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Synthesis, Structure, and Magnetochemical Analysis of Selected First-Row Transition-Metal Anilino- and Anisolesquarate Compounds

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The isomorphous polymeric complexes $\{M(\mu\text{-}C_6H_5NHC_4O_3)_2(CH_3OH)_2\}_n$ [M = Mn (**1**), Co (**2**), Cu (**4**), Zn (**5**)] are produced by reacting the anilinosquarate anion with the appropriate metal nitrates in a methanolic solution. Each of these complexes contains the central metal atom in a slightly distorted octahedral environment, with the coordination polyhedron consisting of four μ-1,2-bridging anilinosquarate ligands and two trans-oriented methanols. The polymer chains propagate to form a two-dimensional net of metal centers, with the conformation of the component sheets in the net being controlled by intramolecular N–H···O and O–H···O hydrogen bonds. Under reaction conditions similar to those used in the synthesis of the polymers **1**, **2**, **4**, and **5**, the nickel(II) monomer $[Ni(C_6H_5NHC_4O_3)_2(H_2O)_4]\cdot 2H_2O$ (**3**) is produced in which each nickel center is attached to two cis-coordinated anilinosquarate and four aqua ligands in a distorted octahedral arrangement. The ligand conformation in **3** is stabilized by both intra- and intermolecular hydrogen bonding, which results in the formation of a sheet polymer having distinct hydrophobic and hydrophilic surfaces. Magnetochemical analysis of **1** and **4** reveals normal paramagnetic behavior for **1** and a very weak ferromagnetic interaction in **4**; the absence of significant magnetic interactions is attributed to the distortion of the C_4 cycle of the anilinosquarate ligand (lower than C_{2v} symmetry) in these complexes. Reaction of anisolesquarate with $M(NO_3)_2\cdot xH_2O$ in acetonitrile produced the set of isomorphous salts $[M(H_2O)_6][CH_3OC_6H_5C_4O_3]_2$ [M = Mn (**6**), Co (**7**), Ni (**8**), Zn (**9**)]. The anisolesquarate anions in **6**–**9** are hydrogen bonded to the $[M(H_2O)_6]^{2+}$ ions to form polymer chains, which are further linked by hydrogen bonds to form complex sheets. Complexation of the anisolesquarate ligand was not observed even when other solvents and reaction conditions were employed.

Introduction

As a continuation of our efforts to identify the factors that influence the complexing properties of monosubstituted squarate ligands and their potential for producing polymeric complexes with desirable electronic and magnetic properties, we have widened our search for suitable ligands that may allow us to achieve these objectives.[1] As part of this initiative, the complexing properties of the phenylsquarate and diphenylaminosquarate ligands and the variable-temperature magnetochemistry of their polymeric first-row transition-metal complexes have already been investigated.[2,3] These magnetochemical investigations revealed a small but measurable antiferromagnetic interaction in manganese(II) diphenylami-

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nosquarate, $\{Mn[(\mu\text{-}(C_6H_5)_2NC_4O_3]_2[H_2O]_2\}_n$, while manganese(II) phenylsquarate, $\{Mn(\mu\text{-}C_6H_5C_4O_3)(C_6H_5C_4O_3)(H_2O)_3\}_n$, exhibited normal magnetic behavior between 2 and 300 K. This antiferromagnetism in manganese(II) diphenylaminosquarate was attributed to the enhanced electron density on the C_4 cycle of the diphenylaminosquarate ligand because of the migration of the nitrogen lone pair. We concluded that the unavailability of mobile electron density in the phenylsquarate ligand, despite an available pathway for electron migration as demonstrated by X-ray structural and spectroscopic analysis,[4] was a major factor in the different magnetic behaviors shown by these two compounds[2,3] (X-ray analysis revealed the conjugation of the phenyl- and C_4-ring π systems resulting from the coplanarity of these rings, while the emission spectroscopy revealed the availability of low-lying π molecular orbitals that extended over the entire phenylsquarate molecule[4]). However, in monosubstituted squarate ligands, electron migration is only demonstrated when the substituents contain an atom with mobile electron density, which results in changes both in the delocalization pattern on the C_4 cycle and in the extent of the electron transfer into the orbitals of the coordinated metal atoms.[1−4] We therefore decided to explore the effect of using (i) a monosubstituted squarate ligand (anisolesquarate) where the substituent contains a group with mobile electron density (viz., OMe) distal to the C_4 cycle and (ii) a monosubstituted squarate ligand (anilinosquarate) having a substituent with a mobile lone pair on an intervening proximal atom. It was anticipated that these studies would allow us to determine the effect of the location of the mobile electron density on the substituent with respect to both (i) the complexing properties of the anisole- and anilinosquarate ligands with first-row transition metals and (ii) the magnetochemical properties of any polymeric complex formed.

Here, we report on the structure and bonding in selected first-row transition-metal compounds of the anilino- and anisolesquarate ligands and the results of a magnetochemical analysis of the manganese(II) and copper(II) anilinosquarate polymers.

