Inorg. Chem. 1990, 29, 5054-5058

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A Tetranuclear Hydroxo-Bridged Copper(II) Cluster of the Cubane Type. Preparation and Structural and Magnetic Characterization of Tetrakis[(2,2'-bipyridyl)(μ-hydroxo)copper(II)] Hexafluorophosphate

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Received April 4, 1990

The title compound, $C_{40}H_{36}N_8Cu_4F_{24}O_4P_4$, noted $[Cu(bpy)(OH)]_4(PF_6)_4$, has been synthesized, and its structure has been determined by X-ray crystallographic methods. Crystal data: monoclinic system, space group $C2/c$, a = 24.494 (7) Å, b = 14.104 (3) Å, c = 16.336 (4) Å, β = 112.65 (2)°, Z = 4. Data up to θ = 26° (Mo Kα radiation) were collected at room temperature on a CAD4 diffractometer. The structure was solved by direct methods and refined by full-matrix least-squares refinement to R = 0.069, including 3667 reflections with $|F_o| > 3\sigma_F$. The complex may be described as two almost planar bpy–Cu–$(OH)_2$–Cu–bpy units held together by long out-of-plane Cu–O(H) bonds (2.486 and 2.585 Å), creating a tetrameric entity with a cubane-like $Cu_4(OH)_4$ core. Within each hydroxo-bridged dinuclear unit both of the crystallographically independent copper atoms form four short equatorial bonds to two hydroxo oxygen atoms (1.947–1.962 Å) and two bipyridyl nitrogen atoms (1.981–1.997 Å). The second axial position around each copper is occupied by a fluorine atom (Cu–F = 2.64 and 2.68 Å), a hexafluorophosphate ion bridging the two copper atoms within a dinuclear unit. The two remaining hexafluorophosphate ions are uncoordinated. The magnetic properties of this compound have been studied in the 4.2–300 K temperature range. They correspond to what is expected for a ferromagnetically coupled CuCu pair with a triplet–singlet energy gap of 12 cm^{-1}. The data may, however, also be fitted to a model that includes weak ferromagnetic interaction between dimers. Magnetization studies have confirmed such an interdinuclear interaction.

Introduction

A number of structural investigations of alkoxo-bridged Cu(II) tetramers with cubane-like Cu_4O_4 cores have been reported, and their magnetic properties have been compared to the ones of the corresponding binuclear complexes.[2-8] The main conclusion that can be inferred from the magnetic studies of oxygen-bridged cubane-like copper(II) clusters is that an overall ferromagnetic or antiferromagnetic behavior results. In most of the cases, this behavior can be adequately described if electron spin–spin interactions among all four copper ions are taken into account. To our knowledge, hydroxo-bridged Cu_4O_4 tetramers have not previously been characterized. However, the parent bis(μ-hydroxo) dinuclear copper(II) complexes are well-known; X-ray structure investigations and studies of magnetic properties have been performed for a great number of such compounds.[9,10] In this family of compounds the correlation between structural parameters and magnetic properties are well established.[9,11] Hatfield and Hodgson have shown that the singlet–triplet energy gap, J, varies linearly with the Cu–O–Cu bridging angle, φ, having a singlet ground state for $\varphi > 97.5°$ and a triplet ground state for $\varphi < 97.5°$. A study of a hydroxo-bridged tetramer is thus of particular interest for elucidating the relationship between molecular structure and magnetic properties in the Cu_4O_4 compounds.

We report here the synthesis and the crystal and molecular structure of the cubane-type complex of formula $[Cu(bpy)OH]_4(PF_6)_4$ and its magnetic properties down to 4.2 K.

Experimental Section

Table I. Crystallographic Data for $[Cu(bpy)OH]_4(PF_6)_4$

chem formula: $C_{40}H_{36}N_8Cu_4F_{24}O_4P_4$
fw: 1526.80
space group: $C2/c$ (No. 15)
a = 24.494 (7) Å
b = 14.104 (3) Å
c = 16.336 (4) Å
β = 112.65 (2)°
V = 5208 (5) Å^3
Z = 4
T = 21 °C
λ = 0.71073 Å
ρ(obsd) = 1.97 g cm^{-3}
ρ(calcd) = 1.947 g cm^{-3}
μ = 18.71 cm^{-1}
transm coeff = 0.77–1.59
$R(F_o)$ = 0.069
$R_w(F_o)$ = 0.080

