literature of a transition-metal complex with $S = 3$.

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Registry No. $[Fe(H_2O)_6](BF_4)_2$, 15279-59-1; $[Fe(\mu_3\text{-}S)_8(PEt_3)_6](BPh_4)_2$, 94347-76-9.

Supplementary Material Available: Listings of atomic thermal parameters, positional parameters of hydrogen atoms, and observed and calculated structure amplitudes (38 pages). Ordering information is given on any current masthead page.

Contribution from the ISSECC, CNR, and Department of Chemistry,
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EPR Spectra of and Exchange Interactions in Trinuclear Complexes. 3. Synthesis, Crystal Structure, and Magnetic Properties of the Oxovanadium(IV) Adduct of a Tetradentate Schiff Base Copper(II) Complex

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The complex $(CuHAPen)_2VO(ClO_4)_2\cdot 3H_2O\cdot{}^1/_2C_2H_5NO_2$, where CuHAPen is (*N*,*N*′-ethylenebis(*o*-hydroxyacetophenone iminato))copper(II), was synthesized and its crystal structure solved at room temperature. It crystallizes in the orthorhombic system, space group $P2_12_12_1$. The lattice constants are $a = 20.928$ (9) Å, $b = 20.065$ (7) Å, and $c = 10.794$ (9) Å, with $Z = 4$. Least-squares refinement of the structure led to a conventional R factor of 0.052. The asymmetric unit comprises a dipositive trinuclear cation, two perchlorate anions, one water, and half of a nitroethane molecule. The two CuHAPen complex ligands bind to a central hexacoordinate oxovanadium(IV) occupying nonequivalent positions in a distorted octahedron. A water molecule acts as the sixth ligand. One of the two CuHAPen complex ligands binds also a water molecule in the axial position. Temperature dependence of the magnetic susceptibility in the range 4.2–300 K showed that the ground state of the trinuclear cation is a spin doublet, with the quartet separated by ~ 3 cm^{-1}, and a second doublet at ~ 90 cm^{-1}. These data were interpreted with a strong ferromagnetic Cu–VO interaction and two weak coupling constants relative to the other Cu–VO and the Cu–Cu interaction. The factors influencing the extent of ferromagnetic coupling between Cu and VO are discussed.

Introduction

Ferromagnetic exchange interactions in oligonuclear transition-metal complexes are much less common than antiferromagnetic interactions.[2-5] It has long been known that the conditions for dominating ferromagnetic coupling require that the interacting magnetic orbitals be orthogonal to each other, with a substantial overlap density,[6-8] which means that the two orbitals must have regions where their product is significantly different from zero. These conditions are rarely met, and only recently Kahn et al.[9] reported a dinuclear copper–oxovanadium species formed by the Schiff base *N*,*N*′-(2-hydroxy-3-carboxybenzylidene)-1,2-diaminoethane, $CuVO(fsa)_2en$, which has a triplet ground state with an excited singlet at 118 cm^{-1}. In the analysis of the data the authors showed that the origin of the strong ferromagnetic coupling is the fulfillment of the orthogonality condition met by the magnetic orbitals of the square-pyramidal copper(II) and oxovanadium(IV) ions bridged by two equatorial ligands.

In order to synthesize other complexes that might give substantial ferromagnetic coupling and investigate the relations between structure and exchange interaction, we reacted tetradentate Schiff base copper(II) complexes with $VO(ClO_4)_2$, since it is known that the copper complexes can act as bidentate ligands toward transition-metal ions.[10,11] With (*NN*′-ethylenebis(*o*-hydroxyacetophenone iminato))copper(II), CuHAPen, we obtained single crystals of formula $(CuHAPen)_2VO(ClO_4)_2\cdot$

Table I. Summary of Crystal Data, Intensity Collection, and Structure Refinement

formula	$C_{36}H_{38}Cl_2N_4O_{14}Cu_2V\cdot 0.5C_2H_5NO_2$
fw	1069.2
space group	$P2_12_12_1$
a, Å	20.928 (9)
b, Å	20.065 (7)
c, Å	10.794 (9)
V, Å^3	4532.61
Z	4
D_{calcd}, g cm^{-3}	1.57
cryst size, mm	0.09 × 0.1 × 0.25
μ(Mo Kα), cm^{-1}	12.55
transmission factors	0.94–0.88
scan type	ω–2θ
scan width ($\Delta(2\theta)$), deg	$0.90 + 0.30\theta$
scan speed, deg min^{-1}	3.6
2θ limits, deg	5–50
data collection range	h,k,l
no. of data	3203
no. of data $F_o^2 > 3\sigma(F_o^2)$	2401
no. of variables	386
R	0.052
R_w	0.053

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$3H_2O\cdot{}^1/_2C_2H_5NO_2$, which we indicate as $Cu_2(HAPen)_2VO$ for short, and determined its X-ray crystal structure and the temperature dependence of its magnetic susceptibility.