Experimental Section

Preparation of the Ligands. (a) Sodium Anilinosquarate. 3-Anilino-4-hydroxycyclobut-3-ene-1,2-dione (anilinosquarate) was first prepared according to the method of Gauger and Manecke[5] as revised by Neuse and Green.[6] However, the best results were obtained using the following modified procedure. A total of 116 mL of a solution of aniline (37.20 g, 0.40 mol) in DMF was added to 120 mL of a solution of 3,4-dihydroxycyclobut-3-ene-1,2-dione (22.80 g, 0.20 mol) in the same solvent. The mixture was allowed to cool in a dry ice/acetone bath for 10 min, followed by the addition of 250 mL of ether that was previously cooled in a similar manner. This mixture was allowed to stand in the cold bath for a further 10 min. The solids were then removed by suction filtration, washed with ether, and dried on a rotary evaporator. The dried solids were then heated for 20 min at 200 °C to give 37.85 g (100%) of crude anilinosquarate.

The sodium salt of the anilinosquarate ligand was then prepared by dissolving the crude compound (37.85 g, 0.20 mol) in 100 mL of 2 M NaOH. The resulting yellow-brown mixture was then stirred for 45 min. The suspension was filtered, the filtrate was pumped down, and the crude sodium salt of the anilinosquarate ligand was recrystallized from hot water: yield 25.75 g (61%); ^1H NMR (400 MHz, DMSO) δ 6.82 (t, $J = 12$ Hz, 1H), 7.19 (m, 2H), 7.66 (d, $J = 12$ Hz, 2H), 9.28 (s, 1H).

(b) Anisolesquarate. 3-(4-Methoxyphenyl)-4-hydroxycyclobut-3-ene-1,2-dione (anisolesquarate) was prepared according to the method of Bellus[7,8] as modified by Law and Bailey.[9]

Preparation of the Compounds. (a) $\{M(\mu\text{-}C_6H_5NHC_4O_3)_2(CH_3OH)_2\}_n$ [M = Mn (1), Co (2), Cu (4), Zn (5)] and $[Ni(C_6H_5NHC_4O_3)_2(H_2O)_4]\cdot 2H_2O$ (3). A 10 mL aliquot of a methanolic solution of $M(NO_3)_2\cdot xH_2O$ (4.74×10^{-4} mol) [M = Mn, Co, Cu, Zn] was added to 30 mL of a methanolic solution of sodium anilinosquarate (0.10 g, 4.74×10^{-4} mol). The preparation of the $\{Ni(C_6H_5NHC_4O_3)_2(H_2O)_4\}\cdot 2H_2O$ complex was similar except that a 1:2 metal/ligand ratio was used in this case (X-ray quality crystals were not obtained with a 1:1 molar ratio). The resulting solution was filtered and left to stand at about 28 °C until crystallization was complete.

$\{Mn(\mu\text{-}C_6H_5NHC_4O_3)_2(CH_3OH)_2\}_n$ (1): pale yellow needles; yield 12%. Anal. Calcd for $C_{22}H_{20}MnN_2O_8$: C, 53.3; H, 4.0; Mn, 11.1; N, 5.7. Found: C, 52.0; H, 4.2; Mn, 10.4; N, 5.5.

$\{Co(\mu\text{-}C_6H_5NHC_4O_3)_2(CH_3OH)_2\}_n$ (2): orange-red needles; yield 17%. Anal. Calcd for $C_{22}H_{20}CoN_2O_8$: C, 52.9; H, 4.0; Co, 11.8; N, 5.5. Found: C, 50.9; H, 4.0; Co, 11.0; N, 5.5.

$[Ni(C_6H_5NHC_4O_3)_2(H_2O)_4]\cdot 2H_2O$ (3): pale blue-green diamond plates; yield 10%. Anal. Calcd for $C_{20}H_{24}N_2NiO_{12}$: C, 44.2; H, 4.4; N, 5.2; Ni, 10.8. Found: C, 44.0; H, 4.6; N, 5.0; Ni, 10.0.

$\{Cu(\mu\text{-}C_6H_5NHC_4O_3)_2(CH_3OH)_2\}_n$ (4): orange-red oval plates; yield 30%. Anal. Calcd for $C_{22}H_{20}CuN_2O_8$: C, 52.4; H, 4.0; Cu, 12.6; N, 5.6. Found: C, 51.7; H, 4.1; Cu, 12.5; N, 5.3.

$\{Zn(\mu\text{-}C_6H_5NHC_4O_3)_2(CH_3OH)_2\}_n$ (5): colorless plates; yield 25%. Anal. Calcd for $C_{22}H_{20}N_2O_8Zn$: C, 52.2; H, 4.0; N, 5.5; Zn, 12.9. Found: C, 51.4; H, 4.0; N, 5.2; Zn, 12.8.

(b) $[M(H_2O)_6][CH_3OC_6H_5C_4O_3]_2$ [M = Mn (6), Co (7), Ni (8), Zn (9)]. A solution of 0.10 g (4.90×10^{-4} mol) of anisolesquarate in 40 mL of acetonitrile was mixed with a solution of $M(NO_3)_2\cdot xH_2O$ (4.90×10^{-4} mol) [M = Mn (**6**), Co (**7**), Ni (**8**), Zn (**9**)] in 25 mL of the same solvent. The resulting mixture was filtered, and the filtrate was allowed to evaporate at room temperature (ca. 28 °C) until crystallization was complete.

$[Mn(H_2O)_6][CH_3OC_6H_5C_4O_3]_2$ (6): colorless needles; yield 8%. Anal. Calcd for $C_{22}H_{26}MnO_{14}$: C, 46.4; H, 4.6; Mn, 9.7. Found: C, 45.7; H, 4.6; Mn, 8.8.

