use of acid conditions as employed in this work.

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Supplementary Material Available: Tables of hydrogen atom positions, bond lengths/angles involving the hydrogen atoms, and anisotropic thermal parameters for γ-$[Cl_2Pt(\mu\text{-dpzm})_2PtCl_2]\cdot 2dmf$ and tables of assigned IR bands and X-ray powder diffraction *d*-spacings and relative intensities for the α-, β-, and γ-platinum(II) complexes (7 pages); a table of observed and calculated structure factors for γ-$[Cl_2Pt(\mu\text{-dpzm})_2PtCl_2]\cdot 2dmf$ (11 pages). Ordering information is given on any current masthead page.

Contribution from the Departament de Química Inorgânica, Facultat de Química de la Universitat de València, Dr. Moliner 50, 46100 Burjassot, València, Spain, Department of Chemistry, University of Bergen, 5007 Bergen, Norway, Laboratoire de Chimie Inorganique, UA No. 420, Université de Paris-Sud, 91405 Orsay, France, and Departament de Química Inorgânica, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain

Exchange Interaction through a Croconato Bridge: Synthesis, Crystal Structure, and Magnetic Properties of (μ-Croconato)bis[{bis(2-pyridylcarbonyl)amido}copper(II)] Trihydrate

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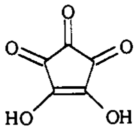
The title compound, denoted as $[Cu_2(bpca)_2(C_5O_5)]\cdot 3H_2O$ (where bpca and $C_5O_5^{2-}$ are the bis(2-pyridylcarbonyl)amide anion, $C_{12}H_8N_3O_2^-$, and the dianion of 4,5-dihydroxy-4-cyclopentene-1,2,3-trione, respectively), has been synthesized, and its structure has been determined by X-ray crystallographic methods. Crystal data: monoclinic system, space group $P2_1/c$, a = 19.535 (2) Å, b = 20.189 (2) Å, c = 7.5167 (6) Å, β = 97.485 (8)°, Z = 4. Data up to θ = 26° (Mo Kα radiation) were collected at room temperature on a CAD-4 diffractometer. The structure was solved by a combination of Patterson and direct methods and refined by full-matrix least-squares refinement to conventional agreement indices R = 0.063 and R_w = 0.080 with 4341 observed reflections [$I \geq 3.0\sigma(I)$]. The structure consists of neutral croconato-bridged copper(II) dinuclear units and crystallization water molecules. The croconate acts as a bis-bidentate ligand bridging two crystallographically independent copper(II) ions separated by 6.824 (1) Å. The bis(2-pyridylcarbonyl)amido group is the end-cap ligand, and it is coordinated to copper(II) through its three nitrogen atoms. Each copper atom forms four short equatorial bonds to the three nitrogen atoms of bpca and one oxygen atom of croconate [1.927 (3)–2.003 (3) Å for Cu(1) and 1.934 (3)–1.997 (3) Å for Cu(2)] and a longer axial bond to an oxygen atom of the croconato bridge [2.585 (3) and 2.477 (3) Å for Cu(1) and Cu(2), respectively]. Cu(1) forms an additional axial bond and Cu(2) has an axial contact to an oxygen atom of respectively a croconato group [2.496 (3) Å] and a carbonyl group of a bpca ligand [2.932 (3) Å] from neighboring molecules. The magnetic behavior of this compound has been investigated in the 4.2–300 K temperature range, and it is as expected for an antiferromagnetically coupled copper(II) dimer with a singlet–triplet energy gap of 9.63 cm^{-1}. Variable-temperature X-band EPR spectra were also recorded. The exchange pathway is analyzed in the light of structural data and extended Hückel MO calculations. The ability of croconate to support a magnetic exchange interaction between two paramagnetic metal ions is compared to that of the related oxalato, squarato, and hydranilato bridges.

Introduction

The dianion of 4,5-dihydroxy-4-cyclopentene-1,2,3-trione (**1**), $C_5O_5^{2-}$, commonly referred to as the croconate anion, is a member of the so-called monocyclic oxocarbon dianions [n = 3 (deltate), 4 (squarate), 5 (croconate), 6 (rhodizonate)] to which considerable attention has been devoted during the last years.[2-4] However, much work remains to be done in order to fully characterize the coordination chemistry of these polyatomic molecules. So, although the first synthesis of deltic acid was reported by West and Eggerding[5] in 1975, its coordinating capability remains unknown. The squarate ligand is the best known of this series. In a recent paper some of us focused on it and characterized structurally its bonding properties to copper(II) ion.[6] Crystal structures of squarate-containing copper(II),[6,7] zinc(II),[8] nickel(II),[9] manganese(II),[8b] chromium(III),[10] iron(III),[11] polyoxomolybdate,[12]



$H_2C_5O_5$

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platinum(II),[13] silver(I),[14] alkaline-earth,[15] and rare-earth[16] cations have been reported. These structural data lead to the conclusion that the squarate ligand cannot act either in a bidentate or in a bis-bidentate fashion toward first-row transition-metal ions because of its high bite parameter.[6] However, the chelation of squarate occurs when metal ions with larger ionic radii, i.e. alkaline- and rare-earth cations,[15,16] are used. As far as the rhodizonate ligand is concerned, no report of structural work on any rhodizonato complex is found in the literature. In fact, rhodizonate solutions are rather unstable; thus, the formation of single crystals by slow evaporation of solvent is not likely. For example, in alkaline medium, rhodizonate has been found to undergo an oxidative process involving ring contraction to yield croconate ion.[17] Very recently, some of us have demonstrated the validity of such an observation by means of X-ray diffraction methods.[18] Finally, the available information on the coordination chemistry of the croconate ligand is limited. To our knowledge, only four structures of croconato transition-metal complexes have been reported: $[M(C_5O_5)(H_2O)_3]$ (M = Cu(II), Zn(II), Mn(II))[19,20] and $[Mn(C_5O_5)(HIm)_2(H_2O)_2]$ (HIm = imidazole).[21] The three first complexes are one-dimensional chains of metal ions bridged by croconate groups, which exhibit unidentate and bidentate coordination modes simultaneously, whereas the latter one is a monomeric species which contains a bidentate croconate.

