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First-Row Transition-Metal Complexes of the 1-Methoxycyclobutenedionate(1−) Ion

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The synthesis and characterization by single-crystal X-ray crystallography of a series of monomeric first-row transition-metal complexes with the 1-methoxycyclobutenedionate(1−) ligand are described. The isomorphous compounds $[M(CH_3OC_4O_3)_2(H_2O)_4]$ (M = Mn, Co, Ni, Zn) are C_2 symmetric and crystallize in the monoclinic space group $C2/c$. The metal atom in each of these complexes is six-coordinate with two cis 1-methoxycyclobutenedionate(1−) ligands, the methoxy substituent being oriented cis with respect to the ligating oxygen atom. The remaining coordination sites are filled by four aqua ligands. Monomers are linked by O−H···O hydrogen bonds to form arrays of stepped tapes. Hydrolysis of the methoxy group on the ligand occurs during the formation of the copper complex and $\{[Cu(C_4O_4)(H_2O)_2]\cdot 0.25H_2O\}_n$ is produced. This complex crystallizes in the tetragonal space group $P4/n$ and has a structure similar to, but differing significantly from, those of a series of 3-dimensional cage squarates which have been reported previously.

Introduction

Contrary to initial expectations, transition-metal squarate complexes in general have not exhibited the desired properties of semiconductivity or molecular magnetism due to poor metal−ligand orbital overlap.[1,2] However, significant antiferromagnetic interactions have been observed in a few binuclear complexes where the squarate ligand is coordinated μ-1,2, the more efficient metal−ligand overlap in this coordination mode being considered responsible for the enhanced interactions.[3,4] An important feature of these latter binuclear species is multiple bond localization which apparently plays some role in facilitating electron transfer between neighboring metal centers.[3−5] We, therefore, considered that linear polymeric complexes containing ligands which possess this feature might thus have the potential to act as semiconductors and molecular magnets and were thus worth investigating.[6] It should be noted that multiple bond localization has also been observed in a series of first-row transition-metal complexes—both monomeric and polymeric—recently synthesized by our group with the monosubstituted squarate ligand 1-methylcyclobutenedione (methylsquarate).[7] Thus, as part of our goal to develop a capability for synthesising complexes with the potential to function as molecular magnets or conducting polymers, we decided to investigate a wide variety of other monosubstituted squarate ligands so as to better understand the effects of the substituents on (i) the nature and extent of electron delocalization on the C_4-rings in complexes of these ligands and (ii) their complexing properties. Here we describe the synthesis and characterization of a number of first-row transition-metal complexes of the monosubstituted squarate ligand 1-methoxycyclobutenedione(1−) (methoxysquarate).

Experimental Section

Preparation of the Ligand. Tetrabutylammonium Methoxysquarate. 3-Amino-4-methoxycyclobut-3-ene-1,2-dione (1.00 g, 7.87 × 10^{-3} mol) prepared according to the method of Cohen and Cohen[8] was dissolved in 100 mL of water, and the resulting solution was filtered. A slight excess of a 1.0 M solution of tetrabutylammonium

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Table 1. Crystallographic Data for Complexes **1**−**5**

data	**1**	**2**	**3**	**4**	**5**
formula	$C_{10}H_{14}MnO_{12}$	$C_{10}H_{14}CoO_{12}$	$C_{10}H_{14}NiO_{12}$	$C_{10}H_{14}O_{12}Zn$	$C_4H_4CuO_6 \cdot 0.25H_2O$
formula weight	381.2	385.1	384.9	391.6	216.1
space group	$C2/c$ (No. 15)	$C2/c$ (No. 15)	$C2/c$ (No. 15)	$C2/c$ (No. 15)	$P4/n$ (No. 85)
T, °C	20	20	20	20	20
a, Å	12.565(1)	12.377(1)	12.292(1)	12.398(2)	16.254(1)
b, Å	13.214(1)	13.151(1)	13.132(1)	13.159(2)	
c, Å	8.859(1)	8.759(1)	8.689(1)	8.751(1)	8.143(1)
β, deg	97.09(1)	96.65(1)	96.44(1)	96.71(1)	
V, Å^3	1459.6(1)	1416.2(2)	1393.6(2)	1417.8(3)	2151.1(3)
Z	4^a	4^a	4^a	4^a	12^b
ρ_{calcd} (g cm^{-3})	1.735	1.806	1.835	1.834	2.002
λ, Å	1.54178	1.54178	1.54178	0.71073	0.71073
μ, cm^{-1}	79.9	101.6	26.7	18.0	30.3
$R_1{}^c$	0.041	0.061	0.035	0.040	0.045
$wR_2{}^d$	0.096	0.121	0.095	0.079	0.113

