Inorg. Chem. **1999,** *38,* 2416−2421

First Row Transition Metal Complexes of 1-Methylcyclobutenedione, a Monosubstituted Squarate Ligand

Bert D. Alleyne, Hazel-Ann Hosein, Hema Jaggernauth, and Lincoln A. Hall*

Department of Chemistry, The University of the West Indies, St. Augustine, Trinidad, West Indies

Andrew J. P. White and David J. Williams*

Chemical Crystallography Laboratory, Department of Chemistry, Imperial College of Science,
Technology and Medicine, South Kensington, London SW7 2AY, U.K.

Received August 21, 1998

Reaction of 1-methylcyclobutenedione with $M(NO_3)_2 \cdot xH_2O$ [M = Co (**1**) and Ni (**2**)] produces isomorphous polymeric complexes of formula $M(CH_3C_4O_3)(NO_3)(H_2O)_4 \cdot 2H_2O$ that crystallize in the monoclinic space group $P2_1/m$ (No. 11) with, for **1**, $a = 6.409(5)$ Å, $b = 14.717(10)$ Å, $c = 7.259(6)$ Å, $\beta = 114.73(4)°$, and $Z = 2$ (the metal atom being positioned on a center of symmetry). In both cases, adjacent metal centers are bridged μ-1,3 by the 1-methylcyclobutenedione ligand, which exhibits distinct multiple bond localization. The positive charges on the polymer chains are in each case balanced by nitrate ions. The metal atoms are six-coordinate with trans-oriented 1-methylcyclobutenedione ligands, and with four aqua ligands completing the coordination sphere. Reduction of the crystallization temperature, however, resulted, with Co, in the formation of the monomeric complex $Co(CH_3C_4O_3)_2 \cdot 4H_2O$ (**4**). Isomorphous Mn (**3**), Cu (**5**), and Zn (**6**) analogues have also been synthesized. These crystallize in the monoclinic space group $P2_1/n$ (No. 14) with, for **3**, $a = 8.8258(8)$ Å, $b = 16.1527(14)$ Å, $c = 9.9084(8)$ Å, $\beta = 93.230(7)°$, and $Z = 4$. The central metal atom in each of these compounds is six-coordinate, being bound to two trans-oriented 1-methylcyclobutenedione ligands and four aqua ligands, the former coordinating in a monodentate fashion via the oxygen atom trans to the methyl substituent. In both the polymeric and monomeric complexes extensive three-dimensional hydrogen-bonded networks are formed in the solid state.

Introduction

In an effort to circumvent the hydrolysis problem encountered in the attempted syntheses of transition metal and lanthanide complexes of the 1-(dialkylamino) derivatives of 3,4-dihydroxycyclobut-3-ene-1,2-dione (squaric acid)[1] we investigated the complexing properties of other monosubstituted squarate ligands having substituents that are not hydrolyzable under the conditions employed in complex synthesis. These experiments were performed with the aim of (i) achieving a greater understanding of the chemistry of monosubstituted squarate ligands[2,3] and (ii) synthesizing polymeric complexes with desirable characteristics such as antiferromagnetism and semiconductivity.[4] Here we report the preparation and structural characterization of selected first row transition metal complexes with 1-methylcyclobutenedione (methylsquarate).

Experimental Section

Preparation of the Ligand. The 1-methylcyclobutenedione was prepared according to the method of Liebeskind et al.[5]

Preparation of the Metal Complexes. $Co(CH_3C_4O_3)(NO_3)(H_2O)_4 \cdot 2H_2O$ (1). A methanolic solution (50 mL) of $Co(NO_3)_2 \cdot 6H_2O$ (0.26 g, 8.93×10^{-4} mol) was added to an equal volume of a methanolic solution of 1-methylcyclobutenedione (0.10 g, 8.93×10^{-4} mol). The mixture was then filtered and left to stand at room temperature until crystallization was complete. Yield: 54%. Anal. Calcd for $C_5H_{15}NO_{12}Co$: C, 17.64; H, 4.41; N, 4.41; Co, 17.32. Found: C, 17.61; H, 4.41; N, 4.04; Co, 17.59.

$Ni(CH_3C_4O_3)(NO_3)(H_2O)_4 \cdot 2H_2O$ (2). A solution (30 mL) of $Ni(NO_3)_2 \cdot 6H_2O$ (0.26 g, 8.9×10^{-4} mol) in water was added to 30 mL of an aqueous solution of 1-methylcyclobutenedione (0.10 g, 8.9×10^{-4} mol). The resulting solution was filtered and left to stand under ambient conditions until crystallization was complete. Yield: 54%.

---

* Authors to whom correspondence should be addressed.

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

(2) Narinesingh, D.; Ramcharitar, N.; Hall, L.; Williams, D. J. *Polyhedron* **1994**, *13*, 45.

(3) Hall, L. A.; Williams, D. J.; Menzer, S.; White, A. J. P. *Inorg. Chem.* **1997**, *36*, 3096.

