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Ten-Membered Rings of Coppers Interconnected by 2,5-Bis(2-pyridyl)pyrazine and Acetate Groups: Synthesis, Crystal Structure, and Magnetic Properties of the Two-Dimensional Polymer *catena*-(Octakis(μ_2-acetato)[2,5-bis(2-pyridyl)pyrazine]tetracopper(II))

Antonia Neels and Helen Stoeckli-Evans*

Institut de Chimie, Université de Neuchâtel,
Avenue de Bellevaux 51, CH-2000 Neuchâtel, Switzerland

Albert Escuer and Ramon Vicente

Departament de Quimica Inorgànica, Universitat de
Barcelona, Diagonal 647, 08028-Barcelona, Spain

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Introduction

Ligands that can serve as molecular bridges between metal centers and that also contain a delocalized π system have received considerable attention in recent years. Binuclear and multinuclear metal complexes, comprising two or more metal centers bridged by multidentate ligands, can exhibit metal−metal interactions, such as energy or electron transfer, magnetic coupling, and intervalence transfer.[1−3] One such ligand is 2,5-bis(2-pyridyl)pyrazine, bppz, which has been used recently in the construction of some interesting supra- or nanomolecular species.[4,5] We were particularly interested in the possibility of using this ligand as a bridge in the formation of coordination polymers. It was shown that binuclear complexes of bppz, with first row transition metals, could be synthesized from aqueous solution when using oxygen rich anions such as nitrates and sulfates[6] and hexafluoroacetylacetonates.[7] It was recently shown that it is possible to form one-dimensional polymers from the reaction of copper acetate monohydrate dimer with 2,2′-bipyridyl[8] and 1,2-diaminoethane.[9] In an attempt to link the [Cu_2(bppz)] binuclear units and so form a polymeric structure we investigated the reaction of bppz with copper(II) acetate monohydrate dimer. It was found not only that it was possible to link the [Cu_2(bppz)] binuclear units to form a polymer chain but that the polymer chains were cross-linked by copper acetate dimers, so forming an extensive two-dimensional polymer structure with ten-membered rings of coppers.

Experimental Section

Materials. All chemicals (Fluka) were used as received without further purification. The synthesis and analytical and spectroscopic data for the ligand bppz have been reported elsewhere.[6] IR spectra were recorded on a Perkin-Elmer IR 521 spectrometer using KBr pellets. C, H, and N microanalyses were carried out by the "Organische-chemisches Mikrolabor" of the Swiss Federal Institute of Technology, Zurich.

Table 1. Crystallographic Data for *catena*-(Octakis(μ_2-acetato)-[2,5-bis(2-pyridyl)pyrazine]tetracopper(II)) (**1**)

chem formula	[$C_{14}H_{12}N_4Cu_2(CH_3CO_2)_4$]-[$Cu_2(CH_3CO_2)_4$]
fw	960.8
a, Å	7.916(1)
b, Å	9.280(3)
c, Å	12.732(4)
α, deg	95.49(1)
β, deg	90.06(1)
γ, deg	106.57(1)
V, Å^3	892.0(4)
Z	1
space group	$P\bar{1}$ (No. 2)
T, °C	20(2)
ϱ_{calcd}, g cm^{-3}	1.788
λ(Mo Kα), Å	0.710 73
μ(Mo Kα), cm^{-1}	24.4
R_F[a]	0.044
R_w[b]	0.062

[a] $R_F = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|^2)]^{1/2}$, where $w = [\sigma^2(F_o) + 0.002(F_o)^2]^{-1}$.