[a] The molecule has crystallographic C_2 symmetry. [b] There are 1.5 formula units in the asymmetric unit. [c] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [d] $wR_2 = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]\}^{1/2}$.

hydroxide in methanol was then added dropwise to the 3-amino-4-methoxycyclobut-3-ene-1,2-dione solution. The mixture was filtered, and the filtrate was evaporated to dryness on a rotary evaporator. The crude product was dissolved in 100 mL of acetonitrile and any undissolved material removed by filtration. The filtrate was then evaporated to dryness on a rotary evaporator and the crude product recrystallized from acetonitrile (yield 2.7 g, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.00 (t, J = 6.7 Hz, 12H), 1.45 (m, 8H), 1.65 (m, 8H), 3.30 (t, J = 6.7 Hz, 8H), 4.30 (s, 3H).

Preparation of the Complexes. All of the complexes were prepared according to the following procedure. The salt tetrabutylammonium methoxysquarate (0.10 g, 2.70×10^{-4} mol) was dissolved in 100 mL of acetonitrile. An equimolar amount (two times in the case of Cu) of the appropriate metal nitrate, $M(NO_3)_2 \cdot xH_2O$ [M = Mn, Co, Ni, Cu, Zn], was then dissolved in a similar volume of acetonitrile, and the metal nitrate solution was added to the ligand solution. The initial fine precipitate formed was removed by filtration and the filtrate allowed to evaporate slowly until crystal formation was complete.

[Mn($CH_3OC_4O_3$)$_2$(H_2O)$_4$]: clear needles (yield, 23%). Anal. Calcd for $C_{10}H_{14}MnO_{12}$: C, 31.5; H, 3.7; Mn 14.4. Found: C, 31.1; H, 3.4; Mn, 14.2.

[Co($CH_3OC_4O_3$)$_2$(H_2O)$_4$]: pink, platy needles (yield, 22%). Anal. Calcd for $C_{10}H_{14}CoO_{12}$: C, 31.2; H, 3.7; Co, 15.3. Found: C, 31.3; H, 3.6; Co, 14.9.

[Ni($CH_3OC_4O_3$)$_2$(H_2O)$_4$]: green, prismatic needles (yield, 21%). Anal. Calcd for $C_{10}H_{14}NiO_{12}$: C, 31.3; H, 3.5; Ni, 15.3. Found: C, 30.8; H, 3.7; Ni, 15.3.

[Zn($CH_3OC_4O_3$)$_2$(H_2O)$_4$]: clear needles (yield, 20%). Anal. Calcd for $C_{10}H_{14}O_{12}Zn$: C, 30.7; H, 3.6; Zn, 16.7. Found: C, 29.8; H, 3.0; Zn, 16.1.

Elemental Analyses. C and H analyses were performed by MEDAC Limited, Brunel University, Uxbridge, Middlesex, U.K. The metal analyses were carried out by flame atomic absorption spectrophotometry using a Unicam 929 atomic absorption spectrometer.

NMR Spectrum. The NMR spectrum was measured on a Bruker DRS 400 spectrometer.

Crystallographic Analyses. Table 1 provides a summary of the crystallographic data for complexes **1**−**5**. The structures were solved by direct methods and were refined by full matrix least-squares based on F^2. In **5** the partial occupancy included water molecule was found to be distributed over four reduced occupancy sites, all of which were refined isotropically. The remaining non-hydrogen atoms in all five structures were refined anisotropically. In complexes **1**−**4** the methyl hydrogen atoms were placed in calculated positions, assigned isotropic thermal parameters, $U(H) = 1.5U_{eq}(C)$, and allowed to ride on their parent atoms. In all five structures the aqua hydrogen atoms were located from ΔF maps and refined isotropically subject to an O−H distance constraint. The hydrogen atoms of the hydrate molecule in **5** could not be located. Computations were carried out using the SHELXTL PC program system.[9]