Experimental Section

Synthesis of the Complex. The ligand complex CuHAPen was synthesized according to literature methods.[12]

Ethanol solutions of oxovanadium(IV) diperchlorate were obtained as follows: aqueous solutions containing equimolar amounts of $VO(SO_4)\cdot5H_2O$ and $Ba(ClO_4)_2$ were mixed, the $BaSO_4$ was filtered, and the filtrate was evaporated to dryness under vacuum at room temperature. Ethanol was then added to the desired volume.

The trinuclear $(CuHAPen)_2VO(ClO_4)_2$ derivative was synthesized by mixing a solution of CuHAPen in chloroform (2 mmol in 200 mL) with an ethanol solution containing the stoichiometric amount of $VO(ClO_4)_2$ (1 mmol in 20 mL). A microcrystalline precipitate formed immediately. It was filtered, washed with chloroform, and recrystallized from nitroethane. The compound was satisfactorily analyzed for C, H, and N as $(CuHAPen)_2VO(ClO_4)_2\cdot3H_2O\cdot{}^1/_2C_2H_5NO_2$. *Caution*! This compound is thermally unstable and may easily explode.

EPR Measurements. Polycrystalline powder EPR spectra were recorded with a Varian E9 spectrometer at X-band (~9 GHz) frequency, using an Oxford Instruments ESR 9 continuous-flow cryostat.

Magnetic Measurements. Magnetic susceptibility measurements were performed with a Faraday balance equipped with a Cahn R-100 microbalance, a Bruker electromagnet, and an Oxford Instruments CF 200 cooling apparatus.

X-ray Structural Determination. Diffraction data for $Cu_2(HAPen)_2VO$ were collected at room temperature on a Philips PW 1100 automated diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). Details on crystal data, intensity collection, and refinement are reported in Table I. Lattice constants were obtained by least-squares fit of 20 reflections in the range $16° < 2\theta < 24°$. Stationary background counts were taken at each end of the scan for a time equal to half the scan time. The intensities of three standard reflections measured every 90 min showed an overall change in intensity less than 3%. The principal computer programs used in the crystallographic calculations are listed in ref 13. Data were processed with use of a p value of 0.03 in the calculation of $\sigma(I)$'s.[14] Correction for Lorentz and polarization effects,[13a] as well as for absorption,[13b] were applied. The space group $P2_12_12_1$ was identified by the systematic absences $h00$ ($h = 2n + 1$), $0k0$ ($k = 2n + 1$), and $00l$ ($l = 2n + 1$). Direct methods (MULTAN) were used to solve the structure. In a first step the program yielded the position of the heavy atoms (Cu1, Cu2, V); chlorine, oxygen, nitrogen, and carbon atoms of the cations and of the ligands and oxygen atoms of water molecules were located by Fourier synthesis. The structure was then refined by combining blocked-full-matrix least-squares techniques and difference Fourier maps. A total of 2401 reflections having $F_o > 6\sigma(F_o)$ were retained during the refinement.

The function minimized was $\sum w(|F_o| - |F_c|)^2$ with weights $w = 1/(\sigma^2(F_o) + 10^{-3}F_o^2)$. The scattering factors for the neutral atoms were taken from ref 15, and anomalous dispersion terms for the metal atoms were included in F_c.[16] All the metal atoms and nitrogen and oxygen atoms bound to the metals as well as chlorine and oxygen atoms of the perchlorate anions were assigned anisotropic temperature factors. All the other atoms in the cation were assigned isotropic thermal parameters. Hydrogen atoms bound to carbon were introduced in calculated positions (C–H = 1.08 Å), and their contributions were included in F_c. Each hydrogen atom was assigned as isotropic temperature factor ca. 20% higher than the isotropic factor of the corresponding C atom. In the final stage of the refinement (R = 0.069) peaks appeared in the difference Fourier maps as high as 1.5 e Å^{-3}, which were assigned to solvate nitroethane molecules according to elemental analysis. The non-hydrogen atoms in the solvate nitroethane molecule were refined isotropically with site occupation factor $^1/_2$. The final values of the discrepancy indices, defined as $R = \sum|F_o| - |F_c|/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$, were R = 0.052 and R_w = 0.053. The highest peaks in the difference Fourier map calculated at the end of the refinement were less than 0.4 e Å^{-3}. Since the space group is noncentrosymmetric, separate refinements were performed on both the enantiomorphs and the solution that gave the smallest R value was retained.

