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Transition-Metal Complexes with Sulfur Atoms as Ligands. 7.[1] Synthesis, Properties, Structure, and Molecular Orbital Calculations of the Paramagnetic Cluster $[Fe_6(\mu_3\text{-}S)_8(PEt_3)_6](BPh_4)_2$

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The reaction of hydrogen sulfide with $[Fe(H_2O)_6](BF_4)_2$ and triethylphosphine in the presence of $NaBPh_4$ gives the paramagnetic cluster $[Fe_6(\mu_3\text{-}S)_8(PEt_3)_6](BPh_4)_2$. The molecular structure has been established by single-crystal X-ray diffraction methods. The crystals are triclinic, space group $P\bar{1}$, with a = 11.837 (6) Å, b = 14.394 (8) Å, c = 15.569 (9) Å, α = 115.19 (9)°, β = 90.16 (8)°, γ = 104.68 (9)°, and Z = 1. The structure was solved by the heavy-atom method and refined by full-matrix least-squares techniques to the conventional R value of 0.058 for 6055 reflections having $I > 3\sigma(I)$. The cation consists of an octahedron of iron atoms with the sulfur ligands triply bridging all the octahedral faces. Moreover, each metal atom is terminally linked to a triethylphosphine group. The inner core of the cation may be considered to possess idealized O_h symmetry with average Fe–Fe and Fe–μ_3-S distances of 2.617 (6) and 2.247 (1) Å, respectively. Different molecular orbital approaches have been performed to account for the magnetic and spectroscopic experimental data. An electronic configuration with six unpaired electrons appears to be the most likely one for the ground state.

Introduction

Owing to the strong "affinity" of transition metals for sulfur, metal–sulfur chemistry has been concerned until recently nearly exclusively with insoluble metal sulfides. Though the growth of organometallic chemistry has led to the isolation of various complexes containing unsubstituted sulfur atoms linked to metals,[3] only in recent years has a new chemistry of soluble metal sulfide clusters been developing,[4] mainly under the stimulus to achieve synthetic models either for active sites of iron–sulfur proteins[5] or for heterogeneous metal sulfide catalysts.[6]

Very recently we have succeeded in synthesizing the metal clusters $[Ni_3(\mu_3\text{-}S)_2(PR_3)_6]^{2+}$ (R = Me, Et),[1] $[Ni_9(\mu_4\text{-}S)_3(\mu_3\text{-}S)_6(PEt_3)_6]^{2+}$,[1] $[Fe_6(\mu_3\text{-}S)_8(PEt_3)_6]^{2+}$,[7] $[Co_6(\mu_3\text{-}S)_8(PEt_3)_6]^{+}$,[8] and $[Co_6(\mu_3\text{-}S)_8(PEt_3)_6]$[9] by reacting the divalent metal aquo ions with hydrogen sulfide, in the presence of mono(tertiary phosphines), according to the "spontaneous self-assembly" strategy first developed by Holm et al.[5] Interest in these compounds is due, beyond the novelty of their structures and unusual properties, to the following reasons. First, the presence of recognizable similar clusters in polymeric sulfides (i.e. the Chevrel phases[10]) suggests that these metal sulfides can provide a bridge between simple molecular compounds and infinite lattices. Moreover, the paramagnetism of some of these complexes suggests that such species could work as multielectron carriers, owing to their reservoir of unpaired electrons.

The synthesis, structure, and properties of the iron cluster $[Fe_6(\mu_3\text{-}S)_8(PEt_3)_6](BPh_4)_2$ are described herein, augmenting a brief report communicated earlier.[7] In order to rationalize the structural, magnetic, and spectral properties, the electronic structure of the title compound has been investigated with use of molecular orbital calculations based on the SCF multiple-scattering Xα (MS-Xα) framework,[11] and the results obtained were compared with the ones provided by an extended Hückel treatment.[12]

Table I. Crystal Data and Data Collection Details

formula	$C_{84}H_{130}B_2Fe_6P_6S_8$
mol wt	1939.0
space group	$P\bar{1}$
a, Å	11.837 (6)
b, Å	14.394 (8)
c, Å	15.569 (9)
α, deg	115.19 (9)
β, deg	90.16 (8)
γ, deg	104.68 (9)
V, Å^3	2303.4
Z	1
d_{calcd}, g cm^{-3}	1.397
d_{obsd}, g cm^{-3}	1.40
color	black
habit	parallelepiped
dimens, mm	0.18 × 0.30 × 0.35
linear abs coeff, cm^{-1}	12.37
transmission factors	0.695–0.832
radiation	Mo Kα (λ = 0.7107 Å)
monochromator	graphite crystal
method	ω–2θ
scan speed, deg/s	0.05
scan width, deg	0.8 + 0.3 tan θ
bkgd time	half the scan time
stds	3 every 120 min
max dev stds, %	1
2θ limits, deg	5 < 2θ < 50
data collected	$\pm h, \pm k, +l$
no. of total data	8105
no. of data used ($I > 3\sigma(I)$)	6055
final no. of variables	218

Finally, a novel theoretical approach, which has been proposed for highly symmetrical metal clusters,[13] was used to interpret the observed EPR spectra and magnetic moment.

Experimental Section

Notwithstanding the air stability of the title compound, the preparation was carried out, initially, under a nitrogen atmosphere in order to prevent oxidation of the phosphine.