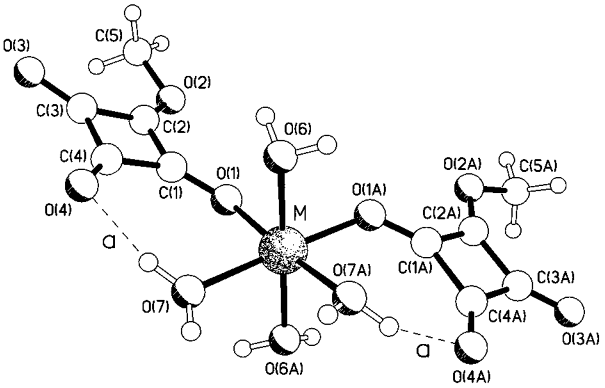

Figure 1. The molecular structure of [M($CH_3OC_4O_3$)$_2$(H_2O)$_4$] (M = Mn, Co, Ni, Zn) (**1**−**4**).

The crystallographic data (excluding structure factors) for the structures reported in Table 1 have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-132433−132437 for **1**−**5**, respectively. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB12 1EZ, UK (Fax intl code +(1223)336-033; e-mail teched@ccdc.cam.ac.uk).

Results and Discussion

The complexing behaviors of the two monosubstituted squarate ligands, methylsquarate and methoxysquarate are seen to differ markedly. The structures of the complexes produced with methoxysquarate are now discussed, and the differences, both in the complexing properties of these two ligands and in the structures of their complexes with first-row transition metals, are described.

Structures of [M($CH_3OC_4O_3$)$_2$(H_2O)$_4$] (M = Mn, Co, Ni, Zn (1−4)). The structures of the tetraaqua complexes formed between Mn, Co, Ni, and Zn and the methoxysquarate ligand were shown by single-crystal X-ray analysis to form an isomorphous series in which pairs of methoxysquarate ligands are cis coordinated via the formally negatively charged oxygen atom immediately cis to the methoxy group (Figure 1). All four structures have crystallographic C_2 symmetry and have their C_4-ring planes inclined by between 29 and 32° to the equatorial coordination plane comprising O(1), O(7), O(1A), and O(7A). The distortions

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(9) SHELXTL PC version 5.03, Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1994.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**−**4**

	1 [M = Mn]	**2** [M = Co]	**3** [M = Ni]	**4** [M = Zn]
M−O(1)	2.148(2)	2.080(4)	2.048(2)	2.077(3)
M−O(6)	2.207(3)	2.110(5)	2.079(2)	2.122(3)
M−O(7)	2.167(3)	2.080(5)	2.043(2)	2.079(3)
O(1)−C(1)	1.242(4)	1.253(7)	1.244(3)	1.240(5)
C(1)−C(2)	1.427(4)	1.417(8)	1.426(3)	1.423(5)
C(1)−C(4)	1.487(4)	1.472(8)	1.488(3)	1.491(5)
C(2)−O(2)	1.307(4)	1.322(7)	1.305(3)	1.317(5)
C(2)−C(3)	1.435(4)	1.426(8)	1.438(3)	1.442(5)
O(2)−C(5)	1.445(4)	1.453(7)	1.447(3)	1.447(5)
C(3)−O(3)	1.245(4)	1.249(7)	1.245(3)	1.241(5)
C(3)−C(4)	1.489(5)	1.489(8)	1.488(3)	1.489(6)
C(4)−O(4)	1.220(5)	1.229(7)	1.225(3)	1.221(5)
O(1)−M−O(1A)	91.32(14)	88.2(2)	86.84(9)	87.9(2)
O(1)−M−O(7A)	175.13(11)	176.2(2)	175.58(7)	174.6(2)
O(1)−M−O(7)	89.48(10)	90.3(2)	90.99(7)	90.64(11)
O(7)−M−O(7A)	90.1(2)	91.3(3)	91.43(10)	91.2(2)
O(1)−M−O(6A)	92.44(11)	91.8(2)	91.78(7)	92.32(14)
O(7)−M−O(6A)	86.02(11)	86.4(2)	86.00(7)	85.39(14)
O(1)−M−O(6)	89.15(11)	90.1(2)	90.23(7)	89.49(14)
O(7)−M−O(6)	92.37(11)	91.8(2)	92.07(7)	92.84(14)
O(6)−M−O(6A)	177.7(2)	177.4(3)	177.24(10)	177.5(2)

from ideal octahedral geometries are small, the largest cis and trans angular variations being in the Zn complex where they range between 85.4(1)−92.8(1)° and 174.6(2)−177.5(2)°, respectively (Table 2). Asymmetries in the bond lengths are likewise quite small, the only noticeable trend being that the metal aqua bonds trans to the methoxysquarate ligand are all consistently shorter than those trans to aqua (Table 2).