(4) (a) Gerstein, B. C.; Habenschuss, M. *J. Appl. Phys.* **1972**, *43*, 5155. (b) Duggan, D. M.; Barefield, E. K.; Hendrickson, D. N. *Inorg. Chem.* **1973**, *12*, 985. (c) Carlin, R. L.; van Duyneveldt, J. *Magnetic Properties of Transition Metal Compounds*; Springer-Verlag: New York, 1977. (d) Wrobleski, J. T.; Brown, D. B. **1979**, *18*, 2738. (e) Willett, R. D., Gatteschi, D., Kahn, O., Reidel, D., Eds. *Magneto-Structural Correlations in Exchange Coupled Systems*; Dordrecht: Holland, 1984. (f) Robl, C.; Weiss, A. *Z. Naturforsch.* **1986**, *41b*, 1485. (g) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 89. (h) Trombe, J.-C.; Petit, J.-F.; Gleizes, A. *New J. Chem.* **1988**, *12*, 97. (i) Chen, Q.; Liu, S.; Zubieta, J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 70. (j) Solans, X.; Aguilo, M.; Gleizes, A.; Faus, J.; Julve, M.; Verdaguer, M. *Inorg. Chem.* **1990**, *29*, 775. (k) Frankenbach, G. M.; Beno, M. A.; Kini, A. M.; Williams, J. M.; Welp, U.; Thompson, J. E.; Whangbo, M.-H. *Inorg. Chim. Acta* **1992**, *192*, 195. (l) Xanthopoulos, C. E.; Sigalas, M. P.; Katsoulos, G. A.; Tsipis, C. A.; Hadjikostas, C. C.; Terzis, A.; Mentzafos, M. *Inorg. Chem.* **1993**, *32*, 3743. (m) Caneschi, A.; David, L.; Ferraro, F.; Gatteschi, D.; Fabretti, A. C. *Inorg. Chim. Acta* **1994**, *217*, 7. (n) Khan, M. I.; Chang, Y.-D.; Chen, Q.; Salta, J.; Lee, Y−S.; O'Connor, C. J.; Zubieta, J. *Inorg. Chem.* **1994**, *33*, 6340. (o) Hilbers, M.; Meiwald, M.; Mattes, R. *Z. Naturforsch.* **1996**, *51B*, 57.

(5) Liebeskind, L. S.; Fengl, R. W.; Wirtz, K. R.; Shawe, T. T. *J. Org. Chem.* **1988**, *53*, 2482.

10.1021/ic981011k CCC: $18.00

Table 1. Crystallographic Data for Complexes **1**−**6**

	1	**2**	**3**	**4**	**5**	**6**
chemical formula	$[C_5H_{11}O_7Co][NO_3]\cdot 2H_2O$	$[C_5H_{11}O_7Ni][NO_3]\cdot 2H_2O$	$C_{10}H_{14}O_{10}Mn$	$C_{10}H_{14}O_{10}Co$	$C_{10}H_{14}O_{10}Cu$	$C_{10}H_{14}O_{10}Zn$
fw	340.1	339.9	349.2	353.1	357.8	359.6
space group, no.	$P2_1/m$, 11	$P2_1/m$, 11	$P2_1/n$, 14	$P2_1/n$, 14	$P2_1/n$, 14	$P2_1/n$, 14
T, °C	20	20	20	27	20	20
a, Å	6.409(5)	6.547(1)	8.826(1)	8.775(1)	8.647(2)	8.793(1)
b, Å	14.717(1)	14.671(2)	16.153(1)	16.021(1)	16.139(4)	15.981(1)
c, Å	7.259(6)	7.269(1)	9.908(1)	9.808(1)	9.656(3)	9.792(1)
β, deg	114.73(4)	114.93(1)	93.23(1)	93.60(1)	94.13(3)	93.61(1)
V, Å^3	621.8(8)	633.2(2)	1410.3(2)	1376.2(1)	1344.0(5)	1373.3(2)
Z	2^a	2^a	4	4	4	4
ρ_{calcd} (g cm^{-3})	1.816	1.783	1.644	1.704	1.768	1.739
λ, Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	1.541 78
μ, cm^{-1}	14.4	15.9	9.8	13.0	16.8	29.8
R1^b	0.064	0.026	0.038	0.036	0.035	0.036
wR2^c	0.164	0.073	0.097	0.075	0.093	0.091

[a] The metal is positioned at a crystallographic center of symmetry. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Anal. Calcd for $C_5H_{15}NO_{12}Ni$: C,17.65; H, 4.41; N, 4.41; Ni, 17.27. Found: C, 17.70; H, 4.41; N, 4.10; Ni, 16.29.

$Mn(CH_3C_4O_3)_2\cdot 4H_2O$ (3). A methanolic solution (25 mL) of $MnCl_2\cdot 6H_2O$ (0.18 g, 8.93 × 10^{-4} mol) was added to a methanolic solution of 1-methylcyclobutenedione (0.10 g, 8.93 × 10^{-4} mol). The solution was evaporated rapidly to 10 mL, filtered, and left to stand until crystal formation was complete. Yield: 34%. Anal. Calcd for $C_{10}H_{14}O_{10}Mn$: C, 34.40; H, 4.04; Mn, 15.73. Found: C, 34.08; H, 3.55; Mn, 15.33.