Preparation. A deoxygenated solution of $[Fe(H_2O)_6](BF_4)_2$ (0.68 g, 2 mmol) in 20 mL of ethanol was added to a deoxygenated solution of PEt_3 (0.71 g, 6 mmol) in 30 mL of methylene chloride, under a nitrogen

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Table II. Positional Parameters ($\times 10^4$)

atom	x	y	z
Fe1	−894 (1)	803 (1)	−168 (1)
Fe2	−1041 (1)	−1251 (1)	−919 (1)
Fe3	−863 (1)	−117 (1)	950 (1)
S1	−922 (1)	−268 (1)	−1730 (1)
S2	−867 (1)	−1834 (1)	190 (1)
S3	−636 (1)	1638 (1)	1435 (1)
S4	−2390 (1)	−488 (1)	−114 (1)
P1	−1895 (2)	1868 (2)	−383 (1)
P2	−2330 (2)	−2785 (1)	−2067 (1)
P3	−1973 (2)	−245 (2)	2118 (1)
C1	−3503 (8)	1356 (8)	−533 (7)
C2	−4027 (9)	1457 (8)	382 (7)
C3	−1643 (7)	3213 (6)	594 (5)
C4	−398 (8)	3977 (8)	804 (7)
C5	−1565 (9)	2059 (8)	−1450 (7)
C6	−2065 (10)	2912 (10)	−1589 (9)
C7	−2478 (7)	−3968 (7)	−1857 (6)
C8	−3287 (8)	−5053 (7)	−2617 (7)
C9	−2016 (7)	−3187 (7)	−3303 (6)
C10	−1025 (9)	−3779 (8)	−3610 (7)
C11	−3858 (7)	−2727 (7)	−2131 (6)
C12	−4039 (8)	−1903 (7)	−2457 (7)
C13	−3179 (6)	346 (6)	2235 (5)
C14	−3958 (8)	296 (7)	3033 (7)
C15	−1096 (9)	368 (8)	3340 (7)
C16	−617 (10)	1452 (10)	3703 (9)
C17	−2656 (6)	−1598 (6)	1959 (5)
C18	−3636 (7)	−2271 (7)	1129 (6)
C19	−2581 (3)	5667 (3)	2122 (3)
C20	−1906 (3)	6003 (3)	1520 (3)
C21	−2328 (3)	5583 (3)	554 (3)
C22	−3426 (3)	4828 (3)	190 (3)
C23	−4101 (3)	4492 (3)	792 (3)
C24	−3679 (3)	4911 (3)	1758 (3)
C25	−2588 (4)	5236 (4)	3651 (4)
C26	−3407 (4)	5235 (4)	4293 (4)
C27	−3735 (4)	4382 (4)	4532 (4)
C28	−3243 (4)	3530 (4)	4129 (4)
C29	−2424 (4)	3530 (4)	3487 (4)
C30	−2096 (4)	4383 (4)	3248 (4)
C31	−732 (5)	6873 (4)	3608 (4)
C32	−356 (5)	7874 (4)	3610 (4)
C33	835 (5)	8443 (4)	3848 (4)
C34	1648 (5)	8011 (4)	4084 (4)
C35	1271 (5)	7010 (4)	4083 (4)
C36	81 (5)	6441 (4)	3845 (4)
C37	−2937 (4)	7139 (4)	3863 (4)
C38	−2535 (4)	7874 (4)	4815 (4)
C39	−3139 (4)	8621 (4)	5307 (4)
C40	−4146 (4)	8632 (4)	4848 (4)
C41	−4548 (4)	7897 (4)	3897 (4)
C42	−3944 (4)	7150 (4)	3404 (4)
B	−2203 (7)	6237 (7)	3311 (6)

atmosphere, and hydrogen sulfide was bubbled through for 10 min. The resulting solution, which became very dark, was stirred overnight; then sodium tetraphenylborate (0.68 g, 2 mmol) was added. The solution became cloudy, and a large amount of whitish solid separated; this was removed by filtration, and the filtrate was evaporated in air. After 12 h black crystals together with a brown solid separated. The filtered material was treated with 30 mL of methylene chloride, in which only the black crystals dissolved. The resulting solution was filtered, and 20 mL of *n*-butanol was added. By slow evaporation of the solvent in air large black crystals precipitated; they were collected on a filter, washed with *n*-butanol and then with petroleum ether, and dried in vacuo; yield 0.13 g, 20%. The compound was recrystallized from methylene chloride/*n*-butanol. Anal. Calcd for $C_{84}H_{130}B_2Fe_6P_6S_8$: C, 52.03; H, 6.76; Fe, 17.28; S, 13.23. Found: C, 51.78; H, 6.75; Fe, 16.70; S, 13.04.

Physical Measurements. Magnetic susceptibilities were measured with use of the Gouy method, the apparatus and experimental technique being those described elsewhere.[14] Powder EPR spectra were recorded with a Varian E-9 spectrometer equipped with X-band (9 GHz) and variable-temperature accessories.

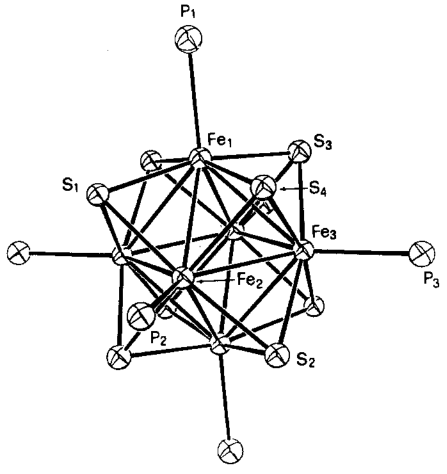

Figure 1. Perspective view of the inner core of the $[Fe_6(\mu_3\text{-}S)_8(PEt_3)_6]^{2+}$ cation with 50% probability ellipsoids.