Synthesis. The title compound was originally obtained as a side product in the course of synthetic work aimed at producing dithiooxamido-bridged dinuclear copper(II) complexes. A procedure similar to that described by Nonoyama et al.[12] for synthesizing dinuclear oxamido-bridged copper(II) complexes was used. After the crystal structure of this side product was solved, we developed a direct synthetic route to obtain such a complex. The procedure is as follows: A Dowex 50W-X8 cationic exchange resin supplied by BDH was used to prepare copper(II) hexafluorophosphate. The resin, which was initially in the hydrogen form, was treated with an aqueous solution of 0.4 mol dm^{-3} copper(II) sulfate in order to exchange H$^+$ by Cu(II). After washing until no sulfate was detected in the waste, a concentrated aqueous solution of KPF_6 (2 mmol) was allowed to drip into the column at a slow rate. Water was used as effluent to pass the hexafluorophosphate solution through the column; effluent and washings (100 mL) were collected. 2,2'-Bipyridyl (1 mmol) was added to this solution with stirring, and a blue solution was obtained after heating at 50 °C for a few minutes. Finally, Na_2CO_3 (0.5 mmol) was added as a solid at room temperature, and the solution turned dark blue, revealing that hydroxo or carbonato complex formation had occurred; the pH of the resulting solution was 8–9. Well-formed blue polyhedral crystals of the tetramer were formed by slow evaporation of this solution at room temperature. Once the crystals were separated, the pH of the aqueous solution had dropped to about 5, which is in agreement with the formation of a hydroxo complex. Anal. Calcd for $C_{40}H_{36}N_8Cu_4F_{24}O_4P_4$: C, 31.47; H, 2.36; N, 7.34; Cu, 16.65. Found: C, 31.40; H, 2.50; N, 7.40; Cu, 17.15.

Physical Techniques. IR spectra were recorded on a Perkin-Elmer spectrophotometer as KBr pellets. Magnetic measurements were carried out on polycrystalline samples in the 4.2–300 K temperature range with a previously described Faraday-type magnetometer,[13] equipped with a helium continuous-flow cryostat. Mercury tetrakis(thiocyanato)cobaltate(II) was used as a susceptibility standard. The correction for the diamagnetism of the complex was estimated from Pascal constants as -390×10^{-6} cm^3 mol^{-1} per dinuclear unit.

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Table II. Atomic Parameters for Non-Hydrogen Atoms[a]

atom	x	y	z	B_{eq}, Å^2
Cu1	0.42660 (3)	0.11153 (6)	0.16322 (6)	2.78 (2)
Cu2	0.51871 (3)	0.23857 (3)	0.15693 (6)	2.74 (2)
P1	0.32336 (9)	0.4959 (2)	0.1118 (2)	3.93 (5)*
P2A	0.0820 (2)	0.3476 (3)	0.0809 (3)	3.30 (8)*
P2B	0.0970 (2)	0.3529 (3)	0.0816 (3)	3.18 (8)*
F1	0.3109 (4)	0.5581 (7)	0.1781 (5)	13.4 (3)
F2	0.3784 (3)	0.5590 (4)	0.1274 (6)	11.4 (3)
F3	0.3398 (4)	0.4405 (7)	0.0435 (5)	14.1 (3)
F4	0.3655 (3)	0.4258 (5)	0.1813 (5)	10.3 (2)
F5	0.2846 (3)	0.5695 (6)	0.0408 (5)	11.2 (2)
F6	0.2709 (3)	0.4332 (5)	0.0914 (7)	13.2 (3)
F7A	0.0574 (6)	0.310 (1)	0.1441 (9)	9.5 (4)*
F8A	0.0340 (7)	0.420 (1)	0.030 (1)	11.5 (5)*
F9A	0.1121 (6)	0.3875 (9)	0.0142 (9)	8.6 (3)*
F10A	0.0524 (5)	0.2713 (9)	0.0123 (8)	8.0 (3)*
F11A	0.120 (1)	0.428 (2)	0.143 (2)	18.2 (8)*
F12A	0.1335 (5)	0.2764 (8)	0.1313 (7)	6.2 (3)*
F7B	0.0284 (4)	0.3114 (7)	0.0258 (7)	5.4 (2)*
F8B	0.0717 (3)	0.4181 (6)	0.1423 (5)	3.6 (2)*
F9B	0.1554 (4)	0.3940 (7)	0.1378 (7)	5.5 (2)*
F10B	0.1095 (6)	0.266 (1)	0.1513 (9)	9.2 (4)*
F11B	0.0808 (5)	0.4372 (8)	0.0144 (7)	6.7 (3)*
F12B	0.1186 (6)	0.292 (1)	0.0220 (9)	9.0 (4)*
O1	0.5078 (2)	0.1034 (3)	0.1695 (3)	2.9 (1)
O2	0.4454 (2)	0.2462 (3)	0.1786 (3)	3.0 (1)
N1	0.3438 (2)	0.1236 (4)	0.1568 (4)	3.2 (1)
N2	0.4062 (2)	−0.0250 (4)	0.1545 (4)	2.8 (1)
N3	0.5299 (2)	0.3742 (4)	0.1352 (4)	3.0 (1)
N4	0.5899 (2)	0.2251 (4)	0.1267 (4)	3.0 (1)
C1	0.3190 (3)	0.0401 (5)	0.1636 (5)	3.0 (2)
C2	0.2665 (3)	0.0377 (6)	0.1739 (6)	4.4 (2)
C3	0.2370 (3)	0.1219 (7)	0.1723 (6)	5.0 (2)
C4	0.2602 (3)	0.2048 (7)	0.1595 (6)	4.9 (2)
C5	0.3142 (3)	0.2035 (6)	0.1531 (6)	4.5 (2)
C6	0.3532 (3)	−0.0435 (5)	0.1591 (5)	3.0 (2)
C7	0.3346 (4)	−0.1360 (6)	0.1566 (6)	4.2 (2)
C8	0.3697 (4)	−0.2089 (6)	0.1517 (6)	5.2 (3)
C9	0.4224 (4)	−0.1887 (6)	0.1483 (6)	4.6 (2)
C10	0.4394 (3)	−0.0948 (6)	0.1483 (6)	4.1 (2)
C11	0.5753 (3)	0.3917 (5)	0.1110 (5)	3.1 (2)
C12	0.5889 (4)	0.4820 (6)	0.0938 (5)	4.3 (2)
C13	0.5561 (4)	0.5559 (6)	0.1040 (7)	5.3 (3)
C14	0.5100 (4)	0.5379 (6)	0.1281 (6)	5.0 (3)
C15	0.4975 (3)	0.4466 (6)	0.1432 (5)	3.8 (2)
C16	0.6090 (3)	0.3068 (6)	0.1047 (4)	3.0 (2)
C17	0.6567 (3)	0.3067 (6)	0.0787 (5)	4.2 (2)
C18	0.6840 (3)	0.2238 (7)	0.0763 (5)	4.7 (2)
C19	0.6646 (3)	0.1397 (6)	0.0993 (5)	4.1 (2)
C20	0.6174 (3)	0.1434 (6)	0.1228 (5)	3.5 (2)

