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Coordination Modes of the Squarate Ligand: Syntheses and Crystal Structures of Six Copper(II) Squarate Complexes

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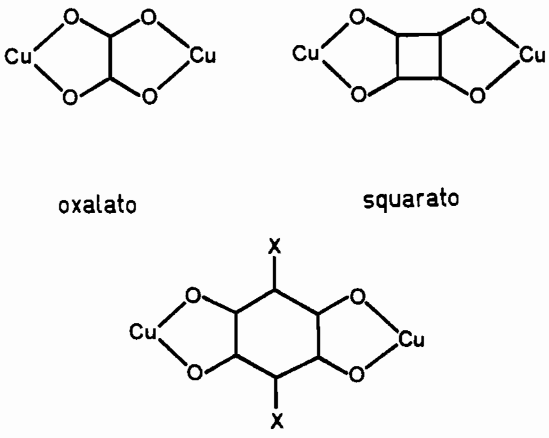
The synthesis and structural characterization of six new copper(II) squarate complexes of formula $[Cu(bpy)(H_2O)(C_4O_4)]\cdot H_2O$ (**1**), $[Cu_2(bpy)_2(H_2O)_2(C_4O_4)](NO_3)_2$ (**2**), $[Cu(phen)(H_2O)_2(C_4O_4)]\cdot 2H_2O$ (**3**), $[Cu(terpy)(H_2O)(C_4O_4)]\cdot H_2O$ (**4**), $[Cu_2(terpy)_2(H_2O)_2(C_4O_4)](ClO_4)_2$ (**5**), and $[Cu_2(pmdien)_2(H_2O)_2(C_4O_4)](NO_3)_2$ (**6**) (where bpy, phen, terpy, pmdien, and $C_4O_4^{2-}$ are 2,2′-bipyridine, 1,10-phenanthroline, 2,2′:6′,2″-terpyridine, 1,1,4,7,7-pentamethyldiethylenetriamine, and the dianion of 3,4-dihydroxycyclobutenedione, respectively), are described. The crystals of **1** are orthorhombic, space group *Pbca*, with $Z = 8$, $a = 17.182$ (3) Å, $b = 13.094$ (3) Å, $c = 12.321$ (2) Å, and $R = 0.053$ ($R_w = 0.058$) for 1874 observed reflections. The crystals of **2** are monoclinic, space group $P2_1/n$, with $Z = 2$, $a = 14.478$ (3) Å, $b = 9.932$ (2) Å, $c = 9.321$ (2) Å, $\beta = 98.09$ (2)°, and $R = 0.040$ ($R_w = 0.049$) for 2867 observed reflections. The crystals of **3** are triclinic, space group $P\bar{1}$, with $Z = 2$, $a = 10.484$ (3) Å, $b = 10.368$ (2) Å, $c = 8.288$ (2) Å, $\alpha = 95.30$ (2)°, $\beta = 83.48$ (2)°, $\gamma = 110.45$ (2)°, and $R = 0.042$ ($R_w = 0.049$) for 2614 observed reflections. The crystals of **4** are monoclinic, space group $P2_1/a$, with $Z = 4$, $a = 19.626$ (3) Å, $b = 11.291$ (2) Å, $c = 8.436$ (2) Å, $\beta = 99.69$ (2)°, and $R = 0.045$ ($R_w = 0.050$) for 1972 observed reflections. The crystals of **5** are monoclinic, space group $P2_1/n$, with $Z = 2$, $a = 14.857$ (3) Å, $b = 13.990$ (3) Å, $c = 8.736$ (2) Å, $\beta = 93.19$ (2)°, and $R = 0.059$ ($R_w = 0.064$) for 2355 observed reflections. The crystals of **6** are monoclinic, space group $P2_1/n$, with $Z = 2$, $a = 15.802$ (3) Å, $b = 12.975$ (2) Å, $c = 8.207$ (2) Å, $\beta = 98.52$ (2)°, and $R = 0.041$ ($R_w = 0.048$) for 2013 observed reflections. The structures of **2**, **5**, and **6** are made of μ-1,3-squarato-bridged copper(II) binuclear units. The structure of **4** consists of one-dimensional chains of μ-1,2-squarato-bridged copper(II) complex units. The structure of **3** is built by mononuclear complex units in which the squarate acts as a monodentate ligand, whereas it acts as in 1,2,3-trismonodentate fashion in **1**, giving a two-dimensional network parallel to the plane (100). The copper(II) ion displays a pyramidal coordination in the discrete structures and a distorted octahedral coordination in the polymeric ones. The squarate ligand is planar in all these complexes. Infrared, UV–visible, and EPR spectra of these compounds are discussed, taking into account their crystal structures. Magnetic susceptibility data for **2**, **4**, and **5** as a function of the temperature show weak exchange interactions as expected from the structures. The ability of the squarate anion to act as a bridging ligand in copper(II) complexes with different terminal ligands is structurally demonstrated. Simple stereochemical considerations allow us to predict that this ligand cannot coordinate to copper(II) and most probably to first-row transition-metal ions either in a bisbidentate or even in a 1,2-bidentate fashion.

Introduction

Increasing interest has been devoted to the study of exchange interactions between transition-metal ions through extended bridging groups by both inorganic and bioinorganic chemists during the last few years.[2] The fundamental understanding of the exchange coupling through multiatom bridges, the search of a limiting distance to the interaction between two transition metal ions, new insights into the electron transfer pathways in biological electron transport chains, and the design of new molecular materials are among the main goals of these efforts.

This paper is a part of our study of exchange interactions propagated by multiatom bridges. We focus here on the squarate ligand, $C_4O_4^{2-}$, to characterize structurally its bonding properties to copper(II) ion and to study and rationalize the exchange interaction through the series shown in Chart I, where the copper–copper distance varies from 5 to 8 Å. Recently, some of us have studied the symmetry factors that govern the overlap of the magnetic orbitals in (μ-oxalato)copper(II) complexes.[3,4] We have shown how to tune the antiferromagnetic coupling in these oxalato compounds in the range −385.4 to ~0 cm^{-1} by playing on the nature of the terminal ligands.[4,5] Very recently, we have found that the counterions could be an a priori unexpected but efficient means to tune the structures and the magnetic properties in copper(II)–oxalato–2,2′-bipyridyl cationic complexes.[6] Chloranilate and bromanilate-bridged copper(II) materials have been structurally characterized by EXAFS; this technique has shown that these compounds have a planar ribbon structure.[7a] The intrachain exchange parameter was determined to be −24.4 and −22.4 cm^{-1} for $Cu(C_6O_4Cl_2)$ and $Cu(C_6O_4Br_2)$, respectively. These structural and magnetic results were confirmed recently on a binuclear copper(II) iodanilate compound.[7b] It has been suggested that the squarate ligand could coordinate to the metal ions in a bisbidentate fashion[5,8,9] like the oxalate dianion. Magnetism and

Chart I



oxalato

squarato

chloranilato (X = Cl)

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Table I. Crystallographic Data for Complexes **1–6**

	1	**2**	**3**	**4**	**5**	**6**
chem formula	$C_{14}H_{12}N_2O_6Cu$	$C_{24}H_{20}N_6O_{12}Cu_2$	$C_{16}H_{16}N_2O_8Cu$	$C_{19}H_{15}N_3O_6Cu$	$C_{34}H_{26}N_6O_{14}Cl_2Cu_2$	$C_{22}H_{50}N_8O_{12}Cu_2$
a, Å	17.182 (3)	14.478 (3)	10.484 (3)	19.626 (3)	14.857 (3)	15.802 (3)
b, Å	13.094 (2)	9.932 (2)	10.368 (2)	11.291 (2)	13.990 (3)	12.975 (2)
c, Å	12.321 (2)	9.321 (2)	8.288 (2)	8.436 (2)	8.736 (2)	8.207 (2)
α, deg	90	90	95.30 (2)	90	90	90
β, deg	90	98.09 (2)	83.48 (2)	99.69 (2)	93.19 (2)	98.52 (2)
γ, deg	90	90	110.45 (2)	90	90	90
V, Å^3	2560 (1)	1327.0 (8)	837.3 (6)	1843 (1)	1813 (1)	1664 (1)
Z	8	2	2	4	2	2
fw	367.8	711.6	427.9	444.9	940.6	745.8
space group	*Pbca*	$P2_1/n$	$P\bar{1}$	$P2_1/a$	$P2_1/n$	$P2_1/n$
T, °C	25	15	15	15	25	15
λ, Å	0.71069	0.71069	0.71069	0.71069	0.71069	0.71069
ρ_{obsd}, g cm^{-3}	1.74	1.81	1.71	1.62	1.73	1.50
ρ_{calcd}, g cm^{-3}	1.760	1.780	1.696	1.603	1.723	1.488
μ, cm^{-1}	16.72	17.48	14.09	12.78	14.47	13.98
$R(F_o)$	0.053	0.040	0.042	0.045	0.059	0.041
$R_w(F_o^2)$	0.058	0.049	0.049	0.050	0.064	0.048

Mössbauer, IR, and electronic spectroscopic studies have been performed on squarate complexes of the first-row transition-metal ions in order to clarify the binding of the squarate in either 1,2-bidentate[9-12] or 1,2-bismonodentate fashion.[9] There are no X-ray diffraction data on complexes of such metal ions that could support the 1,2-bidentate bonding mode for squarate but the 1,2-bismonodentate one has been reported in one binuclear chromium(III) complex[13a] and in a one-dimensional Ni(II) chain compound.[13b] Some structures of polymeric complexes in which the squarate acts as a tetramonodentate[14] and as a 1,3-bismonodentate[15,16] bridging ligand are also known.

We report here the crystal structures of six new Cu(II)–squarate complexes of formulas $[Cu(bpy)(H_2O)(C_4O_4)]\cdot H_2O$ (**1**), $[Cu_2(bpy)_2(H_2O)_2(C_4O_4)](NO_3)_2$ (**2**), $[Cu(phen)(H_2O)_2(C_4O_4)]\cdot 2H_2O$ (**3**), $[Cu(terpy)(H_2O)(C_4O_4)]\cdot H_2O$ (**4**), $[Cu_2(terpy)_2(H_2O)_2(C_4O_4)](ClO_4)_2$ (**5**), and $[Cu_2(pmdien)_2(H_2O)_2(C_4O_4)](NO_3)_2$ (**6**). IR, UV–visible, and EPR spectra of these squarate-containing complexes are discussed in relation with the observed crystal structures. The weak exchange coupling that is observed in complexes **2**, **4**, and **5** is explained in the frame of a localized orbital model. To our knowledge, complex **4** is the first example of a Cu(II) chain with a 1,2-bismonodentate squarate coordination. Neither the bisbidentate nor 1,2-bidentate coordination mode is observed in this series of structures. We show that this bonding behavior originates in the high value of the bite parameter of the squarate.

Experimental Section

Chemicals. Squaric acid, 2,2′-bipyridine, 1,10-phenanthroline, and copper(II) nitrate trihydrate were obtained from Merck. Copper(II) perchlorate hexahydrate, 2,2′:6′,2″-terpyridine and 1,1,4,7,7-pentamethyldiethylenetriamine were purchased from Aldrich, Sigma, and Ames Laboratories, Inc. respectively. All of them were used as received. Analytical data (C, H, N) were performed by the Servei de Microanàlisi Elemental (CSIC, Barcelona, Spain).