Collection and Reduction of X-ray Data. Since the data collection whose results were reported in the preliminary communication was not completely satisfactory, a new set of data was collected. A well-formed crystal delimited by the faces 100, $0\bar{1}0$, 001, and the centrosymmetric faces was used for data collection at 295 K on a Philips PW 1100 automatic diffractometer. Unit cell dimensions were determined from the least-squares refinement of the angular settings of 24 carefully centered reflections. Details of crystal data and data collection are given in Table I. The intensities were corrected for background and assigned standard deviations calculated by using the value of 0.03 for the instability factor K.[15] Of 8105 reflections 6055 having $I > 3\sigma(I)$ were considered observed. Intensity data were corrected for Lorentz and polarization effects and for absorption.[16] The correction for extinction was considered unnecessary.

Solution and Refinement of the Structure. All the calculations was carried out on a Sel 32/70 computer using the SHELX 76[16] and ORTEP[17] programs. Atomic scattering factors of the appropriate neutral atoms were taken from ref 18 for the non-hydrogen atoms and from ref 19 for the hydrogen atoms. Both the $\Delta f'$ and $\Delta f''$ components of the anomalous dispersion correction were included for all the non-hydrogen atoms.[20] The structure was solved by the heavy-atom method, and several Fourier maps revealed all the non-hydrogen atoms. Full-matrix least-squares refinements were carried out, the function $\sum w(|F_o| - |F_c|)^2$ being minimized with the weights w defined as $1/\sigma^2(F_o)$. The phenyl rings of the tetraphenylborate anion were treated as rigid groups, each carbon atom being assigned an individual thermal parameter. The hydrogen atoms were introduced in calculated positions but not refined. The iron, sulfur, and phosphorus atoms were allowed anisotropic thermal vibrations. The refinements converged at the R and R_w factor values of 0.058 and 0.064, respectively. R and R_w factors are defined as $\sum||F_o| - |F_c||/\sum|F_o|$ and $[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. The final positional and thermal parameters are reported in Tables II, SI, and SII (Tables SI and SII are supplementary material).

Results and Disscussion

The reaction of $[Fe(H_2O)_6](BF_4)_2$ with an excess of PEt_3 and H_2S, in the presence of $NaBPh_4$, led to the synthesis of the crystalline dark compound $[Fe_6(\mu_3\text{-}S)_8(PEt_3)_6](BPh_4)_2$. The spontaneous self-assembly of this cluster occurs in mild conditions (room temperature) together with the formation of a considerable amount of unidentified materials. The large excess of phosphine is necessary in order to prevent the formation of the insoluble sulfide FeS. The same reaction performed by using PMe_3 in the place of PEt_3 led to the formation of only intractable materials.

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Table III. Selected Bond Lengths (Å) with Estimated Standard Deviations[a]

	Fe–Fe		
Fe1–Fe2	2.633 (3)	Fe1–Fe3′	2.611 (3)
Fe1–Fe3	2.602 (3)	Fe2–Fe3	2.638 (3)
Fe1–Fe2′	2.612 (3)	Fe2–Fe3′	2.606 (3)
mean	2.617 (6)[b]		
	Fe–μ_3–S		
Fe1–S1	2.253 (4)	Fe2–S4	2.249 (3)
Fe1–S3	2.241 (4)	Fe2–S3′	2.254 (3)
Fe1–S4	2.250 (4)	Fe3–S2	2.239 (3)
Fe1–S2′	2.241 (3)	Fe3–S3	2.248 (3)
Fe2–S1	2.246 (3)	Fe3–S4	2.245 (4)
Fe2–S2	2.246 (3)	Fe3–S1′	2.251 (4)
mean	2.247 (1)		
	Fe–P		
Fe1–P1	2.286 (3)	Fe3–P3	2.289 (4)
Fe2–P2	2.305 (4)		
mean	2.293 (6)		
	S···S		
S1···S4	3.143 (3)	S2···S4	3.126 (3)
S1···S2′	3.152 (4)	S2···S3′	3.166 (3)
S1···S3′	3.180 (3)	S3···S4	3.157 (4)
mean	3.154 (8)		

[a] Primed atoms are related to the corresponding unprimed atoms by the center of symmetry. [b] The estimated errors on the means were calculated according to the formula $[\Sigma_n(d_n - d)^2/n(n-1)]^{1/2}$.