[a] Starred values correspond to atoms that were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter: $B_{eq} = {}^4/_3\sum_i\sum_j\beta_{ij}a_i\cdot a_j$.

Crystallographic Data Collection and Structure Determination. All measurements were carried out at 294 K on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Cell parameters were determined from least-squares refinement of 25 centered reflections in the range 16° < 2θ < 40°. The crystal data are summarized in Table I along with details of the parameters associated with data collection. A full-length table of crystallographic data is given in the supplementary material (Table SI). A total of 5102 unique reflections were recorded in the range 2° < 2θ < 52°. The intensities of three standard reflections measured every 2 h showed no systematic variation. The usual corrections for Lorentz and polarization effects were carried out.

The systematically absent reflections are consistent with space group $C2/c$ or Cc. A centrosymmetric space group is inferred from the intensity distribution and was confirmed in the course of the structure determination. The structure was solved by direct methods and refined with the full-matrix least-squares method. After isotropic refinement, an empirical absorption correction was carried out.[14] Large anisotropic thermal parameters for the fluorine atoms indicated disorder in the PF_6^- groups; for one of the groups a disordered model could be invoked from difference Fourier maps. Two partly populated positions were introduced for each atom in this group. Population parameters refined to approximately 0.5 for each site and were held fixed at this value in the final cycles. Phosphorus atoms and fluorine atoms of the disordered group were isotropically refined, and all other non-hydrogen atoms anisotropically. Hydrogen atoms belonging to the bipyridyl groups were included at calculated positions, while the hydroxo hydrogen atoms were located in a difference Fourier map after anisotropic refinement of non-hydrogen atoms. Hydrogen atoms were not refined; their thermal parameters were adjusted in accordance with those of the atoms to which they are bonded.

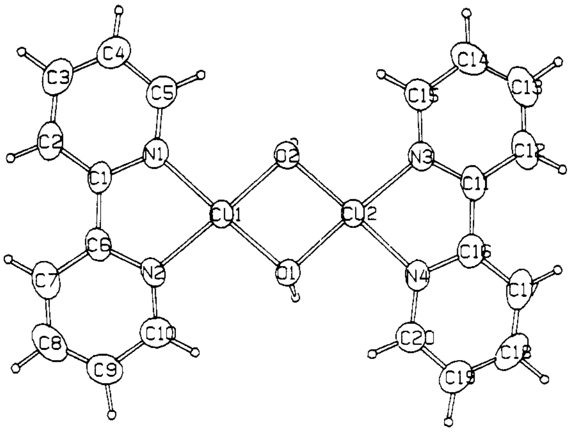

Figure 1. The $[Cu_2(bpy)_2(OH)_2]^{2+}$ moiety with atomic numbering scheme.

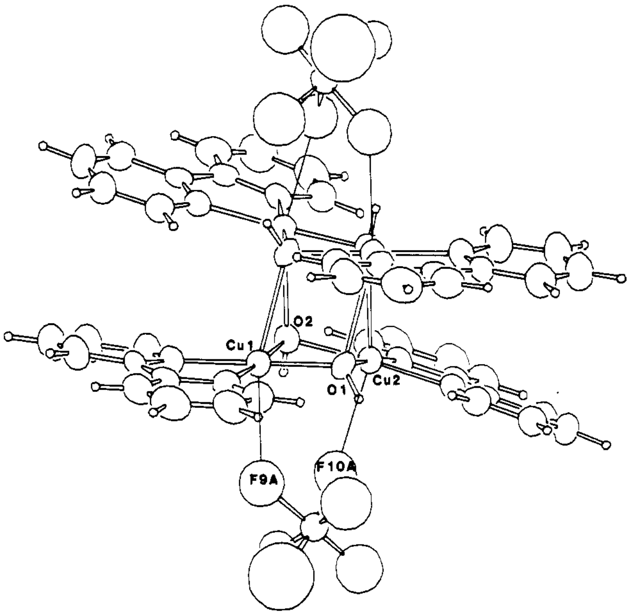

Figure 2. The tetranuclear unit $\{[Cu_2(bpy)_2(OH)_2]_2(PF_6)_2\}^{2+}$.