Preparation of Compounds. $[Cu(bpy)(H_2O)(C_4O_4)]\cdot H_2O$ (1). Copper(II) nitrate trihydrate (483 mg, 2 mmol) and 2,2′-bipyridine (312 mg, 2 mmol) were dissolved in 70 mL of hot water. A warm solution containing lithium squarate (126 mg, 1 mmol) in 10 mL of water was added, forming a green-yellow solution. Brown prismatic crystals (**1**) and green needles were obtained by slow evaporation at room temperature. The former were collected, washed with cold water, and air-dried. Anal. Calcd for $C_{14}H_{12}N_2O_6Cu_2$ (**1**): C, 45.73; H, 3.26; N, 7.61; Cu, 17.28. Found: C, 45.73; H, 3.28; N, 7.67; Cu, 17.10. Analyses of C, H, and N for the latter revealed that they correspond to a pentahydrate of formula $Cu(bpy)(C_4O_4)\cdot 5H_2O$. The loss of water of these crystals at room temperature is accompanied by a color change from green to brown. We did not further study this green compound.

$[Cu_2(bpy)_2(H_2O)_2(C_4O_4)](NO_3)_2$ (2). This compound was synthesized by following the foregoing described procedure with a 10:10:1 copper:2,2′-bipyridine:squarate molar ratio. Dark green prismatic crystals of **2** were obtained by slow evaporation at room temperature; they were collected and air-dried. Anal. Calcd for $C_{24}H_{20}N_6O_{12}Cu_2$ (**2**): C, 40.52; H, 2.81; N, 11.81; Cu, 17.87. Found: C, 40.41; H, 2.96; N, 11.68; Cu, 17.60.

$[Cu(phen)(H_2O)(C_4O_4)]\cdot H_2O$ (3). A solution containing copper(II) nitrate trihydrate (241 mg, 1 mmol) and 1,10-phenanthroline monohydrate (396 mg, 2 mmol) was prepared in 80 mL of 75% aqueous ethanol. A hot aqueous solution of lithium squarate (126 mg, 1 mmol) was added. The initial pale blue solution turned brown, and dark brown prismatic crystals of **3** were obtained by slow evaporation at room temperature. They were filtered and air-dried. Anal. Calcd for $C_{16}H_{16}N_2O_8Cu$ (**3**): C, 44.92; H, 3.74; N, 6.54; Cu, 14.86. Found: C, 44.75; H, 3.79; N, 6.32; Cu, 14.71.

$[Cu(terpy)(H_2O)(C_4O_4)]\cdot H_2O$ (4). A warm solution containing copper(II) nitrate trihydrate (241 mg, 1 mmol) and 2,2′:6′,6″-terpyridine (233 mg, 1 mmol) was prepared in 100 mL of 75% aqueous ethanol. A hot aqueous solution of lithium squarate (126 mg, 1 mmol) was added. The initially blue solution turned dark green. Dark green prismatic crystals were obtained by slow evaporation at room temperature. They were collected, recrystallized from a H_2O–CH_3CN mixture and air-dried. A water molecule was easily lost when the compound was stored in a desiccator over silica gel. Anal. Calcd for $C_{19}H_{15}N_3O_6Cu$ (**4**): C, 51.31; H, 3.37; N, 9.44; Cu, 14.29. Found: C, 51.15; H, 3.42; N, 9.70; Cu, 14.18.

$[Cu_2(terpy)_2(H_2O)_2(C_4O_4)](ClO_4)_2$ (5). Lithium squarate (126 mg, 1 mmol) dissolved in 10 mL of hot water was added to a warm solution containing copper(II) perchlorate hexahydrate (741 mg, 2 mmol) and 2,2′:6′,6″-terpyridine (466 mg, 2 mmol) in 90 mL of water. Brown prismatic crystals of **5** were obtained by slow evaporation of the resulting dark green solution. They were recrystallized from warm water and stored in a desiccator over silica gel. Anal. Calcd for $C_{34}H_{26}N_6O_{14}Cl_2Cu$ (**5**): C, 43.42; H, 2.77; N, 8.93; Cl, 7.54; Cu, 13.51. Found: C, 43.23; H, 2.76; N, 9.22; Cl, 7.30; Cu, 13.38.

$[Cu_2(pmdien)_2(H_2O)_2(C_4O_4)](NO_3)_2$ (6). Lithium squarate (126 mg, 1 mmol) dissolved in a minimum amount of water was added to an aqueous solution containing copper(II) nitrate trihydrate (483 mg, 2 mmol) and 1,1,4,7,7-pentamethyldiethylenetriamine (356 mg, 2 mmol). The resulting dark green solution was filtered, and brown prismatic crystals of **6** were obtained by slow evaporation nearly to dryness. Anal. Calcd for $C_{22}H_{50}N_8O_{12}Cu_2$ (**6**): C, 35.45; H, 6.71; N, 15.03; Cu, 17.05. Found: C, 35.22; H, 6.80; N, 14.89; Cu, 16.88.

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Table II. Final Atomic Fractional Coordinates[a] and Equivalent Isotropic Displacement Parameters[b] for $[Cu(bpy)(H_2O)(C_4O_4)]\cdot H_2O$ (**1**)

atom	x/a	y/b	z/c	B_{eq}, Å^2
Cu	0.40171 (3)	0.09239 (4)	0.36389 (4)	2.26 (3)
O(w1)	0.5140 (2)	0.0673 (2)	0.3476 (3)	2.51 (12)
C(O1)	0.4640 (2)	0.1855 (3)	0.5661 (3)	2.19 (15)
O(O1)	0.4093 (2)	0.1649 (3)	0.5002 (2)	3.21 (13)
C(O2)	0.4687 (2)	0.2557 (3)	0.6564 (3)	2.10 (14)
O(O2)	0.4228 (2)	0.3201 (2)	0.6989 (2)	3.05 (13)
C(O3)	0.5490 (2)	0.2237 (3)	0.6789 (3)	2.15 (14)
O(O3)	0.5993 (1)	0.2484 (2)	0.7461 (3)	2.85 (12)
C(O4)	0.5436 (2)	0.1504 (3)	0.5866 (3)	2.09 (15)
O(O4)	0.5873 (2)	0.0871 (2)	0.5408 (3)	2.59 (13)
N(1)	0.3730 (2)	0.0211 (2)	0.2256 (3)	2.67 (14)
C(2)	0.4231 (4)	−0.0180 (4)	0.1519 (4)	4.03 (22)
C(3)	0.3987 (5)	−0.0676 (5)	0.0606 (5)	5.35 (31)
C(4)	0.3200 (6)	−0.0786 (4)	0.0412 (4)	5.81 (34)
C(5)	0.2683 (4)	−0.0376 (4)	0.1136 (5)	4.69 (25)
C(6)	0.2952 (3)	0.0135 (3)	0.2061 (3)	3.08 (17)
C(7)	0.2465 (2)	0.0647 (3)	0.2875 (4)	2.76 (16)
C(8)	0.1667 (3)	0.0756 (4)	0.2809 (5)	4.42 (24)
C(9)	0.1272 (3)	0.1329 (5)	0.3587 (5)	4.57 (28)
C(10)	0.1687 (3)	0.1764 (4)	0.4421 (5)	3.92 (21)
C(11)	0.2490 (2)	0.1629 (4)	0.4469 (4)	3.07 (18)
N(12)	0.2864 (2)	0.1081 (3)	0.3712 (3)	2.33 (14)
O(w2)	0.2531 (2)	0.2961 (4)	0.6634 (4)	4.99 (21)

[a] Estimated standard deviations in the last significant digits are given in parentheses. [b] $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}\mathbf{a}_i^*\cdot\mathbf{a}_j^*\cdot\mathbf{a}_i\cdot\mathbf{a}_j$.

Table III. Final Atomic Fractional Coordinates[a] and Equivalent Isotropic Displacement Parameters[b] for $[Cu_2(bpy)_2(H_2O)_2(C_4O_4)](NO_3)_2$ (**2**)

atom	x/a	y/b	z/c	B_{eq}, Å^2
Cu	0.23775 (2)	0.03939 (3)	0.36497 (3)	2.84 (2)
O(w)	0.2910 (2)	−0.0432 (2)	0.2027 (2)	3.63 (9)
O(O1)	0.3555 (1)	0.0964 (2)	0.4746 (3)	3.93 (9)
C(O1)	0.4345 (2)	0.0416 (2)	0.4864 (3)	2.67 (9)
C(O2)	0.5175 (2)	0.0578 (2)	0.5929 (3)	2.79 (9)
O(O2)	0.5384 (1)	0.1263 (2)	0.7048 (2)	3.92 (9)
N(1)	0.1708 (1)	0.1652 (2)	0.4827 (2)	2.77 (8)
C(2)	0.2093 (2)	0.2493 (3)	0.5879 (3)	3.39 (11)
C(3)	0.1589 (3)	0.3434 (3)	0.6516 (4)	3.85 (13)
C(4)	0.0642 (2)	0.3516 (3)	0.6060 (3)	3.99 (13)
C(5)	0.0223 (2)	0.2638 (3)	0.5013 (3)	3.48 (11)
C(6)	0.0778 (2)	0.1718 (3)	0.4411 (3)	2.66 (9)
C(7)	0.0412 (2)	0.0739 (3)	0.3279 (3)	2.84 (9)
C(8)	−0.0523 (2)	0.0546 (3)	0.2780 (4)	3.56 (12)
C(9)	−0.0783 (2)	−0.0416 (3)	0.1726 (4)	4.10 (13)
C(10)	−0.0108 (2)	−0.1190 (3)	0.1229 (4)	4.19 (13)
C(11)	0.0817 (2)	−0.0959 (3)	0.1763 (3)	3.46 (11)
N(12)	0.1073 (2)	−0.0014 (2)	0.2756 (2)	2.75 (8)
O(31)	0.2218 (2)	−0.1415 (3)	0.5212 (3)	4.93 (11)
N(32)	0.2360 (2)	−0.2566 (3)	0.4762 (3)	3.73 (10)
O(33)	0.1984 (2)	−0.3567 (3)	0.5209 (3)	4.97 (12)
O(34)	0.2912 (3)	−0.2720 (3)	0.3885 (5)	8.33 (22)

[a] Estimated standard deviations in the last significant digits are given in parentheses. [b] $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}\mathbf{a}_i^*\cdot\mathbf{a}_j^*\cdot\mathbf{a}_i\cdot\mathbf{a}_j$.