Table IV. Selected Bond Angles (deg) with Estimated Standard Deviations

Fe2–Fe1–Fe3	60.5 (1)	Fe1–Fe3–Fe2	60.3 (1)
Fe2–Fe1–Fe2′	90.7 (1)	Fe1–Fe3–Fe1′	90.0 (1)
Fe2–Fe1–Fe3′	59.6 (1)	Fe1–Fe3–Fe2′	60.2 (1)
Fe3–Fe1–Fe2′	60.0 (1)	Fe2–Fe3–Fe1′	59.7 (1)
Fe3–Fe1–Fe3′	90.0 (1)	Fe2–Fe3–Fe2′	90.7 (1)
Fe2′–Fe1–Fe3′	60.7 (1)	Fe1′–Fe3–Fe2′	60.6 (1)
S1–Fe1–S3	167.0 (1)	S2–Fe3–S3	166.7 (1)
S1–Fe1–S4	88.5 (1)	S2–Fe3–S4	88.4 (1)
S1–Fe1–P1	96.7 (1)	S2–Fe3–P3	97.8 (1)
S1–Fe1–S2′	89.1 (1)	S2–Fe3–S1′	89.2 (1)
S3–Fe1–S4	89.3 (1)	S3–Fe3–S4	89.3 (1)
S3–Fe1–P1	96.3 (1)	S3–Fe3–P3	95.5 (1)
S3–Fe1–S2′	89.9 (1)	S3–Fe3–S1′	90.0 (1)
S4–Fe1–P1	100.8 (1)	S4–Fe3–P3	95.8 (1)
S4–Fe1–S2′	165.6 (1)	S4–Fe3–S1′	166.1 (1)
P1–Fe1–S2′	93.5 (1)	P3–Fe3–S1′	98.1 (1)
Fe1–Fe2–Fe3	59.2 (1)	Fe1–S1–Fe2	71.7 (1)
Fe1–Fe2–Fe1′	89.3 (1)	Fe1–S1–Fe3′	70.9 (1)
Fe1–Fe2–Fe3′	59.8 (1)	Fe2–S1–Fe3′	70.8 (1)
Fe3–Fe2–Fe1′	59.6 (1)	Fe2–S2–Fe3	72.0 (1)
Fe3–Fe2–Fe3′	89.3 (1)	Fe2–S2–Fe1′	71.2 (1)
Fe1′–Fe2–Fe3′	59.8 (1)	Fe3–S2–Fe1′	71.3 (1)
S1–Fe2–S2	165.1 (1)	Fe1–S3–Fe3	70.9 (1)
S1–Fe2–S4	88.7 (1)	Fe1–S3–Fe2′	71.1 (1)
S1–Fe2–P2	96.3 (1)	Fe3–S3–Fe2′	70.8 (1)
S1–Fe2–S3′	89.9 (1)		
S2–Fe2–S4	88.1 (1)	Fe1–S4–Fe2	71.6 (1)
S2–Fe2–P2	98.5 (1)	Fe1–S4–Fe3	70.7 (1)
S2–Fe2–S3′	89.4 (1)	Fe2–S4–Fe3	71.9 (1)
S4–Fe2–P2	97.6 (1)		
S4–Fe2–S3′	165.3 (1)		
P2–Fe2–S3′	97.1 (1)		

Table V. Average Distances (Å) within the Isostructural Series $[M_6(\mu_3\text{-}S)_8(PEt_3)_6]^{n+}$ ($n = 2, 1, 0$)

	$[Fe_6(\mu_3\text{-}S)_8(PEt_3)_6]^{2+}$ [a]	$[Co_6(\mu_3\text{-}S)_8(PEt_3)_6]^{+}$ [b]	$[Co_6(\mu_3\text{-}S)_8(PEt_3)_6]$ [c]
M–M	2.617 (6)	2.794 (2)	2.816 (2)
M–S	2.247 (1)	2.234 (2)	2.233 (5)
M–P	2.293 (6)	2.162 (2)	2.135 (3)

[a] This work. [b] Reference 8. [c] Reference 9.

All attempts to reduce the complex by sodium tetrahydroborate or sodium naphthalenide led invariably to the decomposition of the compound.

The complex is air stable and soluble in common polar organic solvents such as methylene chloride, acetone, and nitroethane. In the last solvent the complex behaves as a 1:2 electrolyte.

The molecular structure of the title compound consists of discrete $[Fe_6(\mu_3\text{-}S)_8(PEt_3)_6]^{2+}$ cations and BPh_4^- anions. Figure 1 shows a perspective view of the inner core of the cation, and Tables III and IV report selected bond distances and angles. The complex cation consists of an octahedron of iron atoms with the sulfur ligands triply bridging all the octahedral faces. Moreover, each metal atom is terminally bonded to a triethylphosphine group. Therefore, each metal atom is surrounded by four sulfur atoms and one phosphorus atom in a distorted-square-pyramidal environment and linked to another four iron atoms. The Fe_6S_8 unit may be alternatively described as a slightly distorted cube of sulfur atoms with the metal atoms in the face-centered positions. The sulfur cube has a mean edge of 3.154 (8) Å, and the metal atoms are located just outside the faces of the cube, the deviations from the mean planes containing the sulfur atoms being 0.27, 0.29, and 0.27 Å for Fe1, Fe2, and Fe3, respectively. In this context, in a localized situation description, we can imagine the cluster as built up from six square-pyramidal iron complexes sharing the bridging sulfur ligands.

The $[Fe_6(\mu_3\text{-}S)_8(PEt_3)_6]^{2+}$ cation possesses crystallographic C_i-$\bar{1}$ symmetry, lying on the center of inversion, but the inner core may be considered to posses idealized O_h symmetry. The octahedral iron framework is rather regular, the Fe–Fe distances ranging from 2.602 (3) to 2.638 (3) Å and averaging 2.617 (6) Å. These values lie in the lower range of Fe–Fe distances that have been found for polynuclear compounds containing triangular iron units capped by sulfur ligands.[4c,d,21] Although in the presence of strong bridging ligands it is difficult to discern the real amount of direct metal–metal interaction, a comparison with the related cobalt derivatives $[Co_6(\mu_3\text{-}S)_8(PEt_3)_6]^{+}$[8] and $[Co_6(\mu_3\text{-}S)_8(PEt_3)_6]$[9] seems to indicate that significant metal–metal bonding exists. As a matter of fact, the last two clusters, which are isostructural with the title compound, display average Co–Co distances of 2.794 (2) and 2.816 (2) Å, respectively. Indeed, if we consider this isostructural series (Table V) it appears evident that the increase of the M–M distances is accompanied by the decrease of the M–P and to a lesser extent of the M–S bond distances, indicating that the increase of the total electron number results in a decrease of the metal–metal interactions and in a strengthening of the metal–ligand bonding. Moreover, the metal–sulfur distances appear to be less sensitive to the total electron count than the metal–phosphorus distances.