Equivalent bond lengths within the methoxysquarate ligand do not show any statistically significant variation throughout the isomorphous series. In all cases there is evidence for a pattern of partial delocalisation that extends from the coordinated oxygen O(1) via the methoxy-substituted carbon C(2) to the carbonyl oxygen O(3) (Figure 1). This pattern is different from that observed in the analogous methylsquarate complexes (both monomers and polymers).[7] In the methoxysquarate complexes the ring C−C bonds that are not connected to the substituent are significantly shorter [1.488(3) Å in the Ni complex, Table 2] than their counterparts in the methylsquarate complexes [1.510(2) Å]. Thus, instead of the π-allyl type system exhibited by the methylsquarate complexes, here in the methoxysquarate complexes the electrons are more delocalized over the entire C_4-cycle in a manner similar to that in for example $[Cu_2(SalNEt_2)_2(H_2O)(C_4O_4)](H_2O)$.[3] A noticeable feature of the methoxysquarate ligand is the in-plane orientation of the methoxy group (torsional twist in the range of 2−4°), an orientation analogous to that observed in aryl methoxy compounds which allows the methoxy oxygen lone pairs to migrate to the benzene ring.[10] Accompanying this in-plane orientation is a marked shortening of the C(2)−O(2) bond indicating significant multiple bond character and electron migration into the C_4-ring. Thus, it appears that the increased delocalization observed within the ring in these methoxysquarate complexes results from increased migration of electron density in the form of the labile oxygen lone pairs of the methoxy groups. Hence, it is not surprising that the Δ(C−C) of 0.09 Å seen in the methylsquarate complexes is greater than that (0.05 Å) observed here for the methoxysquarate complexes.

Table 3. H-Bonding Geometries, [O···O], [H···O] (Å), [O−H···O] (deg), for Structures **1**−**4** As Illustrated in Figures 2 and 3

	a O(7)−O(4)	b O(7)−O(4′)	c O(6)−O(3)	d O(6)−O(3′)
Ni	2.75, 1.92, 154	2.78, 1.95, 152	2.77, 1.88, 169	2.83, 1.96, 163
Co	2.77, 1.93, 155	2.79, 1.98, 151	2.78, 1.88, 172	2.82, 1.95, 162
Mn	2.83, 2.06, 143	2.79, 2.01, 144	2.76, 1.86, 175	2.81, 1.93, 165
Zn	2.79, 1.94, 157	2.78, 2.09, 133	2.76, 1.87, 174	2.82, 1.95, 165

The monomer conformation is stabilized by a pair of intramolecular O−H···O hydrogen bonds (a in Figure 1, Table 3) between the cis equatorial aqua ligands and the carbonyl oxygen atoms trans to the methoxy substituent. The monomer molecules are linked via O−H···O hydrogen bonds (b and c, Table 3) to form partially overlapping tapes that extend in the crystallographic *a* direction (Figure 2), the edges of the tapes being bounded by the methoxy substituent. Adjacent tapes are cross-linked above and below by additional O−H···O hydrogen bonds (d, Table 3) using the axial O−H hydrogen atoms not involved in tape formation to form a continuous network of stepped-tapes as illustrated in Figure 3.

In all the complexes **1**−**4** the methoxy substituent on the C_4-ring is oriented cis to the ligating oxygen. In addition, the ligands are also oriented cis with respect to each other. We speculate that after the first ligand coordinates to the hexaaqua metal ion the resulting increased electron density in the direction trans to this initial group, due to migration of the methoxy oxygen lone pairs onto the ligand ring and into the metal orbitals, renders it difficult for nucleophilic attack by a second incoming ligand in the trans direction. The second ligand will therefore attack preferentially in the cis direction and produce complexes with the resulting cis-oriented ligands.