Table IV. Final Atomic Fractional Coordinates[a] and Equivalent Isotropic Displacement Parameters[b] for $[Cu(phen)(H_2O)_2(C_4O_4)]\cdot 2H_2O$ (**3**)

atom	x/a	y/b	z/c	B_{eq}, Å^2
Cu	0.41795 (3)	−0.21055 (3)	0.05584 (4)	2.81 (2)
O(w1)	0.3509 (3)	−0.3407 (3)	0.2802 (3)	3.96 (12)
O(w2)	0.6053 (3)	−0.2141 (3)	0.0263 (3)	3.59 (11)
O(w3)	0.2875 (3)	0.2130 (3)	0.2819 (3)	4.59 (13)
O(w4)	0.0196 (4)	0.1245 (4)	0.4170 (5)	6.96 (21)
O(O1)	0.4571 (2)	−0.0349 (3)	0.1862 (3)	3.69 (10)
O(O2)	0.4969 (2)	0.2135 (2)	0.4579 (3)	3.36 (10)
O(O3)	0.7998 (2)	0.2119 (3)	0.5071 (3)	4.09 (11)
O(O4)	0.7591 (3)	−0.0443 (3)	0.2350 (3)	4.24 (12)
C(O1)	0.5538 (3)	0.0303 (3)	0.2751 (4)	2.79 (12)
C(O2)	0.5694 (3)	0.1447 (3)	0.3968 (4)	2.78 (12)
C(O3)	0.7067 (3)	0.1429 (3)	0.4210 (4)	3.05 (13)
C(O4)	0.6882 (3)	0.0265 (3)	0.2970 (4)	3.05 (12)
N(5)	1.2278 (3)	0.7922 (3)	0.0426 (3)	2.74 (10)
N(16)	1.3534 (3)	0.6281 (3)	0.8875 (3)	2.89 (10)
C(16)	1.1669 (4)	0.8745 (4)	0.1261 (4)	3.40 (13)
C(7)	1.0334 (4)	0.8633 (4)	0.1058 (5)	3.94 (15)
C(8)	0.9608 (4)	0.7665 (4)	−0.0045 (5)	3.87 (15)
C(9)	1.0224 (3)	0.6774 (4)	−0.0954 (4)	3.15 (13)
C(10)	0.9560 (4)	0.5711 (4)	−0.2133 (5)	3.89 (15)
C(11)	1.0203 (4)	0.4887 (4)	−0.2914 (4)	3.89 (14)
C(12)	1.1571 (4)	0.5041 (3)	−0.2652 (4)	3.35 (13)
C(13)	1.2307 (4)	0.4212 (4)	−0.3431 (5)	4.19 (16)
C(14)	1.3595 (5)	0.4438 (4)	−0.3032 (5)	4.52 (18)
C(15)	1.4179 (4)	0.5452 (4)	−0.1885 (4)	3.73 (15)
C(17)	1.2244 (3)	0.6069 (3)	−0.1500 (4)	2.76 (12)
C(18)	1.1561 (3)	0.6949 (3)	0.0657 (3)	2.61 (11)

[a] Estimated standard deviations in the last significant digits are given in parentheses. [b] $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}\mathbf{a}_i^*\cdot\mathbf{a}_j^*\cdot\mathbf{a}_i\cdot\mathbf{a}_j$.

Physical Measurements. Infrared spectra were recorded on a Pye Unicam SP200 spectrometer as KBr pellets. The UV–visible and reflectance spectra were run on a Pye Unicam SP100-8 spectrometer; magnesium oxide was used as the reference for the reflectance spectra.

X-Band EPR spectra were performed, both at room temperature and at 4 K, on a ER 200 Bruker spectrometer equipped with a helium continuous-flow cryostat.

Magnetic measurements were carried out on polycrystalline samples in the 4.2–280 K temperature range with a previously described Faraday-type magnetometer,[7a] equipped with an helium continuous-flow cryostat. Independence of the magnetic susceptibility upon the applied magnetic field was checked at room temperature. Mercury tetrakis(thiocyanato)cobaltate(II) was used as a susceptibility standard.

Crystallographic Data Collection and Structure Determination. Information concerning crystallographic data collection and structures refinement is summarized in Table I. Intensity data were measured with a Philips PW-1100 four-circle computer-controlled diffractometer on single crystals of dimensions 0.10 × 0.10 × 0.15, 0.10 × 0.10 × 0.15, 0.10 × 0.10 × 0.12, 0.10 × 0.10 × 0.15, 0.08 × 0.08 × 0.12, and 0.10 × 0.10 × 0.15 mm for **1–6**, respectively. Graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) and the ω-scan technique were used. The 2θ ranges of the data collections were 4–51° for **1**, 4–60° for **2** and **5** and 4–50° for **3**, **4**, and **6**. The octants of data collected were $+h,+k,+l$ for **1**, $\pm h,\pm k,+l$ for **3**, and $\pm h,+k,+l$ for **2**, **4**, **5**, and **6**. For all the structures, three intensities were collected every 2 h as intensity and orientation control; they showed no significant intensity decay. Lorentz-polarization corrections, but no absorption and extinction corrections, were made. The structures of **1**, **2**, **4**, **5**, and **6** are centrosymmetric according to the observed systematic absences. For 3, space groups $P\bar{1}$ and $P1$ are possible. When its structure was refined in both space groups, very close R values were obtained. However, the former was chosen on the basis of the better standard deviations that were obtained for the atomic coordinates in such a space group. The reflections collected were 1902 (1874), 2964 (2879), 2698 (2614), 2057 (1972), 2473 (2355) and 2154 (2013) for complexes **1–6**, respectively. The values in parentheses correspond to the observed reflections with $I \geq 2.5\sigma(I)$. The estiments of agreement between equivalent reflections were 0.022 for **2**, 0.024 for **4** and **6**, and 0.031 for **5**. Locations for copper atoms in the structures of **1** and **2** were determined by Patterson synthesis, while the remaining non-hydrogen atoms were located from a subsequent Fourier synthesis in **1** and with the DIRDIF computer program[17] in **2**. Structures of **3–6** were solved by direct methods using the MULTAN system of computer programs.[18] All six structures were isotropically and anisotropically refined by full-matrix least-squares methods, using the SHELX computer program;[19] f, f' and f'' were taken from ref 20. A difference synthesis showed a disorder in the localization of the O(w2) water molecule in

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(17) Beurskens, P. T.; Bosman, W. P.; Doesburg, H. M.; Gould, R. O.; Van der Hark, T. E. M.; Prick, P. A. J.; Noordik, J. H.; Beurskens, G.; Parthasarathi, V. DIRDIF, an automatic procedure for phase extension and refinement of diffraction structure factors. Technical Report 1981/2; Crystallographic Laboratory, Toernoiveld: Nijmegen, The Netherlands, 1981.

(18) Main, P.; Fiske, S. J.; Hull, S. L.; Lessinger, L.; Germain, G.; Declercq, S. P. Woolfson, M. M. *MULTAN, an automatic system of computer programs for crystal structure determination from X-ray diffraction data*; Universities of York, England and Louvain, Belgium, 1980.

(19) Sheldrick, G. M. *SHELX, Program for crystal structure determination*; University of Cambridge, England, 1976.

(20) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, pp 99–100, 149.

Table V. Final Atomic Fractional Coordinates[a] and Equivalent Isotropic Displacement Parameters[b] for $[Cu(terpy)(H_2O)(C_4O_4)]\cdot H_2O$ (**4**)

atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{eq}, Å^2
Cu	0.69025 (3)	0.52180 (6)	−0.07443 (9)	2.80 (3)
N(1)	0.6482 (2)	0.4865 (4)	0.1267 (6)	3.04 (21)
C(2)	0.6707 (3)	0.4109 (6)	0.2453 (8)	3.96 (32)
C(3)	0.6380 (4)	0.3970 (6)	0.3791 (8)	4.30 (34)
C(4)	0.5810 (4)	0.4644 (7)	0.3870 (8)	4.38 (34)
C(5)	0.5563 (3)	0.5412 (6)	0.2667 (8)	3.69 (31)
C(6)	0.5915 (3)	0.5522 (5)	0.1384 (7)	2.91 (26)
C(7)	0.5700 (3)	0.6319 (5)	−0.0006 (7)	2.85 (25)
N(8)	0.6131 (2)	0.6315 (4)	−0.1071 (6)	2.45 (19)
C(9)	0.6022 (3)	0.6966 (5)	−0.2417 (7)	2.63 (24)
C(10)	0.5446 (3)	0.7702 (5)	−0.2731 (9)	3.67 (30)
C(11)	0.5003 (3)	0.7734 (6)	−0.1626 (9)	4.22 (32)
C(12)	0.5120 (3)	0.7036 (6)	−0.0262 (8)	3.83 (31)
C(13)	0.6560 (3)	0.6816 (5)	−0.3429 (7)	3.04 (25)
N(14)	0.7046 (2)	0.6007 (4)	−0.2850 (6)	2.94 (21)
C(15)	0.7555 (3)	0.5777 (6)	−0.3669 (8)	3.80 (31)
C(16)	0.7585 (4)	0.6342 (7)	−0.5097 (9)	4.65 (37)
C(17)	0.7091 (4)	0.7172 (7)	−0.5710 (9)	4.68 (36)
C(18)	0.6571 (4)	0.7418 (6)	−0.4848 (8)	4.17 (32)
C(O1)	0.6234 (3)	0.2688 (5)	−0.2065 (6)	2.37 (23)
O(O1)	0.6202 (2)	0.3795 (3)	−0.2219 (5)	3.50 (20)
C(O2)	0.6735 (3)	0.1836 (5)	−0.1301 (7)	2.68 (24)
O(O2)	0.7352 (2)	0.1889 (3)	−0.0528 (5)	3.38 (18)
C(O3)	0.6260 (3)	0.0876 (5)	−0.1799 (9)	4.19 (32)
O(O3)	0.6267 (3)	−0.0218 (4)	−0.1599 (10)	9.53 (38)
C(O4)	0.5752 (3)	0.1727 (5)	−0.2588 (7)	3.21 (27)
O(O4)	0.5151 (2)	0.1668 (4)	−0.3383 (6)	4.83 (23)
O(w1)	0.7680 (2)	0.4137 (4)	−0.0456 (6)	3.85 (24)
O(w2)	0.5920 (5)	−0.0398 (10)	0.2226 (15)	6.73 (63)
O(w2)′[c]	0.5789 (6)	0.0121 (9)	0.3989 (16)	6.99 (65)

[a] Estimated standard deviations in the last significant digits are given in parentheses. [b] $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}\cdot\mathbf{a}_i^*\cdot\mathbf{a}_j^*\cdot\mathbf{a}_i\cdot\mathbf{a}_j$. [c] Primed atom refers to two positions of the noted atom.

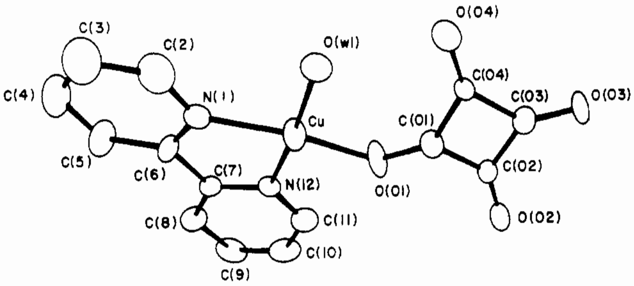

Figure 1. ORTEP view of complex **1** with the atom-labeling scheme. Thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms are not shown for simplicity.

complex **4**; two oxygen atoms of perchlorate groups of structure **5** were located in two disorder sites; disorder was also present in the nitrate groups of complex **6**. In all these cases, an occupancy factor of 0.5 was assigned to each site according to the Fourier map height of the respective peak. Hydrogen atoms in the six structures were located by difference synthesis and refined with an overall isotropic temperature factor[21] while the remaining atoms were refined anisotropically.