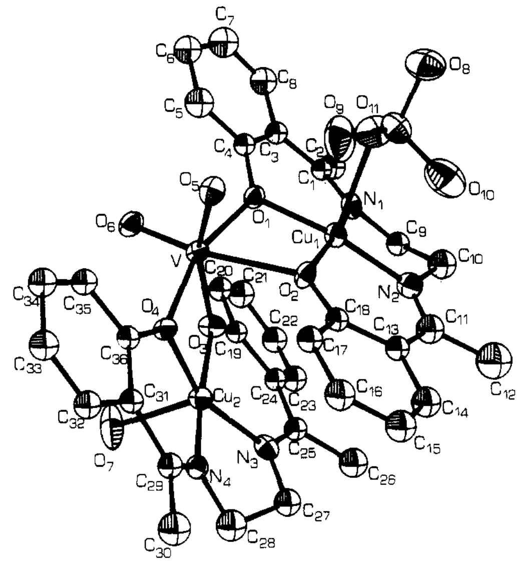

Figure 1. ORTEP drawing of the trinuclear cation in $Cu_2(HAPen)_2VO$.

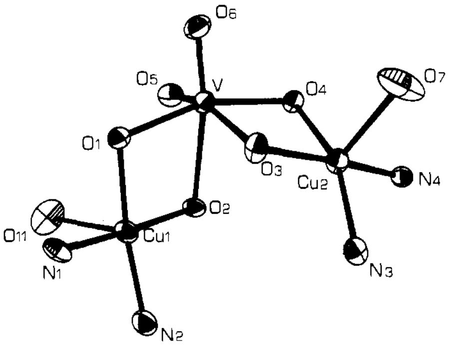

Figure 2. ORTEP drawing of the chromophores present in the trinuclear cation in $Cu_2(HAPen)_2VO$.

The final atomic positional parameters for the non-hydrogen atoms are listed in Table II. Thermal parameters and positional parameters of the hydrogen atoms are listed in Tables SI and SII, respectively.[17] A listing of the observed and calculated structure amplitudes is available.[17]

Description of the Structure

In $Cu_2(HAPen)_2VO$ the asymmetric unit comprises a trinuclear cation together with one perchlorate anion, one water, and half of a nitroethane molecule as described in the Experimental Section. An ORTEP view of the cation is shown in Figure 1. In Table III are given the relevant bond distances and angles around the three metal ions in the cation. In Figure 2 are shown only the metals and the atoms directly bound to them. The central oxovanadium(IV) group is coordinated to four oxygen atoms of two ligand complex molecules, CuHAPen, and a water molecule to yield a distorted octahedron. The two CuHAPen molecules occupy cis positions in the octahedron: in particular the oxygen atoms of Cu1, O1 and O2, occupy an equatorial and an axial position, respectively, while those of Cu2, O3 and O4, occupy equatorial positions. The bond distances to vanadium of O1, O3, and O4 are relatively similar to each other, while the V–O2 bond, which is opposite to the V=O bond, is much longer, 2.349 (8) Å, as expected. The three similar V–O bond distances compare well with the values reported for a vanadium–phenolic oxygen bond in the similar heterodinuclear copper–vanadyl complex[9] CuVO(fsa)$_2$en. The V–OH$_2$ bond compares well with the values reported for other vanadyl complexes.[18]

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[17] Supplementary material.

Table II. Positional Parameters for the Non-Hydrogen Atoms for $Cu_2(HAPen)_2VO(ClO_4)_2 \cdot 3H_2O \cdot {}^1/_2C_2H_5NO_2$[a,b]