Taking into account the analogies between croconate and oxalate groups (planar stereochemistry, oxygen donor atoms, identical overall charge) and the work which has been carried out with oxalato-containing copper(II) complexes from a magneto–structural point of view,[22,23] we have investigated the possibility of synthesizing croconato-bridged copper(II) complexes in order to characterize new coordination modes of this ligand and to check its efficiency to transmit electronic effects at longer distances.

In this paper, we report the synthesis and the crystal and molecular structure of the complex of formula $[Cu_2(bpca)_2(C_5O_5)]\cdot 3H_2O$ [bpca = the bis(2-pyridylcarbonyl)amido anion] and its magnetic properties down to 4.2 K. The structure provides the first example of a bis-bidentate croconato bridge. IR and EPR spectra are also discussed in relation with the observed crystal structure.

Experimental Section

Materials. Potassium croconate and diaqua[bis(2-pyridylcarbonyl)amido]copper(II) nitrate dihydrate were prepared according to reported procedures.[24,25] Elemental analyses (C, H, N) were performed by the Servicio de Análisis Elemental de la Universidad Autónoma de Madrid, Madrid, Spain.

Synthesis of $[Cu_2(bpca)_2(C_5O_5)]\cdot 3H_2O$. This complex was prepared as a blue-greenish microcrystalline powder by treatment of a warm aqueous solution (40 mL) of $[Cu(bpca)(H_2O)_2]NO_3\cdot 2H_2O$ (0.106 g, 0.25 mmol) with solid $K_2C_5O_5$ (0.027 g, 0.125 mmol). The precipitate was filtered out, washed with water, ethanol, and ether, and stored over calcium chloride. Anal. Calcd for $C_{29}H_{22}N_6O_{12}Cu_2$: C, 45.02; H, 2.84; N, 10.86. Found: C, 44.95; H, 2.78; N, 10.75. Polyhedral dark blue crystals were grown from diluted solutions of $[Cu(bpca)(H_2O)_2]^+$ and $C_5O_5^{2-}$ (2:1 molar ratio) by slow evaporation at room temperature.

Table I. Crystallographic Data for $[Cu_2(bpca)_2(C_5O_5)]\cdot 3H_2O$

chem formula	$C_{29}H_{22}N_6O_{12}Cu_2$	Z	4
fw	773.61	T, °C	21
space group	$P2_1/c$ (No. 14)	λ, Å	0.71073
a, Å	19.535 (2)	ρ_{calcd}, g cm^{-3}	1.748
b, Å	20.189 (2)	μ, cm^{-1}	15.26
c, Å	7.5167 (6)	transm coeff	0.73–0.69
β, deg	97.485 (8)	$R(F_o)$	0.063
V, Å^3	2939.2 (8)	$R_w(F_o)$	0.080

Physical Techniques. IR spectra were recorded on a Perkin-Elmer 1750 FTIR spectrophotometer as KBr pellets in the 4000–225-cm^{-1} region. Variable-temperature magnetic measurements were carried out on polycrystalline samples of the title compound in the temperature range 4.2–300 K by means of a previously described pendulum-type apparatus[26] equipped with a helium-continuous-flow cryostat. The uncertainty in the data is lower than 0.1 K for temperatures and 2×10^{-5} cm^3 mol^{-1} for susceptibilities. Mercury tetrakis(thiocyanato)cobaltate(II) was used as a susceptibility standard. Experimental susceptibilities were corrected for diamagnetism of the constituent atoms by the use of Pascal's constants (-357×10^{-6} cm^3 mol^{-1}/dinuclear unit) and for the temperature-independent paramagnetism (60×10^{-6} cm^3 mol^{-1}/copper(II) ion). Variable-temperature X-band EPR spectra were recorded with a Bruker ER 200D spectrometer equipped with a nitrogen cryostat.

Crystallographic Data Collection and Structure Determination. Diffraction data were collected at 294 K with an Enraf-Nonius CAD-4 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 $12 < \theta < 24°$. Crystal parameters and refinements results are summarized in Table I. Complete crystal data and experimental details are deposited as supplementary material (Table S1). A total of 6937 unique reflections were recorded in the range $0 < 2\theta < 52°$. Three reference reflections monitored throughout data collection showed no significant sign of crystal deterioration. The usual corrections for Lorentz and polarization effects were carried out. Correction for absorption was done by the Gaussian integration method.