R ($\sum|\Delta F|/\sum|F_o|$) and R_w ($[\sum w(\Delta F)^2/\sum wF_o^2]^{1/2}$) factors are given in Table I. The function minimized was $\sum w|\Delta F|^2$ where $w = [\sigma^2|F_o| + k|F_o|^2]^{-1}$. The k values were 0.0331, 0.0105, 0.021, 0.0042, 0.0009, and 0.010 for **1**–**6**, respectively. The values of the residual electron density were 0.4 e Å^{-3} for complexes **1**, **3**, **4**, and **5** and 0.3 e Å^{-3} for **2** and **6**. Tables II–VII present the final atomic positional parameters for non-hydrogen atoms of all the six compounds. Full crystallographic data, anisotropic thermal parameters, and final hydrogen coordinates are listed in Tables SI–SXIII.[22]

Results

Table VI. Final Atomic Fractional Coordinates[a] and Equivalent Isotropic Displacement Parameters[b] for $[Cu_2(terpy)_2(H_2O)_2(C_4O_4)](ClO_4)_2$ (**5**)

atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{eq}, Å^2
Cu	0.08651 (4)	0.25200 (4)	0.64410 (8)	3.80 (3)
O(w)	−0.0604 (3)	0.2464 (4)	0.6801 (7)	4.9 (2)
C(O1)	0.0372 (4)	0.4375 (4)	0.5067 (7)	3.7 (2)
O(O1)	0.0854 (2)	0.3637 (2)	0.5113 (4)	4.0 (2)
C(O2)	−0.0462 (4)	0.4691 (4)	0.5718 (7)	3.7 (2)
O(O2)	−0.1012 (3)	0.4333 (3)	0.6550 (5)	4.6 (2)
N(1)	0.0760 (3)	0.1539 (3)	0.4731 (6)	4.1 (2)
C(2)	0.0394 (4)	0.1653 (5)	0.3296 (9)	4.8 (3)
C(3)	0.0354 (5)	0.0933 (5)	0.2217 (9)	5.4 (3)
C(4)	0.0719 (5)	0.0051 (5)	0.2631 (12)	5.8 (4)
C(5)	0.1084 (5)	−0.0079 (5)	0.4109 (11)	5.3 (4)
C(6)	0.1107 (4)	0.0655 (4)	0.5124 (8)	4.2 (3)
C(7)	0.1490 (4)	0.0602 (4)	0.6710 (8)	4.3 (3)
C(8)	0.1921 (5)	−0.0162 (5)	0.7444 (12)	5.7 (4)
C(9)	0.2259 (5)	−0.0069 (5)	0.8949 (11)	6.1 (4)
C(10)	0.2187 (4)	0.0790 (5)	0.9713 (10)	5.7 (4)
C(11)	0.1741 (4)	0.1547 (4)	0.8931 (8)	4.5 (3)
N(12)	0.1400 (3)	0.1429 (3)	0.7506 (6)	3.8 (2)
C(13)	0.1621 (4)	0.2519 (5)	0.9553 (7)	4.4 (3)
N(14)	0.1212 (3)	0.3133 (4)	0.8529 (6)	4.3 (2)
C(15)	0.1060 (5)	0.4038 (4)	0.8979 (9)	4.9 (3)
C(16)	0.1294 (5)	0.4346 (6)	1.0445 (9)	5.6 (4)
C(17)	0.1708 (5)	0.3736 (6)	1.1474 (9)	5.8 (4)
C(18)	0.1886 (5)	0.2808 (6)	1.1035 (9)	5.6 (4)
Cl	0.1527 (1)	−0.2757 (1)	0.9463 (3)	6.2 (1)
O(1)	0.1753 (12)	−0.2406 (19)	0.8066 (30)	7.9 (10)
O(2)	0.0890 (17)	−0.2201 (18)	0.9900 (29)	10.2 (15)
O(3)	0.2119 (4)	−0.3262 (4)	1.0532 (8)	9.3 (4)
O(4)	0.0848 (6)	0.6612 (7)	0.8972 (12)	14.8 (6)
O(1)′[c]	0.2167 (11)	0.7626 (19)	0.8467 (38)	9.3 (11)
O(2)′[c]	0.1264 (16)	0.8110 (12)	1.0451 (25)	8.0 (11)

[a] Estimated standard deviations in the last significant digits are given in parentheses. [b] $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}\cdot\mathbf{a}_i^*\cdot\mathbf{a}_j^*\cdot\mathbf{a}_i\cdot\mathbf{a}_j$. [c] Primed atom refers to two positions of the noted atom.

Table VII. Final Atomic Fractional Coordinates[a] and Equivalent Isotropic Displacement Parameters[b] for $[Cu_2(pmdien)_2(H_2O)_2(C_4O_4)](NO_3)_2$ (**6**)

atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{eq}, Å^2
Cu	0.09793 (3)	0.25506 (4)	0.74092 (7)	2.38 (3)
O(w)	−0.0036 (2)	0.1941 (3)	0.5492 (5)	3.5 (2)
C(O1)	0.0286 (3)	0.5642 (4)	0.5606 (6)	3.0 (2)
O(O1)	0.0973 (2)	0.3993 (3)	0.6633 (5)	3.4 (1)
C(O2)	0.0428 (3)	0.4542 (4)	0.5738 (6)	2.6 (2)
O(O2)	−0.0614 (2)	0.3582 (3)	0.3650 (5)	4.2 (2)
N(1)	0.0278 (3)	0.2972 (3)	0.9271 (5)	3.2 (2)
C(11)	−0.0603 (4)	0.3341 (5)	0.8682 (9)	4.0 (3)
C(12)	0.0757 (4)	0.3802 (5)	1.0281 (9)	4.3 (3)
C(2)	0.0251 (4)	0.2040 (5)	1.0304 (8)	4.0 (3)
C(3)	0.1100 (4)	0.1482 (5)	1.0457 (7)	3.8 (3)
N(4)	0.1279 (2)	0.1241 (3)	0.8750 (5)	2.7 (2)
C(41)	0.0798 (4)	0.0326 (4)	0.8101 (9)	3.9 (3)
C(5)	0.2205 (3)	0.1091 (4)	0.8726 (7)	3.3 (2)
C(6)	0.2366 (3)	0.1213 (4)	0.6964 (7)	3.4 (2)
N(7)	0.2043 (2)	0.2233 (3)	0.6318 (5)	2.8 (2)
C(71)	0.1835 (5)	0.2203 (7)	0.4483 (8)	4.8 (3)
C(72)	0.2701 (4)	0.3029 (5)	0.6819 (9)	3.9 (3)
O(1)	0.7122 (3)	0.6761 (4)	−0.1166 (7)	7.1 (3)
N(2)	0.6902 (3)	0.5925 (4)	−0.1801 (7)	4.5 (3)
O(3)	0.3747 (14)	0.4513 (15)	0.1349 (26)	5.9 (7)
O(4)	0.7205 (20)	0.5627 (21)	−0.2874 (35)	15.8 (20)
O(3)′[c]	−0.1174 (15)	0.0727 (18)	0.6928 (41)	11.3 (16)
O(4)′[c]	−0.2584 (7)	0.5365 (14)	0.7576 (27)	7.4 (8)

[a] Estimated standard deviations in the last significant digits are given in parentheses. [b] $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}\cdot\mathbf{a}_i^*\cdot\mathbf{a}_j^*\cdot\mathbf{a}_i\cdot\mathbf{a}_j$. [c] Primed atom refers to two positions of the noted atom.

Description of the Structures. $[Cu(bpy)(H_2O)(C_4O_4)]\cdot H_2O$ (1). The structure of **1** consists of discrete molecules of $[Cu(bpy)(H_2O)(C_4O_4)]$ linked by weak metal–ligand and hydrogen-bond interactions. The copper(II) ion displays a distorted square-planar coordination. The largest deviation from the mean plane of Cu, N(1), N(12), O(O1), and O(w1) is 0.032 (1) Å for Cu. The copper(II) ion is linked to the two nitrogen atoms of

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(21) In the structure of **4**, only 13 hydrogen atoms were obtained from a difference synthesis, and they were refined with an overall isotropic temperature factor.

(22) Supplementary material.

Table VIII. Selected Bond Distances (Å) and Angles (deg) for **1**[a]

	Distances		
Cu-O(w1)	1.967 (3)	C(O1)-C(O2)	1.446 (5)
Cu-O(O1)	1.933 (3)	C(O2)-O(O2)	1.267 (5)
Cu-N(1)	2.005 (3)	C(O2)-C(O3)	1.468 (5)
Cu-N(12)	1.995 (4)	C(O3)-O(O3)	1.240 (4)
Cu-O(O3)^{i}	2.541 (3)	C(O3)-C(O4)	1.491 (5)
Cu-O(O4)^{ii}	2.634 (3)	C(O4)-O(O4)	1.252 (5)
C(O1)-O(O1)	1.270 (4)	C(O4)-C(O1)	1.465 (5)
	Angles		
O(O1)-Cu-O(w1)	96.0 (1)	C(O4)-C(O1)-O(O1)	137.2 (3)
N(1)-Cu-O(w1)	94.4 (1)	C(O4)-C(O1)-C(O2)	90.8 (3)
N(1)-Cu-O(O1)	169.6 (1)	C(O4)-C(O3)-O(O3)	136.1 (3)
N(12)-Cu-O(w1)	175.0 (1)	C(O3)-C(O4)-C(O1)	89.3 (3)
N(12)-Cu-O(O1)	88.7 (1)	O(O4)-C(O4)-C(O1)	133.6 (3)
N(12)-Cu-N(1)	80.9 (1)	O(O4)-C(O4)-C(O3)	137.0 (3)
O(w1)-Cu-O(O3)^{i}	94.9 (1)	C(O1)-O(O1)-Cu	135.2 (2)
O(O1)-Cu-O(O3)^{i}	95.4 (1)	O(O2)-C(O2)-C(O1)	134.9 (3)
N(1)-Cu-O(O3)^{i}	84.0 (1)	C(O3)-C(O2)-C(O1)	90.9 (3)
N(12)-Cu-O(O3)^{i}	86.2 (1)	C(O3)-C(O2)-C(O2)	134.1 (3)
O(w1)-Cu-O(O4)^{ii}	80.0 (1)	O(O3)-C(O3)-C(O2)	135.0 (3)
O(O1)-Cu-O(O4)^{ii}	92.6 (1)	C(O4)-C(O3)-C(O2)	88.9 (3)
N(1)-Cu-O(O4)^{ii}	88.9 (1)	C(2)-N(1)-Cu	126.2 (3)
N(12)-Cu-O(O4)^{ii}	98.3 (1)	C(6)-N(1)-Cu	115.1 (3)
O(O3)^{i}-Cu-O(O4)^{ii}	170.9 (1)	C(7)-N(12)-Cu	115.0 (3)
C(O2)-C(O1)-O(O1)	132.0 (3)	C(11)-N(12)-Cu	124.2 (3)

[a] Roman numeral superscripts refer to the following symmetry operations: i = $1 - x, {}^{1}/_{2} - y, z - {}^{1}/_{2}$; ii = $1 - x, \bar{y}, 1 - z$.

bipyridine in a bidentate fashion, to a water molecule, and to an oxygen atom of the squarate ligand. A perspective view of **1** is depicted in Figure 1 and main bond distances and angles are given in Table VIII. The Cu-O(O1) bond length (1.933 (1) Å) is shorter than the Cu-O(w1) bond distance (1.967 (3) Å); this is due to the electronegative character of the $C_4O_4^{2-}$ ligand and leads to slight differences in copper-nitrogen bond lengths (1.995 (4) and 2.005 (3) Å for Cu-N(12) and Cu-N(1), respectively. The weaker metal-ligand interactions are Cu-O(O3)^{i} = 2.541 (3) Å and Cu-O(O4)^{ii} = 2.634 (3) Å, achieving a 4 + 2 distorted octahedral geometry around the copper(II) ion.

The squarate ligand is planar. The largest deviation from the mean plane is 0.004 (5) Å. The C-C and C-O average bond lengths and C-C-C and C-C-O average bond angles are 1.257 (12) and 1.467 (16) Å and 90.0 (9) and 135.2 (17)°, respectively. Large differences are observed in the C-C-O bond angles. The dihedral angle between the C_4O_4 and CuN_2O_2 mean planes is 19.2 (3)°.

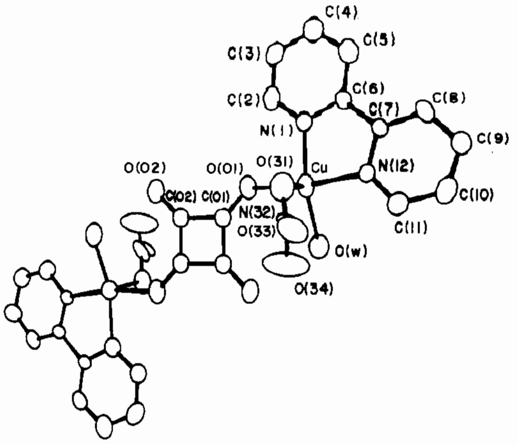

Figure 2. ORTEP view of complex **2** with the atom-numbering scheme.