$Co(CH_3C_4O_3)_2\cdot 4H_2O$ (4). A methanolic solution (50 mL) of $Co(NO_3)_2\cdot 6H_2O$ (0.26 g, 8.93 × 10^{-4} mol) was added to an equal volume of a methanolic solution of 1-methylcyclobutenedione (0.10 g, 8.93 × 10^{-4} mol). The mixture was then filtered and left to stand at approximately 15 °C until crystallization was complete. Yield: 21%. Anal. Calcd $C_{10}H_{14}O_{10}Co\cdot H_2O$: C, 32.34; H, 4.31; Co, 15.87. Found: C, 32.55; H, 4.05; Co, 16.42.

$Cu(CH_3C_4O_3)_2\cdot 4H_2O$ (5). A methanolic solution (25 mL) of $Cu(NO_3)_2\cdot 3H_2O$ (0.26 g, 8.94 × 10^{-4} mol) was added to a methanolic solution of 1-methylcyclobutenedione (0.20 g, 1.79 × 10^{-3} mol). The resulting blue-green solution afforded turquoise blocks on standing. Yield: 32%. Anal. Calcd for $C_{10}H_{14}O_{10}Cu$: C, 33.57; H, 3.94; Cu, 17.76. Found: C, 33.53; H, 3.90; Cu, 17.13.

$Zn(CH_3C_4O_3)_2\cdot 4H_2O$ (6). A solution (30 mL) of $Zn(NO_3)_2\cdot 6H_2O$ (0.26 g, 8.9 × 10^{-4} mol) in acetone was added to 30 mL of an acetone solution of 1-methylcyclobutenedione (0.05 g, 4.5 × 10^{-4} mol). The resulting solution was filtered and left to stand until crystal formation was complete. Yield: 12%. Anal. Calcd for $C_{10}H_{14}O_{10}Zn$: C, 33.40; H, 3.92; Zn, 18.18. Found: C, 33.15; H, 3.84; Zn, 18.05.

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

Crystallographic Analyses. Table 1 provides a summary of the crystal data and refinement parameters for complexes **1**−**6**. Structures **3**−**6** were solved by direct methods while **1** and **2** were solved by the heavy-atom method. In each structure all of the non-hydrogen atoms were refined anisotropically by full-matrix least squares based on F^2. In **2** the nitrate ion was found to be disordered about a crystallographic mirror plane: this was modeled as two half-occupancy anions each straddling the mirror plane. In complexes **3**−**6** the methyl hydrogen atoms were located from ΔF maps, assigned isotropic thermal parameters, $U(H) = 1.5U_{eq}(C)$, and allowed to ride on their parent atoms. In **1** and **2** the methyl hydrogen atoms were found to be disordered about the crystallographic mirror plane, and so a single idealized orientation of half-occupancy atoms was used with $U(H) = 1.5U_{eq}(C)$. In all six structures the hydrogen atoms of the aqua ligands were located from ΔF maps—in **1** and **3**−**6** they were refined isotropically, whereas in **2** they were assigned isotropic thermal parameters, $U(H) = 1.2U_{eq}(O)$—and refined subject to an O−H distance constraint. Computations were carried out using the SHELXTL PC program system.[6]

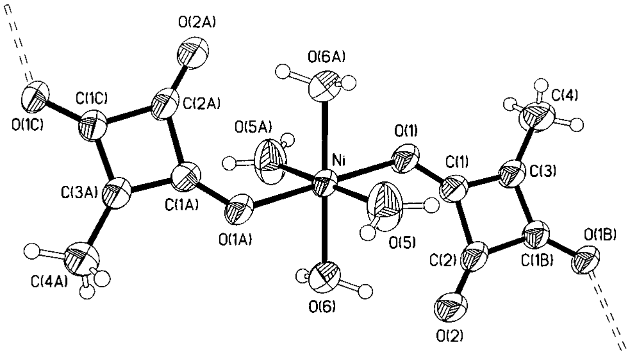

Figure 1. Molecular structure of the cation in **2** (80% probability ellipsoids).

Results and Discussion

Because of the resistance to hydrolysis of the methyl substituent in 1-methylcyclobutenedione (methylsquarate) during complexation with first row transition elements, this ligand was used as a viable alternative to the 1-(dialkylamino) derivatives of squaric acid in the furtherance of achieving our stated goals of understanding and exploiting the properties of the transition metal complexes of monosubstituted squarate ligands. These compounds, the first ever complexes of transition metals with a monosubstituted squarate ligand, provide valuable insights into the effects of monosubstitution of the parent acid and upon its complexing properties.