Preparation of *catena*-(Octakis(μ_2-acetato)[2,5-bis(2-pyridyl)pyrazine]tetracopper(II)) (1). Bppz (50 mg, 0.21 mmol) was added to a solution of $Cu(OAc)_2 \cdot H_2O$ (170 mg, 0.85 mmol) in 20 mL of acetonitrile at 50 °C and stirred for 1 h. The green insoluble precipitate (170 mg, 83%) was filtered out, washed with acetonitrile, and dried in vacuo. The filtrate was allowed to evaporate slowly. After several days dark-green rectangular crystalline blocks formed (5 mg, 2%, mp 226.7 °C). The microanalysis of the insoluble precipitate corresponds to the stoichiometry of the crystals. Selected IR data (cm^{-1}): 2927 w, 1633 s, 1617 s, 1564 s, 1469 w, 1442 s, 1403 s, 1366 w, 1336 w, 1283 w, 1188 w, 1167 m, 1062 w, 1026 m, 937 w, 781 m, 732 w, 684 m. Anal. Calcd for $C_{30}H_{34}N_4O_{16}Cu_4$: C, 37.5; H, 3.6; N, 5.8. Found: C, 37.5; H, 3.6; N, 6.32.

X-ray Crystallography. A crystal of dimensions 0.46 × 0.23 × 0.15 mm was mounted on a Stoe AED2 four-circle diffractometer equipped with graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å). Data were collected using ω/θ scans out to 50° in 2θ. The lattice parameters were optimized from a least-squares refinement of the settings angles of 19 reflections and their equivalents in the range of $28° < 2\theta < 33°$. Crystallographic data are summarized in Table 1. The structure was solved by direct methods using SHELXS-86.[10] The NRCVAX system[11] was used for all further calculations. Neutral complex atom scattering factors in NRCVAX are from ref 12. The H atoms were located from difference maps and refined isotropically. The non-hydrogen atoms were refined anisotropically using weighted full-matrix least-squares. No corrections were made for absorption or extinction. Final atomic coordinates are given in Table 2, and selected bond distances and angles in Table 3. The structural diagram was drawn using the programme SCHAKAL92.[13]

Magnetic Measurements. Variable-temperature magnetic measurements were carried out on polycrystalline samples using a Quantum Design SQUID susceptometer. The diamagnetic corrections were estimated from the Pascal tables. ESR spectra were recorded at X-band frequencies with a Brucker ESP-300E spectrometer in the temperature range 298−4 K.

Results and Discussion

Description of the Structure. The structure of *catena*-(octakis(μ_2-acetato)[2,5-bis(2-pyridyl)pyrazine]tetracopper(II) (**1**),

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Table 2. Atomic Parameters x, y, z and B_{iso} (Å^2) for *catena*-(Octakis(μ_2-acetato)[2,5-bis(2-pyridyl)pyrazine]tetracopper(II)) (**1**)

	x	y	z	B_{iso}[a]
Cu1	0.11538(9)	0.71449(8)	0.54645(5)	2.58(3)
Cu2	0.40944(9)	0.92703(8)	0.91306(5)	2.59(3)
O1	−0.1246(6)	0.6643(5)	0.5962(4)	3.64(22)
O2	0.2123(7)	0.5850(5)	0.4269(4)	4.10(23)
O3	0.2633(6)	0.8009(5)	0.7771(3)	2.93(18)
O4	0.1945(6)	0.6098(5)	0.6512(3)	3.29(19)
O5	0.2538(6)	1.0559(5)	0.9517(4)	3.88(22)
O6	0.6023(6)	0.8290(5)	0.9002(3)	3.37(20)
O7	0.5491(6)	1.0895(5)	0.8333(3)	3.93(23)
O8	0.2993(6)	0.7932(5)	1.0200(3)	3.51(20)
N1	0.3513(6)	0.8932(5)	0.5304(4)	2.31(19)
N2	0.0440(6)	0.8270(5)	0.4336(4)	2.58(20)
C1	0.3447(7)	0.9694(6)	0.4466(4)	2.09(22)
C2	0.5056(8)	0.9234(7)	0.5833(5)	2.44(23)
C3	0.1701(7)	0.9367(6)	0.3940(4)	2.26(22)
C4	0.1359(9)	1.0099(7)	0.3117(5)	2.9(3)
C5	−0.0330(9)	0.9722(8)	0.2689(6)	3.6(3)
C6	−0.1610(9)	0.8617(8)	0.3093(5)	3.4(3)
C7	−0.1191(8)	0.7907(8)	0.3905(6)	3.4(3)
C8	−0.2338(8)	0.5367(7)	0.6026(5)	2.8(3)
C9	0.5938(12)	1.5435(13)	0.6507(9)	4.9(5)
C10	0.2342(7)	0.6642(6)	0.7466(4)	2.4(3)
C11	0.2479(12)	0.5534(9)	0.8220(6)	3.8(4)
C12	0.6633(9)	1.1952(7)	0.8829(5)	3.1(3)
C13	0.7715(17)	1.3189(11)	0.8225(8)	5.5(5)
C14	0.2760(8)	1.1471(7)	1.0310(5)	3.0(3)
C15	0.1472(12)	1.2396(11)	1.0457(9)	4.5(4)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