The hydrogen-bonded network involving the two water molecules and the oxygen atoms O(O2)^{i}, O(O2)^{iii}, O(O4)^{iv}, and O(O3)^{v} is characterized in Table IX. These hydrogen-bonding interactions and the observed ones in the other five structures are illustrated by means of the corresponding stereodrawings (Figures SI-SVI).[22] The shortest intermolecular copper-copper distances are 5.340 (2) and 7.123 (2) Å for Cu···Cu^{ii} and Cu···Cu^{vi}, respectively (symmetry code vi = $x, y - {}^{1}/_{2}, {}^{1}/_{2} - z$).

[$Cu_2(bpy)_2(H_2O)_2(C_4O_4)$]($NO_3$)$_2$ (2). The structure of **2** is made of centrosymmetrical (μ-1,3-squarato)copper(II) binuclear units. A perspective view of the molecule is shown in Figure 2. Selected bond lengths and angles are given in Table X. The environment of each copper(II) ion is square pyramidal. The basal plane is built by two nitrogen atoms of bipyridine and two oxygen atoms, one of a water molecule and the other one of the squarate, whereas the apical position is occupied by an oxygen atom of a nitrate group. The Cu-N and Cu-O(w) bond distances are similar to those observed in the foregoing mononuclear complex. However, the C(O1)-O(O1) bond length (1.258 (3) Å) is slightly shorter than the one observed in this complex (1.270 (4) Å), which could explain the lengthening of the Cu-O(O1) bond (1.946 (2) Å in the binuclear compound and 1.933 (3) Å in the mononuclear one). The apical Cu-ONO$_2$ bond distance (2.344 (3) Å) is intermediate

Table IX. Hydrogen-Bonding Interactions[a,b] in Complexes **1-6**

compd	hydrogen atom	receptor atom	receptor atom position	H···O, Å	O···O, Å	angle, deg
1	H1(w1)-O(w1)	O(O2)	i	1.77 (6)	2.591 (5)	161 (4)
	H2(w1)-O(w1)	O(O4)	iv	1.89 (6)	2.706 (5)	164 (4)
	H1(w2)-O(w2)	O(O2)	iii	2.32 (6)	2.965 (5)	139 (5)
	H2(w2)-O(w2)	O(O3)	v	2.27 (6)	2.891 (6)	154 (5)
2	H1(w)-O(w)	O(33)	viii	2.14 (5)	2.808 (2)	149 (3)
	H2(w)-O(w)	O(O2)	ii	1.54 (5)	2.631 (2)	160 (3)
3	H2(w1)-O(w1)	O(O2)	ix		2.790 (4)	
	H2(w1)-O(w1)	O(O3)	ix		2.792 (4)	
	H1(w2)-O(w2)	O(w3)	ix	1.87 (4)	2.671 (4)	151 (3)
	H2(w2)-O(w2)	O(O4)	x	1.74 (4)	2.603 (4)	164 (3)
	H1(w3)-O(w3)	O(O2)	ix	1.84 (4)	2.769 (4)	166 (3)
	H2(w3)-O(w3)	O(w4)	iv	1.98 (4)	2.767 (4)	172 (3)
	H2(w3)-O(w4)	O(O3)	xi		2.762 (4)	
	H2(w3)-O(w4)	O(w4)	vii		2.917 (5)	
4	H1(w1)-O(w1)	O(O2)	iv	1.66 (7)	2.609 (6)	179 (6)
	H2(w1)-O(w1)	O(O3)	xiii	2.08 (7)	2.549 (6)	176 (6)
	H1(w2)-O(w2)	O(O4)	x		2.859 (9)	
	H1(w2)′-O(w2)′	O(O4)	x		2.721 (9)	
5	H1(w)-O(w)	O(2)	xv	2.16 (9)	2.96 (4)	169 (9)
	H1(w)-O(w)	O(2)′	xv	2.01 (9)	2.76 (4)	156 (9)
	H2(w)-O(w)	O(O2)	iv	2.36 (7)	2.690 (6)	119 (6)
6	H1(w)-O(w)	O(O2)	iv	1.81 (6)	2.692 (5)	170 (5)
	H2(w)-O(w)	O(3)	iv	1.98 (8)	2.86 (1)	172 (7)
	H2(w)-O(w)	O(3)′	iv	1.91 (8)	2.78 (1)	157 (7)

[a] Primed atom refers to two positions of the noted atom. [b] iii = $1 - x, {}^{1}/_{2} - y, z - {}^{1}/_{2}$; iv = x, y, z; v = ${}^{3}/_{2} - x, y, z - {}^{1}/_{2}$; vii = $\bar{x}, \bar{y}, 1 - z$; viii = ${}^{1}/_{2} - x, {}^{1}/_{2} + y, {}^{1}/_{2} - z$; ix = $1 - x, 1 - y, \bar{z}$; x = $1 - x, \bar{y}, \bar{z}$; xi = $x - 1, y, z$; xiii = ${}^{3}/_{2} - x, {}^{1}/_{2} + y, \bar{z}$; xv = $\bar{x}, 1 - y, 2 - z$.

Table X. Selected Bond Distances (Å) and Angles (deg) for **2**

Distances			
Cu–O(w)	1.972 (2)	C(O1)–O(O1)	1.248 (3)
Cu–O(O1)	1.946 (2)	C(O2)–C(O1)	1.456 (4)
Cu–N(1)	2.000 (2)	C(O2)^{vii}–C(O1)	1.465 (4)
Cu–N(12)	1.993 (2)	O(O2)–C(O2)	1.247 (3)
Cu–O(31)	2.344 (3)		
Angles			
O(O1)–Cu–O(w)	96.5 (1)	C(O2)–C(O1)–O(O1)	131.7 (2)
N(1)–Cu–O(w)	162.4 (1)	C(O2)^{vii}–C(O1)–O(O1)	137.5 (2)
N(1)–Cu–O(O1)	89.2 (1)	C(O2)^{vii}–C(O1)–C(O2)	90.8 (2)
N(12)–Cu–O(w)	92.6 (1)	O(O2)–C(O2)–C(O1)	135.3 (2)
N(12)–Cu–O(O1)	170.7 (1)	C(O1)^{vii}–C(O2)–C(O1)	89.2 (3)
N(12)–Cu–N(1)	81.6 (1)	O(O2)–C(O2)–C(O1)^{vii}	135.4 (2)
O(31)–Cu–O(w)	103.9 (1)	C(2)–N(1)–Cu	127.2 (2)
O(31)–Cu–O(O1)	93.0 (1)	C(7)–N(12)–Cu	114.3 (2)
O(31)–Cu–N(1)	92.4 (1)	C(6)–N(1)–Cu	114.4 (2)
O(31)–Cu–N(12)	86.2 (1)	C(11)–N(12)–Cu	125.9 (2)
C(O1)–O(O1)–Cu	129.8 (2)	N(32)–O(31)–Cu	117.4 (2)

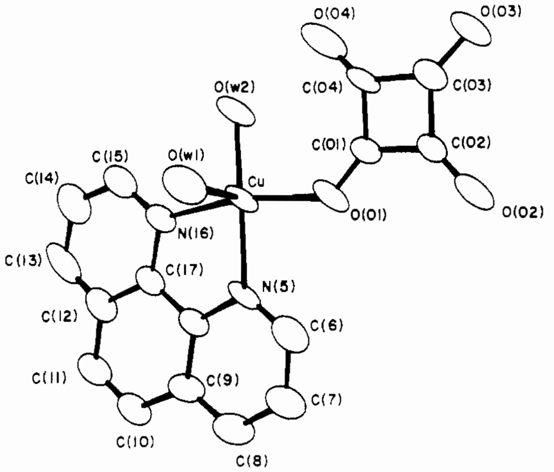

Figure 3. ORTEP view of complex **3** with the atom-labeling scheme.

between the one observed in the five-coordinate complex (nitrato)(trichloroacetato)bis(2,9-dimethyl-1,10-phenanthroline)copper(II) trichloroacetic acid solvate (2.15 (4) Å),[23] and the observed in the six-coordinated complex (nitrato)(salicylaldehydato)(1,10-phenanthroline)copper(II) (2.402 (3) Å).[24] Another oxygen atom of the nitrate group (O(34)) is weakly linked to the copper(II) ion (2.998 (3) Å), at opposite to O(31). This fact has also been observed in the last-mentioned compound where the Cu–ONO2 distance is equal to 2.781 (3) Å. The squarate is planar (largest deviation from the mean plane is −0.004 (3) Å for C(O2)^{vii}). The dihedral angle between the basal copper plane and the squarate plane is 18.3°.

The packing of the molecules is due to van der Waals forces and to hydrogen bonds between O(w)–H2(w)···O(O2)^{ii} and O(w)–H1(w)···O(33)^{viii} (see Table IX). The intramolecular Cu···Cu^{vii} separation is 7.690 (1) Å while the shortest intermolecular Cu···Cu^{viii} distance amounts to 5.441 (1) Å.

Table XI. Selected Bond Distances (Å) and Angles (deg) for **3**

Distances			
Cu–O(w2)	1.964 (2)	C(O2)–O(O2)	1.252 (4)
Cu–O(O1)	1.967 (2)	C(O2)–C(O3)	1.482 (4)
Cu–N(5)	2.019 (2)	C(O3)–O(O3)	1.245 (3)
Cu–N(16)	2.048 (2)	C(O3)–C(O4)	1.484 (4)
Cu–O(w1)	2.297 (2)	C(O4)–O(O4)	1.257 (4)
C(O1)–O(O1)	1.257 (3)	C(O4)–C(O1)	1.456 (4)
C(O1)–C(O2)	1.460 (4)		
Angles			
O(w2)–Cu–O(w1)	95.9 (1)	C(O4)–C(O1)–O(O1)	136.6 (3)
O(w1)–Cu–O(O1)	93.5 (1)	C(O4)–C(O1)–C(O2)	91.8 (2)
O(w2)–Cu–O(O1)	97.4 (1)	C(O1)–C(O2)–O(O2)	135.7 (2)
O(w1)–Cu–N(5)	92.5 (1)	C(O3)–C(O2)–O(O2)	135.2 (2)
O(w2)–Cu–N(5)	169.8 (1)	C(O3)–C(O2)–C(O1)	89.2 (2)
O(O1)–Cu–N(5)	87.9 (1)	C(O2)–C(O3)–O(O3)	135.1 (3)
O(w1)–Cu–N(16)	96.2 (1)	C(O4)–C(O4)–O(O3)	135.1 (3)
O(w2)–Cu–N(16)	91.8 (1)	C(O4)–C(O3)–C(O2)	89.8 (2)
O(O1)–Cu–N(16)	165.9 (1)	C(O1)–C(O4)–O(O4)	135.2 (3)
N(5)–Cu–N(16)	81.5 (1)	C(O3)–C(O4)–O(O4)	135.5 (3)
C(O2)–C(O1)–O(O1)	131.7 (3)	C(O3)–C(O4)–C(O1)	89.3 (2)

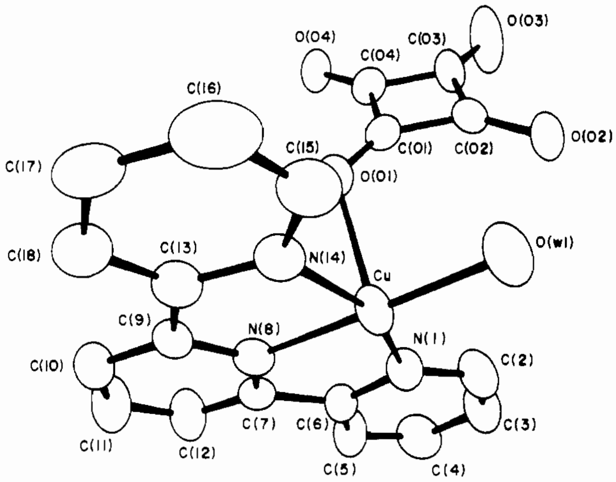

Figure 4. ORTEP view of complex **4** with the atom-numbering scheme.