The structure was solved by a combination of Patterson and direct methods and refined by the full-matrix least-squares method. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the bis(2-pyridylcarbonyl)amido group were localized in difference-Fourier maps and were included in the refinement with isotropic thermal parameters. Water molecules have high thermal parameters, and their hydrogen atoms are not included. The final full-matrix least-squares refinement, minimizing $\sum[w(F_o - F_c)^2]$ and including 4341 reflections with $I \geq 3\sigma(I)$, converged at $R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.063$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.080$ with a weighting scheme $w = 1/\sigma_F{}^2$ ($\sigma_F = \sigma_I(ILp)^{-1/2}$; $\sigma_I = [\sigma_C{}^2 = [\sigma_C{}^2 + (0.02N_{net})^2]^{1/2}$). The scattering curves, with anomalous dispersion terms included, were those of Cromer and Waber.[27] All calculations were done on a MICRO-VAX II computer using the Enraf-Nonius structure determination programs.[28]

The refined final coordinates for non-hydrogen atoms and selected bond distances and angles are listed in Tables II and III, respectively. Tables of anisotropic temperature parameters, remaining bond distances and angles, deviations of atoms from their least-squares planes and dihedral angles between these planes, and observed and calculated structure factor amplitudes are deposited as supplementary material (Tables S2–S6).

Results and Discussion

Description of the Structure. The crystal structure is built from neutral dinuclear units of formula $[Cu_2(bpca)_2(C_5O_5)]$, which are associated into chains through a long axial Cu–O bond. In addition there are three molecules of water of hydration per dimer.

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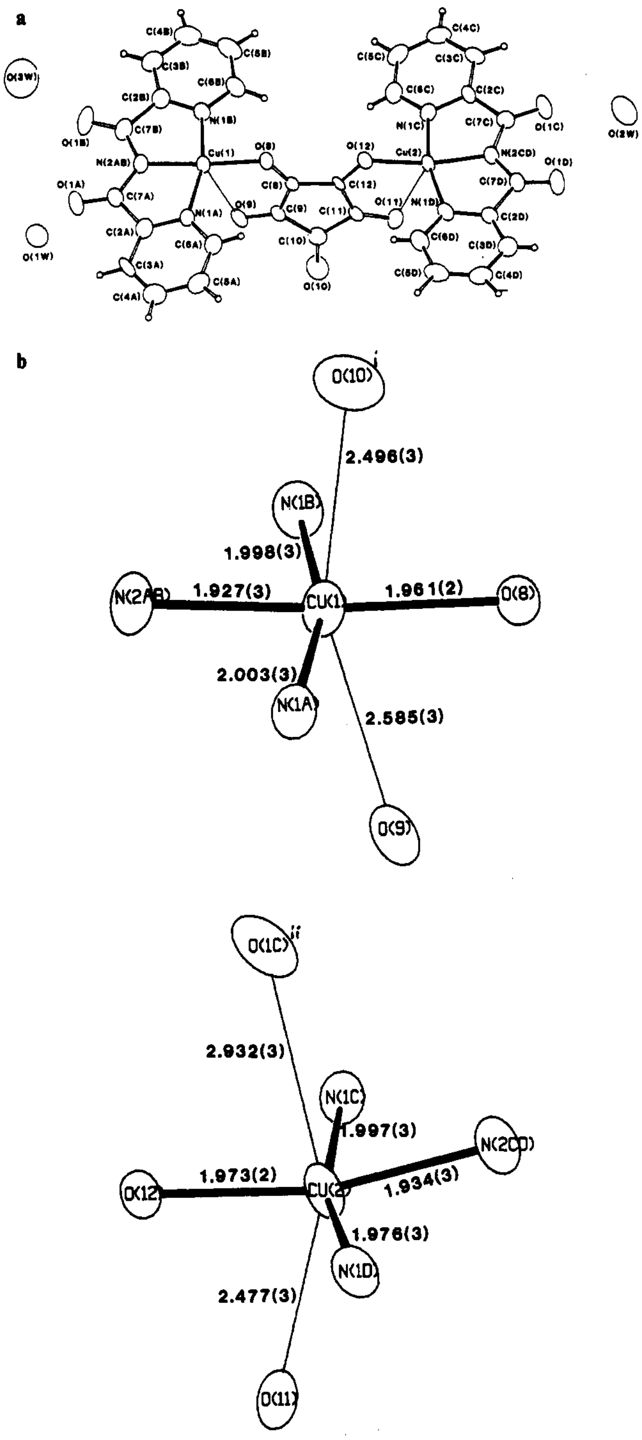

Figure 1. (a) ORTEP drawing of the complex $[Cu_2(bpca)_2(C_5O_5)]\cdot 3H_2O$ along with the atom-numbering scheme. Thermal ellipsoids are plotted at the 50% probability level. Hydrogen atoms are given an arbitrary radius. (b) Coordination geometry of the two independent copper atoms in $[Cu_2(bpca)_2(C_5O_5)]\cdot 3H_2O$. Roman numeral superscripts refer to the following symmetry codes: (i) $x, y, z + 1$; (ii) $= x, {}^3/_2 - y, {}^1/_2 + z$.

An ORTEP view of the dinuclear unit is depicted in Figure 1a.

The two crystallographically independent copper(II) ions within a dinuclear unit are bridged by a croconato group in a bis-bidentate fashion; one short equatorial [1.961 (2), 1.973 (2) Å] and one long axial Cu–O bond [2.585 (3), 2.477 (3) Å] being formed between croconate and each copper(II) ion. The remaining equatorial positions are occupied by the bpca nitrogen atoms, the bis(2-pyridylcarbonyl)amido groups acting as tridentate outer ligands and preventing the formation of the one-dimensional (μ-croconato)copper(II) trihydrate polymer.[19] Cu–N(pyridyl) distances range from 1.976 (3) to 2.003 (3) Å, while the Cu–N(amido) bonds are significantly shorter [1.927 (3) and 1.934 (3) Å]. This shortening, which is also observed in other bpca-containing copper(II) complexes,[7a,25,29–32] can be related to the stronger

