2)	O5–V–O9	102.5(2)
O3–V–O9	100.1(2)	O6–V–Ow1	164.0(2)
O4–V–O5	81.4(2)	O6–V–O9	99.4(2)
O4–V–O6	82.2(2)		
	Oxalate Ligands		
C16–O1	1.213(6)	C18–O5	1.276(6)
C16–O3	1.294(6)	C18–O7	1.227(7)
C17–O2	1.285(6)	C19–O6	1.272(7)
C17–O4	1.234(6)	C19–O8	1.216(8)
C16–C17	1.529(8)		
O1–C16–O3	125.9(5)	O5–C18–O7	125.3(6)
O2–C17–O4	124.9(5)	O6–C19–O8	125.1(6)

Results and Discussion

Infrared Data. The [CuVO] compound exhibits bands corresponding to the bidentate oxalato ligand [1720, 1670, 1650 cm^{-1} (ν_{as}(CO)); 1415, 1280 cm^{-1} (ν_s(CO)); 780 cm^{-1} (δ(OCO)] and the bisbidentate oxalato ligand [1645 cm^{-1} (ν_{as}(CO)), 1360, 1315 cm^{-1} (ν_s(CO)); 800 cm^{-1} (δ(OCO))]. The [CuVOCu] compound exhibits bands corresponding to both the bisbidentate oxalato ligand and the perchlorate ion, these latter at 1100 and 630 cm^{-1}. Both show the band of the vanadyl group at 970 cm^{-1}.

Description of the Structure. The molecular geometry together with the atom-labeling scheme for the [CuVO] compound is shown as an ORTEP[23] drawing in Figure 1.

The structure of the complex molecule consists of discrete heterometallic dimers formulated as [(terpy)Cu(ox)VO(H_2O)(ox)]·H_2O. The aquobis(oxalato)oxovanadate(IV) anion, [VO(ox)$_2$(H_2O)]$^{2-}$, bridges to the [Cu(terpy)]$^{2+}$ cationic complex through one of its two oxalato ligands. The copper coordination geometry is a distorted square pyramid with three nitrogen atoms of the terpy ligand [Cu–N1,N2,N3 = 2.017(5), 1.921(5), 2.034(5) Å] and one oxygen atom of the oxalato bridging group [Cu–O2 = 1.966(4) Å] in the basal position. The apical site is occupied by a second oxygen atom of this oxalato group [Cu–O1 = 2.297(4) Å]. The vanadium atom is hexacoordinated (VO_6). One of the oxygen atoms is provided by a water molecule [V–Ow1 = 2.016(5) Å]; this and three oxygen atoms of the two oxalato groups [V–O3,O5,O6 = 2.002(4), 1.983(4), 1.986(4) Å] form the equatorial plane. As shown in Figure 1, the two oxalato groups have a *cis* arrangement. The vanadium atom is elevated from the equatorial plane by 0.342 Å and forms a short bond with one axial oxygen [V–O9 = 1.586(5) Å]. The shortness of this bond shows the evidence of multiple bonding, and it is typical of the vanadyl group found in other structures.[24,25] The length of the other axial bond [V–O4 = 2.264 Å] is a further example of