So far we have been unable to prepare any polymeric complexes with the methoxysquarate ligand. One possible reason for the absence of polymer formation via ligation of the O(3), O(3A) oxygen atoms (Figure 1) could be the steric constraint of the in-plane methoxy group which hinders the approach of a second hexaaqua metal species, a necessary step for any chain propagation. Another could be that any resulting polymer will have all of the methoxy groups pointing in the same direction which will make such a structure unstable. It should be noted that the polymeric complexes with the methylsquarate ligands both had the methyl substituent pointing in alternate directions along the polymer chain.[7]

The Structure of $\{[Cu(C_4O_4)(H_2O)_2]\cdot 0.25H_2O\}_n$ (5). Attempts to synthesize the analogous Cu member of the series under conditions similar to those used in the synthesis of complexes **1**−**4** resulted in the methoxy group on the ligand being hydrolyzed and the formation of a complex pseudo-cubic cage network that is similar but differs significantly from those reported by Weiss et al.[11] and Lee et al.[2f] The principal difference between the present tetragonal structure, **5**, and the cubic [Co,[2f] Ni,[11] and Zn[11]], rhombohedral [Fe[2f]], and triclinic [Mn[11] and Zn[11]] structures lies in the relative orientation of the squarate rings on the three pairs of opposite faces of the cubes. Here, in **5**, two of these have staggered relationships while the third is eclipsed (Figure 4). By contrast in the cubic structures of Weiss[11] and Lee[2f] the opposite squarate rings are all staggered, and in the rhombohedral and triclinic cases they are all eclipsed. Another interesting feature of the structure of **5** is that it contains two independent copper atoms (one lying on an inversion center, the other in a general position), three independent squarate C_4-rings (Figure 5) and two alternating independent cages, A and B, of different dimensions (both of which have the same staggered/eclipsed relationships for their opposite faces).

The coordination geometry at each copper center is slightly distorted octahedral, with in each case the copper atom being

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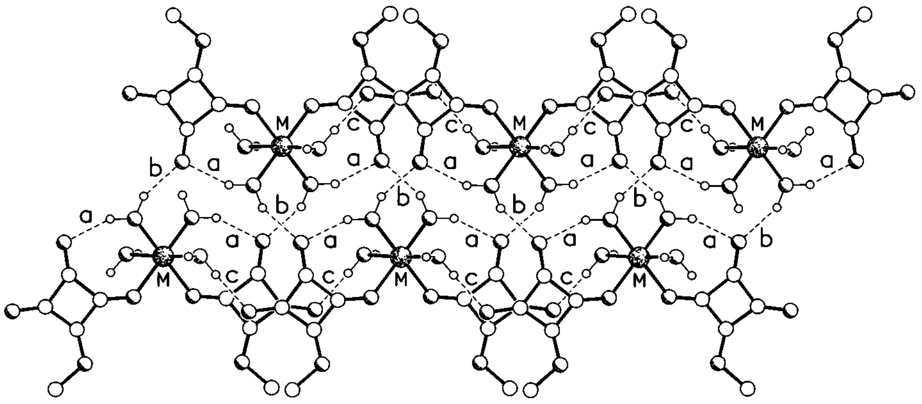

Figure 2. Part of one of the partially overlapping hydrogen-bonded tapes present in the structures of **1**−**4**; H-bonding geometries (a, b, c) in Table 3.

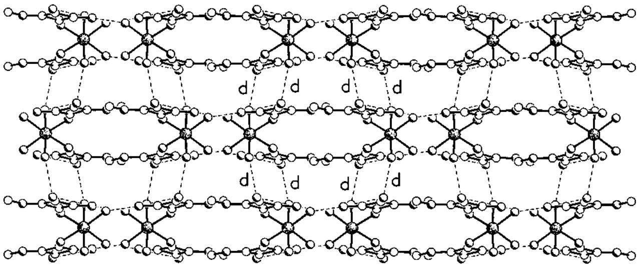

Figure 3. The cross-linking of stepped tapes present in the structures of **1**−**4** viewed down the tape direction; H-bonding geometries (d) are given in Table 3.