Structures of $M(CH_3C_4O_3)(NO_3)(H_2O)_4\cdot 2H_2O$ [M = Co (1) and Ni (2)]. The X-ray analyses of **1** and **2** show the complexes to be isomorphous and polymeric with the squarate ligand adopting a μ-1,3 bridging role linking adjacent metal centers (Figure 1). The metal atom lies on a crystallographic inversion center with a consequent trans orientation for the two squarate ligands. The remaining four coordination sites are occupied by aqua ligands. The coordination geometry is only slightly distorted octahedral with the largest deviations being in the cis angles of the Ni complex (in the range 84.28(4)−95.72(4)°, Table 2). The metal−aqua coordination distances 2.0340(11), 2.0410(11) Å (M = Ni) and 2.037(4), 2.074(4) Å (M = Co) are significantly shorter than those to the respective methylsquarate ligand oxygen atoms, 2.0839(9) and 2.128(4) Å. The equivalent bond lengths of the methylsquarate ligands in **1** and **2** do not differ significantly. (As the structures are isomorphous, the subsequent discussion will center on the Ni

---

(6) *SHELXTL PC*, version 5.03; Siemens Analytical X-Ray Instruments, Inc.: Madison, WI, 1994.

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

	1 (M = Co)	**2** (M = Ni)		**1** (M = Co)	**2** (M = Ni)
M−O(1)	2.128(4)	2.0839(9)	M−O(5)	2.074(4)	2.041(1)
M−O(6)	2.037(4)	2.034(1)	C(1)−O(1)	1.242(7)	1.249(2)
C(1)−C(2)	1.506(8)	1.510(2)	C(1)−C(3)	1.428(8)	1.421(2)
C(2)−O(2)	1.218(10)	1.215(2)	C(3)−C(4)	1.479(12)	1.480(3)
O(6)−M−O(6A)	180.0	180.0	O(6)−M−O(5A)	90.5(2)	90.53(5)
O(6)−M−O(5)	89.5(2)	89.47(5)	O(5)−M−O(5A)	180.0	180.0
O(6)−M−O(1A)	84.5(2)	84.28(4)	O(5)−M−O(1A)	90.8(2)	89.33(4)
O(6)−M−O(1)	95.5(2)	95.72(4)	O(5)−M−O(1)	89.2(2)	90.67(4)
O(1)−M−O(1A)	180.0	180.0			

complex, which has significantly higher precision.) The ligand is positioned about a crystallographic mirror plane that passes through the C(2) carbonyl group and the C(3) methyl group. There is a marked asymmetry in the pattern of bonding within the C_4 ring. The original C(1)−C(3) formal double bond has retained some of its multiple-bond character [1.421(2) Å] but with significant delocalization extending into the immediately adjacent C(3)−C(1B) bond [1.421(2) Å], previously a formal single bond. There is therefore a π-allyl system that extends over the C(1)−C(3)−C(1B) assembly of atoms while the other two C_4-ring bonds are normal single bonds each with length 1.510(2) Å. This multiple-bond localization is similar to that observed in $[Cu_2(SalNEt_2)_2(H_2O)(C_4O_4)]\cdot H_2O$, $NH_4[V_2O_2(OH)(C_4O_4)_2(H_2O)_3]\cdot H_2O$, and a series of anionic complexes of V and Mo synthesized by Mattes et al.[4l,n,o] The Δ(C−C) of 0.09(1) Å in **1** and **2** is greater than the value of 0.06(1) Å and equal to that of 0.09(1) Å observed in $[Cu_2(SalNEt_2)_2(H_2O)(C_4O_4)]\cdot H_2O$ and $NH_4[V_2O_2(OH)(C_4O_4)_2(H_2O)_3]\cdot H_2O$, respectively. In these latter two complexes the multiple-bond localization results from the μ-1,2 bridging mode adopted by the squarate ligand.[4l,n] However, in complexes **1** and **2**, although the ligand bridges μ-1,3, the observed difference in bond lengths must be an effect of the substituent. The pattern of delocalization within the methylsquarate ligand in **1** and **2** is consistent with the resonance hybrid that can be written from its two canonical resonance forms. It must be noted that when the unsubstituted squarate ion bridges μ-1,3 it does not show multiple-bond localization.[4k,7−10]

There is a significant lengthening of the coordinated C(1) carbonyl bond [1.249(2) Å], but the C(2) carbonyl bond length is normal at 1.215(2) Å. This pattern of delocalization, which extends from one Ni center through O(1), C(1), C(3), C(1B), O(1B) to the next, offers the potential for electron transfer between adjacent metal centers. It is also worth noting that the Ni−O bond [2.084(1) Å] by which the methylsquarate ligand is attached to the metal in **1** is significantly shorter than the equivalent Co−O bond of 2.128(4) Å in **2**. This we assume is due to the greater extent of electron flow into the orbitals of the smaller Ni^{2+} ion.

The polymer chain, which propagates via a combination of the crystallographic 2_1 screw axis and a mirror plane, has a zigzag conformation which is stabilized by both intra- and intermolecular O−H···O hydrogen bonds, the former between one of the aqua ligands and the ketonic oxygen atom (**a** in Figure 2, Table 3) and the latter between the other independent aqua ligand and the nitrate ion (**b** in Figure 2). The nitrate ion is slightly disordered about the crystallographic mirror plane, leading to two orientations and the alternate hydrogen bonds illustrated in Figure 2. The nitrate ion and the C_4 ring are approximately parallel to each other (6° inclination) and are overlaid with a mean interplanar separation of 3.25 Å, indicative of a strong $\pi-\pi$ interaction.[7,11] This interaction extends in the crystallographic *a* direction to include lattice-translated polymer chains, the interchain $\pi-\pi$ separation being 3.28 Å. The included water molecules link adjacent polymer chains via O−H···O hydrogen bonds to form the approximately hexagonal close-packed arrangement illustrated in Figure 3. The geometry about each water molecule is pseudotetrahedral with each water donating two hydrogen bonds, one to the coordinated O(1), the other to a nitrate oxygen atom, and accepting two bonds, one from each of the aqua ligand hydrogen atoms not utilized in intrachain interactions. The metal atoms in complexes **1** and **2** are linearly arranged when viewed along the polymer chain, and it is the orientation of the ligands that is responsible for the overall zigzag nature of the chains.