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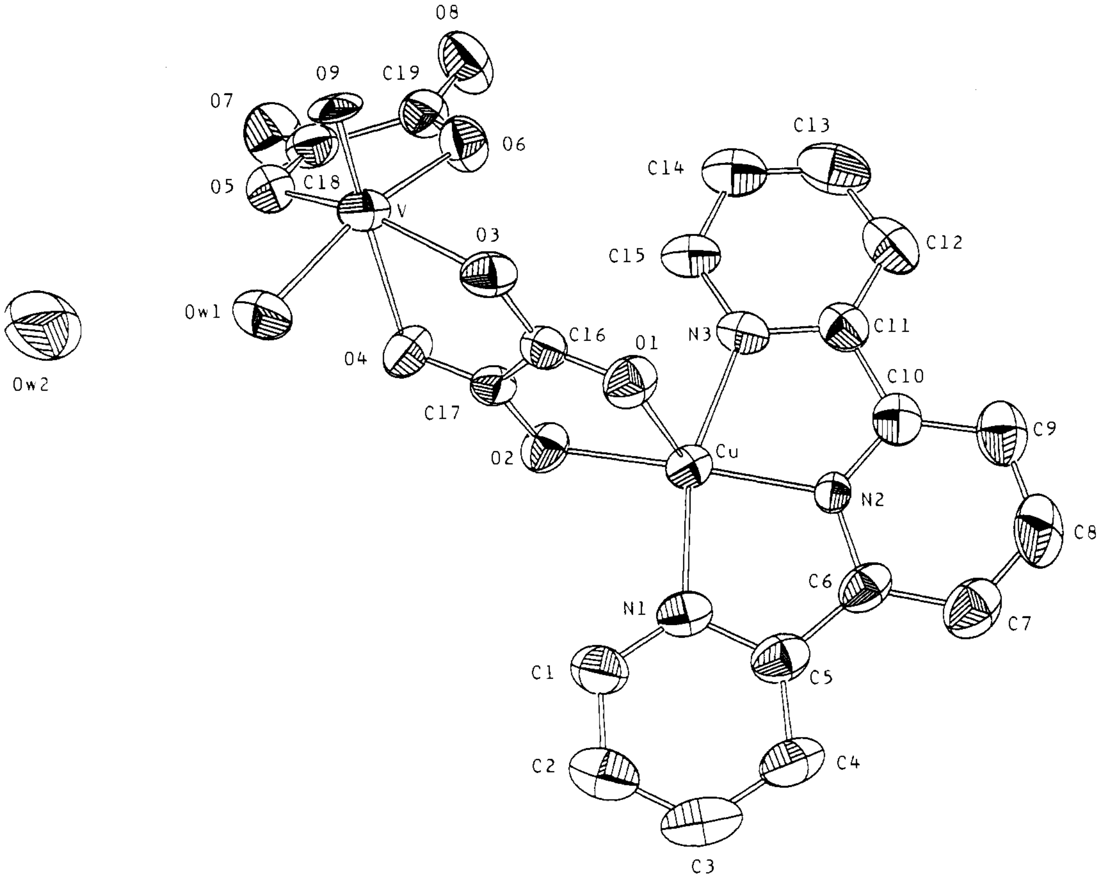

Figure 1. Molecular structure of [(terpy)Cu(ox)VO(ox)(H_2O)]·H_2O ([CuVO]), showing the atom numbering.

the *trans* influence of the vanadyl ion. Deviations from the idealized topologies for the copper (pentacoordinated) and vanadium (hexacoordinated) atoms have been evaluated by the Muetterties and Guggenberger[26] model. The results $\Delta = 0.81$ (CuN_3O_2) and $\Delta = 0.03$ (VO_6) show a good accord with square pyramidal and octahedral topologies, respectively (see supplementary material). Inside the V–μ-oxalato–Cu framework, the original bonding of the μ-oxalato presents V–O3 and Cu–O2 short bonds and V–O4 and Cu–O1 long bonds in *trans* positions. This framework is not far from planarity, with the V–O5 and Cu–N2 bonds forming dihedral angles of 12.5 and 14.0° with respect to the plane.

With respect to the oxalato groups, the two noncoordinated oxygens of the terminal group show the shortest C–O bonding distances [C18–O7 = 1.227(8) Å; C19–O8 = 1.216(8) Å]. A consequence of the *trans* effect is that a stronger C–O bond occurs where the O atom concerned is *trans* to the oxygen atom of the vanadyl group [C17–O4 = 1.234(6) Å]. The C–C lengths are in agreement with values generally found in oxalato complexes.[27,28] The bridging oxalato group, in contrast to the terminal oxalato, is planar itself. The terpyridine ligand maintains its characteristic rigidity and planarity.[29–31]

ESR Spectroscopy and Magnetic Properties. The Q-band ESR spectra of [CuVO] and [CuVOCu] compounds, as powdered samples at 77 K, are shown in Figure 2 together with those of the corresponding Cu(terpy)(H_2O)(ClO_4)$_2$ (named [Cu–]) and (NH_4)$_2$[VO(ox)$_2$(H_2O)] (named [–VO]) precursor complexes.