The refinement based on 3667 reflections with $|F| > 3\sigma_F$ converged at R = 0.069 and R_w = 0.080, with a standard deviation in an observation of unit weight s = 3.94. The scattering curves, with anomalous dispersion terms included, were those of Cromer and Waber.[15] All calculations were carried out on a PDP 11/55 computer using the Enraf-Nonius Structure Determination Programs.[16]

The refined coordinates and isotropic equivalent thermal parameters are listed in Table II. Tables of anisotropic temperature factors, hydrogen parameters, and structure factors are found in Tables SII, SIII, and SIV, respectively, of the supplementary material.

Results

Description of Structure. The $[Cu_2(OH)_2(bpy)_2]^{2+}$ bis(hydroxo)-bridged dinuclear unit is depicted in Figure 1, showing the atomic numbering scheme used. Two of these entities, related by a crystallographic 2-fold axis, are connected by long axial Cu–O

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Table III. Bond Distances (Å) within the Cluster^a

Cu1–F9A^{ii}	2.681 (8)	N4–C20	1.349 (5)
Cu1–O1	1.956 (2)	C1–C2	1.360 (5)
Cu1–O1^{i}	2.585 (3)	C1–C6	1.465 (5)
Cu1–O2	1.947 (2)	C2–C3	1.386 (6)
Cu1–N1	1.997 (3)	C3–C4	1.353 (6)
Cu1–N2	1.981 (3)	C4–C5	1.367 (6)
Cu2–F10A^{ii}	2.643 (7)	C6–C7	1.377 (5)
Cu2–O1	1.947 (2)	C7–C8	1.361 (6)
Cu2–O2	1.962 (2)	C8–C9	1.344 (6)
Cu2–O2^{i}	2.486 (3)	C9–C10	1.388 (6)
Cu2–N3	1.984 (4)	C11–C12	1.373 (5)
Cu2–N4	1.995 (4)	C11–C16	1.479 (6)
N1–C1	1.349 (5)	C12–C13	1.365 (7)
N1–C5	1.328 (5)	C13–C14	1.356 (7)
N2–C6	1.354 (5)	C14–C15	1.367 (6)
N2–C10	1.306 (5)	C16–C17	1.386 (5)
N3–C11	1.341 (5)	C17–C18	1.354 (6)
N3–C15	1.331 (5)	C18–C19	1.384 (6)
N4–C16	1.345 (5)	C19–C20	1.354 (6)

^{a}Roman numeral superscripts refer to the following equivalent positions relative to x, y, z: (i) $1 - x, y, {}^1/_2 - z$; (ii) ${}^1/_2 - x, {}^1/_2 - y, -z$.

Table IV. Selected Bond Angles (deg) within the Cluster^a

F9A^{ii}–Cu1–O1	89.2 (2)	F10A^{ii}–Cu2–N3	86.8 (2)
F9A^{ii}–Cu1–O1^{i}	163.8 (2)	F10A^{ii}–Cu2–N4	91.3 (2)
F9A^{ii}–Cu1–O2	95.9 (2)	O1–Cu2–O2	82.1 (1)
F9A^{ii}–Cu1–N1	90.9 (2)	O1–Cu2–O2^{i}	86.3 (1)
F9A^{ii}–Cu1–N2	87.3 (2)	O1–Cu2–N3	175.7 (1)
O1–Cu1–O1^{i}	74.8 (1)	O1–Cu2–N4	95.8 (1)
O1–Cu1–O2	82.2 (1)	O2–Cu2–O2^{i}	76.7 (2)
O1–Cu1–N1	178.5 (1)	O2–Cu2–N3	100.3 (1)
O1–Cu1–N2	99.8 (1)	O2–Cu2–N4	175.1 (1)
O1^{i}–Cu1–O2	83.50 (9)	O2^{i}–Cu2–N3	97.9 (1)
O1^{i}–Cu1–N1	105.3 (1)	O2^{i}–Cu2–N4	107.0 (2)
O1^{i}–Cu1–N2	94.1 (2)	N3–Cu2–N4	81.6 (1)
O2–Cu1–N1	96.2 (1)	Cu1–O1–Cu1^{i}	105.0 (1)
O2–Cu1–N2	176.3 (1)	Cu1–O1–Cu2	96.6 (2)
N1–Cu1–N2	81.7 (1)	Cu1^{i}–O1–Cu2	90.79 (9)
F10A^{ii}–Cu2–O1	89.8 (2)	Cu1–O2–Cu2	96.4 (2)
F10A^{ii}–Cu2–O2	84.9 (2)	Cu1–O2–Cu2^{i}	93.7 (1)
F10A^{ii}–Cu2–O2^{i}	161.6 (2)	Cu2–O2–Cu2^{i}	103.0 (2)

^{a}Roman numeral superscripts refer to the following equivalent positions relative to x, y, z: (i) $1 - x, y, {}^1/_2 - z$; (ii) ${}^1/_2 - x, {}^1/_2 - y, -z$.

bonds into a tetranuclear entity with a cubane-like $Cu_4(OH)_4$ core. The tetramer, including the weakly coordinated, bridging hexafluorophosphate groups, is shown in Figure 2. The second PF_6^- ion in the asymmetric unit is uncoordinated. Bond distances and selected angles within the cluster are listed in Tables III and IV: distances and angles within the PF_6^- units are found in Table SV (supplementary material), and a complete set of angles within the cluster is given in Table SVI (supplementary material).