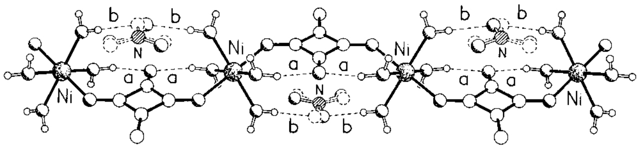

Figure 2. Part of the extended polymer chain present in the structures of **1** and **2** showing the hydrogen bonding within the chain and to the nitrate ions. (In **1** the nitrate ion is ordered.)

Table 3. Hydrogen-Bonding Geometries [O···O, H···O distances (Å) and O−H···O Angles (deg)] for Complexes **1** and **2**[a]

	1 (M = Co)	**2** (M = Ni)
a	2.73, 2.10, 125	2.73, 1.86, 163
b	2.90, 2.38, 117	2.79, 1.90, 169
c	2.91, 2.05, 159	2.87, 1.99, 165
c′	n/a	2.93, 2.03, 170
d	2.87, 1.99, 164	2.92, 2.03, 168
e	2.76, 1.92, 155	2.75, 1.86, 176
f	2.72, 1.84, 166	2.76, 1.88, 167

[a] Linkages **a** and **b** are depicted in Figure 2 and **c**−**f** in Figure 3. O−H distances normalized to 0.90 Å, **c** and **c′** respresent the contacts to the two 50% occupancy positions of the nitrate oxygen atoms in **2**.

Structure of $M(CH_3C_4O_3)_2\cdot 4H_2O$ [M = Mn (3), Co (4), Cu (5), and Zn (6)]. The X-ray analyses of the Mn, Cu, and Zn complexes with 1-methylcyclobutenedione synthesized at ambient temperature and analysis of the Co complex synthesized at 15 °C revealed in each case the formation of isomorphous monomeric species rather than the polymeric compounds observed for **1** and **2** (Figure 4). Furthermore, in these monomeric complexes, although the methylsquarate ligands are again trans coordinated, bonding to the metal is through a ketonic oxygen and not a deprotonated hydroxyl. Within the

---

(7) Weiss, A.; Riegler, E.; Alt. I.; Bohme, H.; Robl, C. *Z. Naturforsch.* **1986**, *41b*, 18.

(8) Robl, C.; Weiss, A. *Z. Naturforsch.* **1986**, *41b*, 1341.

(9) Ooijen, J. A. C.; Reedijk, J.; Spek, A. L. *Inorg. Chem.* **1979**, *18*, 1184.

(10) Yaghi, O. M.; Li, G.; Groy, T. L. *J. Chem. Soc., Dalton Trans.* **1995**, 727.

(11) Braga, D.; Grepioni, F. *Chem. Commun.* **1998**, 911.

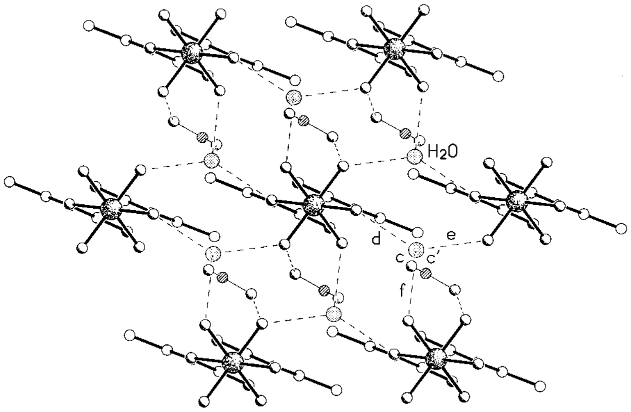

Figure 3. Close-packed hexagonal array of polymer chains in **1** and **2** viewed end-on showing the cross-linking by the included water molecules.

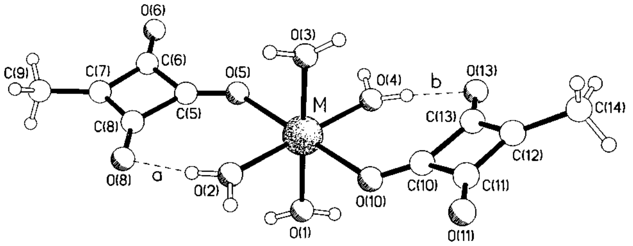

Figure 4. Molecular structure of $M(CH_3C_4O_3)_2{\cdot}4H_2O$ [M = Mn (**3**), Co (**4**), Cu (**5**), and Zn (**6**)].