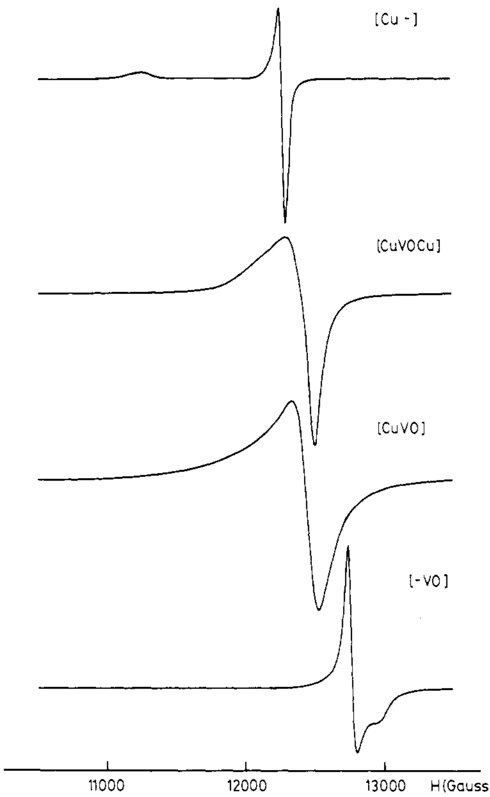

Figure 2. Q-Band ESR spectra of polycrystalline samples of the [Cu–], [CuVOCu], [CuVO], and [–VO] compounds at 77 K.

The spectrum of [Cu–] is typical of a noncoupled copper(II) ion in an elongated tetragonal environment, having the *g* values

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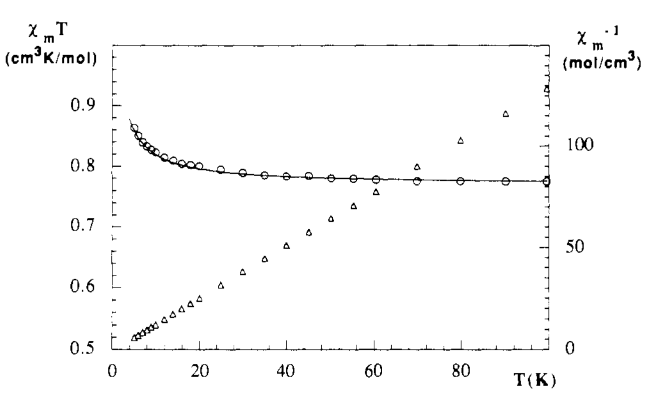

Figure 3. Thermal variation of reciprocal susceptibility and χ_mT for the [CuVO] complex.

$g_\parallel = 2.256$ and $g_\perp = 2.058$. The spectrum of [-VO] is typical of a noncoupled vanadyl ion, with the values $g_\parallel = 1.945$ and $g_\perp = 1.978$. The corresponding [CuVOCu] compound possesses an average $g = 2.068$ obtained from the gravity center of the absorption spectrum. The spectrum of [CuVO] exhibits a quasi-isotropic feature with $g = 2.033$. These two latter spectra are not the superposition of those of the [Cu-] and [-VO] species. Therefore, the metal ions cannot be considered as noninteracting, and the observed resonance occurs in the quartet–doublet and triplet states of the trio and pair, respectively.