Within each dinuclear unit, the Cu–O–Cu bridging angles are 96.6 and 96.4°. The two crystallographically independent copper atoms have similar coordination geometries: both are (4 + 2)-coordinated, the short equatorial bonds being those to hydroxyl bridges within the dimer (Cu–O = 1.947–1.962 Å) and to bipyridyl nitrogen atoms (Cu–N = 1.981–1.995 Å). The axial Cu–O bond lengths differ significantly (2.486 and 2.585 Å), and this is reflected in the deviations of the Cu atoms from the equatorial planes (planes through N1, N2, O1, O2, and N3, N4, O1, O2, respectively): Cu2 is displaced by 0.063 Å to the same side as the axial oxygen ligand, while Cu1 is displaced 0.026 Å to the opposite side. The second axial position around each copper is occupied by a fluorine atom, a weakly coordinated hexafluorophosphate ion bridging the two copper atoms within a dinuclear unit. A similar type of anion bridging has previously been observed with perchlorate in two hydroxo-bridged copper(II) dimers.[17,27]

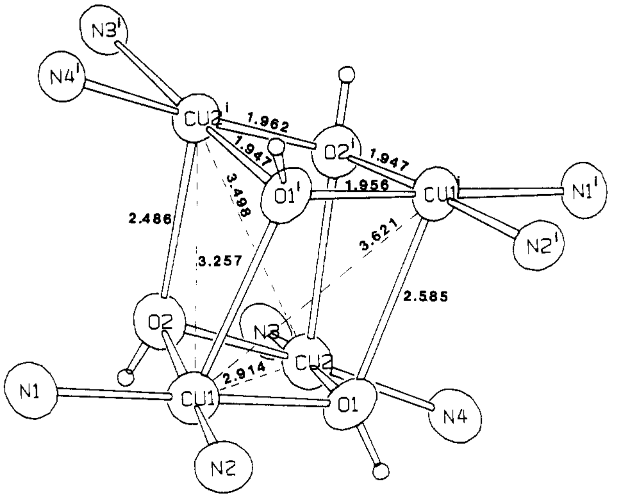

Figure 3. Core of the tetranuclear unit. (i: $1 - x, y, {}^1/_2 - z$.)

Due to the disorder, the errors in the Cu–F distances are high. The shortest contacts between copper atoms and disordered fluorine atoms are 2.64 Å (Cu2–F10A) and 2.68 Å (Cu1–F9A). The closest approaches between copper and the alternative fluorine sites in the disordered model are 2.84 Å (Cu2–F7B) and 2.92 Å (Cu1–F11B). The shortest contacts between hydroxo groups and the disordered fluorine atoms are O1- - -F11B = 3.01 Å, O2- - -F12B = 3.09 Å and O1- - -F8A = 3.035 Å, O2- - -F10A = 3.15 Å. This may indicate weak hydrogen-bond interaction and alternate bonding schemes of weak hydrogen bonding—weak coordination to Cu may perhaps explain the disorder in the hexafluorophosphate group.

In the $Cu_4(OH)_4$ core there are two short Cu1- - -Cu2 separations of 2.914 Å (within each binuclear unit) and four long separations: Cu1- - -Cu1^i = 3.621 Å, Cu2- - -Cu2^i = 3.498 Å, Cu1- - -Cu2^i = Cu2- - -Cu1^i = 3.257 Å, where superscript "i" refers to symmetry operation ($1 - x, y, {}^1/_2 - z$) (Figure 3). There is a slight bending within each binuclear unit, the dihedral angle between the O–Cu–O planes being 16.5°.

Infrared Spectrum. An extensive amount of data concerning IR spectra of hydroxo-bridged copper(II) compounds are available.[18] The IR spectra of the tetranuclear complex exhibits a doublet at 3610 and 3620 cm^{-1}, which is assigned to the bridging OH stretch in full accordance with the literature. The fact that we are dealing with an anhydrous compound makes easy the interpretation in the 3500-cm^{-1} region. Sharp bands of medium intensity are observed at about 1600, 1500, 1475, and 1450 cm^{-1}. These bands involve the ring C–C and C–N vibrations of 2,2′-bipyridyl,[19] and they are observed at lower frequencies in the free ligand. Additional bands of medium intensity are found at 1320 and 1160 cm^{-1} and in the 1070–1020-cm^{-1} region. The absorption in the 1000-cm^{-1} region has been attributed[19,20] to the pyridine breathing mode in the free 2,2′-bipyridyl ligand. It has been pointed out that upon chelation such a band is shifted to higher frequencies and is intensified. A weak band at 970 cm^{-1} is tentatively assigned to the bending OH vibration.[18] The presence of this band together with the observed ones in the 3500-cm^{-1} region are in agreement with the existence of the $Cu(OH)_2Cu$ unit as shown by X-ray diffraction. The out-of-plane CH bending vibrations are observed at 735 and 770 cm^{-1} as sharp bands of