$[Co(H_2O)_6][CH_3OC_6H_5C_4O_3]_2$ (7): colorless needles; yield 21%. Anal. Calcd for $C_{22}H_{26}CoO_{14}$: C, 46.1; H, 4.5; Co, 10.3. Found: C, 45.9; H, 4.5; Co, 10.2.

$[Ni(H_2O)_6][CH_3OC_6H_5C_4O_3]_2$ (8): colorless needles; yield 18%. Anal. Calcd for $C_{22}H_{26}NiO_{14}$: C, 46.1; H, 4.5; Ni, 10.2. Found: C, 45.9; H, 4.5; Ni, 9.3.

$[Zn(H_2O)_6][CH_3OC_6H_5C_4O_3]_2$ (9): colorless needles; yield 18%. Anal. Calcd for $C_{22}H_{26}O_{14}Zn$: C, 45.6; H, 4.5; Zn, 11.3. Found: C, 44.1; H, 4.4; Zn, 10.6.

Variable-Temperature Magnetic Measurements. Variable-temperature magnetic data for **1** and **4** (2−300 K) were obtained using a Quantum Design MPMS5S Squid magnetometer operating

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Table 1. Crystallographic Data for Compounds **1**−**9**[a]

data	**1**	**2**	**3**
chemical formula	$C_{22}H_{20}N_2O_8Mn$	$C_{22}H_{20}N_2O_8Co$	$C_{20}H_{20}N_2O_{10}Ni$
solvent			$2H_2O$
fw	495.34	499.33	543.12
T (°C)	−123	−123	−123
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)
a (Å)	9.7356(8)	9.753(2)	12.4987(3)
b (Å)	11.4568(8)	11.3372(12)	9.2437(2)
c (Å)	9.3523(6)	9.0443(10)	40.2057(14)
β (deg)	99.044(3)	97.506(4)	97.4167(10)
V (Å^3)	1030.18(13)	991.5(2)	4606.3(2)
Z	2[b]	2[b]	8
ρ_{calcd} (g cm^{-3})	1.597	1.673	1.566
λ (Å)	0.71073[c]	0.71073[c]	0.71073[c]
μ (mm^{-1})	0.696	0.923	0.911
R_1[e]	0.034	0.053	0.034
wR_2[f]	0.081	0.127	0.078

data	**4**	**5**	**6**
chemical formula	$C_{22}H_{20}N_2O_8Cu$	$C_{22}H_{20}N_2O_8Zn$	$C_{22}H_{26}O_{14}Mn$
solvent			
fw	503.94	505.77	569.37
T (°C)	−123	−123	−123
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a (Å)	9.6094(3)	9.8369(6)	6.7380(4)
b (Å)	11.5090(3)	11.2936(6)	8.4952(6)
c (Å)	9.2534(2)	9.1740(4)	21.7946(14)
β (deg)	99.0713(14)	98.862(2)	91.651(5)
V (Å^3)	1010.58(5)	1007.01(9)	1247.02(14)
Z	2[b]	2[b]	2[b]
ρ_{calcd} (g cm^{-3})	1.656	1.668	1.516
λ (Å)	0.71073[c]	0.71073[c]	0.71073[c]
μ (mm^{-1})	1.137	1.276	0.601
R_1[e]	0.035	0.036	0.058
wR_2[f]	0.079	0.078	0.133

data	**7**	**8**	**9**
chemical formula	$C_{22}H_{26}O_{14}Co$	$C_{22}H_{26}O_{14}Ni$	$C_{22}H_{26}O_{14}Zn$
solvent			
fw	573.36	573.14	579.80
T (°C)	−90	20	−90
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a (Å)	6.6557(5)	6.6536(5)	6.6694(9)
b (Å)	8.4202(6)	8.3936(9)	8.4190(11)
c (Å)	21.970(2)	22.297(2)	21.901(4)
β (deg)	92.146(8)	91.580(5)	91.932(12)
V (Å^3)	1230.41(16)	1244.8(2)	1229.0(4)
Z	2[b]	2[b]	2[b]
ρ_{calcd} (g cm^{-3})	1.548	1.529	1.567
λ (Å)	1.54178[d]	1.54178[d]	1.54178[d]
μ (mm^{-1})	6.120	1.769	2.041
R_1[e]		0.043	
wR_2[f]		0.110	

[a] Details in common: graphite-monochromated radiation and refinement based on F^2. [b] The molecule has crystallographic C_i symmetry. [c] Nonius Kappa CCD diffractometer. [d] Siemens P4 rotating-anode diffractometer. [e] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [f] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

in the range of 0.01−1.0 T. Calibrations were carried out with a palladium standard cylinder and $[H_2TMEN][CuCl_4]$ [H_2TMEN = $(CH_3)_2HNCH_2CH_2NH(CH_3)_2^{2+}$].[10]

X-ray Crystallography. Table 1 provides a summary of the crystallographic data for compounds **1**−**9**. For compounds **7** and **9**, only the unit cells were determined. CCDC 228124 to 228130.

Elemental Analysis. C, H, and N analyses were performed by MEDAC Limited, Brunel Science Centre, Egham, Surrey, U.K. The Mn, Co, Ni, Cu, and Zn analyses were done by flame atomic absorption spectrophotometry using a Unicam 929 atomic absorption spectrometer.