Table 3. Selected Distances (Å) and Angles (deg) for *catena*-(Octakis(μ_2-acetato)[2,5-bis(2-pyridyl)pyrazine]tetracopper(II)) (**1**)[a]

Cu1···Cu2	5.167(2)	Cu1···Cu1^{iii}	3.941(2)
Cu1···Cu1^{i}	7.026(2)	Cu1···Cu1^{iv}	6.287(2)
Cu2···Cu2^{ii}	2.665(2)		
Cu1−N1	2.140(4)	Cu2−O3	2.131(4)
Cu1−N2	2.024(5)	Cu2−O5	1.980(4)
Cu1−O1	1.945(4)	Cu2−O6	1.987(4)
Cu1−O2	2.128(4)	Cu2−O7	1.967(5)
Cu1−O4	1.926(4)	Cu2−O8	1.966(4)
O1−Cu1−O2	125.62(20)	O3−Cu2−O5	98.05(17)
O1−Cu1−O4	93.28(19)	O3−Cu2−O6	95.07(17)
O1−Cu1−N1	145.15(18)	O3−Cu2−O7	93.87(18)
O1−Cu1−N2	89.47(19)	O3−Cu2−O8	98.92(17)
O2−Cu1−O4	89.19(19)	O5−Cu2−O6	166.74(18)
O2−Cu1−N1	86.85(18)	O5−Cu2−O7	87.97(21)
O2−Cu1−N2	89.15(19)	O5−Cu2−O8	89.64(20)
O4−Cu1−N1	100.16(18)	O6−Cu2−O7	89.27(20)
O4−Cu1−N2	177.25(19)	O6−Cu2−O8	90.19(19)
N1−Cu1−N2	77.56(18)	O7−Cu2−O8	167.20(18)
Cu1−N1−C1	113.1(3)	Cu2^{ii}−Cu2−O3	177.40(11)
Cu1−N1−C2	128.4(4)	Cu2^{ii}−Cu2−O5	83.32(13)
Cu1−N2−C3	118.1(4)	Cu2^{ii}−Cu2−O6	83.63(12)
Cu1−N2−C7	123.6(4)	Cu2^{ii}−Cu2−O7	88.39(13)
Cu1−O1−C8	129.7(4)	Cu2^{ii}−Cu2−O8	78.85(13)
Cu1−O2−C8^{iii}	146.7(4)	Cu2−O3−C10	129.1(4)
Cu1−O4−C10	124.0(4)	Cu2−O5−C14	124.3(4)
		Cu2−O6−C14^{ii}	122.9(4)
		Cu2−O7−C12	117.8(4)
		Cu2−O8−C12^{ii}	129.0(4)

[a] Symmetry operations: (i) $1 - x, 2 - y, 1 - z$; (ii) $1 - x, 2 - y, 2 - z$; (iii) $-x, 1 - y, 1 - z$; (iv) $-x, 2 - y, 1 - z$.