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Table V. Structural Data and Isotropic Exchange Parameters for Hydroxo-Bridged (2,2′-Bipyridyl)Copper(II) Complexes[a]

compd	Cu–O, Å	Cu–Cu, Å	Cu–O–Cu, deg	OCuO/OCuO, deg	J, cm^{-1}	ref
$[Cu_2(bpy)_2(OH)_2](NO_3)_2$	1.922	2.847	95.6	0.0	+172	25, 29
$[Cu_2(bpy)_2(OH)_2](ClO_4)_2$	1.918	2.871	96.9	0.0	+93	27, 29
$[Cu_2(bpy)_2(OH)_2](C_4O_4)\cdot 4H_2O$	1.927	2.870	96.4	0.0	+145	28
$[Cu_2(bpy)_2(OH)_2](SO_4)\cdot 5H_2O$	1.939	2.893	96.5	6.1	+49	26, 29
$[Cu_2(bpy)_2(OH)_2](PF_6)_2$	1.953	2.914	96.5	16.5	+12	this work

[a] Average bond distances and angles are given for each structure.

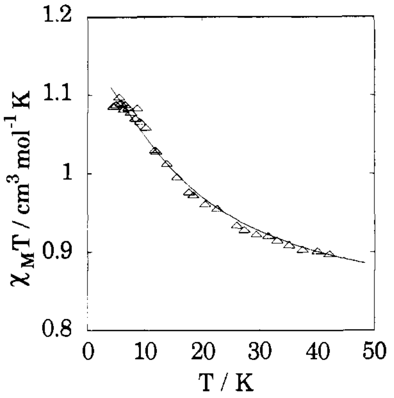

Figure 4. Temperature dependence of $\chi_M T$ for the tetranuclear complex: (△) experimental data; (—) calculated curve per two copper(II) ions.

medium intensity. It is well-known that, upon chelation, splitting of such bending vibrations at about 750 cm^{-1} occurs. A medium absorption band at 490 cm^{-1} and a weak one at 280 cm^{-1} are assigned to asymmetric Cu–O and Cu–N stretching vibrations in the light of data for related hydroxo-bridged copper(II) complexes.[18,21] A prominent and broad band centered at 840 cm^{-1} and a strong sharp band at 560 cm^{-1} can be assigned to the stretching $\nu_3(F_{1u})$ and bending $\nu_4(F_{1u})$ modes, respectively, of the PF_6^- anion in O_h symmetry.[22-24] A shoulder at 865 cm^{-1} and a weak peak at 890 cm^{-1} in the former vibration, as well as a shoulder at about 540 cm^{-1} in the latter one, indicate a lowering of O_h symmetry in the hexafluorophosphate anion, in agreement with the semicoordination to copper atoms and weak hydrogen bonding to hydroxo groups.

Magnetic Properties. The magnetic behavior of the title compound is shown in Figure 4 in the form of the $\chi_M T$ vs T plot, χ_M being the magnetic susceptibility per two copper(II) ions and T the temperature. At room temperature $\chi_M T$ is equal to 0.849 cm^3 mol^{-1} K, a value that corresponds to the expected one for two noncoupled copper(II) ions. A Curie law is observed between room temperature and 50 K. $\chi_M T$ increases very smoothly upon further cooling and reaches a value of 1.09 cm^3 mol^{-1} K at 4.2 K. This behavior is characteristic of a ferromagnetic interaction with a high-spin ground state. In a first approach, we interpret the magnetic behavior in terms of a binuclear formulation via a simple Bleaney–Bowers equation. The energy gap J between the triplet ground state and the singlet state is deduced from the magnetic data through the theoretical expression

$$\chi_M = \frac{2N\beta^2 g^2}{kT}[3 + \exp(-J/kT)]^{-1} \qquad (1)$$

where N, β, k, and g have their usual meanings. J and g values were determined by minimizing the reliability factor $R = \sum[(\chi_M T)^{obsd} - (\chi_M T)^{calcd}]^2/\sum[(\chi_M T)^{obsd}]^2$ and found as $J = 12$ cm^{-1} and $g = 2.10$. R is then equal to 9.18×10^{-5}, showing that a good fit is obtained when only interaction within dimers is considered. In a second approach, the possible interaction between the two dinuclear units is considered. In our model the interdinuclear interaction is treated as a perturbation and is characterized by the J' value. We used the following Hamiltonian to determine the energies of the low-lying states: $H = -J(S_1S_2 + S_3S_4) - J'(S_1 + S_2)(S_3 + S_4)$. A good agreement is obtained by least-squares fit of the experimental data for the values $g = 2.07$, $J = 15.1$ cm^{-1}, and $J' = 0.16$ cm^{-1}, with $R = 6.33 \times 10^{-5}$. The quality of the fit is slightly improved; it confirms the ferromagnetic nature of the intradinuclear interaction, and it indicates that a ferromagnetic interaction is operative between the two low-lying triplet states, leading to a $S = 2$ ground state with an excited triplet state at $2J'$ and a singlet state at $3J'$ energy values. Preliminary magnetization studies at 4.2 K are consistent with the existence of a quintuplet low-lying state. An EPR single-crystal study is needed to fully characterize the spin states arising from the above mentioned triplet–triplet interaction.