[Cu(phen)(H_2O)$_2$(C_4O_4)]·2H_2O (3). The crystal structure of **3** consists of mononuclear units in which the copper(II) ion surrounding is square pyramidal. An oxygen atom (O(w1)) from a water molecule is in the apical position. Two nitrogen atoms (N(5) and N(16)) from phen and two oxygen atoms, one from the squarate (O(O1)) and the other one from a water molecule, (O(w2)) build the basal plane (see Figure 3). Main bond distances and angles for non-hydrogen atoms are listed in Table XI. N(5), N(16), O(O1), and O(w2) atoms fall on a plane: the largest deviation from the mean plane is −0.017 (3) Å for N(5). The copper(II) ion is −0.158 (2) Å out of this plane. The average value for the copper–nitrogen distance is 2.033 (14) Å, which is shorter than the observed one (2.05 (1) Å) in the complex *trans*-bis(1,10-phenanthroline)copper(II)[25] and larger than the reported one (1.998 (11) Å) for other (1,10-phenanthroline)copper(II) complexes.[24,26,27] The Cu–O(O1) bond length in **3** (1.967 (2) Å) is larger than the corresponding one in **1** (1.933 (3) Å) probably due to the lengthening of the trans copper–nitrogen bond (2.048 (2) and 1.995 (4) Å in **3** and **1**, respectively). C(O1)–O(O1) bond distances in **3** and **1** are nearly identical (1.275 (3) and 1.270 (4) Å respectively), but they are larger than the other carbon–oxygen bond lengths of the squarate. This lengthening is due to the coordination of O(O1) to the metal ion. The squarate is planar. The largest deviation from the mean plane is 0.016 (11) Å for O(O3). The dihedral angle between the copper basal plane and the squarate plane is only 9.3°.

Distances and angles for hydrogen-bonding interactions are listed in Table IX. The shortest intermolecular Cu···Cu^{x} distance is 4.244 (1) Å.

[Cu(terpy)(H_2O)(C_4O_4)]·H_2O (4). The crystal structure of **4** is made of chains of Cu(terpy)(H_2O) units built up by 1,2-squarato-bridged copper(II) ions. Each copper(II) ion displays a distorted octahedral coordination. It is linked to three nitrogen atoms (N(1), N(8), N(14)) and an oxygen atom O(w1) from a water molecule in the equatorial plane; the largest deviation from the mean plane is 0.011 (6) Å for N(14) and N(1) atoms. Two oxygen atoms, O(O1) and O(O2)^{xii}, from different squarates are

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Table XII. Selected Bond Distances (Å) and Angles (deg) for **4**[a]

	Distances		
Cu–N(1)	2.047 (5)	C(O1)–C(O2)	1.448 (7)
Cu–N(8)	1.940 (4)	C(O2)–O(O2)	1.276 (6)
Cu–N(14)	2.048 (5)	C(O2)–C(O3)	1.445 (8)
Cu–O(w1)	1.936 (4)	C(O3)–O(O3)	1.246 (7)
Cu–O(O1)	2.333 (4)	C(O3)–C(O4)	1.462 (8)
Cu–O(O2)^{xii}	2.514 (4)	C(O4)–O(O4)	1.257 (6)
C(O1)–O(O1)	1.257 (6)	C(O4)–C(O1)	1.458 (7)
	Angles		
N(8)–Cu–N(1)	80.1 (2)	C(O4)–C(O1)–O(O1)	133.7 (5)
N(14)–Cu–N(1)	159.5 (2)	C(O4)–C(O1)–C(O2)	89.9 (4)
N(14)–Cu–N(8)	79.4 (2)	O(O2)–C(O2)–C(O1)	135.3 (5)
O(O1)–Cu–N(1)	91.4 (2)	C(O3)–C(O2)–C(O1)	90.7 (4)
O(O1)–Cu–N(8)	89.3 (2)	C(O3)–C(O2)–O(O2)	134.0 (5)
O(O1)–Cu–N(14)	89.5 (2)	O(O3)–C(O3)–C(O2)	135.4 (6)
O(w1)–Cu–N(1)	101.1 (2)	C(O4)–C(O3)–C(O2)	89.8 (5)
O(w1)–Cu–N(8)	178.8 (2)	C(O4)–C(O3)–O(O3)	134.7 (6)
O(w1)–Cu–N(14)	99.4 (2)	C(O3)–C(O4)–C(O1)	89.6 (4)
O(w1)–Cu–O(O1)	90.8 (2)	O(O4)–C(O4)–C(O1)	134.7 (5)
O(O2)^{xii}–Cu–N(1)	94.6 (2)	O(O4)–C(O4)–C(O3)	135.6 (5)
O(O2)^{xii}–Cu–N(8)	88.1 (2)	C(2)–N(1)–Cu	128.2 (4)
O(O2)^{xii}–Cu–N(14)	83.4 (2)	C(6)–N(1)–Cu	113.9 (4)
O(O2)^{xii}–Cu–O(O1)	172.8 (2)	C(7)–N(8)–Cu	118.3 (4)
O(O2)^{xii}–Cu–O(w1)	91.4 (2)	C(9)–N(8)–Cu	118.8 (4)
C(O2)–C(O1)–O(O1)	136.4 (5)	C(O1)–O(O1)–Cu	128.0 (3)

[a] Roman numeral superscript xii refers to equivalent position $^3/_2 - x$, $y + {}^1/_2$, $1 - z$.

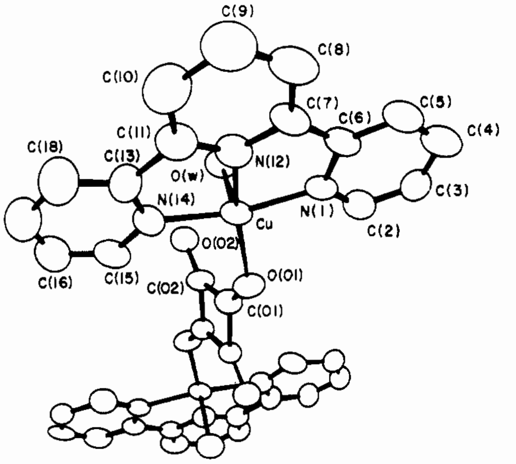

Figure 5. ORTEP view of the binuclear cation $[Cu_2(terpy)_2(H_2O)_2(sq)]^{2+}$ with the atom-labeling scheme.

located in the apical sites. A view of the molecule, along with the numbering scheme, is shown in Figure 4. Selected bond lengths and angles are listed in Table XII. The copper–nitrogen distances vary from 2.047 (5) and 2.048 (5) Å for nitrogen atoms in the trans position to 1.940 (4) Å for the nitrogen atom in the trans position to the oxygen atom from the coordinated water molecule. This variation is also observed in the structure of complex **5**. The observed angles range from 79.4 (2) (N(14)–Cu–N(8)) to 110.1 (2)° (O(w1)–Cu–N(1). The five-membered rings C_2N_2Cu have an envelope form with C(7) (for the Cu, N(1), C(6), C(7), and N(8) ring) and N(8) (for the Cu, N(14), C(13), C(9), and N(8) ring) atoms out of the plane defined by the remaining four atoms (N(8)–Cu–N(1)–C(6) and Cu–N(14)–C(13)–C(9) torsion angles equal to 0.0 (2)°. The squarate is planar (largest deviation from the mean plane is 0.019 (6) Å for O(O1)), and it does not exhibit the large differences in the C–C–O angles as observed in the other five structures reported herein. The dihedral angle between the squarate and Cu(terpy)(H_2O) mean planes is 76.6°. The distance between the mean planes of two adjacent terpy ligands is 3.61 (1) Å.

The oxygen atom O(w1) from the coordinated water molecule acts as a proton donor to O(O2)^{iv} and O(O3)^{xiii} atoms, whereas the oxygen atom O(w2) of the disordered water molecule is hydrogen bonded to O(O4)^{x} (see Table IX).

Table XIII. Selected Bond Distances (Å) and Angles (deg) for **5**[a]

	Distances		
Cu–O(O1)	1.946 (3)	C(O1)–O(O1)	1.255 (6)
Cu–N(1)	2.029 (5)	C(O1)–C(O2)	1.461 (7)
Cu–N(12)	1.935 (4)	C(O2)–O(O2)	1.230 (6)
Cu–N(14)	2.055 (5)	C(O1)–C(O2)^{xvi}	1.486 (6)
Cu–O(w)	2.224 (5)		
	Angles		
O(O1)–Cu–O(w)	97.9 (2)	C(O2)^{xvi}–C(O1)–O(O1)	132.2 (5)
N(1)–Cu–O(w)	92.5 (2)	C(O2)^{xvi}–C(O1)–C(O2)	90.8 (5)
N(1)–Cu–O(O1)	96.1 (2)	C(O1)^{xvi}–C(O2)–C(O1)	89.2 (5)
N(12)–Cu–O(w)	106.5 (2)	O(O2)–C(O2)–C(O1)	135.5 (5)
N(12)–Cu–O(O1)	155.5 (2)	O(O2)–C(O2)–C(O1)^{xvi}	135.3 (5)
N(12)–Cu–N(1)	80.4 (2)	C(2)–N(1)–Cu	128.0 (4)
N(14)–Cu–O(w)	95.1 (2)	C(6)–N(1)–Cu	114.3 (4)
N(14)–Cu–O(O1)	100.8 (2)	C(7)–N(12)–Cu	118.4 (4)
N(14)–Cu–N(1)	160.3 (2)	C(11)–N(12)–Cu	118.5 (4)
N(14)–Cu–N(12)	80.8 (2)	C(13)–C(14)–Cu	113.7 (4)
C(O1)–O(O1)–Cu	131.7 (3)	C(15)–N(14)–Cu	127.8 (5)
C(O2)–C(O1)–O(O1)	137.0 (5)		

[a] Roman numeral superscript xvi refers to equivalent position $\bar{x}$, $1 - y$, $1 - z$.

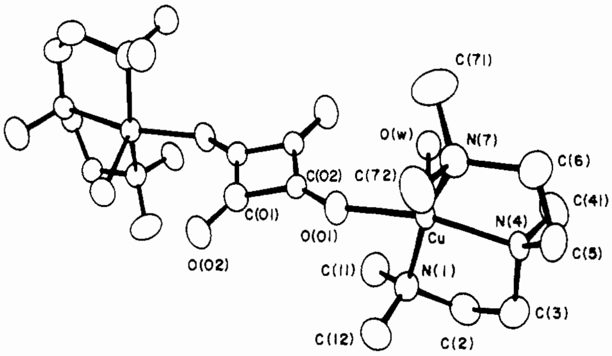

Figure 6. ORTEP view of the binuclear cation $[Cu_2(pmdien)_2(H_2O)_2(sq)]^{2+}$ with the atom numbering scheme.

The shortest intrachain Cu···Cu^{xiv} separation is 7.770 (1) Å (symmetry code xiv = $\bar{x}$, $1 - y$, $\bar{z}$).