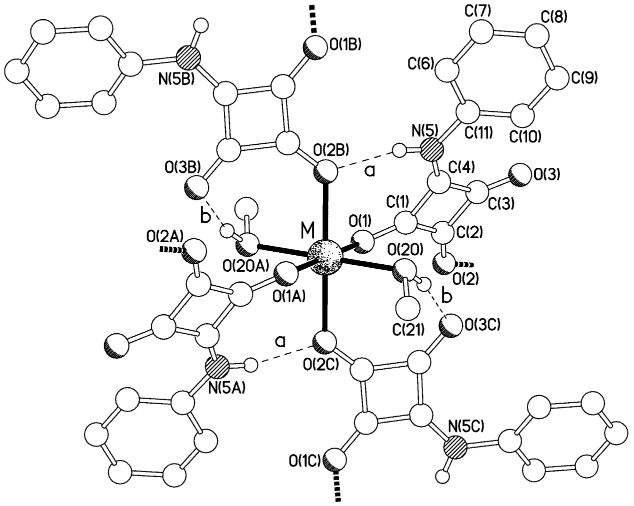

Figure 1. Metal environment in the polymeric complexes $\{M(\mu\text{-}C_6H_5\text{-}NHC_4O_3)_2(CH_3OH)_2\}_n$, M = Mn (**1**), Co (**2**), Cu (**4**), Zn (**5**). The hydrogen-bonding geometries [X···O], [H···O] (Å), [X−H···O] (deg) for **1**, **2**, **4**, and **5** respectively are (a) 2.94, 2.06, 166; 2.90, 2.04, 159; 2.81, 1.93, 166; 2.89, 2.01, 167 and (b) 2.66, 1.78, 165; 2.64, 1.76, 165; 2.64, 1.75, 171; 2.65, 1.76, 170.

Results and Discussion

Reaction of the methanolic solutions of sodium anilinosquarate with $M(NO_3)_2\cdot xH_2O$ (M = Mn, Co, Ni, Cu, Zn) produced crystalline products, which were characterized by single-crystal X-ray diffraction. These structural studies showed the complexes with Mn, Co, Cu, and Zn to be isomorphous and polymeric, whereas that formed with Ni was found to be monomeric. The polymeric structures have the constitution $\{M(\mu\text{-}C_6H_5NHC_4O_3)_2(CH_3OH)_2\}_n$ [M = Mn (**1**), Co (**2**), Cu (**4**), Zn (**5**)] with the metal coordinated to two *trans*-methanol ligands and four O-bonded anilinosquarate ligands in a centrosymmetric arrangement (Figure 1). Two of the anilinosquarate ligands bind to the metal center via the ketonic oxygen atom cis to the amino center, whereas the other two bond via the trans oxygen atom. There is, however, only one crystallographically unique anilinosquarate ligand, with the others being generated by symmetry, so each adopts a μ-1,2-bridging role. The geometry at the metal center is slightly distorted octahedral with cis angles in the ranges 87.49(5)−92.51(5)°, 88.43(11)−91.57(11)°, 86.49(6)−93.51(6)°, and 88.42(6)−91.58(6)° for Mn, Co, Cu, and Zn, respectively. As expected, the Cu complex **4** exhibits the normal Jahn−Teller tetragonal distortion, with the bonds to the oxygen atoms [O(2B) and O(2C)] of the “trans”-coordinated anilinosquarate ligands being significantly longer (by ca. 0.4 Å) than those of their “cis” equatorial counterparts. Interestingly, there are also small axial/equatorial differences in the M−O distances in the Mn, Co, and Zn complexes but, in these, the differences in bond lengths range between only ca. 0.05 and 0.08 Å.

A comparison of the bond lengths within the C_4 ring shows that there is a high degree of consistency throughout the isomorphous series (Table 2). However, it is noticeable that

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Table 2. Selected Comparative Bond Lengths (Å) for Compounds **1**−**5**

	1 (M = Mn)	**2** (M = Co)	**3** (M = Ni)[a]	**4** (M = Cu)	**5** (M = Zn)
M−O(1)	2.1215(14)	2.056(3)	2.042(2) 2.047(2)	1.9489(14)	2.0553(15)
M−O(2B)	2.2020(14)	2.105(3)	*b*	2.3570(15)	2.1355(15)
M−O(20)	2.2002(15)	2.092(3)	*b*	2.005(2)	2.103(2)
C(1)−C(2)	1.456(3)	1.456(6)	1.463(3) 1.472(3)	1.463(3)	1.456(3)
C(1)−C(4)	1.443(3)	1.445(5)	1.428(3) 1.427(3)	1.445(3)	1.447(3)
C(2)−C(3)	1.486(3)	1.479(5)	1.487(3) 1.485(3)	1.491(3)	1.490(3)
C(3)−C(4)	1.459(3)	1.452(5)	1.463(3) 1.454(3)	1.463(3)	1.457(3)
C(4)−N(5)	1.329(3)	1.330(5)	1.338(3) 1.338(3)	1.322(3)	1.320(3)
N(5)−C(11)	1.419(2)	1.423(4)	1.407(2) 1.404(2)	1.422(2)	1.420(2)

[a] The nickel complex has two independent anilinosquarate ligands. [b] Complex **3** is not centrosymmetric and has aqua ligands instead of CH_3OH ligands and thus has no directly equivalent bond lengths. The nickel aqua coordination distances are given in Table 4.