atom	*x*	*y*	*z*
Cu1	−4567 (1)	−2515 (1)	−1802 (1)
Cu2	−3074 (1)	−2832 (1)	1215 (1)
V	−3081 (1)	−2637 (1)	−1554 (2)
O1	−3779 (4)	−2222 (4)	−2538 (7)
O2	−4041 (3)	−3206 (4)	−1165 (8)
O3	−3347 (4)	−2186 (4)	16 (7)
O4	−2647 (4)	−3175 (4)	−226 (7)
O5	−3046 (4)	−3425 (4)	−2803 (8)
O6	−2500 (4)	−2197 (4)	−2034 (8)
O7	−2310 (4)	−2128 (7)	1946 (12)
N1	−5001 (4)	−1694 (5)	−2281 (10)
N2	−5299 (5)	−2756 (6)	−816 (10)
N3	−3798 (5)	−2680 (5)	2301 (9)
N4	−2860 (4)	−3609 (5)	2214 (9)
C1	−4801 (6)	−1241 (6)	−2983 (12)
C2	−5136 (7)	−574 (7)	−2995 (15)
C3	−4255 (6)	−1341 (6)	−3764 (13)
C4	−3775 (6)	−1825 (6)	−3549 (11)
C5	−3273 (8)	−1902 (8)	−4387 (14)
C6	−3232 (8)	−1510 (7)	−5462 (15)
C7	−3733 (8)	−1047 (9)	−5652 (17)
C8	−4209 (8)	−948 (8)	−4845 (15)
C9	−5559 (6)	−1631 (6)	−1456 (12)
C10	−5826 (7)	−2301 (7)	−1131 (16)
C11	−5349 (7)	−3252 (8)	−64 (14)
C12	−6008 (9)	−3362 (10)	578 (19)
C13	−4833 (6)	−3719 (6)	143 (12)
C14	−4946 (7)	−4243 (7)	998 (14)
C15	−4509 (7)	−4747 (7)	1219 (15)
C16	−3928 (7)	−4729 (7)	618 (13)
C17	−3793 (6)	−4225 (6)	−224 (12)
C18	−4222 (6)	−3698 (6)	−429 (12)
C19	−3739 (6)	−1663 (6)	291 (12)
C20	−3694 (7)	−1101 (7)	−480 (13)
C21	−4078 (7)	−531 (8)	−228 (16)
C22	−4465 (7)	−556 (7)	793 (14)
C23	−4543 (7)	−1095 (7)	1495 (13)
C24	−4165 (6)	−1681 (6)	1304 (12)
C25	−4232 (6)	−2246 (7)	2142 (12)
C26	−4853 (7)	−2295 (8)	2875 (14)
C27	−3871 (7)	−3226 (7)	3170 (13)
C28	−3219 (7)	−3548 (7)	3376 (15)
C29	−2497 (6)	−4091 (6)	1954 (12)
C30	−2418 (7)	−4661 (7)	2810 (14)
C31	−2139 (6)	−4108 (6)	767 (11)
C32	−1657 (6)	−4609 (6)	626 (12)
C33	−1278 (7)	−4640 (7)	−409 (12)
C34	−1333 (6)	−4171 (6)	−1351 (13)
C35	−1787 (5)	−3666 (6)	−1233 (13)
C36	−2197 (5)	−3650 (6)	−215 (11)
Cl1	218 (2)	−1234 (2)	−6027 (4)
O8	4 (6)	−1030 (5)	−4854 (10)
O9	862 (5)	−1004 (6)	−6216 (14)
O10	−182 (6)	−959 (6)	−6938 (11)
O11	205 (5)	−1934 (4)	−6122 (10)
Cl2	−1562 (2)	−3328 (2)	−4815 (4)
O12	−1647 (10)	−2706 (6)	−4360 (23)
O13	−998 (6)	−3556 (10)	−4304 (15)
O14	−1527 (6)	−3354 (8)	−6131 (11)
O15	−2068 (4)	−3765 (6)	−4378 (9)
C37*	−3091 (24)	627 (22)	−8069 (44)
C38*	−2602 (23)	450 (23)	−8470 (39)
N5*	−2293 (29)	−140 (36)	−8029 (62)
O16*	−2261 (22)	−470 (24)	−9294 (46)
O17*	−2607 (20)	−612 (20)	−8166 (39)
O18*	−1507 (10)	−1600 (10)	−6302 (22)

[a] Coordinates multiplied by 10^4. [b] Atoms marked with an asterisk belong to nitroethane molecules.

Table III. Selected Bond Distances (Å) and Angles (deg) around the Three Metal Ions in $Cu_2(HAPen)_2VO$

Cu1–O1	1.923 (8)	Cu1–N1	1.95 (1)
Cu1–O2	1.898 (8)	Cu1–N2	1.93 (1)
Cu1–O11	2.54 (1)		
Cu2–O3	1.919 (8)	Cu2–N3	1.94 (1)
Cu2–O4	1.921 (8)	Cu2–N4	1.95 (1)
Cu2–O7	2.27 (1)		
V–O1	1.989 (8)	V–O4	2.011 (8)
V–O2	2.349 (9)	V–O5	2.079 (8)
V–O3	2.001 (8)	V–O6	1.589 (9)
O1–Cu1–O2	82.8 (3)	O1–Cu1–N1	91.9 (4)
O1–Cu1–N2	170.7 (4)	O1–Cu1–O11	86.0 (3)
O2–Cu1–N1	169.2 (4)	O2–Cu1–N2	94.5 (4)
O2–Cu1–O11	96.3 (3)	N1–Cu1–N2	89.3 (4)
N1–Cu1–O11	92.6 (4)	N2–Cu1–O11	103.2 (4)
O3–Cu2–O4	80.5 (3)	O3–Cu2–O7	91.4 (4)
O3–Cu2–N3	93.9 (4)	O3–Cu2–N4	169.3 (4)
O4–Cu2–O7	100.2 (4)	O4–Cu2–N3	155.3 (4)
O4–Cu2–N4	93.1 (4)	O7–Cu2–N3	104.0 (4)
O7–Cu2–N4	98.2 (4)	N3–Cu2–N4	88.3 (4)
O1–V–O2	70.7 (3)	O1–V–O3	93.3 (3)
O1–V–O4	159.6 (3)	O1–V–O5	89.9 (3)
O1–V–O6	98.9 (4)	O2–V–O3	80.2 (3)
O2–V–O4	89.9 (3)	O2–V–O5	77.1 (3)
O2–V–O6	169.3 (4)	O3–V–O4	76.4 (3)
O3–V–O5	154.6 (3)	O3–V–O6	103.7 (4)
O4–V–O5	92.2 (3)	O4–V–O6	100.7 (4)
O5–V–O6	100.7 (4)		