Discussion

As noted above, a good agreement between the observed and calculated susceptibilities down to 4.2 K is obtained by considering that our tetranuclear complex is formed by two separate and equal dinuclear units with a small interaction between them in the temperature range studied. The structural origin of this behavior can be found in the classification of the Cu_4O_4 core complex by Haase et al.,[2] which is based on their work on alkoxo-bridged species. Those of type I, in their classification, have structures similar to that of the present compound: two dinuclear units connected with four approximately parallel, long axial Cu–O bonds, as shown in Figure 3, which corresponds to the title compound. They conclude that the exchange interaction between the two dinuclear units in such a structure is vanishingly small.[5] This can be understood as follows: The Cu1 and Cu2 magnetic orbitals (which are located in the quasi-planar Cu1, O1, O2, Cu2 network) and the corresponding ones of Cu1^i and Cu2^i (lying in the Cu1^i, O1^i, O2^i, Cu2^i network) overlap only weakly, leading to a very small coupling. Our results are consistent with a weak ferromagnetic coupling between the dinuclear units.

Each dinuclear unit within the tetranuclear complex has a structure that conforms closely to the structures observed in hydroxo-bridged copper(II) dinuclear complexes with 2,2′-bipyridyl as outer ligands and counterions such as nitrate,[25] sulfate,[26] perchlorate,[27] and squarate,[28] the main differences being slightly longer Cu–O(hydroxyl) bonds in the present structure (average 1.953 Å as compared to 1.931 Å) and slightly more acute O–Cu–O angles (average 82.2° as compared to 83.5°). We have gathered in Table V reported structural and magnetic data concerning the hydroxo-bridged (2,2′-bipyridyl)copper(II) dinuclear complexes. The average value for the Cu–OH–Cu bridging angle in our compound (96.5°) lies within the range found in such a series of dinuclear complexes, whereas its intramolecular copper–copper separation is the largest one. All these complexes exhibit a ferromagnetic interaction, our complex exhibiting the smallest one. Hodgson, Hatfield, and co-workers have noted a linear relationship between the singlet–triplet splitting and the Cu–OH–Cu angle in hyroxo-bridged dinuclear complexes with various outer ligands, the magnetic interaction being ferromagnetic for bridge angles smaller than 97.6°.[9,29] According to the proposed relationship, a J value of 78 cm^{-1} would be expected for the hexafluorophosphate complex, a value that is greater than the observed one ($J = 15.1$ cm^{-1}). This disagreement may be related to the long copper–oxygen distance in the present compound (see Table V), causing a smaller spin density on the hydroxo bridge. Another structural factor to be taken into account is the planarity of the Cu(OH)Cu unit: the values for the dihedral angle between the

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OH-Cu-OH planes is 16.5 and 6.1° for hexafluorophosphate and sulfate complexes, respectively, and in both cases the observed *J* values are lower than predicted from the linear relationship. In the centrosymmetric nitrate, perchlorate, and squarate complexes, no bending is present. Evidence of attenuation in the antiferromagnetic coupling has been found in two hydroxo-bridged dinuclear compounds with OCuO/OCuO dihedral angles of 147.5 and 132.9°, respectively.[30-32]

We would finish this structural discussion with a brief comment on the key role of the counterion in such a series of complexes. In all these complexes the counterion is semicoordinated: the perchlorate and sulfate complexes are built of isolated $[(bpy)Cu(OH)_2Cu(bpy)]^{2+}$ units containing bismonodentate perchlorate and monodentate sulfate respectively; for the nitrate and squarate complexes, a one-dimensional arrangement of $[(bpy)Cu(OH)_2Cu(bpy)]^{2+}$ is observed, the squarate acting in a 1,3-bismonodentate fashion and the nitrate linking a copper atom of a dinuclear unit with a hydroxo group of another unit through two of its oxygen atoms. Finally, when hexafluorophosphate is used as a counterion, the tetranuclear entity herein described is obtained. To summarize, this series provides an example of the relevant structural role of the counterion and consequently of its influence on the magnetic properties of the resulting compounds.

Acknowledgment. We thank the Comisión Interministerial de Ciencia y Technologia (Spain) (Project PB88-0490) and the Programme d'Actions Integrées Franco-Espagnoles for partial financial support. We are also indebted to Professor O. Kahn for his continuous interest in this work.

Supplementary Material Available: Crystallographic data (Table SI), anisotropic thermal parameters (Table SII), hydrogen coordinates (Table SIII), bond distances and angles within the PF_6^- ions (Table SV), bond angles in the cluster (Table SVI), and a crystal packing diagram (Figure S1) (8 pages); observed and calculated structure factors (Table SIV) (17 pages). Ordering information is given on any current masthead page. A listing of experimental magnetic data is available from the authors on request.