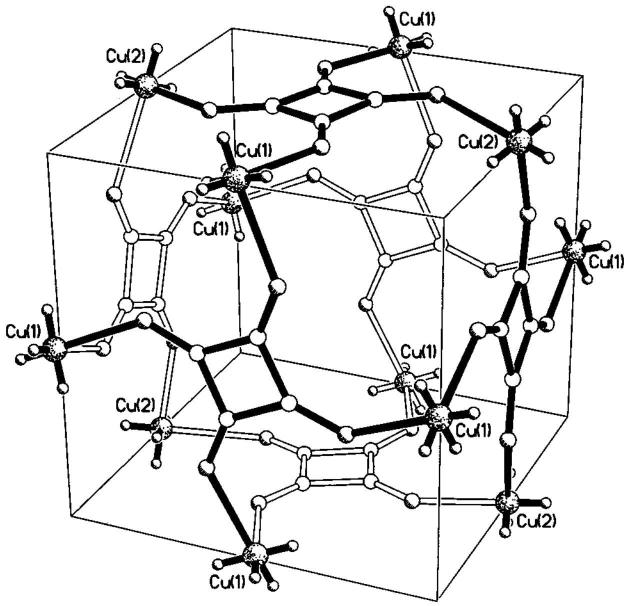

Figure 4. One of the cube-like arrays present in the structure of $\{[Cu(C_4O_4)(H_2O)_2]\cdot 0.25H_2O\}_n$ (**5**) showing the two staggered and one eclipsed relationship of diametrically opposite pairs of squarate rings. The bounding cube is drawn for comparison with the Weiss[11] representation and does not represent the crystallographic unit cell.

bonded to four squarate ligands and two trans oriented aqua ligands. Although the angular distortions at the two independent copper centers are small [cis angles ranging between 83.1(2) and 96.6(2)° at Cu(1), and 82.9(2) and 97.1(2)° at Cu(2)] (see Table 4), the patterns of bonding are different. At Cu(1) there are four long [to the squarate ligands, ranging from 2.142(5) to 2.169(5) Å], and two short Cu−O distances [to the aqua ligands, 1.949(4) and 1.963(4) Å]. In contrast, at Cu(2) there are two long [to a pair of squarate ligands, 2.351(4) Å] and four short Cu−O distances [two to the other pair of squarate ligands, 1.980(4) Å, and two to the aqua ligands, 1.955(4) Å]. A feature of the A and B type cages present in **5** is that in the A type cage two pairs of opposite faces are slightly concave with centroid−centroid separations of 7.87 Å, the third pair of faces being separated by 8.14 Å. Thus the B type cages have a larger volume than the A type (the corresponding dimensions are 8.38 and 8.14 Å). These cage distortions are almost certainly a consequence of the partial inclusion of water, the larger B type cages being those containing the water molecules while the A type cages are empty.

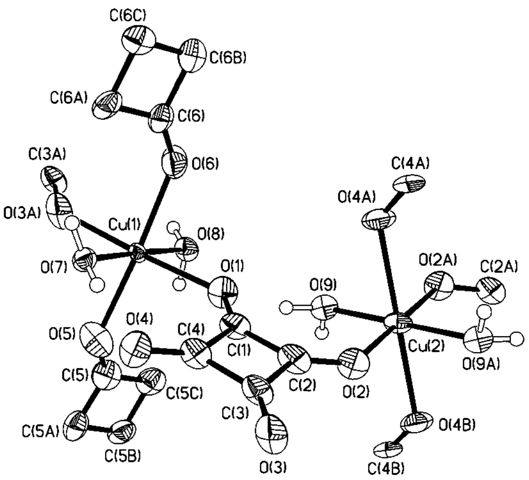

Figure 5. The coordination environments of the two crystallographically independent copper atoms in the structure of **5** (50% probability ellipsoids).

Hydrolysis of the Methoxy Substituent. As indicated above, there is evidence for migration of electron density into the methoxysquarate ligand ring. The C−O bonds utilized in coordinating to the metal are also significantly longer than in the analogous monomeric complexes with the methylsquarate ligand suggesting greater migration of electron density into the metal orbitals in complexes **1**−**4** than in the methylsquarate counterparts.[7] It is assumed that the increasing electron transfer from the methoxysquarate ligand orbitals into the metal orbitals with decreasing size of the metal cation as the period is traversed makes the methoxy substituent sufficiently susceptible to hydrolysis in the Cu complex. A similar hydrolysis occurred when attempts were made to synthesize first-row transition metal complexes with dialkylaminosquarate ligands.[12] In the syntheses involving the dialkylaminosquarates, hydrolysis of the dialkylamino groups occurred for all of the transition metals studied

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(12) Hosein, H.-A.; Hall, L. A.; Lough, A. J.; Desmarais, W.; Vela.; Foxman, B. M. *Inorg. Chem.* **1998**, *37*, 4184.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **5**