The equatorial oxygen atoms O1, O3, O4, and O5 define to a good approximation a plane, the maximum deviation from it being 0.05 Å. The vanadium atom lies 0.38 Å above this plane, as usually found in octahedral vanadyl complexes.

The coordination environments of the two copper ions are different from each other: both are five-coordinate, but the fifth axial position is occupied by the oxygen of a perchlorate for Cu1 and by a water molecule for Cu2. Beyond this there are not large differences in the copper–oxygen and copper–nitrogen bonds, the values comparing well with the data reported in the literature for similar mono-, bi-, and trinuclear[19–21] complexes. The N_2O_2 atoms around Cu1 define to a good approximation a plane, the coordination plane, the maximum deviation being 0.006 Å. The copper atom is 0.16 Å out of this plane. The N_2O_2 atoms around Cu2, on the other hand, show large deviations from planarity, with opposite atoms moving in the same direction, causing a tetrahedral distortion. The atoms show deviations up to 0.13 Å from the least-squares plane. The copper atom also deviates from this plane by 0.29 Å toward the axial water molecule. The water molecule is on the same side of the V═O bond, as previously found in $CuVO(fsa)_2en$.[9] Looking in more detail at the structure in the bridge regions, we see that the Cu2–V bridge is rather symmetric, as far as both the bond distances and the bond angles are concerned. In fact, the Cu2–O3–V angle is 100.5 (4)°, and the Cu2–O4–V angle is 100.1 (3)°. The corresponding angles in $CuVO(fsa)_2en$ were slightly smaller than this (98.9 (7) and 98.4 (6)°). On the other hand, the Cu1–O1–V angle is larger (106.3 (4)°) and the Cu1–O2–V angle is smaller (94.4 (3)°).

The coordination plane around Cu1 makes an angle of 74° with the equatorial plane of the vanadyl ion, while that around Cu2 makes an angle of 138° with it. It is worth noting here that the corresponding dihedral angle in $CuVO(fsa)_2en$ is much closer to 180° (190°).[9] Also the two Cu–V distances are different from each other, the shorter being Cu2–V (3.015 (2) Å). This value is only slightly longer than the copper–vanadium distance seen in $CuVO(fsa)_2en$ (2.989 (3) Å) while the Cu1–V distance is significantly longer than this (3.132 (3) Å).[9] The two copper atoms are relatively close to each other, 4.558 (3) Å, this distance being very close to that observed in $(CuSALen)_2Cu(H_2O)_2(ClO_4)_2 \cdot H_2O$ (CuSALen being (*N,N'*-ethylenebis(salicylaldiminato))copper(II)), where the central metal atom is also hex-

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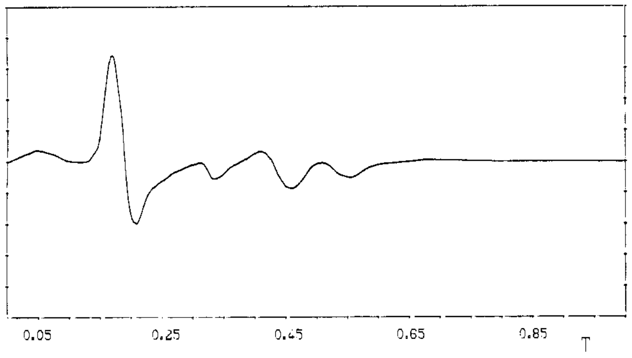

Figure 3. Polycrystalline powder EPR spectrum (9 GHz) of $Cu_2(HAPen)_2VO$ at 4.2 K.