Table II. Non-Hydrogen Atoms Positional Parameters for $[Cu_2(bpca)_2(C_5O_5)]\cdot 3H_2O$ with Estimated Standard Deviations in Parentheses

atom	*x/a*	*y/b*	*z/c*
Cu(1)	0.17081 (4)	0.42735 (4)	0.6382 (1)
Cu(2)	0.39053 (4)	0.63625 (4)	0.2780 (1)
O(1A)	0.0626 (3)	0.2662 (3)	0.7495 (8)
O(1B)	−0.0099 (3)	0.3851 (3)	0.8123 (8)
O(1C)	0.4457 (3)	0.8192 (2)	0.1397 (8)
O(1D)	0.5516 (3)	0.7249 (3)	0.0940 (8)
O(1w)	−0.0595 (3)	0.2294 (3)	0.4970 (8)
O(2w)	0.5896 (3)	0.8662 (3)	0.159 (1)
O(3w)	−0.1448 (4)	0.3925 (5)	0.879 (1)
O(8)	0.2472 (2)	0.4836 (2)	0.5836 (6)
O(9)	0.1621 (2)	0.4240 (2)	0.2923 (7)
O(10)	0.2187 (3)	0.4563 (3)	−0.0472 (7)
O(11)	0.3203 (2)	0.5661 (2)	0.0533 (6)
O(12)	0.3448 (2)	0.5748 (2)	0.4292 (6)
N(1A)	0.2156 (3)	0.3383 (3)	0.6309 (7)
N(1B)	0.1037 (3)	0.5009 (3)	0.6561 (8)
N(1C)	0.3229 (3)	0.7102 (3)	0.2841 (7)
N(1D)	0.4724 (3)	0.5824 (3)	0.2453 (8)
N(2AB)	0.0959 (3)	0.3752 (3)	0.7069 (8)
N(2CD)	0.4450 (3)	0.7057 (3)	0.1884 (8)
C(2A)	0.1728 (4)	0.2887 (4)	0.6617 (9)
C(2B)	0.0464 (4)	0.4818 (4)	0.7237 (9)
C(2C)	0.3489 (3)	0.7700 (3)	0.2468 (9)
C(2D)	0.5232 (3)	0.6165 (3)	0.181 (1)
C(3A)	0.1923 (4)	0.2225 (3)	0.646 (1)
C(3B)	−0.0042 (4)	0.5249 (4)	0.758 (1)
C(3C)	0.3133 (4)	0.8278 (3)	0.263 (1)
C(3D)	0.5840 (4)	0.5878 (4)	0.152 (1)
C(4A)	0.2561 (4)	0.2082 (4)	0.603 (1)
C(4B)	0.0043 (4)	0.5915 (4)	0.721 (1)
C(4C)	0.2487 (4)	0.8246 (4)	0.317 (1)
C(4D)	0.5948 (4)	0.5212 (4)	0.189 (1)
C(5A)	0.3006 (4)	0.2592 (4)	0.575 (1)
C(5B)	0.0620 (4)	0.6118 (4)	0.651 (1)
C(5C)	0.2205 (4)	0.7638 (4)	0.348 (1)
C(5D)	0.5430 (4)	0.4857 (4)	0.250 (1)
C(6A)	0.2776 (4)	0.3235 (4)	0.588 (1)
C(6B)	0.1100 (4)	0.5653 (4)	0.619 (1)
C(6C)	0.2593 (4)	0.7083 (4)	0.332 (1)
C(6D)	0.4823 (4)	0.5175 (4)	0.276 (1)
C(7A)	0.1040 (4)	0.3069 (4)	0.712 (1)
C(7B)	0.0409 (4)	0.4074 (4)	0.755 (1)
C(7C)	0.4191 (4)	0.7681 (3)	0.186 (1)
C(7D)	0.5087 (4)	0.6895 (3)	0.148 (1)
C(8)	0.2540 (3)	0.4918 (3)	0.4196 (8)
C(9)	0.2110 (3)	0.4605 (3)	0.2734 (9)
C(10)	0.2367 (4)	0.4796 (4)	0.1016 (9)
C(11)	0.2895 (3)	0.5312 (3)	0.1525 (9)
C(12)	0.3003 (3)	0.5352 (3)	0.3471 (9)

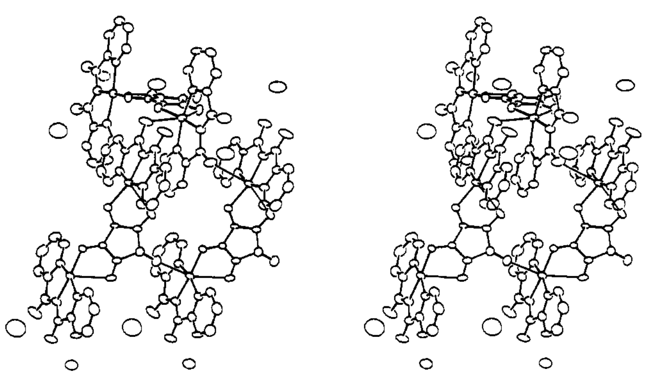

Figure 2. Stereoscopic view of the complex $[Cu_2(bpca)_2(C_5O_5)]\cdot 3H_2O$, showing three dinuclear units. The interdimer Cu–O contacts are drawn as bonds.