The value of the average Fe–μ_3-S bond distance, 2.247 (1) Å, compares well with those reported for polynuclear compounds containing triply bridging sulfur ligands.[4c,d,21]

Molecular clusters of the type M_6X_8 have been reported in the literature,[22] but as far as we know, no similar compound containing iron has been previously described. Moreover, another peculiarity of this compound is its large paramagnetism.

Indeed, the magnetic susceptibility of the cluster follows the Curie–Weiss law in the range 100–300 K, with a Θ value of about −3.7 K, and the related effective magnetic moment slowly decreases from 6.04 μ_B (at room temperature) to 5.66 μ_B (at liquid-nitrogen temperature) as shown in Figure 2. This magnetic moment could appear indicative of five unpaired electrons, for which the spin-only formula provides $\mu_{eff} = 5.91\ \mu_B$, but this does not agree with the even number of electrons in the whole cluster (total number of electrons 372).

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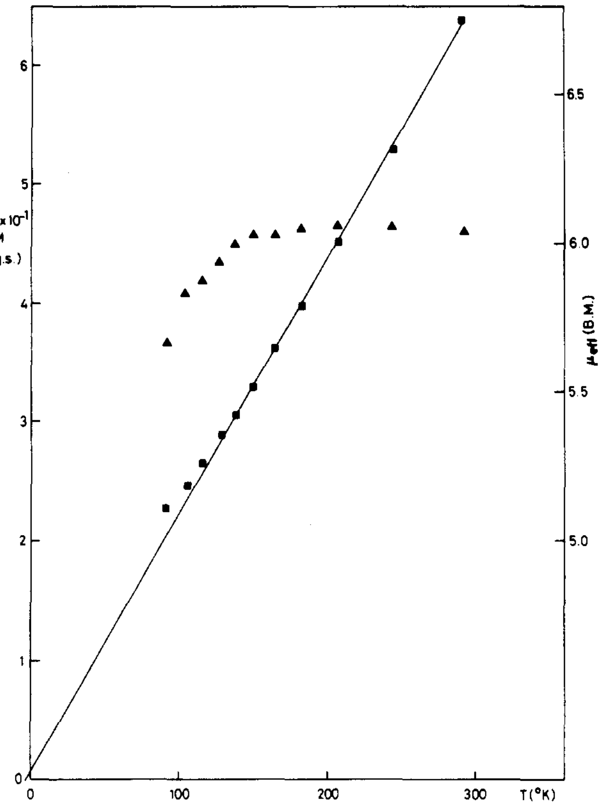

Figure 2. Magnetic effective moment (▲) and susceptibility (■) vs. temperature for $[Fe_6(\mu_3\text{-}S)_8(PEt_3)_6](BPh_4)_2$.

In addition, Mössbauer spectra[23] in the range 7–300 K have revealed no phase transition or magnetic interaction. They are only slightly affected by temperature and are characterized by small values of the quadrupole splittings and of the isomer shift (0.268 and 0.281 mm/s, respectively, at 7 K), these being typical of highly covalent compounds.[24]

Good powder EPR spectra are obtained at 4 K (Figure 3) and show two strong resonances at about $g = 4.9$ and $g = 2.0$ plus other weaker signals at about $g = 11.0$, 9.4, and 7.0. The strongest signal at $g = 4.9$ disappears at $T > 200$ K.

Finally, electronic spectra show only one intense peak at 243 nm and a broad shoulder at about 650 nm.

Looking at the above results, one can easily realize that it is not a trivial matter to find a model that can account simultaneously for the different experimental data.

A crude, but intuitive, model could be based upon the following considerations.

The formal charge of each iron atom, as results from the stoichiometry, is 3+, while the approximate stereochemistry is a square pyramid (C_{4v} point group symmetry). Five-coordinated iron(III) complexes with soft ligands, like S or P, are commonly expected to be low spin[25] with a single unpaired electron. Therefore, if a weak interaction among the six iron "complexes", constituting the cluster, is assumed, six unpaired electrons are expected for the whole cluster.

Such an electronic configuration could give useful suggestions for interpreting our experimental results. In fact, an axial spin Hamiltonian

$$H = D[\hat{S}_z^2 - \tfrac{1}{3}S(S + 1)] + g_{\parallel}\beta H_z\hat{S}_z + g_{\perp}\beta(H_x\hat{S}_x + H_y\hat{S}_y) \qquad (1)$$

with $S = 3$ and small D values ($D \approx 0.2$ cm^{-1}) seems to us, at the present, the only possibility of explanation of the EPR and magnetic susceptibility data.

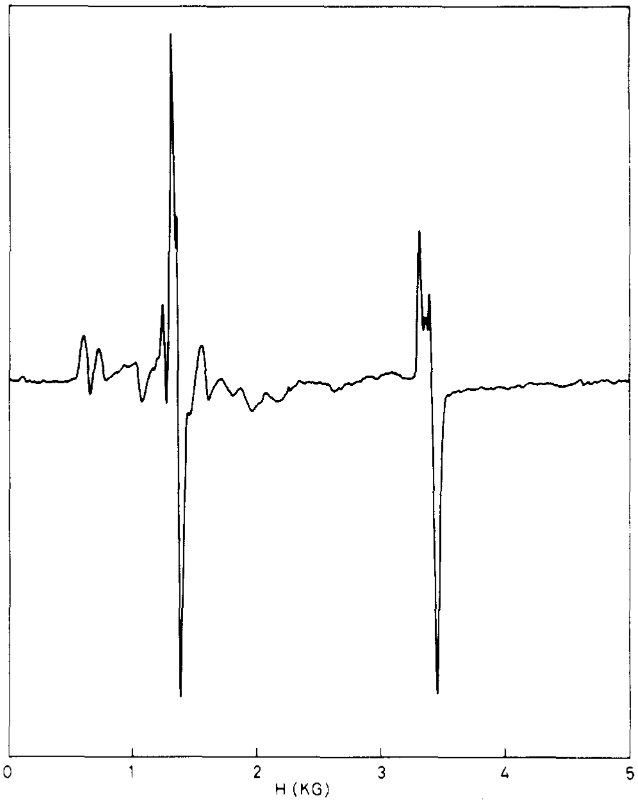

Figure 3. Powder EPR spectrum of $[Fe_6(\mu_3\text{-}S)_8(PEt_3)_6](BPh_4)_2$ recorded at liquid-helium temperature.