Table 3. Selected Bond Angles (deg) for Compounds **1**, **2**, **4**, and **5**

	1 (M = Mn)	**2** (M = Co)	**4** (M = Cu)	**5** (M = Zn)
O(1)−M−O(2B)	89.39(6)	88.43(11)	88.62(6)	88.42(6)
O(1)−M−O(2C)	90.61(6)	91.57(11)	91.38(6)	91.58(6)
O(1)−M−O(20)	89.30(6)	89.88(13)	89.03(6)	89.72(6)
O(1)−M−O(20A)	90.70(6)	90.12(13)	90.97(6)	90.28(6)
O(2B)−M−O(20)	87.49(5)	90.05(12)	86.49(6)	89.32(6)
O(2B)−M−O(20A)	92.51(5)	89.95(12)	93.51(6)	90.68(6)

these bond lengths fall into a pattern of one "short", two "short medium", and one "long", indicative of a distortion and a consequent change in the symmetry of the C_4 ring to lower than C_{2v}. The difference between the diametrically opposite longest and shortest bonds is still only ca. 0.04 Å, thus indicating an appreciable degree of delocalization within the C_4 cycle. This pattern of bonding contrasts with that seen, for example, in the first-row transition-metal diphenylaminosquarate complexes, where the ring contains just two adjacent short and two adjacent long bonds.[3] However, in this latter series of complexes, all of the diphenylaminosquarate ligands are bonded to the metal center via the oxygen donors cis to the amino substituent, whereas here in the anilinosquarate complexes, we have a combination of cis and trans geometries (vide infra). The only other example that we have observed where a combination of cis and trans coordination occurs is in the dimeric lanthanide complexes of diphenylaminosquarate.[1e] In these latter structures, a distortion of the C_4 ring similar to that seen in the current anilinosquarate complexes is observed, with there being one "short", one "short-medium", one "long-medium", and one "long" bond. The most obvious explanation for these different patterns of bonding within the C_4 cycle is that in the "cis−cis" case there exists a delocalization pathway that extends from the amino N atom to both of the coordinated metal centers, whereas in the "cis−trans" case (the geometry that we observe in **1**, **2**, **4**, and **5**) there is only one such pathway that extends from N(5) via C(4), C(1), and O(1) to the metal center (Table 3). A feature of the ligand geometry that differs significantly from that seen in its diphenylamino counterpart[3] is a noticeably increased double-bond character for the C_4−N linkage, which here has lengths that range from 1.320(3) Å in the zinc complex **5** to 1.330(5) Å in the cobalt analogue **2**. In the manganese and copper diphenylaminosquarate polymer complexes, this C−N bond has values of 1.367(5) and 1.357(3) Å, respectively; similar longer C−N bonds are also observed in the dimeric lanthanide diphenylaminosquarate complexes.[1e] In the anilinosquarate complexes, although the plane of the phenyl ring is rotated significantly (by ca. 27°) out of the plane of its associated C_4 cycle, we believe the shortening of the C_4−N bond is still a consequence of a pattern of delocalization that extends to include the phenyl ring. In the case of the diphenylaminosquarate complexes, this is apparently not possible because of the enforced larger rotation of the planes of the pair of aromatic rings out of the plane of the C_4 ring (ca. 38°).

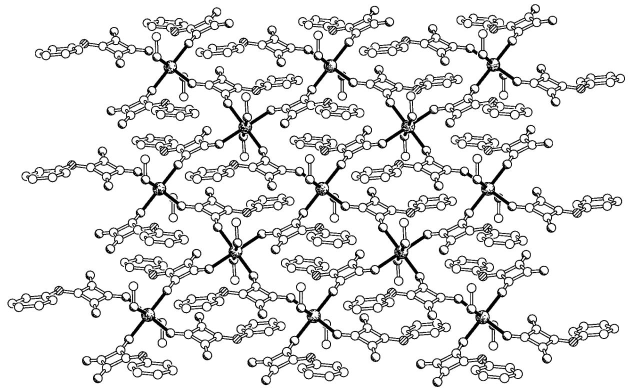

Figure 2. Part of one of the contiguous polymeric sheets in the structures of $\{M(\mu\text{-}C_6H_5NHC_4O_3)_2(CH_3OH)_2\}_n$, M = Mn (**1**), Co (**2**), Cu (**4**), Zn (**5**).

As was observed for the manganese and copper diphenylaminosquarate complexes, the polymer chains in **1**, **2**, **4**, and **5** propagate to form a 2-D net of metal centers linked by a single bridging ligand (Figure 2).[3] In the case of the diphenylaminosquarate complexes, the bridging is μ-1,3, whereas here for the anilinosquarate case, the bridging is μ-1,2. This series of complexes represents the first example of polymeric first-row transition-metal complexes of monosubstituted squarate ligands exhibiting μ-1,2 bridging.[1c,2,3] The sheet conformation is to a large extent controlled by the presence of intramolecular N−H···O and O−H···O hydrogen bonds within each complex (a and b in Figure 1). There are no intrasheet $\pi-\pi$ interactions to note or any intersheet stacking interactions.