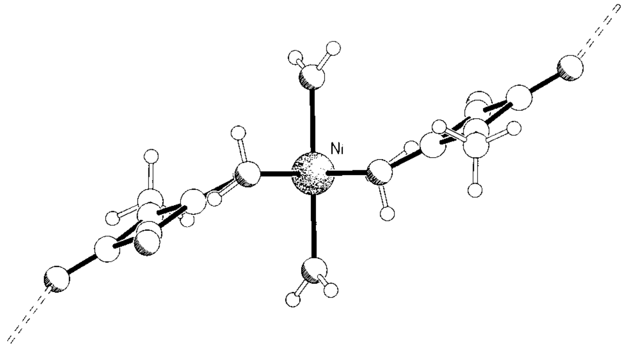

Figure 5. Diagram showing the orientations of the planes of the methylsquarate units in **2** with respect to the equatorial metal coordination plane.

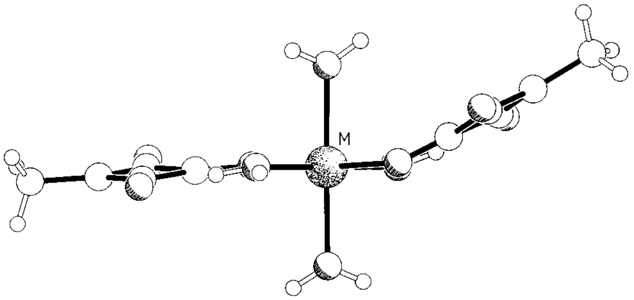

Figure 6. Diagram showing the orientations of the planes of the methylsquarate units in **3**−**6** with respect to the equatorial metal coordination plane.

isomorphous series of complexes the distortions from octahedral coordination geometry are small, the largest departures from 90° cis geometries being in the zinc complex, where the angles range between 86.22(9)° and 93.26(9)° (Table 4). The largest differences in the bond lengths occur in the copper complex, which exhibits a normal Jahn−Teller tetragonal distortion.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Complexes **3**−**6**

	3 (M = Mn)	**4** (M = Co)	**5** (M = Cu)	**6** (M = Zn)
M−O(1)	2.145(2)	2.049(2)	1.963(2)	2.053(2)
M−O(2)	2.155(1)	2.057(2)	1.987(2)	2.063(2)
M−O(3)	2.181(2)	2.089(2)	1.988(2)	2.099(2)
M−O(4)	2.151(1)	2.052(2)	1.977(2)	2.050(2)
M−O(5)	2.223(1)	2.175(2)	2.361(2)	2.178(2)
M−O(10)	2.225(1)	2.159(2)	2.311(2)	2.170(2)
O(5)−C(5)	1.216(2)	1.223(3)	1.212(4)	1.214(4)
C(5)−C(8)	1.506(2)	1.502(4)	1.510(4)	1.511(4)
C(5)−C(6)	1.512(2)	1.514(4)	1.505(4)	1.512(4)
C(6)−O(6)	1.238(2)	1.245(3)	1.243(4)	1.246(4)
C(6)−C(7)	1.425(2)	1.422(4)	1.420(4)	1.424(4)
C(7)−C(8)	1.424(2)	1.423(4)	1.420(4)	1.423(4)
C(7)−C(9)	1.473(3)	1.481(4)	1.469(4)	1.471(4)
C(8)−O(8)	1.244(2)	1.248(3)	1.251(4)	1.244(4)
O(10)−C(10)	1.217(2)	1.220(3)	1.211(4)	1.220(4)
C(10)−C(11)	1.497(2)	1.501(4)	1.496(4)	1.493(4)
C(10)−C(13)	1.507(2)	1.513(4)	1.516(4)	1.506(4)
C(11)−O(11)	1.240(2)	1.237(3)	1.241(4)	1.246(4)
C(11)−C(12)	1.423(2)	1.430(4)	1.434(4)	1.424(4)
C(12)−C(13)	1.427(2)	1.424(4)	1.423(4)	1.424(4)
C(12)−C(14)	1.476(3)	1.482(4)	1.478(4)	1.478(4)
C(13)−O(13)	1.237(2)	1.243(3)	1.248(4)	1.240(4)
O(1)−M−O(4)	90.72(6)	90.57(8)	90.41(9)	90.74(9)
O(1)−M−O(2)	89.17(6)	89.45(8)	89.18(9)	89.58(9)
O(4)−M−O(2)	179.36(6)	179.53(8)	179.50(9)	179.30(9)
O(1)−M−O(3)	178.08(6)	178.70(8)	178.70(9)	178.14(9)
O(4)−M−O(3)	89.63(6)	90.15(8)	90.78(9)	90.25(9)
O(2)−M−O(3)	90.46(6)	89.83(8)	89.62(10)	89.42(9)
O(1)−M−O(5)	92.67(5)	92.17(8)	92.43(9)	93.26(9)
O(4)−M−O(5)	90.75(5)	89.05(8)	88.40(8)	88.96(8)
O(2)−M−O(5)	89.89(5)	91.42(7)	91.31(8)	91.64(8)
O(3)−M−O(5)	89.21(6)	88.93(8)	88.12(9)	88.33(9)
O(1)−M−O(10)	90.35(6)	90.06(8)	88.39(9)	89.45(9)
O(4)−M−O(10)	91.72(5)	92.76(8)	92.81(8)	93.16(9)
O(2)−M−O(10)	87.65(5)	86.76(8)	87.48(8)	86.22(9)
O(3)−M−O(10)	87.75(6)	88.81(8)	91.04(9)	88.92(9)
O(5)−M−O(10)	176.07(5)	177.11(8)	178.54(8)	176.54(9)