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Table III. Selected Interatomic Distances (Å) and Bond Angles (deg) for $[Cu_2(bpca)_2(C_5O_5)]\cdot 3H_2O$[a]

Environment of Copper Atoms			
Distances			
Cu(1)–N(1A)	2.003 (3)	Cu(2)–N(1D)	1.976 (3)
Cu(1)–N(1B)	1.998 (3)	Cu(2)–N(1C)	1.997 (3)
Cu(1)–N(2AB)	1.927 (3)	Cu(2)–N(2CD)	1.934 (3)
Cu(1)–O(8)	1.961 (2)	Cu(2)–O(12)	1.973 (2)
Cu(1)–O(9)	2.585 (3)	Cu(2)–O(11)	2.477 (3)
Cu(1)–O(10)^{i}	2.496 (3)	Cu(2)–O(1C)^{ii}	2.932 (3)
Angles			
N(1A)–Cu(1)–N(1B)	164.2 (1)	N(1D)–Cu(2)–N(1C)	164.3 (1)
N(1A)–Cu(1)–N(2AB)	82.4 (1)	N(1D)–Cu(2)–N(2CD)	82.2 (1)
N(1B)–Cu(1)–N(2AB)	81.9 (1)	N(1C)–Cu(2)–N(2CD)	82.1 (1)
N(1A)–Cu(1)–O(8)	99.6 (1)	N(1D)–Cu(2)–O(12)	99.2 (1)
N(1B)–Cu(1)–O(8)	96.2 (1)	N(1C)–Cu(2)–O(12)	96.1 (1)
N(1A)–Cu(1)–O(9)	85.4 (1)	N(1D)–Cu(2)–O(11)	89.2 (1)
N(1B)–Cu(1)–O(9)	97.4 (1)	N(1C)–Cu(2)–O(11)	97.7 (1)
N(1A)–Cu(1)–O(10)^{i}	97.2 (1)	N(1D)–Cu(2)–O(1C)^{ii}	94.5 (1)
N(1B)–Cu(1)–O(10)^{i}	86.0 (1)	N(1C)–Cu(2)–O(1C)^{ii}	85.1 (1)
O(8)–Cu(1)–N(2AB)	176.2 (1)	O(12)–Cu(2)–N(2CD)	165.4 (1)
O(8)–Cu(1)–O(9)	75.91 (8)	O(12)–Cu(2)–O(11)	77.36 (9)
O(8)–Cu(1)–O(10)^{i}	82.05 (9)	O(12)–Cu(2)–O(1C)^{ii}	78.34 (9)
O(9)–Cu(1)–N(2AB)	107.6 (1)	O(11)–Cu(2)–N(2CD)	117.3 (1)
O(9)–Cu(1)–O(10)^{i}	157.93 (8)	O(11)–Cu(2)–O(1C)^{ii}	155.70 (8)
O(10)^{i}–Cu(1)–N(2AB)	94.5 (1)	O(1C)^{ii}–Cu(2)–N(2CD)	87.0 (1)
Croconato Bridge			
Distances			
O(8)–C(8)	1.268 (4)	O(12)–C(12)	1.278 (4)
O(9)–C(9)	1.228 (4)	O(11)–C(11)	1.238 (4)
O(10)–C(10)	1.223 (4)	C(8)–C(12)	1.419 (4)
C(8)–C(9)	1.440 (4)	C(11)–C(12)	1.453 (5)
C(9)–C(10)	1.497 (5)	C(10)–C(11)	1.480 (5)
Angles			
O(8)–C(8)–C(9)	124.0 (3)	O(12)–C(12)–C(11)	121.5 (3)
O(8)–C(8)–C(12)	127.4 (3)	O(12)–C(12)–C(8)	128.9 (3)
C(9)–C(8)–C(12)	108.5 (3)	C(11)–C(12)–C(8)	109.6 (3)
O(9)–C(9)–C(8)	124.1 (3)	O(11)–C(11)–C(12)	123.8 (3)
O(9)–C(9)–C(10)	127.5 (3)	O(11)–C(11)–C(10)	128.4 (3)
C(8)–C(9)–C(10)	108.5 (3)	C(12)–C(11)–C(10)	107.8 (3)
O(10)–C(10)–C(9)	126.9 (3)	O(10)–C(10)–C(11)	128.1 (3)
C(9)–C(10)–C(11)	105.0 (3)	Cu(1)^{iii}–O(10)–C(10)	169.9 (3)
Cu(1)–O(8)–C(8)	117.3 (2)	Cu(2)–O(12)–C(12)	116.4 (2)
Cu(1)–O(9)–C(9)	98.7 (2)	Cu(2)–O(11)–C(11)	100.6 (2)

[a] Roman numeral superscripts refer to the following equivalent positions relative to x, y, z: (i) $x, y, z + 1$; (ii) $x, {}^{3}/_{2} - y, {}^{1}/_{2} + z$; (iii) $x, y, z - 1$.

basic character of the amido–nitrogen atom. The copper coordination spheres are shown in Figure 1b. Around the Cu(1) there is a sixth coordinated atom, a croconate oxygen atom from a neighboring molecule, translated one unit cell along the *c*-axis (Cu(1)–O(10)^{i} = 2.486 (3) Å). Thus, the dinuclear units are linked into chains by this long axial Cu–O bond, as shown in Figure 2, and the croconate ion has hence a unidentate function in addition to its previously described bis-bidentate binding mode. At Cu(2) the sixth position is occupied by a carbonyl-oxygen atom from a *c*-glide-related molecule. The Cu(2)–O(1C)^{ii} distance of 2.932 (3) Å is on the long side even for semicoordination, but as illustrated in Figure 1b, the coordination of the two independent copper atoms becomes strikingly similar when this atom is taken into account.