Table VI. Atomic Positions and MS–Xα Parameters[a]

Atomic Positions

Fe: $\pm a, 0, 0; 0, \pm a, 0; 0, 0, \pm a$
S: $\pm b, \pm b, \pm b$
P: $\pm c, 0, 0; 0, \pm c, 0; 0, 0, \pm c$
$a = 3.507$ au; $b = 3.030$ au; $c = 7.847$ au

Sphere Radii (au) and α Parameters

$R_{Fe} = 2.4871$	$\alpha_{Fe} = 0.71151$
$R_S = 2.6867$	$\alpha_S = 0.72475$
$R_P = 3.1185$	$\alpha_P = 0.72620$
$R_{OS} = 10.9655$	$\alpha_{OS} = 0.72005$

[a] The atomic positions were derived from the preliminary communication's parameters.[7]

The occurrence of an electronic structure with six unpaired electrons is actually provided, on a qualitative basis, by an extended Hückel MO treatment,[12] at least at room temperature: the proposed configuration is $a_{1g}{}^1e_g{}^2t_{2u}{}^3$, where a_{1g}, e_g, and t_{2u} are one-electron orbitals in increasing energy order. When the temperature is decreased, alternative arrangements of the six "excess" electrons are possible, depending upon the interelectronic repulsion, and spin multiplicities $S = 2$ and $S = 0$ can also occur.

To get more information as to the electronic structure of the present cluster, we started on a MO calculation adopting the SCF MS–Xα approach, which had provided useful indications for similar clusters.[26]

The idealized cubic cluster $[Fe_6S_8P_6]^{2+}$ was assumed for the calculation. To reduce the computational time, phosphorus atoms instead of triethylphosphine were considered. Iron and phosphorus atoms are situated on the corners of two concentric octahedra, respectively, while sulfur atoms are disposed on the corners of a cube. In Table VI we report atomic positions together with the

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Table VII. Ground-State Energy (eV) and Charge Distribution for $[Fe_6S_8P_6]^{2+}$

level	energy	% contribns Fe	S	P	int	out	% Fe angular contribns
$7e_g$	−0.114	1	1	2	45	51	
$8t_{2g}$	−0.312	1	3	3	43	51	
$11t_{1u}$	−0.780	1	3	3	51	42	
$7a_{1g}$	−1.368	8	6	2	57	27	
$3a_{2u}$	−4.082	56	36	0	7	0	100 (d)
$7t_{2g}$	−4.853	55	36	1	8	0	1 (p), 99 (d)
$6e_g$	−5.036	53	17	23	6	1	3 (p), 97 (d)
$2e_u$	−5.207	51	41	0	8	0	100 (d)
$10t_{1u}$	−5.277	54	16	24	5	1	6 (p), 94 (d)
$4t_{1g}$	−6.751	42	2	48	8	0	100 (d)
$5t_{2u}$	−6.857	20	7	63	10	1	1 (p), 99 (d)
$9t_{1u}$	−6.912	30	10	49	11	1	3 (p), 97 (d)
$6t_{2g}$	−6.974	23	5	60	11	1	1 (p), 99 (d)
$4t_{2u}$	−7.022	85	13	0	2	0	1 (p), 99 (d)
$3t_{1g}$	−7.222	36	45	15	4	0	4 (p), 96 (d)
$6a_{1g}$	−7.500	45	1	44	8	1	42 (p), 58 (d)
$1a_{2g}$	−7.546	98	0	0	2	0	100 (d)
$5e_g$	−7.960	90	5	1	3	0	1 (s), 1 (p), 98 (d)
$8t_{1u}$	−8.370	38	17	38	7	0	1 (s), 10 (p), 89 (d)
$5t_{2g}$	−8.694	63	9	22	5	0	2 (p), 98 (d)
$3t_{2u}$	−8.759	76	0	19	5	0	100 (d)
$2t_{1g}$	−9.284	26	40	24	10	0	19 (p), 81 (d)
$7t_{1u}$	−9.389	39	55	1	6	0	2 (s), 16 (p), 82 (d)
$4e_g$	−10.083	40	1	58	0	1	5 (s), 9 (p), 85 (d)
$6t_{1u}$	−10.266	37	3	59	0	1	9 (s), 10 (p), 81 (d)
$1e_u$	−10.445	51	49	0	0	0	100 (d)
$4t_{2g}$	−10.651	26	69	1	4	0	44 (p), 56 (d)
$5a_{1g}$	−10.799	53	3	43	0	1	7 (s), 93 (d)
$2t_{2u}$	−11.053	25	60	5	10	0	36 (p), 64 (d)
$2a_{2u}$	−11.479	39	61	0	0	0	100 (d)
$3t_{2g}$	−11.535	46	52	2	1	0	4 (p), 96 (d)
$3e_g$	−12.081	33	55	7	5	0	35 (s), 1 (p), 64 (d)
$5t_{1u}$	−12.174	32	64	2	2	0	39 (s), 10 (p), 51 (d)
$4a_{1g}$	−12.429	26	70	0	4	0	81 (s), 19 (p)
$3a_{1g}$	−16.898	9	2	89	0	0	
$4t_{1u}$	−16.942	8	2	90	0	0	
$2e_g$	−17.019	9	1	90	0	0	
$2t_{2g}$	−19.766	12	88	0	0	0	56 (p), 44 (d)
$1a_{2u}$	−19.793	14	86	0	0	0	100 (d)
$3t_{1u}$	−20.355	15	84	1	0	0	47 (s), 42 (p)
$2a_{1g}$	−21.318	20	79	1	0	0	85 (s), 2 (p)
$1t_{1g}$	−59.570	100	0	0	0	0	100 (p)
$2t_{1u}$	−59.601	99	0	0	0	0	100 (p)
$1t_{2u}$	−59.610	100	0	0	0	0	100 (p)
$1e_g$	−59.616	99	0	1	0	0	100 (p)
$1t_{2g}$	−59.700	99	1	0	0	0	100 (p)
$1t_{1u}$	−59.716	99	0	0	0	0	100 (p)
$1a_{1g}$	−59.745	99	0	1	0	0	100 (p)