Similarly the equivalent bond lengths within the methylsquarate ligands do not show any significant statistical variation throughout the series. Furthermore, there is no difference between the methylsquarate ligand geometries observed in this monomeric series and those in the polymers. The pattern of delocalization in the polymers, which extends between the two oxygen atoms cis to the methyl substituent and includes the ring carbon to which the methyl group is bonded, is still present in the monomers but, because of the difference in coordination, does not extend to include the metal center. Indeed for the only metal (Co) where both monomeric and polymeric species have been obtained, the Co−O distance in the polymer is significantly shorter than that in the monomer, indicative of a greater migration of electron density into the metal orbitals in the polymeric complexes.

In the polymeric structures the planes of the squarate ring are equally inclined (by ca. 31°) to one of the metal coordination planes (Figure 5), whereas in the monomers there is a distinct asymmetry with one squarate ring [C(10)−C(13)] being inclined by between 29°and 30° while the other lies almost within this coordination plane (inclined by between 8° and 10°, Figure 6). Despite these differences in orientation there are intramolecular O−H···O hydrogen bonds between trans equatorial aqua hydrogen atoms and anti-disposed methylsquarate oxygen atoms (Figure 7, Table 5). The principal difference between the intramolecular hydrogen bonding in the polymers and that in the monomers is that in the former it is the ketonic oxygen trans to the methyl substituent that is involved whereas in the monomers it is one of the oxygen atoms cis to the methyl group that is utilized.

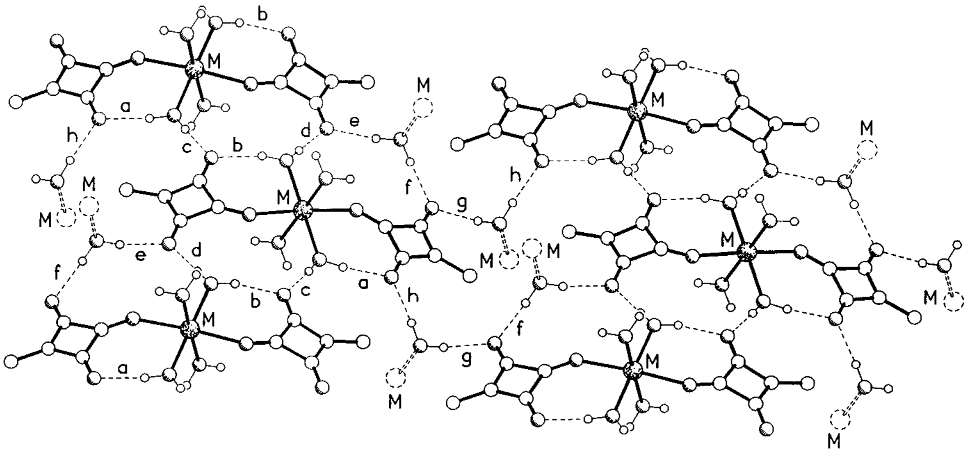

Figure 7. Part of a pair of lattice-translated cross-linked tapes present in the structures of the monomers **3**−**6**.

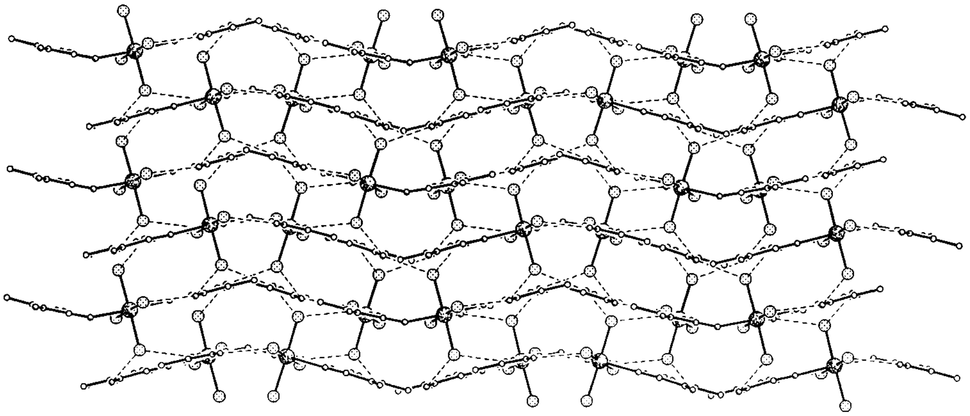

Figure 8. Diagram showing corrugated sheets of monomeric units present in the structures of **3**−**6**.