The equatorial ligand atoms of Cu(1) deviate by 0.040–0.047 Å from a least-squares plane defined by these atoms, and the corresponding values for equatorial atoms at Cu(2) are 0.092–0.125 Å. The metal atoms are displaced by 0.015 and 0.138 Å toward O(9) and O(11), respectively. The dihedral angle between the equatorial planes is 15.8°. The bridging croconate group shows a slight deviation from planarity, and the dihedral angles between this plane and the equatorial planes are 81.3 and 85.5°. Each pyridyl ring is planar, the dihedral angle between rings within the same bpca group being 10.6 Å. Bond distances and angles of the bpca ligand are similar to those reported earlier and therefore will not be further discussed. Although there is no symmetry restriction on the croconate bridge, this group possesses close to 2-fold symmetry (see Table III). The C–O bond distances are markedly different: long when O is equatorially coordinated to Cu, short when O forms a long axial bond to Cu. The structure of the related squarato-bridged Cu(bpca) dinuclear complex[7a] shows that the squarate acts as a bis-unidentate ligand in contrast to what is observed for the croconate. This different coordinating behavior can be explained on the basis of stereochemical constraints (vide infra).

The intramolecular Cu(1)···Cu(2) separation is 6.824 (1) Å, whereas the shortest intermolecular copper–copper distance is 5.935 (1) Å and occurs between Cu(2) atoms related by the *c*-glide translation. These molecules are laced through the very long axial Cu(2)–O(1C)^{ii} connections (2.932 (3) Å) (see Figures 1b and 2). A separation of 7.338 (1) Å occurs between centrosymmetrically related Cu(1) atoms: Cu(1)···Cu(1)^{iv} (where iv denotes the equivalent coordinates $-x, 1 - y, 1 - z$). Furthermore, between molecules related through a unit cell translation along *c* and connected through the axial Cu(1)–O(10)^{i} bond, the Cu(1)–Cu(2)^{i} separation is 7.346 (1) Å.

As hydrogen atoms belonging to water molecules could not be located, a detailed description of the hydrogen bonding scheme is not possible. The O···O contacts listed at the end of Table S3 (supplementary material) suggest that all these water molecules participate in hydrogen bonds interlacing symmetry-related complex units.

Infrared and EPR Spectra. The infrared spectrum of the title complex exhibits a broad and intense absorption located in the range 3600–3300 cm^{-1} and attributed to the OH stretching frequency of the water molecules and a sharp medium absorption at 1630 cm^{-1}, which is assigned to the ν_{HOH} bending vibration.[33] A strong and sharp feature observed at 1715 cm^{-1} is consistent with the presence of the imide group in the bpca ligand.[25,29,30,34] A shoulder at 1730 cm^{-1} can be attributed to the occurrence of three weakly coordinated carbonyl groups of croconate which have considerable double-bond character.[35] Strong and broad absorptions occurring in the range 1600–1350 cm^{-1} are characteristic of the salts of $C_nC_n^{2-}$ ions,[36] and in the present case they can be assigned to vibrational modes representing mixtures of C–O and C–C stretching motions. The coordinated C–O groups of croconate are characterized by medium absorptions at 1660 and 1650 cm^{-1} as observed in other croconato complexes.[21] In the far IR region of the spectrum several absorptions between 330 and 500 cm^{-1} occur, which may be attributed to the ν_{Cu-O}(croconate) and ν_{Cu-N}(bpca) stretching frequencies.[37]

The X-band powder EPR spectrum of $[Cu_2(bpca)_2(C_5O_5)]\cdot 3H_2O$ at 100 K looks like an isolated axial copper(II) ion with $g_{\parallel}$ and $g_{\perp}$ values of 2.22 and 2.07, respectively. The fact that intensity of the signals decreases upon cooling from room temperature to 100 K confirms that the resonance occurs within the triplet excited state. Furthermore, the spectrum shows the $\Delta M_s = 2$ forbidden transition in the $g = 4$ region, whose intensity is very weak when compared to the one of the feature in the $g = 2$ region. The shape of the spectrum of in the $g = 2$ region and the weak intensity of the half-field transition reveal that the zero-field splitting within the triplet state is almost negligible with respect to the incident quantum (~0.3 cm^{-1}). The nondetection of the zero-field splitting in the triplet state deserves a brief comment. Both the dipolar interaction and the anisotropic exchange[38] contribute to the zero-field splitting in a symmetrical copper(II) dinuclear complex (a C_{2v} symmetry may be roughly assumed for $[Cu_2(bpca)_2(C_5O_5)]\cdot 3H_2O$). The former contribution which would arise from the dipolar interaction between the two local doublets separated by 6.8 Å is[39] 6.1 × 10^{-3} cm^{-1}, a value

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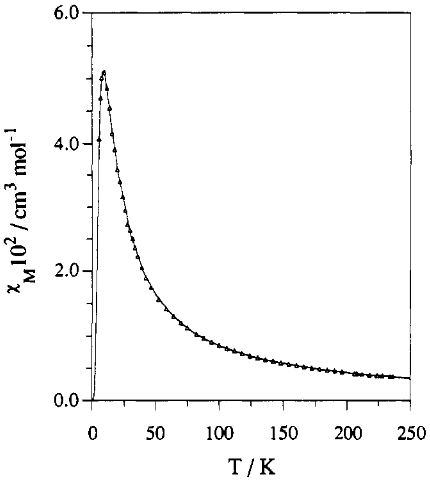