MS–Xα parameters. The mean value of the bond distances was assumed, and the statistical exchange parameters were obtained from Schwarz's tabulation.[27] Atomic sphere radii were increased to obtain 20% (for iron and sulfur) and 29% (for iron and phosphorus) overlapping spheres. This latter value could appear too large, but it should compensate for the substitution of triethylphosphine by phosphorus atoms, since sp^3 hybridization should produce a much more extended electronic cloud along the P–Fe axis than in the case of a single phosphorus atom. A Watson sphere having the same radius as the outer sphere and bearing a charge of 2− was used to simulate the effect of an external stabilizing electrostatic field. SCF calculations were converged to better than ±0.001 Ry on each level.

Valence electron energies are displayed in Figure 4, where the orbital levels are labeled according to the irreducible representations of the point group O_h. In Table VII energies and charge distribution of the orbitals are reported. The total charges in the shperes are as follows: Q(Fe) = 25.836; Q(S) = 15.785; Q(P) = 14.438; Q(outer sphere) = 0.24; Q(intersphere) = 3.836. If the charge of the intersphere and outer sphere is fully attributed to the ligand atoms, the atomic charge of the Fe is +0.164 e, while a slight negative charge is present at the sulfur atoms. Instead, phosphorus atoms are positively charged. In fact, even if the outer-sphere charge is fully attributed to P and the intersphere one is equally distributed between P and S, the atomic charge of P is +0.248 e, while that of S is −0.059 e, which is consistent with the electronegative character of the latter element. The positive charge on the phosphorus together with the small charge on the iron indicates a strong charge transfer from P to Fe, and this fact could explain the stabilization of the cluster only in the presence of phosphine.

The highest occupied molecular orbital is the level $4t_{2u}$, which is essentially Fe 3d like and is occupied by four electrons. Therefore, in a strictly octahedral stereochemistry a paramagnetic ground state with $S = 1$ has to be expected even at very low temperature. However, the very crowded distribution of one-electron orbitals around 7 eV suggests the possibility of higher spin multiplicities when interelectronic repulsion is taken into account: for instance, the configuration $3t_{1g}{}^5 4t_{2u}{}^3 6t_{2g}{}^2$ provides six unpaired electrons (see Figure 3).

The present Xα calculation gives a level scheme for the highest occupied orbitals at variance with the extended Hückel treatment[12] because the level ordering for the Fe–Fe bonding is reversed for the orbitals a_{2g} and e_g and, moreover, these levels are separated from the highest occupied t_{2u} level by two intermediate metal–ligand mixed orbitals.

Above the highest occupied and the low-lying empty orbitals (around 7 eV) two groups of molecular orbitals occur at about 5 and 1 eV, respectively. One-electron energy differences among the ground-state orbitals can be used to interpret tentatively the electronic spectra, because the extensive delocalization of these molecular orbitals should assure small relaxation effects so that transition-state calculations can be avoided.[28,29] With this approximation two absorption bands are calculated at about 650 and 210 nm, which compare satisfactorily with the experimental ones at 650 and 243 nm.

Although both extended Hückel and Xα treatments do not disagree with an electronic configuration with six unpaired electrons, which appears to be the most suitable to interpret the magnetic data, they are not able to supply, at the present stage of calculation, a definitive description of the electronic structure of the cluster. Therefore, at last we wish to present an alternative approach, recently proposed by one of us[13] for general metal clusters, which could provide the right electronic configuration.

Owing to the highly delocalized charge distribution commonly observed for the highest occupied orbitals in symmetrical metal clusters, it has been proposed that the valence electron cloud is subjected to a central spherical potential, which arises from nuclei and core electrons. Consequently, the same filling order of the orbitals as in free atoms can be assumed, while crystal field effects are introduced as successive perturbations.