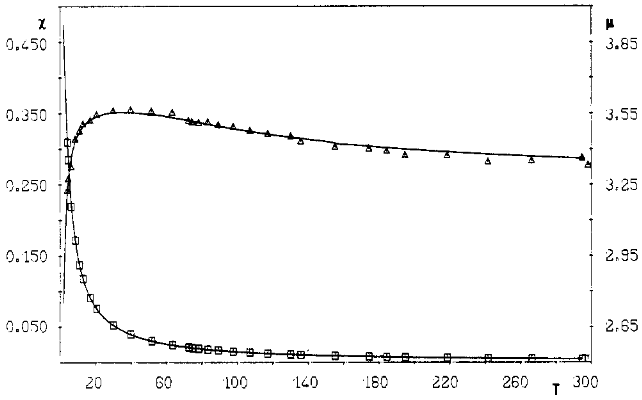

Figure 4. Temperature dependence of the magnetic susceptibility and of the effective magnetic moment of $Cu_2(HAPen)_2VO$. The curves were calculated as described in the text.

acoordinate,[19] but longer than the corresponding distance in $(CuHAPen)_2Cu(H_2O)(ClO_4)_2$, where the central metal atom is five-coordinate.[19] The three metal ions Cu1, V, and Cu2 define a triangle with the Cu1–V–Cu2 angle close to 90° (95.7°), which again compares well with the values observed in $(CuSALen)_2Cu(H_2O)_2(ClO_4)_2{\cdot}H_2O$ (97.3°), while it is much smaller than the value observed for $(CuHAPen)_2Cu(H_2O)(ClO_4)_2$ (156.2°).

EPR Spectra

Polycrystalline powder EPR spectra of $Cu_2(HAPen)_2VO$ at 4.2 K are shown in Figure 3. The number of features that are present in the spectrum and their positions are indicative of a spin quartet, but the presence also of a doublet cannot be ruled out, due to the signals that are observed in the $g = 2$ region. The fact that the spectra of the quartet are seen at 4.2 K suggests that the quartet is either the ground state or is separated from that by a small energy difference.

The analysis of the spectra appears to be difficult, since **g** and **D** are presumably not parallel to each other: as a consequence several forbidden transitions may steal intensity in the polycrystalline powder EPR spectra.[22] We prefer to delay the detailed assignment to a time when single crystals suitable to record EPR spectra will be available. If tentatively the two signals at 650 and 5550 G are assigned to the same fine-structure transition, the third being at ~3200 G, then a first-order analysis yields $g = 2.10$, $D = 0.115$ cm^{-1}. We feel that these figures give at least a rough estimation of the value of the zero-field splitting in this complex.

Magnetic Data

The temperature dependences of the magnetic susceptibility and of the effective magnetic moment of $Cu_2(HAPen)_2VO$ are shown in Figure 4. The magnetic susceptibility increases indefinitely with decreasing temperature in the range 4.2–300 K, while the magnetic moment increases to reach a maximum at 20 K and then decreases.

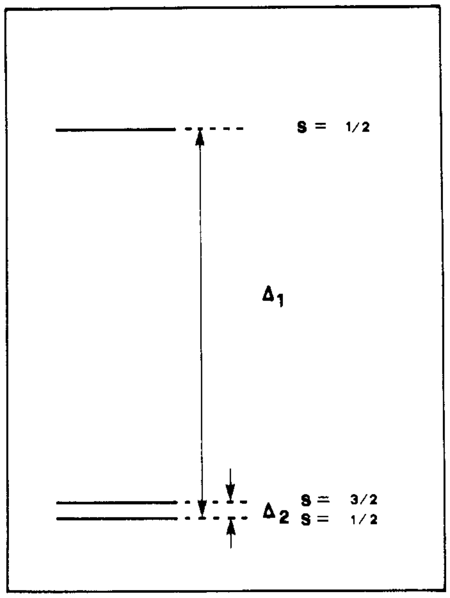

Figure 5. Energy level diagram for the two spin doublets and the spin quartet originating from the interaction of $S_1 = S_2 = S_3 = {}^1/_2$.

The spin Hamiltonian that is appropriate for a completely asymmetric trinuclear species is

$$\hat{H} = J_{12}\hat{S}_1{\cdot}\hat{S}_2 + J_{13}\hat{S}_1{\cdot}\hat{S}_3 + J_{23}\hat{S}_2{\cdot}\hat{S}_3 \qquad (1)$$

Since the three individual spins S_i are equal to ${}^1/_2$, there will be two resulting spin doublets and one spin quartet. the energies of these states can be easily expressed as $E({}^3/_2) = (J_{12} + J_{23} + J_{13})/4$ and $E({}^1/_2) = -(J_{12} + J_{23} + J_{13})/4 \pm {}^1/_2[J_{12}^2 + J_{23}^2 + J_{13}^2 - J_{12}J_{23} - J_{13}J_{23} - J_{12}J_{13}]^{1/2}$. When (1) is used for the fitting of the temperature dependence of the magnetic susceptibility, however, a problem arises: three J_{ij} parameters are required by (1), but only two energy differences are needed to determine the temperature dependence of the magnetic susceptibility. It is apparent therefore that the three J_{ij} parameters must be highly correlated, and a least-squares fitting procedure is bound to fail. Alternatively we decided to fit the experimental data by expressing the magnetic susceptibility as a function of the Δ_1 and Δ_2 energy differences defined in Figure 5. The Δ_1 and Δ_2 parameters obtained from the fit were then related to the J_{ij} constants in order to have parameters comparable to those usually reported in the literature.