Figure 3. Experimental (Δ) and calculated (—) temperature dependences of the molar magnetic susceptibility, χ_M, of the dinuclear complex $[Cu_2(bpca)_2(C_5O_5)]\cdot 3H_2O$. J and g values from the best fit are -9.63 cm^{-1} and 2.17 (see text).

clearly undetectable due to the line widths. As far as the anisotropic exchange is concerned, it is due to the spin–orbit coupling and is proportional to the interaction between the ground state of an ion and the excited states of the other.[38] For a quasi-planar system, the most efficient ground–excited interaction is of the type $(xy) - (x^2 - y^2)$ involving in-plane orbitals.[38,40] In the title compound we are dealing with $x^2 - y^2$ magnetic orbitals centered on each copper(II) ion (vide infra). This interaction, which is purely ferromagnetic, may be large for $Cu^{II}X_2Cu^{II}$ entities, X being a monoatomic bridge which leads to a copper–copper separation close to 3 Å. Such an interaction quickly approaches to zero when the metal–metal distance increases by using polyatomic bridges.[23] Undetected intermolecular exchange coupling in the present complex could be also responsible for the lack of zero-field splitting.

Magnetic Properties. The variation of the molar magnetic susceptibility χ_M vs the temperature T for the title compound is shown in Figure 3. A maximum of χ_M is observed at 9 K, which is characteristic of an antiferromagnetic interaction. The experimental data were fitted to the simple Bleaney–Bowers expression (eq 1) for a dinuclear copper(II) complex, where J is the

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

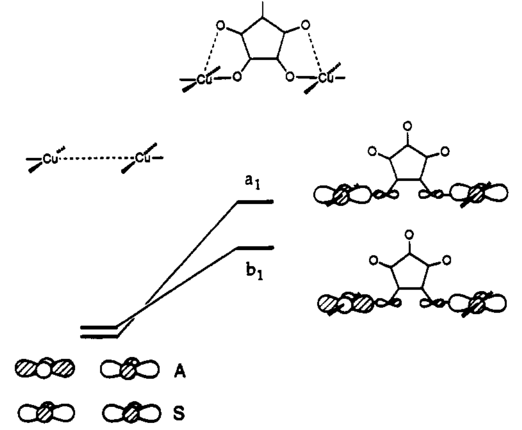
singlet–triplet energy gap defined by the phenomenological Hamiltonian with quantum spin operators S_1 and S_2 (eq 2). J

$$H = -JS_1 \cdot S_2 \qquad (2)$$

expresses the intramolecular exchange interaction. In eq 1, N, g, β, and T have their usual meaning. The minimization of $R = \sum (\chi_M^{obsd} - \chi_M^{calcd})^2 / \sum (\chi_M^{obsd})^2$ leads to J and g values of -9.63 cm^{-1} and 2.17, respectively. The fit is excellent as shown in Figure 3 ($R = 1.26 \times 10^{-5}$).

When undertaking this work, we addressed ourselves two main questions: (i) Is it possible to demonstrate structurally the bis-bidentate coordination mode of croconate between copper(II) ions? (ii) If so, what would be its ability to transmit magnetic interaction between the metal ions? This second question is posed keeping in mind the remarkable efficiency of related oxalate[22,23] and hydranilate bridges.[42] Our experimental results allow us to answer yes to the first question. In fact, the bite parameter [$b = d(O\cdots O)/d(Cu\cdots O)$] of the croconate is 1.45 (the shortest O···O and Cu–O distances are used), a value which is close to the calculated for oxalate (1.34) and hydranilate derivatives (1.33) but significantly smaller than the one of squarate (1.70).[6] So, it is not surprising that the croconate can act as a chelating bidentate and bis-bidentate ligand. In the present case, it acts in an asymmetrical bis-bidentate fashion because three of the four short coordinating sites are occupied by the nitrogen atoms of bpca. It is well-known that copper(II) prefers nitrogen donor ligands to oxygen ones, and due to the Jahn–Teller effect, only four short distances are found around copper(II). If a bidentate N-donor ligand were used as end-cap ligand, the croconate group could act in a symmetrical chelating or bis-chelating fashion. Preliminary results of an X-ray structure investigation of a copper bipyridyl croconato complex indicates the presence of the former coordination mode.[43]

As far as the second question is concerned, the weak coupling (-9.63 cm^{-1}) that we have determined for the title compound reveals that the croconato bridge is more efficient than the related squarato group[6] but less than the parent oxalato[22,23] and hydranilato[42] bridges. As the structure of the present compound consists of dinuclear units linked into chains by long axial Cu–O bonds, 2.496 (3) and 2.932 (2) Å for $Cu(1)-O(10)^i$ and $Cu(2)-O(1C)^{ii}$, respectively, and the shortest intermolecular $Cu(2)\cdots Cu(2)^{ii}$ contact of 5.935 Å is shorter than the intramolecular Cu(1)···Cu(2) separation, both intra- and intermolecular exchange pathways are possible. Qualitative molecular orbital analysis based on extended Hückel calculations[44,45] shows that the magnetic orbitals are essentially of $d_{x^2-y^2}$ symmetry with a negligible admixture of d_{z^2}. This allows us to conclude that no efficient pathway exists between dimers and that the observed coupling is most likely of intramolecular nature. The molecular orbitals containing the unpaired electrons and therefore responsible for the antiferromagnetic coupling of $[Cu_2(bpca)_2(C_5O_5)]\cdot 3H_2O$ are depicted in **2**, where only the major contributions from the copper