Table 5. Hydrogen-Bonding Geometries [O···O, H···O Distances (Å) and O−H···O Angles (deg)] for **3**−**6**[a]

	3 (M = Mn)	**4** (M = Co)	**5** (M = Cu)	**6** (M = Zn)
a	2.70, 1.81, 170	2.69, 1.80, 169	2.70, 1.81, 169	2.68, 1.79, 167
b	2.73, 1.85, 166	2.70, 1.82, 165	2.73, 1.83, 171	2.71, 1.82, 165
c	2.76, 1.86, 176	2.77, 1.87, 173	2.78, 1.89, 176	2.78, 1.89, 167
d	2.73, 1.83, 176	2.72, 1.83, 172	2.73, 1.83, 174	2.73, 1.84, 169
e	2.71, 1.82, 168	2.71, 1.82, 170	2.68, 1.79, 169	2.70, 1.82, 167
f	2.75, 1.85, 177	2.75, 1.86, 171	2.77, 1.87, 175	2.75, 1.86, 173
g	2.80, 1.90, 171	2.83, 1.93, 176	2.80, 1.94, 170	2.83, 1.94, 170
h	2.76, 1.84, 175	2.73, 1.83, 177	2.72, 1.82, 175	2.74, 1.85, 174

[a] Linkages **a**−**h** are depicted in Figure 7. O−H distances normalized to 0.90 Å.

The packing of the monomers is controlled by an extensive network of O−H···O hydrogen bonds utilizing all eight potential aqua donor hydrogen atoms. The "in-plane" aqua ligands link *n*-glide related monomeric units (links **a**, **b**, **c**, and **d** in Figure 7, Table 5) to form tapes. Adjacent lattice-translated tapes are cross-linked via the "axial" aqua ligands belonging to equivalent tapes that lie above and below those illustrated in the Figure 7 (links **e**, **f**, **g**, and **h**). The combined effect of these hydrogen-bonding interactions is to produce corrugated sheets of monomeric units which are held together by the axial hydrogen bonds described above and illustrated in Figure 8. We conjecture that the asymmetry in the methylsquarate ligand orientations with respect to the coordination plane in these monomeric complexes is controlled by the maximization of the hydrogen-bonding donor and acceptor capabilities of these complexes.

As in **1** and **2** a similar disparity in C−C bond lengths on the C_4 ring is also observed in **3**−**6** with Δ(C−C) = 0.09(1) Å. There is no significant change in bond length of either the shorter or longer ring C−C bonds throughout this series of complexes. The shorter ring C−C bond is ca. 1.42 Å while the longer one is ca. 1.51 Å as was observed for **1** and **2**.

Conclusions

This study of the series of complexes **1**−**6** demonstrates that multiple-bond localization, a phenomenon previously observed in μ-1,2-bridged metal squarates,[4l,n,o] can alternatively readily be achieved by simply utilizing a monosubstituted squarate ligand instead of the unsubstituted parent compound. Additionally, the transition metal polymers synthesized with monosubstituted squarate ligands appear to have potential as precursors for low-dimensional polymeric conductors or molecular magnets,[4d,h,k] properties that simple polymers of squaric acid did not possess. We are currently carrying out a variable-temperature magnetochemical investigation of these polymeric complexes to determine if there is any antiferromagnetic coupling as was observed for the μ-1,2-bridged copper and vanadium squarate complexes.[4l,n] We also intend to investigate the π interactions and the semiconducting properties of the polymers as well as their potential as directional conductors in view of the fact that the π interactions occur in a direction different from the direction of delocalization along the polymer chain.[13,14]

We do not fully understand what is responsible for the difference in coordination modes shown by the methylsquarate ligand and consequently the factors that determine optimum

---

(12) Solans, X.; Aguilo, M.; Gleizes, A.; Faus, J.; Julve, M.; Verdaguer, M. *Inorg. Chem.* **1990**, *29*, 775.

conditions for polymer formation, although, as demonstrated by the cobalt complexes **1** and **4**, temperature appears to be a contributory factor. The relative stabilities of the different canonical forms of the ligand may also be important. However, it is clear that the chain propagation necessary for polymer formation is dependent on the orientation of the substituent relative to the ligating oxygen.

Monosubstitution also appears to be an effective means of controlling the extent of delocalization on the C_4 ring and its geometry, which in complexes **1**−**6** was shown to be solely dependent on the substituent and independent of the mode of coordination and the identity of the metal.

Supporting Information Available: X-ray crystallographic files in CIF format for complexes **1**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC981011K

---

(13) (a) Collman, J. P.; McDevitt, J. T.; Yee, G. T.; Leidner, C. R.; McCullough, L. G.; Little, W. A.; Torrance, J. B. T. *Proc. Natl. Acad. Sci. U.S.A.* **1986**, *83*, 4581. (b) Collman, J. P.; McDevitt, J. T.; Yee, G. T.; Leidner, C. R.; Yee, G. T.; Torrance, J. B. T.; Little, W. A. *J. Am. Chem. Soc.* **1987**, *109*, 4606.

(14) Blake, A. J.; Champness, N. R.; Khlobystov, A. N.; Lemenovskii, D. A.; Li, W.-H.; Schroder, M. *Chem. Commun.* **1997**, 1339.