The expression for the susceptibility we used is

$$\chi = \frac{N\mu_B^2g^2}{k(T + \Theta)}F(\Delta,T) \qquad (2)$$

where

$$F(\Delta,T) = \frac{{}^1\!/_2 + {}^1\!/_2 \exp(-\Delta_1/kT) + 5\exp(-\Delta_2/kT)}{2 + 2\exp(-\Delta_1/kT) + 4\exp(-\Delta_2/kT)} \qquad (3)$$

and $\Theta = -zJ'[F(\Delta,T)]/k$ takes into account possible intercluster interactions,[24] defined by the coupling constant J' and by the number of nearest neighbors z.

For the sake of simplicity we used only one g value for the three multiplets, although in principle three different values would be required.[25,26] Also in the fitting procedure we fixed at first Θ to zero and only when the best fit of χT was found did we let it vary freely. The best parameters for $\Theta = 0$ are $\Delta_1 = 87$ (1) cm^{-1}, $\Delta_2 = 2.25$ (2) cm^{-1}, and $g = 2.176$ (1), with R, defined as

$$(\textstyle\sum_i(\chi_i^{\text{obsd}} - \chi_i^{\text{calcd}})^2T_i^2/\sum(\chi_i^{\text{obsd}}T_i)^2)^{1/2}$$

equalling 8.9×10^{-3}. Letting also Θ vary, we found $\Delta_1 = 95$ (2)

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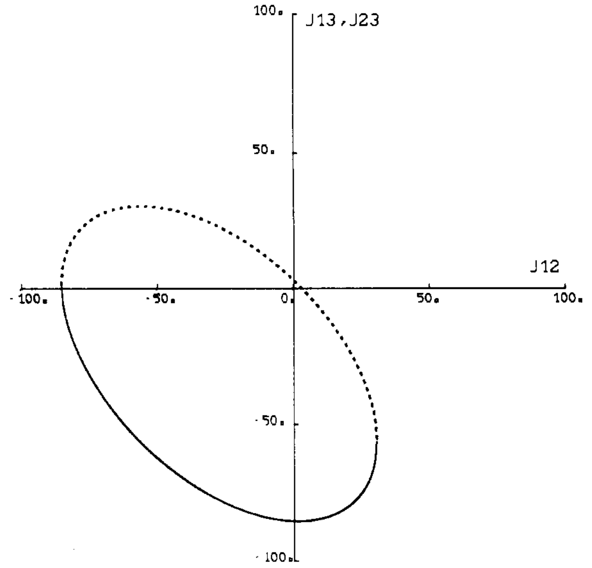

Figure 6. Calculated J_{13} (—) and J_{23} (---) as a function of J_{12}.

cm^{-1}, $\Delta_2 = 2.87$ (9) cm^{-1}, $zJ' = +0.32$ cm^{-1}, and $g = 2.168$ (2), with $R = 8.7 \times 10^{-3}$. Since the fit was not substantially improved by adding a fourth parameter, we prefer to use the one with $\Theta = 0$, and the curve in Figure 4 was calculated with that. The values of the Δ_i parameters show that the ground state is a doublet, with the quartet very close in energy, at $\sim$2 cm^{-1}. The fact that the ground state is a doublet indicates that at least one J_{ij} constant is antiferromagnetic, while the fact that the quartet is so close in energy to the ground state indicates that one J_{ij} constant must be strongly ferromagnetic.

Since Δ_1 and Δ_2 are determined by three independent parameters J_{ij}, there is no way of obtaining the latter values unambiguously. However, it is possible to estimate ranges of allowed values by fixing arbitrarily one J_{ij} constant and determining the other two using the relations

$$\begin{aligned}\Delta_1 &= (J_{12}^2 + J_{13}^2 + J_{23}^2 - J_{12}J_{13} - J_{13}J_{23} - J_{12}J_{23})^{1/2} \\ \Delta_2 &= (J_{12} + J_{13} + J_{23} + \Delta_1)/2\end{aligned} \tag{4}$$

Letting J_{12} vary between -100 and $+100$ cm^{-1}, we found real solutions only in the range -85 to $+30$ cm^{-1}, as is shown in Figure 6. Since it is known that the exchange interaction between the two external copper ions must be small, we considered as acceptable only those solutions that give at least one small J_{ij} value. We found that in fact if one J_{ij} value is small also a second one is such and that in this case the third J_{ij} value is only slowly varying. Acceptable fits therefore yield $J_{12} = -85 \pm 1$ cm^{-1}, $J_{13} = 0 \pm 10$ cm^{-1}, and $J_{23} = 0 \pm 10$ cm^{-1}.