Figure 1, consists of symmetrical [Cu_2(bppz)] binuclear units linked by two acetate groups coordinating in the syn−syn mode, so forming a one-dimensional polymer chain. These one-dimensional chains are then linked to the copper acetate dimer by an acetate anion coordinating in a syn−anti mode, so forming the two-dimensional network. The Cu1···Cu1^{iii} bridging distance is 3.941(2) Å, and distances Cu1−O1 and Cu1−O2 are 1.945(4) and 2.128(4) Å, respectively. The Cu1···Cu2 cross-linking distance is 5.167(2) Å, while the Cu2···Cu2^{ii} distance in the copper acetate dimer is 2.665(2) Å. The [Cu_2(bppz)] binuclear unit has a slightly different geometry compared to that found in the binuclear complex, **2**, formed by the reaction of copper nitrate with bppz.[6] In both compounds the Cu atoms are pentacoordinate. In **1** the geometry of the copper atom is a highly distorted trigonal-bipyramid (TBP) with the atom Cu1 almost lying (0.027(4) Å) in the plane of atoms N1, N2, O4, while atoms O1 and O2 are displaced from this plane by 1.091(9) and −2.099(6) Å, respectively. In **2** the geometry of the copper atom is square pyramidal (SP). This is consistent with the calculation of the degree of distortion of coordination polyhedra ($\tau = 1$ for TBP, $\tau = 0$ for SP[14]) which gives a value of $\tau = 0.535$ for **1** and 0.07 for **2**. In **1** the intramolecular Cu1···Cu1^{i} distance is 7.026 Å compared to 6.760 Å in **2**.[6] The ligand bppz is more planar in the title compound with a pyrazine−pyridine dihedral angle of 4.2(3)°, compared to 8.5(1)° in **2**. The Cu−N_{pyz} distance of 2.140(4) Å in **1** is significantly longer than the same distance in **2** (2.021(3) Å), while the Cu−N_{py} distances are comparable, 2.024(5) Å in **1** compared to 2.012(3) Å in **2**. This results in a smaller N_{pyz}−Cu−N_{py} bite angle in **1** of 77.6(2)° compared to 81.0(1)° in **2**.

The geometry of atom Cu2 in the copper acetate dimers is square pyramidal. The copper atom is displaced by −0.223(3) Å from the best plane through atoms O5, O6, O7, and O8 and toward atom O3 which is itself displaced by −2.352(5) Å from the same plane. The overall geometry is very similar to that observed for the one-dimensional polymer formed by the reaction of 2,2′-bipyridine with copper acetate monohydrate dimer.[8] Here, as in **1**, a binuclear copper complex is linked by an axial acetate group to the dimeric copper acetate core. The cross-linking Cu···Cu distance is longer, 5.441 Å, compared to 5.167 Å in **1**. The Cu···Cu distance in the copper acetate dimer is very similar to that in **1**, *i.e.* 2.669 Å.

In the crystal of **1** the two-dimensional polymer sheets are separated by approximately 6.6 Å. The pyridine rings of neighboring sheets overlap almost perfectly with a separation of 4.07(1) Å. The shortest interplane metal···metal distance, Cu1···Cu1^{iv}, is 6.287 Å.

Magnetic Results. The molar χT product *vs* T of **1** is given in Figure 2. The $\chi_M T$ value (1.52 cm^3 K mol^{-1} at room temperature) decreases rapidly when the temperature is lowered and tends to stabilize below 100 K. Below 25 K $\chi_M T$ decreases abruptly reaching a value of 0.19 cm^3 K mol^{-1} at 2 K. Between 300 and 2 K the χ_M *vs* T plot increases continuously, but no maximum was observed. There are four superexchange J parameters and two local g values present in the polymer plane. These superexchange pathways are the four syn−syn carboxylate bridges of the tetraacetate group (J_1), a syn−anti single carboxylate bridge that relates a copper atom of the tetraacetate fragment with a copper atom bridged to the bppz ligand (J_2), two syn−syn carboxylates between two copper atoms bonded to the bppz (J_3), and finally the bppz ligand (J_4); see Figure 1.