In the case of the Ni complex, the single-crystal structure analysis revealed the formation of the monomeric compound $[Ni(C_6H_5NHC_4O_3)_2(H_2O)_4]\cdot 2H_2O$ (**3**). The complex comprises two cis-coordinated anilinosquarate and four aqua ligands in a distorted octahedral geometry [cis angles in the range of 80.37(7)−97.05(7)°]. In each case, the coordinated oxygen atom of the anilinosquarate ligand is cis to the amino nitrogen atom. The complex has approximate noncrystallographic C_s symmetry about a plane that bisects the O(1)−Ni−O(21) angle and includes the aqua ligands O(34) and O(35) (Figure 3). The Ni coordination distances range between 2.042(2) and 2.077(2) Å, with there being no differentiation between $Ni-O_{aqua}$ and $Ni-O_{anilinosquarate}$ (Table

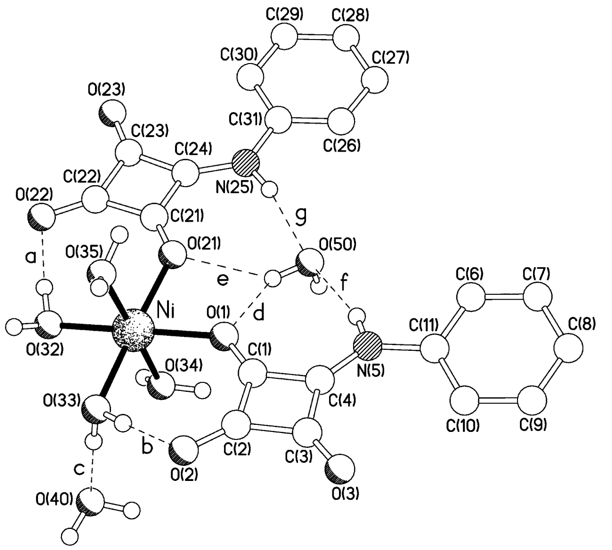

Figure 3. Molecular structure of the monomeric Ni complex **3**. The hydrogen-bonding geometries are given in Table 5.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Compound **3**

Ni−O(32)	2.050(2)	Ni−O(33)	2.077(2)
Ni−O(34)	2.046(2)	Ni−O(35)	2.053(2)
O(1)−Ni−O(34)	87.84(7)	O(1)−Ni−O(21)	80.37(7)
O(34)−Ni−O(21)	89.94(7)	O(1)−Ni−O(32)	173.74(7)
O(34)−Ni−O(32)	86.91(7)	O(21)−Ni−O(32)	96.21(7)
O(1)−Ni−O(35)	93.41(7)	O(34)−Ni−O(35)	178.12(7)
O(21)−Ni−O(35)	91.66(7)	O(32)−Ni−O(35)	91.93(7)
O(1)−Ni−O(33)	97.05(7)	O(34)−Ni−O(33)	90.65(7)
O(21)−Ni−O(33)	177.33(7)	O(32)−Ni−O(33)	86.43(7)
O(35)−Ni−O(33)	87.80(7)		

4). The bond lengths within the two independent C_4 cycles do not differ significantly from those observed in the polymeric complexes **1**, **2**, **4**, and **5** other than a shortening of the C(1)−C(4) and C(21)−C(24) distances to 1.428(3) and 1.427(3) Å, respectively. There is also a similar shortening of the N(5)−C(11) and N(25)−C(31) bond lengths relative to their counterparts in **1**, **2**, **4**, and **5**, indicating a possible increase in the pattern of conjugation that extends from the phenyl ring of each independent ligand to include the Ni center. The inclination of each phenyl ring to its associated C_4 cycle is also in both of the cases appreciably reduced (to ca. 6 and 17°). The ligand conformation is stabilized by hydrogen bonding between the oxygen atoms trans to each anilino substituent and a pair of cis-coordinated aqua ligands (a and b in Figure 3) and between the two amino N−H groups and one of the molecules of water of crystallization O(50) (interactions d−g in Figure 3).

The cis coordination of the two anilinosquarate ligands results in the molecule having its aqua ligands dominating one face. Three of the aqua hydrogen atoms, two of them on O(35) and one of them on O(34), and one of them of the included water molecule [O(40)] form intermolecular hydrogen bonds to the noncoordinated oxygen atoms of symmetry-related anilinosquarate ligands (see Table 5). These interactions give rise to the formation of a hydrogen-bonded sheet polymer having one face populated entirely by oxygen atoms and the other by the phenyl rings of the anilinosquarate ligands. The hydrophilic face of one sheet is hydrogen bonded via O−H···O hydrogen bonds to the equivalent face of its centrosymmetrically related counterpart, employing the aqua and H_2O hydrogen atoms not utilized in the initial sheet formation. The hydrophobic surface of the resulting hydrophobic−hydrophilic−hydrophilic−hydrophobic sandwich is illustrated in Figure 4 as a space-filling representation. The geometry of this surface is stabilized by face-to-face stacking interactions between the C_4 cycles of the two independent anilinosquarate ligands (a in Figure 5) supplemented by further stacking interactions (b in Figure 5) between the phenyl ring of one anilinosquarate ligand and the opposite face of one of the C_4 cycles.