In this "quasi-atomic" framework the electronic configuration $nf^6(n + 2)s^2$, which leads to the ground state ^7F, is obtained for the $[Fe_6S_8P_6]^{2+}$ cluster. When a cubic ligand field is introduced, the above level splits into the three levels $^7A_1$, $^7T_1$, and $^7T_2$, the level $^7A_1$ being the ground state for a cubic (eight-coordination) geometry. This level spans the irreducible representations Γ_2, Γ_4, and Γ_5 of the cubic point symmetry. Using such a basis, we can easily obtain an approximate evaluation of the magnetic moment. In fact, if no coupling between the ground and excited levels is assumed, the application of the magnetic field Hamiltonian $H = 2\beta HS$ upon the above spin functions readily provides a constant μ_{eff} value of 5.86 μ_B.[13] The introduction of zero-field splitting and coupling to excited levels could explain the slight temperature dependence of μ_{eff}. The EPR spectrum too can be interpreted in this picture: in fact, owing to the absence of orbital contributions in the $^7A_1$ level, we may consider only the effect of the magnetic field upon a spin system with $S = 3$. With the spin Hamiltonian (1) assuming $D = 0.15$ cm^{-1} and $g = 2.0$, two lines at $g = 4.98$

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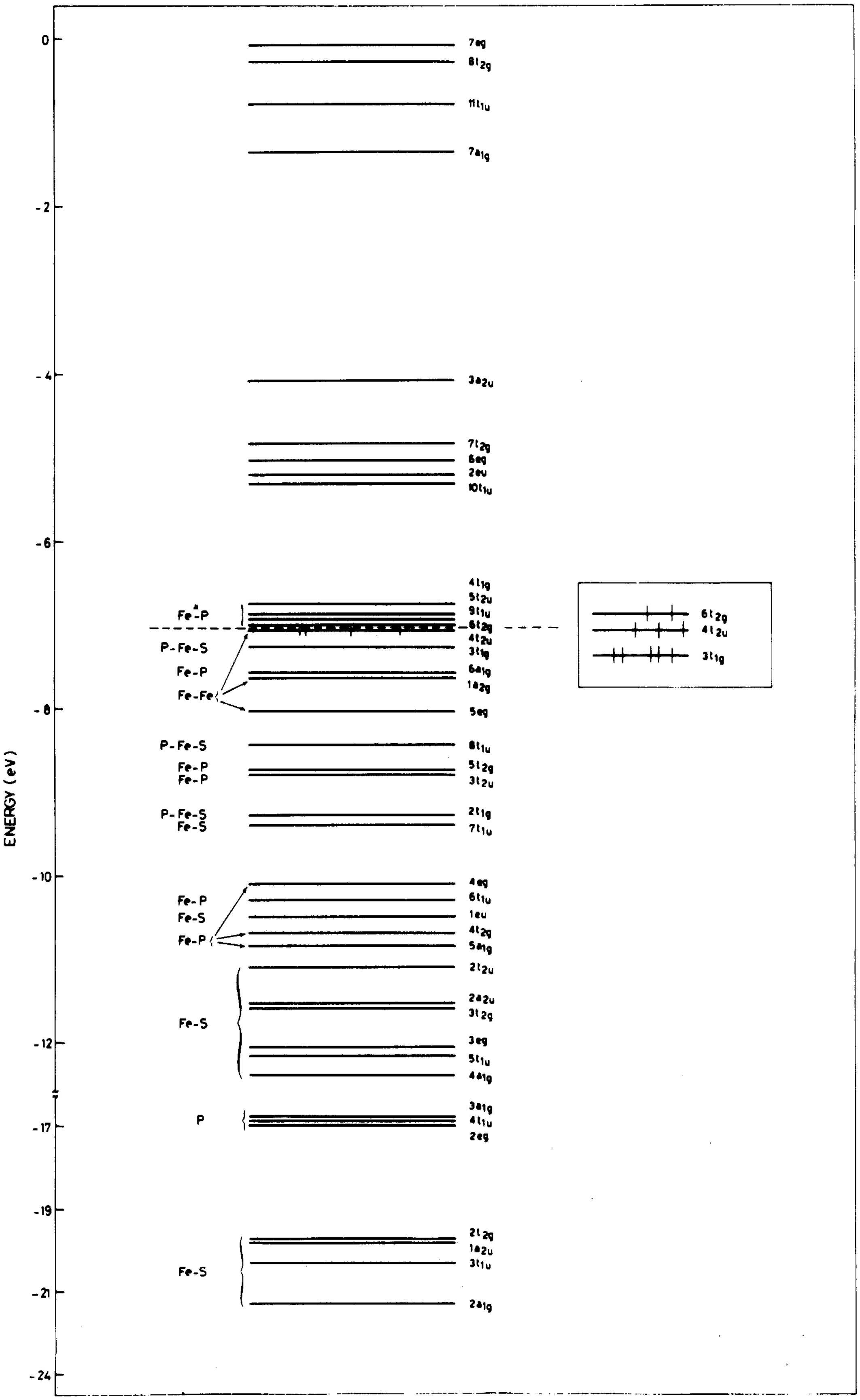

Figure 4. Ground-state valence energy levels of $[Fe_6S_8P_6]^{2+}$. The highest occupied level is $4t_{2u}$. In the inset a plausible electronic configuration with six unpaired electrons is shown.

and $g = 1.93$ are calculated for H parallel to x or y.

Unfortunately the lack of further information concerning the relevant parameters, which characterize the "pseudoatomic" level ^7F, prevents a deeper analysis.

In conclusion, the present experimental data and theoretical studies seem to support a delocalized electronic structure with six unpaired electrons for the cluster $[Fe_6(\mu_3\text{-}S)_8(PEt_3)_6]^{2+}$, which represents, to our knowledge, the first example reported in the literature of a transition-metal complex with $S = 3$.

Acknowledgment. Thanks are expressed to Prof. J. Weber, University of Geneva, for supplying us a copy of the SCF Xα calculation program. We thank also Drs. A. Vera and E. Buluggiu, University of Parma, and Dr. A. Bencini, ISSECC CNR, for helpful discussions concerning EPR spectra.

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 $\sim$3 cm^{-1}, and a second doublet at $\sim$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)$_2$en, 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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