Obviously no exact treatment can be made for this two-dimensional compound in order to determine the six variable parameters (neglecting interplane interactions or paramagnetic impuritie parameters). However, some approximations can be made on the basis of the relative values of the different J parameters. For example, in a recent report[15] the superexchange parameter found for a tetraacetate group with a carboxylate

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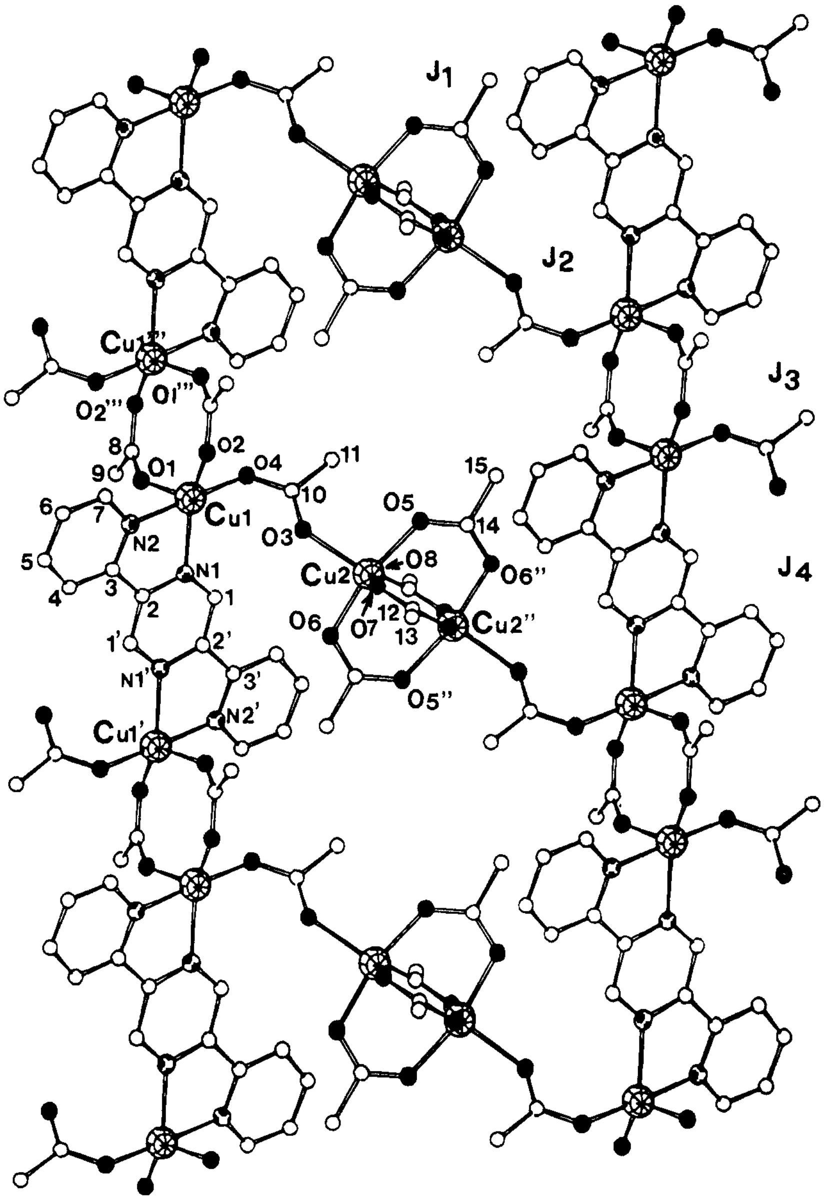

Figure 1. Two-dimensional network for *catena*-(octakis(μ_2-acetato)[2,5-bis(2-pyridyl)pyrazine]tetracopper(II)) (**1**), showing the numbering scheme and the four superexchange J parameters.