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Synthesis and Structural Characterization of Binuclear Ruthenium Aquo, Hydroxy, and Oxo Complexes Incorporating the Anionic Tripod Ligand $[(\eta^5\text{-}C_5H_5)Co\{(CH_3CH_2O)_2P{=}O\}_3]^-$

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Received June 6, 1990

The two-phase reaction of NaL_{OEt} ($L_{OEt}^- = [CpCo\{(EtO)_2P{=}O\}_3]^-$) in 1% H_2SO_4 with RuO_4 in CCl_4 generates the Ru^{IV}–Ru^{IV} edge-sharing bioctahedral complex $[L_{OEt}(H_2O)Ru(\mu\text{-}O)_2Ru(OH_2)L_{OEt}][SO_4]$, in the aqueous phase. This bis(aquo) dication can be isolated as the PF_6^- salt or, alternatively, treated with excess Na_2CO_3 to produce the neutral bis(hydroxo) species $[L_{OEt}(HO)Ru(\mu\text{-}O)_2Ru(OH)L_{OEt}]$ in 50% yield, which in turn can be treated with CF_3SO_3H to regenerate the bis(aquo) complex $[L_{OEt}(H_2O)Ru(\mu\text{-}O)_2Ru(OH_2)L_{OEt}][CF_3SO_3]_2$ quantitatively. The reaction of $[L_{OEt}(HO)Ru(\mu\text{-}O)_2Ru(OH)L_{OEt}]$ with RuO_4 in CCl_4 produces the Ru^V–Ru^V–dioxo species $[L_{OEt}(O)Ru(\mu\text{-}O)_2Ru(O)L_{OEt}]$ in 65% yield. $[L_{OEt}(H_2O)Ru(\mu\text{-}O)_2Ru(OH_2)L_{OEt}][CF_3SO_3]_2$, $[L_{OEt}(HO)Ru(\mu\text{-}O)_2Ru(OH)L_{OEt}]$, and $[L_{OEt}(O)Ru(\mu\text{-}O)_2Ru(O)L_{OEt}]$ have been characterized by X-ray crystallography. The Ru^{IV}–Ru^{IV} species exhibit a substantial metal–metal interaction (Ru–Ru is 2.452 Å in $[L_{OEt}(HO)Ru(\mu\text{-}O)_2Ru(OH)L_{OEt}]$ and 2.505 Å in $[L_{OEt}(H_2O)Ru(\mu\text{-}O)_2Ru(OH_2)L_{OEt}][CF_3SO_3]_2$), while the Ru^V–Ru^V complex, although diamagnetic, shows a relatively weak interaction (2.912 Å). Crystal data: $[L_{OEt}(H_2O)Ru(\mu\text{-}O)_2Ru(OH_2)L_{OEt}][CF_3SO_3]_2$, $Ru_2Co_2C_{36}H_{74}O_{28}P_6S_2F_6$, triclinic, $P\bar{1}$, with $a = 10.510$ (6) Å, $b = 13.475$ (6) Å, $c = 14.132$ (9) Å, $\alpha = 101.50$ (5)°, $\beta = 117.99$ (5)°, $\gamma = 101.42$ (5)°, $V = 1630.6$ (16) Å^3, $Z = 1$, $R(F_o) = 0.0483$; $[L_{OEt}(HO)Ru(\mu\text{-}O)_2Ru(OH)L_{OEt}]\cdot 4C_6H_5CH_3$, $Ru_2Co_2C_{62}H_{104}O_{22}P_6$, monoclinic, $P2_1/n$, with $a = 13.187$ (5) Å, $b = 23.103$ (8) Å, $c = 13.455$ (6) Å, $\beta = 113.82$ (4)°, $V = 3750$ (3) Å^3, $Z = 2$, $R(F_o) = 0.0563$; $[L_{OEt}(O)Ru(\mu\text{-}O)_2Ru(O)L_{OEt}]$, $Ru_2Co_2C_{34}H_{70}O_{22}P_6$, monoclinic, $C2/c$, with $a = 27.486$ (7) Å, $b = 11.849$ (5) Å, $c = 17.268$ (7) Å, $\beta = 109.11$ (3)°, $V = 5314$ (5) Å^3, $Z = 4$, $R(F_o) = 0.0610$.

Introduction

Interest in high-valent ruthenium oxo complexes has stemmed in part from the realization that the ruthenyl (Ru=O) center can be stabilized by judicious choice of ancillary ligand without greatly decreasing its oxidizing power. In this context, the successful use of oxidatively robust nitrogen-based ligands such as porphyrins, polypyridyls, and macrocyclic tertiary amines has led to a range of structurally characterized high-valent ($Ru^{IV} \rightarrow Ru^{VI}$) oxo derivatives.[1] In virtually all of these systems the ancillary ligands preferentially occupy the equatorial sites of an octahedral ruthenium center. While the oxidizing potential of these ruthenium complexes is found to vary somewhat with the electronic nature of the ligand, a more profound effect might be brought about by changing the coordination requirements of the ancillary ligand. Indeed, Meyer and others have noted that *cis*-dioxoruthenium(VI) complexes should be more powerful oxidants than their trans counterparts.[2] Apart from two recent reports of such complexes that utilize bulky polypyridyls to confer a cis configuration on the oxo ligands,[2c,d] very little effort has been directed at the search for alternate ligand systems[3]—not only for this specific case but

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