The thermal variations of the reciprocal susceptibiliy and of χ_mT for the [CuVO] compound in the 4.2–100 K temperature range are shown in Figure 3. High-temperature magnetic susceptibility data for this compound follow a Curie–Weiss law, with a Curie constant of 0.79 cm^3 K mol^{-1} and a Weiss temperature of +1.5 K. At lower temperatures, χ_mT increases when the sample is cooled, reaching a value of 0.87 cm^3 K mol^{-1} at 4.2 K. All these data suggest a weak ferromagnetic behavior for the complex. The experimental susceptibility data for [CuVO] were fitted to the Bleaney–Bowers[32] equation, derived from the isotropic spin Hamiltonian $H = -JS_{Cu}{\cdot}S_{VO}$. The best fit (solid line in Figure 3) was obtained for the values of $J = +1.35$ K and $g = 2.027$, this last in good accord with the ESR results. The agreement factor, defined as SE $= [\Phi/(n - K)]^{1/2}$, where n is the number of data points (23), K is the number of adjustable parameters (2), and $\Phi = \Sigma(\chi_mT_{obs} - \chi_mT_{calc})^2$ is the sum of squares of the residuals, equal to 4.1×10^{-3}.

The magnetic susceptibility of [CuVOCu] follows a Curie–Weiss law over the entire temperature interval (4.2–100 K), with a χ_mT value of 1.20 cm^3 K mol^{-1}. The observed behavior could indicate either that the metal ions do not interact through the oxalato bridge or that the doublet and quartet states arising from the intramolecular interaction are almost accidentally degenerate with a $|J|$ gap smaller than 1 cm^{-1}. Taking into account the latter hypothesis, the average g value can be calculated from the Curie constant according to the expression $\chi_mT = Ng^2\beta^2/2k$. The value obtained is $g = 2.073$ for the [CuVOCu] compound, in reasonable accord with the ESR results.

If we consider a value of the exchange coupling constant $J = 0$ for the [CuVOCu] system, the ESR spectrum of this compound will exhibit two signals at $H_1 = h\nu/\beta g_{Cu}$ and $H_2 = h\nu/\beta g_{VO}$. Therefore, although the spectrum is formally associated with quartet–doublet states of the trio, which are accidentally degenerate, it is identical to what is expected for two non interacting local doublet states. The ESR spectrum of the [CuVOCu] compound exhibits only one signal, and it is exactly what is expected for $|J| > 0$ with a g value intermediate between those of g_{Cu} and g_{VO}. On the basis of the magnetic data described before, which gave a higher limit for $|J|$, it is possible to conclude that 0 cm^{-1} < $|J|$ < 1 cm^{-1}; however, the sign cannot be specified.

Concluding Remarks

Two heterometallic Cu^{II}–V^{IV}O complexes, namely [CuVO] and [CuVOCu], have been synthesized by using a metal complex ion as a ligand to coordinate another one, giving a simple metal salt. The former has been structurally characterized. The disposition of the copper and vanadyl ions in the [CuVO] system, with their magnetic orbitals in practically parallel planes, necessarily leads to weak orbital interactions transmitted through the oxalato ligand, which is perpendicular to these planes. This can be explained by considering the original situation of the V–μ-oxalato–Cu framework in the compound (Figure 1), where the unique unpaired electron of VO^{2+} (d^1, t$_{2g}$) is interacting with a π molecular orbital of the oxalato ligand with a strong participation of a p$_z$ orbital of O3 (z being perpendicular to the oxalato plane),[33] whereas the Cu^{2+} unpaired electron (d^9, e$_g$) is delocalized on a σ molecular orbital of the oxalato ligand with a strong participation of a p$_{x,y}$ orbital of O2, within the plane of the oxalato ligand (x and y are in that plane).[18] Hence, the overlap between the two singly occupied VO and Cu orbitals is strictly zero (strict orthogonality); however the overlap density between them is weak but sufficiently high on some points of the oxalato bridge to explain the observed ferromagnetism. This original situation is then at the origin of the ferromagnetic interactions observed for this compound. The unobserved presence of orbital interactions in the trinuclear [CuVOCu] compound may be explained by considering slight antiferromagnetic interactions of the second copper(II) ion with respect to the vanadyl ion. Multiple attempts to obtain good-quality crystals of this compound have failed. The ESR spectra of both compounds clearly indicate that the metal ions must be considered as interacting.

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Supplementary Material Available: Listings of anisotropic thermal parameters, hydrogen positions, and distortions of the coordination polyhedra (4 pages). Ordering information is given on any current masthead page.

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