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atoms and the croconato ligand are shown. In the absence of the bridging croconato ligand, the symmetric (S) and antisymmetric (A) combinations of the Cu $d_{x^2-y^2}$ orbitals are practically degenerate, given the long Cu···Cu distance (6.82 Å). Introduction of the croconato bridge results in two copper–croconato antibonding molecular orbitals a_1 and b_1, clearly nondegenerate, with a_1 roughly 0.1 eV above b_1. Thus, the small calculated energy gap must be

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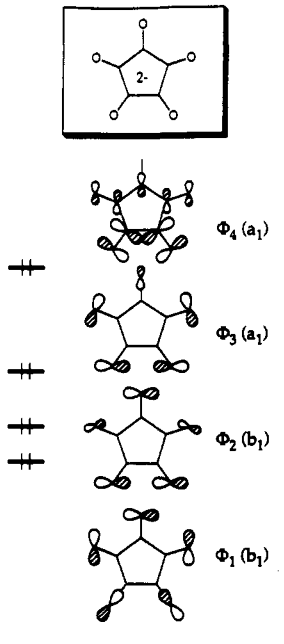
at the origin of the tiny separation found experimentally between the singlet and triplet states and can be clearly attributed to the interaction of the $d_{x^2-y^2}$ orbitals through the croconato bridge.

To be sure that the splitting of the a_1 and b_1 orbitals is intrinsic to this dinuclear system and not an artifact of the computational procedure employed, a more detailed analysis of the orbital interactions giving rise to the a_1 and b_1 molecular orbitals is needed. The molecular orbitals of the croconato anion which interact with the $d_{x^2-y^2}$ orbitals of the copper atoms (S and A in **2**) to give a_1 and b_1 are shown in **3** (Φ_1–Φ_4). The remarkable feature of such orbitals is that those of A_1 symmetry appear at higher energy than those of B_1 character, resulting in a better energy match for the S/Φ_3 and S/Φ_4 interactions than for the A/Φ_1 and A/Φ_2 ones. A direct consequence is the higher energy of the a_1 molecular orbital. However, the overlap between A and the corresponding croconato orbitals is somewhat higher, compensating in part the difference in the energy match and avoiding a large HOMO–LUMO separation.



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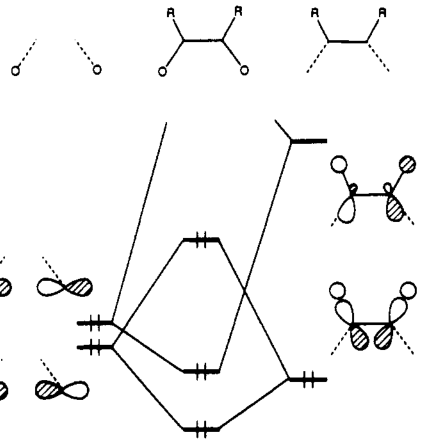
The fact that the A_1 orbitals of croconato have higher energies than the B_1 can be seen to be intrinsic to its molecular structure. From the croconate ion we can isolate the fragment which is relevant for the magnetic coupling between the copper atoms, an ORC–CRO group (and take R = H for model calculations). Let us consider the p orbitals of the highly electronegative oxygen atoms carrying the lone pairs (**4**). Their A_1 combination has the right symmetry to interact with an occupied orbital of the carbonaceous skeleton with π_{CC} (and some σ_{CR}) character, hence with low energy. In contrast, their B_1 combination can mix with an empty orbital of π^*_{CC} and σ^*_{CR} character of higher energy, resulting in a poorer interaction. As a consequence, the A_1 combination of the oxygen lone pairs has higher energy than the B_1 one, exactly as found for the croconato ion. We can conclude that such orbital ordering is due to fundamental reasons such as electronegativity and topology and must be the same for any bridging ligand which can be idealized as an ORC–CRO fragment. Such ligands, when acting in the coordination mode shown in **4**, should induce a weak antiferromagnetic coupling similar to that reported here for $[Cu_2(bpca)_2(C_5O_5)]\cdot 3H_2O$.



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The very weak exchange coupling reported for analogous (μ-1,3-squarato)copper(II) complexes[6,7a] is due to the fact that for this family the overall overlap integral between the magnetic orbitals is practically zero. However, in the case of oxalato- and hydranilato-bridged copper(II) complexes, the great efficiency of such bridging groups is due to the large overlapping between the in-phase and out-of-phase combinations of d_{xy} metal orbitals and the two HOMO's of the bridging ligand, of b_{1g} and b_{2u} symmetries. The larger intermolecular copper–copper separation together with the smaller overlapping for μ-hydranilato complexes (~7.6 Å) when compared to that for the μ-oxalato species (~5.1 Å) accounts for the different value of the exchange coupling (maximum values of −26 and −380 cm^{-1} for the hydranilato and oxalato complexes, respectively).[22c,42]

To conclude, we want to stress that this study clearly establishes for the first time that the croconate ligand can act as a bis-bidentate bridge and it is able to mediate weak but significant magnetic coupling between copper(II) ions separated by 6.8 Å.

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Registry No. **1**, 15110-70-0; $[Cu_2(bpca)_2(C_5O_5)]\cdot 3H_2O$, 140110-94-7; $[Cu(bpca)(H_2O)_2]NO_3$, 127887-62-1; $[Cu_2(NH_3)_6(C_5O_5)]^{2+}$, 140110-95-8.

Supplementary Material Available: Tables S1–S5, listing full crystallographic data, thermal parameters, hydrogen coordinates, nonessential bond distances and angles, and least-squares planes and deviations therefrom (16 pages); Table S6, listing calculated and observed structure factors (32 pages). Ordering information is given on any current masthead page.