Table 5. Hydrogen-Bonding (X−H···Y) Geometries for Compound **3**[a]

	X	Y	X···Y (Å)	H···Y (Å)	X−H···Y (deg)
			Intramolecular (Including Solvent, See Figure 3)		
a	O(32)	O(22)	2.717(2)	1.82	174
b	O(33)	O(2)	2.705(2)	1.81	175
c	O(33)	O(40)	2.682(3)	1.78	178
d	O(50)	O(1)	2.956(3)	2.18	145
e	O(50)	O(21)	2.946(3)	2.21	138
f	N(5)	O(50)	3.118(3)	2.24	165
g	N(25)	O(50)	3.050(3)	2.16	168
			Intermolecular		
	O(32)	O(33)	2.813(2)	1.92	170
	O(34)	O(23)	2.799(2)	1.91	172
	O(34)	O(40)	2.758(2)	1.90	159
	O(35)	O(3)	2.750(3)	1.85	176
	O(35)	O(23)	2.806(3)	1.91	171
	O(40)	O(22)	2.763(2)	1.88	166
	O(40)	O(2)	2.756(2)	1.87	168

[a] All of the O−H and N−H are located from Δ*F* maps and fixed at 0.90 Å.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for Compounds **6** and **8**

	6 (M = Mn)	**8** (M = Ni)
M−O(21)	2.166(3)	2.051(2)
M−O(22)	2.170(3)	2.047(2)
M−O(23)	2.193(3)	2.072(2)
C(1)−C(2)	1.488(5)	1.491(4)
C(2)−C(3)	1.496(5)	1.491(4)
C(3)−C(4)	1.439(5)	1.442(4)
C(4)−C(1)	1.434(5)	1.433(4)
O(21)−M−O(22)	88.28(11)	88.94(12)
O(21)−M−O(23)	90.81(11)	90.57(10)
O(21)−M−O(22A)	91.72(11)	91.05(12)
O(21)−M−O(23A)	89.19(11)	89.43(10)
O(22)−M−O(23)	89.62(11)	88.72(11)
O(22)−M−O(23A)	90.38(11)	91.28(11)

In the case of Ni, the formation of a monomer containing just a pair of cis-oriented anilinosquarate ligands, with the other coordination sites occupied by aqua ligands instead of a polymeric structure isomorphous with **1**, **2**, **4**, and **5**, is reminiscent of anomalies that we have observed for complexes of other monosubstituted squarate ligands.[1d,2,3] The reasons for the absence of coordinated methanol ligands in **3** are unclear, especially because this complex was prepared under experimental conditions similar to those for the Mn, Co, Cu, and Zn complexes. However, it should be noted that, in the case of a series of first-row transition-metal complexes of the methylsquarate ligand synthesized in methanolic solution, no coordinated methanols were observed.[1c] The cis orientation of the two coordinated anilinosquarate ligands

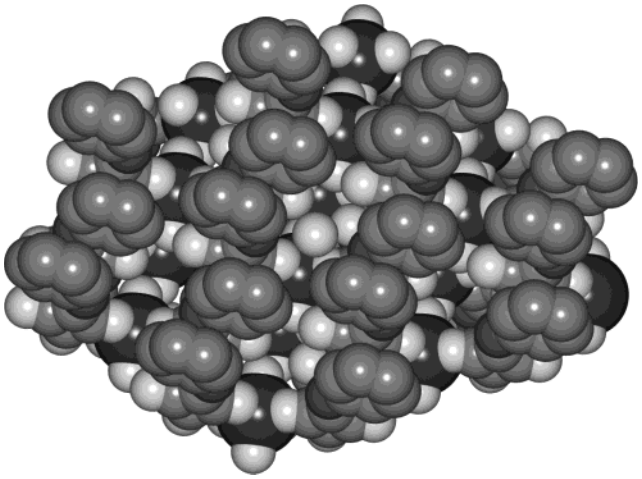

Figure 4. Space-filling representation showing the hydrophobic surface of the hydrogen-bonded polymeric-sheet structure adopted by **3** in the solid state. Hydrogen atoms have been omitted for clarity. The Ni atoms, which occupy the central hydrophilic region of the sheets, are depicted in black, and the oxygen atoms, in pale gray.

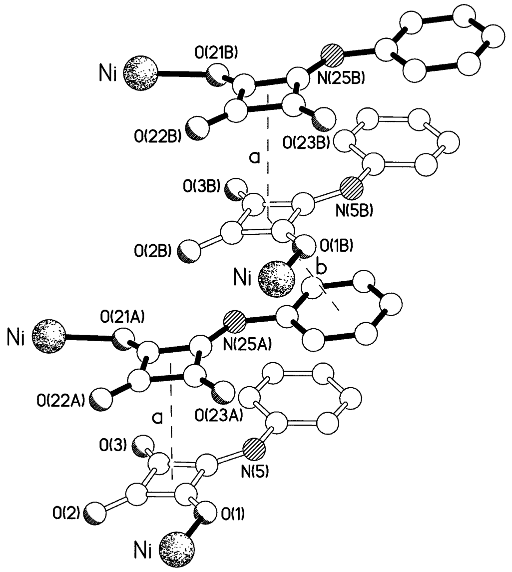

Figure 5. $C_4\cdots C_4$ and $C_4\cdots C_6$ stacking interactions between the anilinosquarate ligands in the hydrogen-bonded sheets in the structure of **3**. The centroid⋯centroid and mean interplanar separations (Å) are (a) 3.45, 3.36 and (b) 3.63, 3.36; the constituent rings are inclined by 4 and 9°, respectively.

in **3** is analogous to that observed in a series of monomeric complexes of the methoxysquarate ligand (M = Mn, Co, Ni, Zn).[1d] In that case, we argued that the methoxysquarate ligand had a cis-directing effect resulting from the migration of the lone pair of electrons on the oxygen atom of the methoxy group. The anilinosquarate ligand also possesses a similar mobile lone pair, which we assume would thus have an equivalent cis-directing effect. It should be noted that in the cases of two series of first-row transition-metal monomeric complexes of the methyl- and phenylsquarate ligands, which do not possess such lone pairs, only trans coordination is observed.[1c,2]