Cu(1)−O(7)	1.949(4)	Cu(1)−O(8)	1.963(4)	Cu(1)−O(6)	2.142(5)
Cu(1)−O(3)#1	2.142(5)	Cu(1)−O(1)	2.166(4)	Cu(1)−O(5)	2.169(5)
Cu(2)−O(9)#2	1.955(4)	Cu(2)−O(9)	1.955(4)	Cu(2)−O(2)#2	1.980(4)
Cu(2)−O(2)	1.980(4)	Cu(2)−O(4)#3	2.351(4)	Cu(2)−O(4)#4	2.351(4)
C(1)−O(1)	1.254(7)	C(1)−C(2)	1.441(9)	C(1)−C(4)	1.472(7)
C(2)−O(2)	1.269(8)	C(2)−C(3)	1.458(7)	C(3)−O(3)	1.256(8)
C(3)−C(4)	1.466(9)	O(3)−Cu(1)#5	2.142(5)	C(4)−O(4)	1.234(7)
O(4)−Cu(2)#6	2.351(4)	C(5)−O(5)	1.259(8)	C(5)−C(5)#7	1.449(10)
C(5)−C(5)#8	1.449(10)	C(6)−O(6)	1.250(8)	C(6)−C(6)#3	1.482(9)
C(6)−C(6)#6	1.482(9)				
O(7)−Cu(1)−O(8)	178.0(2)	O(7)−Cu(1)−O(6)	96.6(2)	O(8)−Cu(1)−O(6)	85.0(2)
O(7)−Cu(1)−O(3)#1	84.7(2)	O(8)−Cu(1)−O(3)#1	96.4(2)	O(6)−Cu(1)−O(3)#1	88.9(2)
O(7)−Cu(1)−O(1)	95.7(2)	O(8)−Cu(1)−O(1)	83.2(2)	O(6)−Cu(1)−O(1)	88.3(2)
O(3)#1−Cu(1)−O(1)	177.3(2)	O(7)−Cu(1)−O(5)	83.1(2)	O(8)−Cu(1)−O(5)	95.4(2)
O(6)−Cu(1)−O(5)	176.4(2)	O(3)#1−Cu(1)−O(5)	87.5(2)	O(1)−Cu(1)−O(5)	95.2(2)
O(9)#2−Cu(2)−O(9)	180.0	O(9)#2−Cu(2)−O(2)#2	95.4(2)	O(9)−Cu(2)−O(2)#2	84.6(2)
O(9)#2−Cu(2)−O(2)	84.6(2)	O(9)−Cu(2)−O(2)	95.4(2)	O(2)#2−Cu(2)−O(2)	180.0
O(9)#2−Cu(2)−O)(4)#3	97.1(2)	O(9)−Cu(2)−O(4)#3	82.9(2)	O(2)#2−Cu(2)−O(4)#3	87.3(2)
O(2)−Cu(2)−O(4)#3	92.7(2)	O(9)#2−Cu(2)−O(4)#4	82.9(2)	O(9)−Cu(2)−O(4)#4	97.1(2)
O(2)#2−Cu(2)−O(4)#4	92.7(2)	O(2)−Cu(2)−O(4)#4	87.3(2)	O(4)#3−Cu(2)−O(4)#4	180.0

(except for $[Mn(H_2O)_6][HC_4O_3NH_2]_2\cdot 2H_2O$ where complexation was not achieved)[12] while with the methoxysquarate ligand the hydrolysis occurred only at Cu. This we can rationalize as due to the fact that oxygen (which holds the lone pairs in the methoxy group) is smaller than nitrogen (which holds the lone pairs in the dialkylamino groups) and therefore electron withdrawal from the nitrogen would be more facile causing hydrolysis to occur more readily.

Conclusions

The results of this study indicate that the nature of the substituent on the ligand ring affects the extent of delocalization on the ring. The methoxy substituent which has lone pairs that can migrate into the ring apparently causes an increase in the amount of delocalization and a corresponding decrease in the extent of the multiple bond localization relative to the methyl substituent which has no such available lone pairs. In addition, such electron migration apparently causes (i) a cis-directing effect and a consequent decrease in the probability of polymer formation, (ii) a cis orientation of the substituent with respect to the ligating atom, and (iii) hydrolysis of the substituent when the extent of electron migration into the metal orbitals is adequate. This study therefore provides valuable information about the effects of the ring substituent on the complexing properties of monosubstituted squarate ligands and increases our capability of synthesising complexes with predictable and desirable properties.

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Supporting Information Available: X-ray crystallographic files, in CIF format, containing data for the structures of **1**−**5** and ORTEP representations. This material is available free of charge via the Internet at http://pubs.acs.org.

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