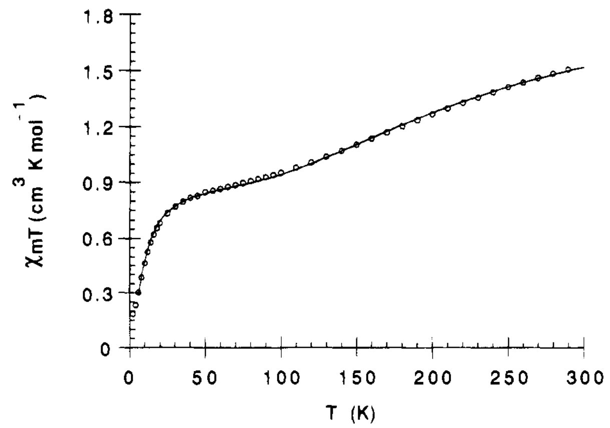

Figure 2. Experimental (○) and theoretical (—) temperature dependence of $\chi_M T$ for *catena*-(octakis(μ_2-acetato)[2,5-bis(2-pyridyl)pyrazine]-tetracopper(II)) (**1**).

group bonded to the axial position was -318 cm^{-1}. Consequently, a value of around -300 cm^{-1} can be expected for J_1. The remainder of the $|J|$ coupling parameters should be low: syn−syn and syn−anti carboxylate bridges between distorted square-pyramidal copper atoms from the basal to axial positions shows typically very weak ferro- or antiferromagnetic behavior.[16] The interactions through the pyrazine ligand are also normally very weak.[17−19] In **1** the geometry of the copper(II) polyhedron is intermediate between square pyramidal and trigonal bipyramidal (τ 0.535); hence, the orbital ground state of the copper(II) atoms should have a significant admixture of the $dx^2 - y^2$ and dz^2 orbitals. Permitting a certain overlap of the ligand $\pi(b1_g)$ orbitals and the $dx^2 - y^2$ orbitals should give rise to weak antiferromagnetism.[19] Accordingly, for this structure J_4 should be negative in sign and low in value, as reported previously for TBP binuclear Cu(II) pyrazine bridged compounds.[20−24]

Below 100 K, the absolute coupling of the tetraacetate fragments isolates the remainder of the copper atoms as an

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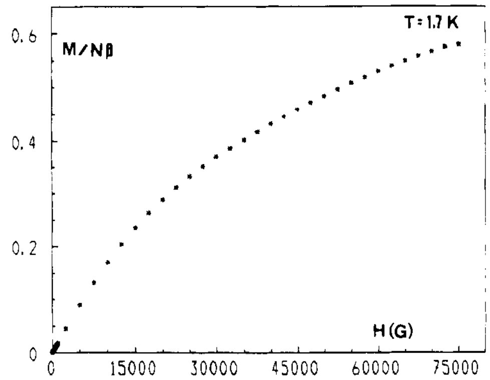

Figure 3. Magnetization isotherm plot at 1.7 K from 0 to 7.5 T for *catena*-(octakis(μ_2-acetato)[2,5-bis(2-pyridyl)pyrazine]tetracopper(II)) (**1**).

alternating chain defined by J_3 and J_4. In this situation J_2 is not operative and its sign is unimportant in determining the magnetic properties of the compound. An approximate fit was performed considering the system as a strongly coupled dimer added to a weakly coupled chain ($J_1 >>> J_{3,4}$, $J_2 = 0$). Considering the chain as an uniform system ($J_3 = J_4$) or taking the chain as an alternating system gave similar results. The expression used was

$$\chi_M T = 2N\beta/k[g_1^2(\exp(x)/(1 + 3\exp(x)) + g_2^2(0.25 + 0.074975y + 0.05235y^2)/(1 + 0.9931y + 0.172135y^2 + 0.757825y^3)]$$