$[Cu_2(terpy)_2(H_2O)_2(C_4O_4)](ClO_4)_2$ (5). The structure of **5** consists of (μ-1,3-squarato)copper(II) binuclear cations and perchlorate groups. A view of the binuclear cation $[Cu_2(terpy)_2(H_2O)_2(C_4O_4)]^{2+}$ is depicted in Figure 5. A crystallographic inversion center stands at the middle of the C_4O_4 mean plane of the squarate. Each copper(II) ion is surrounded by a pyramid, the square basis of which is formed by O(O1), N(1), N(12), and N(14) atoms (largest deviation from the mean plane equal to −0.013 (7) Å); the apical position is occupied by the oxygen atom O(w) of a water molecule. Selected bond distances and angles are listed in Table XIII.

The Cu–O(O1) bond length (1.946 (3) Å) is shorter than the corresponding one in compound **4**. The squarate ligand is planar (largest deviation from the main plane is 0.005 (3) Å for O(O2)^{xvi}). The C(O1)–O(O1) bond length (1.255 (6) Å) is larger than the C(O2)–O(O2) distance (1.230 (6) Å) observed in complex **2** (1.258 (3) and 1.247 (3) Å, respectively). The coordination of O(O1) to the copper(II) ion causes this lengthening in the carbon–oxygen bond length. The remaining bond distances and angles of this ligand are similar to the ones observed in **2**, showing also the large differences in the C–C–O angles. The angle between the copper basal plane and the squarate plane is 62.4 (3)°.

The perchlorate anions are hydrogen bonded to apical water molecules (see Table IX). The shortest intramolecular Cu···Cu^{xvi} distance is 7.770 (1) Å.

$[Cu_2(pmdien)_2(H_2O)_2(C_4O_4)](NO_3)_2$ (6). The structure of **6** consists of (μ-1,3-squarato)copper(II) binuclear cations and uncoordinated nitrate anions. A view of the binuclear unit with numbering scheme is shown in Figure 6. A crystallographic inversion center stands in the middle of the C_4O_4 mean plane of the squarate. The environment of each copper(II) ion is square pyramidal: the three nitrogen atoms N(1), N(4), and N(7) of the triamine and the oxygen atom O(O1) of the squarate build

Table XIV. Selected Bond Distances (Å) and Angles (deg) for **6**

	Distances		
Cu–O(O1)	1.977 (3)	C(O1)–O(O1)	1.265 (5)
Cu–N(1)	2.089 (4)	C(O1)–C(O2)	1.446 (6)
Cu–N(4)	2.041 (3)	C(O2)–O(O2)	1.250 (5)
Cu–N(7)	2.059 (4)	C(O2)–C(O1)^{xvi}	1.476 (6)
Cu–O(w)	2.220 (4)		
	Angles		
O(O1)–Cu–O(w)	98.1 (1)	O(O1)–C(O1)–C(O2)^{xvi}	136.3 (3)
N(1)–Cu–O(w)	101.9 (1)	C(O2)–C(O1)–C(O2)^{xvi}	90.6 (3)
N(1)–Cu–O(O1)	90.6 (2)	C(O2)–C(O1)–O(O1)	133.1 (4)
N(4)–Cu–O(w)	99.8 (1)	C(11)–N(1)–Cu	114.8 (4)
N(4)–Cu–O(O1)	162.1 (1)	C(12)–N(1)–Cu	108.3 (3)
N(4)–Cu–N(1)	85.9 (2)	C(2)–N(1)–Cu	105.6 (3)
N(7)–Cu–O(w)	99.8 (1)	C(3)–N(4)–Cu	105.6 (3)
N(7)–Cu–O(O1)	90.9 (1)	C(41)–N(4)–Cu	114.3 (3)
N(7)–Cu–N(1)	157.8 (2)	C(5)–N(4)–Cu	104.6 (3)
N(7)–Cu–N(4)	85.9 (2)	C(6)–N(7)–Cu	106.4 (3)
C(O1)–O(O1)–Cu	133.7 (3)	C(71)–N(7)–Cu	111.8 (3)
C(O1)–C(O2)–C(O1)^{xvi}	89.4 (3)	C(72)–N(7)–Cu	108.9 (3)
C(O1)^{xvi}–C(O2)–O(O2)	135.3 (3)		

Table XV. IR Bands Attributable to the Squarate Ligand in the 1850–1500-cm^{-1} Region and Electronic Spectral Data for Complexes **1–6**

	infrared^a			
compd	ν(C=O)	ν(C=C)	ν[(C–C) + (C–O)]	visible^b reflectance
1	1780 w	1620 w	1520 s, br 1490 s 1450 s	680 405
2	1730 w	1610 m	1525 s 1480 s	660 410
3	1715 w	1580 m	~1500 s, br	710 420
4	1710 w	1600 m	1530 s, br	705 380
5	1705 w 1780 w	1610 m	1530 s, br	700 430
6	1740 w	1600 m	1535 s 1500 s	650 415

^{a}Band assignment after ref 11b. Key: br = broad, m = medium intensity, w = weak intensity. ν values are given in cm^{-1}. $^b\lambda$ values are given in nm.

the basal plane; the apical site is occupied by the oxygen atom O(w) of a water molecule. The largest deviation from the mean basal plane is –0.039 (7) Å and the copper(II) ion is –0.351 (4) Å out of this plane. Selected bond lengths and angles are listed in Table XIV.

The squarate is planar (largest deviation –0.0117 Å) as in the preceding structures. The dihedral angle between the basal plane and the squarate plane is 92.0 (4)°. This value is larger than the ones found in the other two (μ-1,3-squarato)copper(II) binuclear compounds, complexes **5** (62.4 (3)°) and **2** (18.7 (4)°). This structural feature could be attributed to the increasing steric hindrance between terminal amine ligands and squarato bridge, when going from diamines (bpy) to triamines (terpy or pmdien). The C(O1)–O(O1) and C(O2)–O(O2) bond distances are similar (1.250 (5) and 1.265 (5) Å, respectively) as in complex **2**. Hydrogen-bonding interactions are listed in Table IX. The shortest intramolecular Cu···Cu^{xvi} distance is 7.874 (1) Å.

Infrared and Electronic Spectra. The IR bands attributable to the squarate ligand in the region 1800–1500 cm^{-1} are given in Table XV for complexes **1–6**. All of them show strong bands at ca. 1500 cm^{-1} and two other bands in the 1620–1600- and 1800–1700-cm^{-1} regions. Both position and intensity of these bands are similar to the reported ones for squaric acid.[28] The presence of localized C=O bonds is evidenced by the occurrence of the weak bands at higher energy. Some differences are observed in the lower energy bands: only one strong band at 1500 cm^{-1} is observed for the binuclear compound **5** whereas this band is split for the binuclear compounds **2** and **6**. The IR spectra in the 1800–1500-cm^{-1} region for **4** and **5**, in which the squarate acts as 1,2-bismonodentate and 1,3-bismonodentate bridging ligands, respectively, are nearly identical. The mononuclear compound **3** shows a strong band centered at 1500 cm^{-1}; however, for compound **1** this band is split into three peaks (1520, 1490, and 1450 cm^{-1}) probably due to the chain structure.

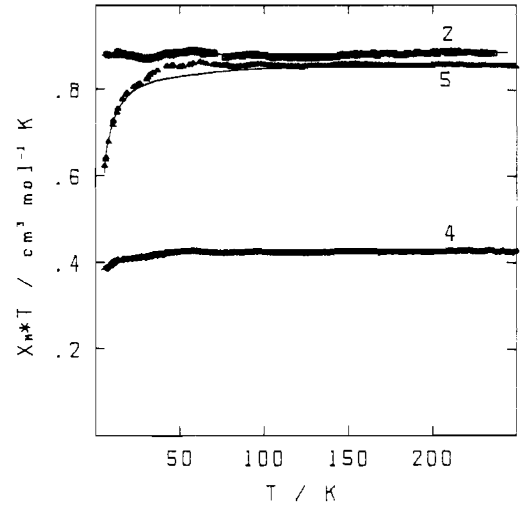

Figure 7. Thermal variation of the molar susceptibility of compounds **2**, **4**, and **5**. The solid line represents the best fit to data.

Table XVI. EPR Data for Complexes **1–6**

	1	**2**	**3**	**4**	**5**	**6**
g, g_1	2.17	2.19	2.26	2.23	2.05	2.21
g, g_2	2.05	2.13	2.08	2.08	2.02	2.08
g_3	2.01	2.05				
half-field transition		yes	yes	yes	yes	yes

Reflectance data of the visible electronic spectra for complexes **1–6** are summarized in Table XV. All six complexes exhibit two bands in the regions 710–650 and 430–380 nm, which correspond to d–d and charge-transfer bands respectively.

The visible spectra of compounds **1**, **2**, **4**, and **6** in methanol are very similar to the spectra of the crystalline complexes. Small differences are only observed in spectra of compound **4**, which could be due to structural modifications and solvent effects when this polymeric compound is dissolved in methanol. The UV spectra of all complexes display a band centered at ca. 270 nm corresponding to an absorption within the squarate dianion. The position of this band is insensitive to the mode of coordination as was already pointed out.[9]

Conductivity measurements of complexes **1**, **2**, **4**, **5**, and **6** in methanolic solutions revealed that **1** and **4** are nonconductors, whereas **2**, **5**, and **6** exhibited conductivity values within the normal range of 2:1 electrolytes.[29] Thus, it appears that the binuclear nature of compounds **2**, **5**, and **6** is preserved in this medium. Because of limited solubility, the conductivity of complex **3** could not be measured.

Magnetic Properties and EPR Spectra. The thermal variation of the molar magnetic susceptibility of complexes **2**, **4**, and **5** reveals weak copper(II)–copper(II) exchange interactions (Figure 7). The product $\chi_M T$ versus T remains practically constant between room temperature and 20 K with a small decrease down to 4.2 K ($J \sim 0$ for **2**; $J = -0.35$ cm^{-1} and $g = 2.075$ for **4**; $J = -3.6$ cm^{-1} and $g = 2.13$ for **5**). This magnetic behavior can be easily understood by considering the weak overlap between the magnetic orbitals through the μ-1,3-bismonodentate or μ-1,2-bismonodentate squarate bridging ligand as illustrated in Figure 8. In all the cases the overall overlap integral between the magnetic orbitals is practically zero. In the approximation where

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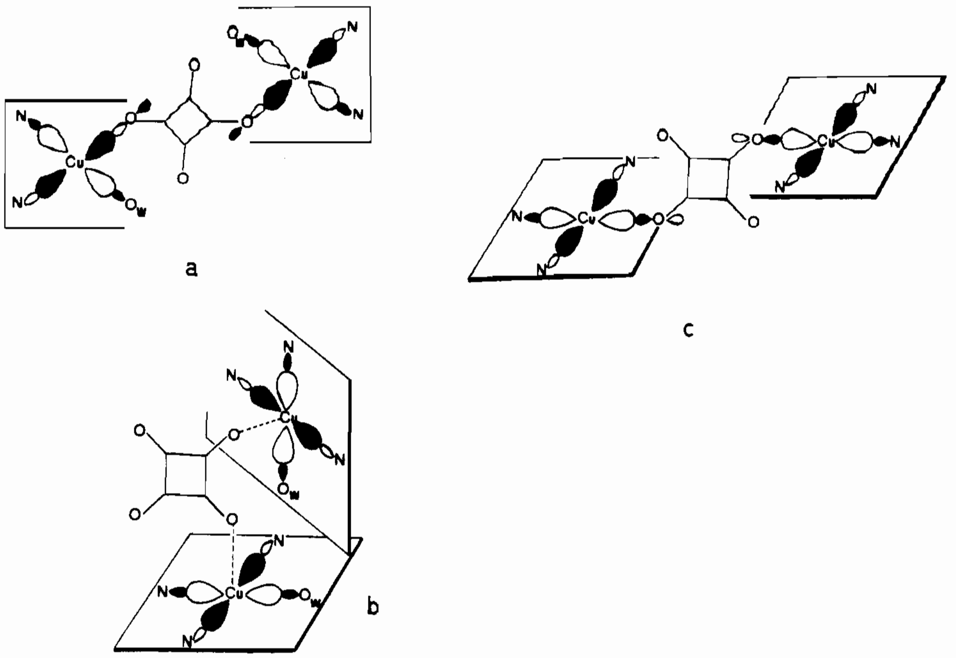

Figure 8. Schematic drawings of magnetic orbitals showing the weakness of overlap in complexes **2**, **4**, and **5**. (a) In **2**, magnetic orbitals are coplanar; (b) in **4**, magnetic orbitals are practically in perpendicular planes; (c) in **5**, magnetic orbitals are in roughly parallel planes.