The Exchange Interaction

The magnetic data show that the quartet state is very close in energy to the ground doublet state. The order of the levels is determined by a large ferromagnetic constant J_{12}, and two small ones, which remain largely undetermined as far as the value and the sign are concerned. The fitting procedure does not tell us unambiguously to which metal–metal interaction J_{12} is referred, but an analysis of the crystal structure using the known criterion for the exchange gives us a clear indication on this purpose.

In fact, excluding as we did in the previous section that J_{12} is referred to the interaction of the two external copper atoms, since this has been proven to be small in other similar complexes,[19,27] J_{12} can be associated with either the Cu1–V or the Cu2–V interaction. We strongly advocate the second choice on the following basis. As we observed in the description of the structure, the geometry of the bridge in the Cu2–V region is similar to that observed for CuVO (fsa)$_2$en,[9] where a strong ferromangetic coupling was reported to be operative. The considerations that apply in the case of CuVO(fsa)$_2$en to justify ferromagnetic coupling, i.e. orthogonality of the magnetic orbitals on the two metal centers, apply also in the present case. In fact the magnetic orbital on Cu2 is $x^2 - y^2$, with the axes roughly parallel to the copper–donor directions, while that on V is xy, approximately bisecting the equatorial donor–vanadium–donor angles. The geometry of the bridge in the Cu2–V region is not far from having C_{2v} symmetry; therefore, the two magnetic orbitals can be reasonably assumed to be orthogonal to each other, spanning different representations in C_{2v} symmetry. If on the other hand we look at the geometry of the Cu1–V bridge, we find a completely different coordination environment. In fact the two magnetic orbitals lie on planes that are roughly orthogonal to each other, rather than roughly parallel to each other as was the case for Cu2–V. Indeed, the overlap density at the O2 oxygen atom must be rather small; therefore, the coupling must be essentially determined by the O1 bridge atom. The geometry of the bridge in this case is such that the p oxygen orbital which overlaps best with the xy vanadium orbital is different from that which overlaps best with the $x^2 - y^2$ copper orbital. Therefore also the overlap density at O1 must be small. As a conclusion a weak coupling is predicted between V and Cu1, and either J_{13} or J_{23} can describe it.

The coupling constant relative to the Cu2–V interaction is smaller than that observed in CuVO(fsa)$_2$en. For a ferromagnetic coupling like the one observed in these two compounds no dependence on the Cu–O–V angle is anticipated in the limit of symmetry-determined orthogonality of the magnetic orbitals.[9] On the other hand, if the symmetry requirement is removed, it must be expected that the ferromagnetic coupling decreases as the Cu–O–V angle, α, increases. Indeed α is larger in Cu$_2$(HAPen)$_2$VO as compared to CuVO(fsa)$_2$en. Another relevant parameter, affecting the overlap density on the oxygen atoms, might be the metal–oxygen distance. The metal–oxygen distances are slightly longer in our case as far as the vanadium ion is concerned while the copper–oxygen distances are slightly shorter, so the balance is difficult to evaluate.

Another factor that may affect the extent of ferromagnetic coupling is the dihedral angle, ϕ, between the two equatorial planes of the two square pyramids. On the grounds of simple overlap considerations it can be assumed that the ferromagnetic coupling decreases as ϕ moves from 180°. In fact, if we consider the limit of $\phi = 90°$, we see that the vanadium xy and the copper $x^2 - y^2$ orbitals cannot overlap to the same p oxygen orbital, thus giving a vanishingly small overlap density on the bridges. Since this angle is definitely smaller in our case (138 vs. 190°), it is probably this parameter that justifies the observed smaller splitting in Cu$_2$(HAPen)$_2$VO as compared to that in CuVO(fsa)$_2$en.

Conclusions

The analysis of the crystal structure and of the temperature dependence of the magnetic susceptibility of Cu$_2$(HAPen)$_2$VO showed that one coupling constant in the trinuclear unit is definitely moderately ferromagnetic, thus confirming the prediction on the sign of the coupling between square-pyramidal copper and oxovanadium dinuclear species bridged through two equatorial donors.[9] Several factors may affect the ferromagnetic coupling between the two magnetic orbitals; presumably the dihedral angle between the two equatorial planes may play a major role, yielding the most efficient pathway when the two planes are parallel to each other. We are now trying to grow suitable single crystals to study the EPR spectra of Cu$_2$(HAPen)$_2$VO, in order to have more detailed information on the nature of the lowest lying states of the trinuclear species.

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Registry No. (CuHAPen)$_2$VO(ClO$_4$)$_2$·3H$_2$O·$^1/_2$C$_2$H$_5$NO$_2$, 93895-68-2; CuHAPen, 21350-69-6.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes, atomic thermal parameters (Table SI), and positions of hydrogen atoms (Table SII) (17 pages). Ordering information is given on any current masthead page.

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