where N, β, and k have the usual meanings, $x = J_1/kT$, and $y = |J_{3,4}|/kT$. The best fitting parameters obtained are $J_1 = -297$ cm^{-1}, $g_1 = 2.38$, $J_{3,4} = -6.8$ cm^{-1}, $g_2 = 2.23$, and $R = 6 \times 10^{-4}$, R being the quality factor defined as $R = \sum(\chi_M^{\text{calcd}} - \chi_M^{\text{obs}})^2/(\chi_M^{\text{obs}})^2$.

The molar magnetization data recorded at 1.7 K from 0 to 7.5 T are shown in Figure 3. It shows uniform magnetization from low fields and is far from saturation at maximum field. A significant value around 0.5 in M/Nβ units at 7.5 T is reached, indicating a weak antiferromagnetic coupling. The plot does not show the typical sigmoid shape that would be expected for a system in which the intrachain coupling parameter J is close to -7 cm^{-1}. This nonsigmoid magnetization should probably be attributed to very weak interchain or interplane antiferromagnetic interactions. On the other hand, the value of 0.5 in M/Nβ units at the highest applied field supports the existence of weak intrachain antiferromagnetic coupling, as indicated by the susceptibility data.

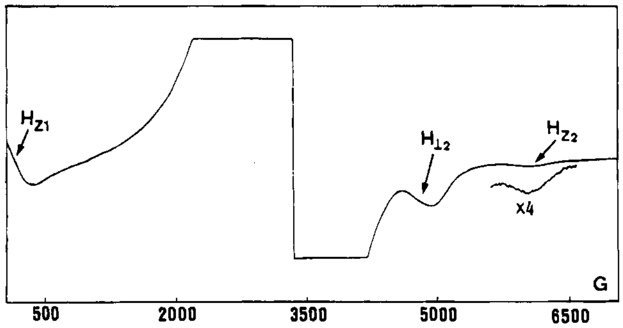

Figure 4. X-band ESR spectra of the polycrystalline powder of *catena*-(octakis(μ_2-acetato)[2,5-bis(2-pyridyl)pyrazine]tetracopper(II)) (**1**) at room temperature, showing the position of the partially resolved triplet spectra.

Electron Spin Resonance. The X-band ESR powder spectra of **1** exhibit two overlapping sets of signals; one centered around $g = 2$ and a second group of bands of lower intensities, in a wide range of fields (100–6000 G). The intensities of the signals in the $g = 2$ region (2.24 and 2.05 at room temperature) show no significant variation when the temperature is lowered and can be attributed to the copper atoms bonded to the bppz ligand. The second group of bands overlaps with the former signals and correspond to a partially resolved triplet with axial symmetry and relatively high D value. The components of this triplet spectrum at room temperature appear at 110 G (H_{z1}), 4800 G ($H_{\perp 2}$), and 5900 G (H_{z2}) (Figure 4). From these data, and with the assumption $E = 0$, the D and g parameters can be evaluated from the expressions[25]

$$H_{z1} = g_e/g_z(H_0 - D) \qquad H_{z2} = g_e/g_z(H_0 + D)$$

$$H_{\perp 2} = g_e/g_\perp[(H_0 + D)H_0]^{1/2}$$

The values obtained are $D = 0.335$ cm^{-1}, $g_z = 2.40$, and $g_x = g_y = 2.06$. The absence in the spectrum of the $H_{\perp 1}$ signals at low field is indicative of the common $H_0 < D$ relation and compares well with previously reported tetraacetate copper(II) systems.[26,27] On cooling, the intensity of the triplet signals decreases. At 77 K it is undetectable.

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Supplementary Material Available: Tables giving crystal data and details of the structure determination, bond lengths and angles, anisotropic thermal parameters, and hydrogen atom coordinates and thermal parameters (5 pages). Ordering information is given on any current masthead page.

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