$J_{ST} \propto S^2$,[30] the singlet–triplet gap is very small.

Main features of X-band EPR spectra for all six complexes are given in Table XVI. The spectra remain unchanged when the temperature is decreased, and they are characteristic of axial symmetry with $g_\parallel > g_\perp$. The half-field forbidden transition appears at room temperature and at low temperatures in complexes **2**–**6**. In the binuclear complexes **2**, **5**, and **6**, it could be interpreted as a $\Delta M_s = 2$ forbidden transition in the triplet, but this interpretation is no longer valid in the structurally characterized mononuclear complex **3** and in the chain complex **4**, where interactions between Cu(II) at larger distances occur. Such a situation is not rare and has been observed and commented on by some of us.[31]

Discussion

The versatility of squarate as a ligand is illustrated by the variety of the structures reported herein. However, this ligand always coordinates to the metal ion through only one oxygen atom and never in a bidentate fashion. It occupies an equatorial position of the coordination sphere of the metal ion in complexes **1** and **3**, yielding a short copper–oxygen bond (average value 1.95 Å), whereas it fills an axial position in complex **4**, yielding a weaker interaction with copper(II) (2.333 (4) Å for the Cu–O(O1) bond distance). It deserves to be noted that in this complex a water molecule occupies an equatorial position, giving a shorter copper–oxygen bond.

The squarate dianion is potentially a good bridging ligand due to the availability of its four oxygen donor atoms. In fact, only complex **3** is strictly mononuclear. In complex **4**, each squarate acts in an asymmetrically 1,2-bismonodentate fashion, filling two axial positions of two copper(II) ions to yield one-dimensional chains. Complex **1** consists of a polymeric arrangement of Cu(bpy)(H_2O)(C_4O_4) units in which the squarate is asymmetrically linked to three copper(II) ions.

Complexes **1** and **4** are easily soluble in methanol, leading to nonconductor solutions that could contain mononuclear species. Curiously, complex **3** is sparingly soluble in methanol, probably due to the network of hydrogen bonds that occur in the crystal.

Complexes **2**, **5**, and **6** are binuclear, the squarate acting in a symmetrical 1,3-bismonodentate fashion and occupying equatorial positions in the coordination sphere of the metal ions. Conductivity measurements support the existence of these binuclear units in methanolic solution. Nevertheless, a study that we have carried out on the interaction between Cu(bpy)$^{2+}$ and sq^{2-} in dilute aqueous solutions reveals the formation of only a mononuclear species.[32] In fact, complex **1** is the only species that is obtained from aqueous solutions containing Cu(bpy)$^{2+}$ and sq^{2-} at different copper–squarate molar ratios. A Cu(bpy)$^{2+}$:sq^{2-} 1:2 molar ratio has been used in the synthetic procedure of complex **1** because under these conditions X-ray suitable crystals of **1** are obtained. Only the presence of a great excess of Cu(bpy)$^{2+}$ allowed us to obtain crystals of **2**.

On the contrary, **5** and **6** are isolated easily from aqueous solutions containing the reagents in the stoichiometric ratio. This fact can be related to structural features: the squarate occupies axial positions in the mononuclear species involving terpy and probably pmdien ligands, whereas it fills equatorial positions in the binuclear complexes. This behavior is different from the observed one for the bpy system.

We would like to comment on the IR data of squarato complexes in view of our structural results. It has been pointed out that infrared spectra of squarate-containing complexes are characteristic of the coordination mode.[9,10,11b] complexes of squarate anion with M(II), where M = Mn, Fe, Co, Ni, and Zn, are isostructural and the squarate acts as a tetramonodentate ligand through all four oxygen atoms.[14a] The IR spectra of these compounds show a strong band at ca. 1500 cm^{-1}, which has been assigned to a mixture of C–C and C–O stretching vibrations.[33] The highest IR band of the squarate ligand in a structurally characterized (μ-1,3-squarato)nickel(II) chain[16a] occurred at 1480 cm^{-1}. IR data were used to predict the binding of the squarate ligand either in a 1,2-bismonodentate or in a 1,2-bidentate fashion in coordination compounds of Ti(IV),[34] V(III),[10] and Fe(III).[11] However, these predictions have not been confirmed by X-ray diffraction data. On the basis of IR, magnetism, and EPR data a series of mononuclear and binuclear copper(II)–squarate complexes,[9] it has been suggested that the squarate ligand could coordinate in a 1,2-bidentate fashion for the mononuclear complexes and in a 1,2-bismonodentate fashion for the binuclear ones. It has been also postulated that the squarate is binding in a

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Table XVII. Structural Parameters for Squarate and Related Ligands

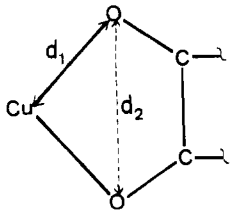
bridging ligand	d(C–O), Å	d(C–C), Å	∠O–C–C, deg	d_1, Å	d_2, Å	bite parameter
oxalate[a]	1.24	1.56	115.5	1.97	2.63	1.34
chloranilate;[b] (iodanilate)[c]	1.26 (1.27)	1.54 (1.52)	116 (115)	1.96 (1.95)	2.61 (2.50)	1.33 (1.28)
squarate[d]	1.26	1.465	137.2	1.95	3.31	1.70

[a] Averaged values from refs 3–5. [b] Averaged values from refs 7 and 35. [c] Values from ref 6b. [d] This work.

bisbidentate fashion in the compounds [Cu$_2$(Etdien)$_2$sq)](BF$_4$)$_2$,[5] [Ni$_2$(macro)$_2$sq](ClO$_4$)$_2$[8] and [Cu$_2$(Et$_4$dien)$_2$sq](PF$_6$)$_2$.[9] All three complexes show a strong band in the 1800–1500-cm^{-1} region. Very recently, it has been assumed that the HC$_4$O$_4^-$ anion acts in a 1,2-bidentate fashion in compounds or formula [M(HC$_4$O$_4$)Cl(EtOH)]$_2$·EtOH[12] where M = Fe(II) and Ni(II). Nevertheless, our results clearly show that these conclusions are imprudent or at least questionable: a comparison of the IR spectra with the molecular structures of the six copper(II) squarato complexes herein reported shows no general correlation between the coordination mode of the squarate ligand and the number and position of the IR bands, illustrating once more the risks associated with assignments of structures from IR data, when a structure is unavailable.

When undertaking this work, we addressed ourselves to two main questions: (i) Is it possible to demonstrate structurally the binding ability of the squarate dianion between two copper(II) ions in a binuclear complex or in a chain? If so, is it possible to provide evidence for the bidentate and the bisbidentate characters of the squarate ligand that have been often suggested but never demonstrated?

Our experimental results enable us to answer yes to the first question, but unfortunately, we could not demonstrate the bidentate and a fortiori the bisbidentate character of the squarate ligand. One means to characterize the chelating ability is to compute the bite parameter,[36] $b = d_2/d_1 = d(\mathrm{O{-}O})/d(\mathrm{Cu{-}O})$, for



The calculated values of the bite parameter for the squarate and related oxalate, chloranilate, and iodanilate ligands are given in Table XVII. The average values of the carbon–oxygen and copper–oxygen distances are very close for all three ligands whereas large differences are observed in the magnitudes of the O–C–C angle, d_2, and C–C distances of the squarate with respect to the ones in oxalate, chloranilate, and iodanilate. The estimated value of the bite parameter for a bidentate squarate ligand is 1.70, whereas the greatest reported value for a bidentate ligand is only 1.52.[36] A value of 2.47 Å is obtained for d_1 when we use the values of the bite parameter of the oxalate and the d_2 bite of the squarate. Therefore, we can conclude that the squarate ligand could act as a bidentate ligand only in an asymmetric fashion or in a symmetric one with an average copper–oxygen distance of about 2.47 Å. This value is out of the normal range for nearest neighbor copper–oxygen bond lengths.

On the other hand a value of 1.70 for the bite parameter of the squarate involves significant problems to action of the ligand in a bidentate fashion because the copper–carbon and the copper–double-bond carbon–carbon distances will be about 2.07 and 1.96 Å respectively. The former value would correspond to a short copper–oxygen bond distance and the latter to a π interaction between the copper and the double carbon–carbon bond. Finally, from theoretical energetic calculations that have been carried out on complexes of formula $[(\widehat{\mathrm{N\,N}})\mathrm{Cu(C_4O_4)}]$, where $\widehat{\mathrm{N\,N}}$ represents a bidentate ligand trans to a bidentate squarate group, a minimum of energy is obtained for a puckered configuration, keeping constant the bite parameter of the bidentate ligands. The result is that this configuration around the metal ion is close to a tetrahedral one, fact which is not common in the coordination chemistry of copper(II).

These simple stereochemical and energetic considerations along with the structures herein reported enable us to conclude that despite the suggestions made by several authors, the squarate ligand does not seem to act in a bidentate fashion and a fortiori in a bisbidentate fashion with copper(II) and most probably with first-row transition-metal ions. However, the magnitude of the calculated d_1 value (2.47 Å) enables us to predict that (a) when the oxygen atom is exchanged by a larger substituent such as sulfur, the resulting ligands could act in a bidentate fashion as has been already reported,[37,38] (b) when metal ions with larger ionic radii are used, the bidentate coordination could be achieved. Indeed, in cases of chelation of squarate with alkaline-earth cations[39] and cerium(III)[40] have been reported recently. It deserves to be pointed out that there are two kinds of squarate ligands in the structure of the Ce(III) complex: one acts in a bisbidentate fashion whereas the other one is chelating on one end and unidentate on the other with one oxygen atom remaining uncoordinated. The d_1 average values are 2.69 and 2.62 Å, respectively. They are close to the predicted one (2.47 Å) for a chelating squarate group that has been calculated from the bite parameter of the oxalate ligand and the d_2 value of the squarate.

Safety Note

Perchlorate complexes are potentially explosive and every attempt should be made to substitute anions such as the fluoro sulfonates for the perchlorates. We used in our syntheses only small amounts of material, and the starting perchlorate salt was an aquo complex. The dilute solutions were handled with care and evaporated slowly at room temperature in an open hood (cf. ref 41).

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Supplementary Material Available: Tables SI–SXIV, listing full crystallographic data, thermal parameters, derived hydrogen positions, and nonessential bond lengths and angles, Tables SXXI–XXII, listing susceptibility/temperature data, and stereoviews of complexes **1–6** (Figures SI–SVI) (28 pages); Tables SXV–SXX, listing calculated and observed structure factors (59 pages). Ordering information is given on any current masthead page.

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