First-Row Transition-Metal Compounds of Anisolesquarate. Single-crystal structure analysis of the products obtained from the attempted syntheses of the Mn(II), Co(II), Ni(II), and Zn(II) anisolesquarate complexes showed all of them to be isomorphous compounds of the formula

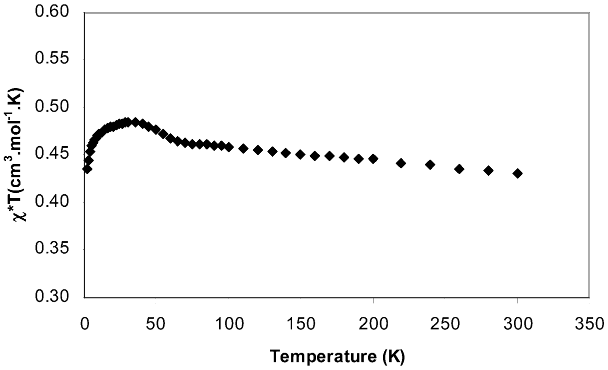

Figure 6. Graph of χ^*T versus temperature (K) for **4**.

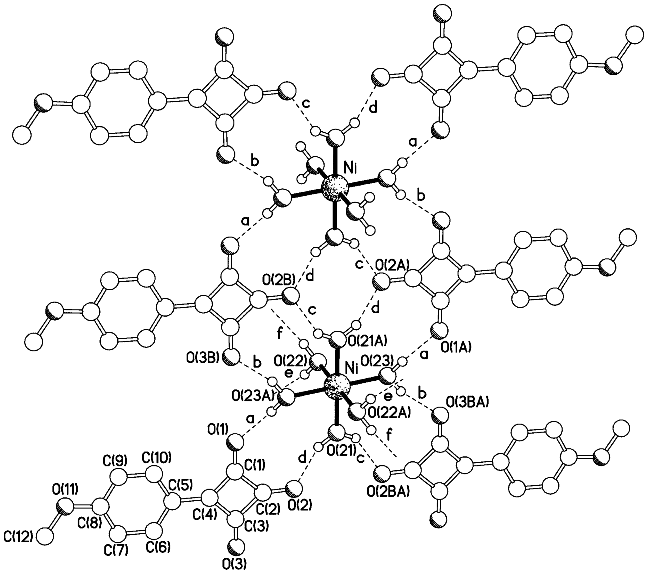

Figure 7. Molecular structure of the hydrogen-bonded salt **8**. The hydrogen-bonding geometries [O⋯O], [H⋯O] (Å), [O−H⋯O] (deg) are (a) 2.78, 1.90, 167; (b) 2.79, 1.92, 162; (c) 2.74, 1.94, 148; (d) 2.80, 1.95, 158; (e) 2.75, 1.85, 171; and (f) 2.72, 1.83, 171.

$[M(H_2O)_6][CH_3OC_6H_5C_4O_3]_2$ [M = Mn (**6**), Co (**7**), Ni (**8**), Zn (**9**)]. An analysis of the nickel product showed the anisolesquarate "ligand" not to be directly bonded to the nickel center, with a simple hexaaquanickel(II) anisolesquarate salt having been formed (Table 6). The anisolesquarate anions are, however, linked directly to the $Ni(H_2O)_6$ "core" by the O−H⋯O hydrogen bonds, i.e., second-sphere coordination (Figure 7). The hydrogen-bonded chain polymer that is formed is linked by further O−H⋯O hydrogen bonds to the chains lying immediately above and below to form a fairly complex hydrogen-bonded sheet, with the methoxy groups populating the upper and lower surfaces. Adjacent sheets, however, do not exhibit interleaving of the anisolesquarate units, with the methoxy groups in each sheet just abutting each other. The structure observed here is very reminiscent of that observed previously for the salt formed between phenylsquarate and $[Pt(NH_3)_4]^{2+}$.[2]

Decreasing the polarity of the solvent with a view to reducing the stabilities of the cation/anion pair and thus increasing the possibility of a complex formation proved futile. We then attempted a synthesis with anhydrous nickel(II) chloride and the anisolesquarate ligand in acetonitrile, but the previously reported complex *trans*,*trans*,*trans*-Ni-

$(CH_3CN)_2Cl_2(H_2O)_2$ (**10**)[11] was the only crystalline product we were able to isolate (Tables S1 and S2 in the Supporting Information provide crystal data and bond lengths and angles, respectively, CCDC 228131). Attempted syntheses using sodium anisolesquarate, on the basis of the assumption that the anisolesquarate ion would be a stronger ligand than the neutral anisolesquarate, also produced salts. It appears that any enhanced possibility of complexation because of the expected increased ligand strength of the anilinosquarate ion was effectively counteracted by the stability of the salts.

The anisolesquarate ligand is the first example of a monosubstituted squarate ligand where complexation was not achieved with any of these four metals: Mn, Co, Ni, Zn. Previously, only three examples of salt formation in attempted syntheses of metal complexes with monosubstituted squarate ligands have been reported. These were $[Mn(H_2O)_6][H_2NC_4O_3]_2 \cdot 2H_2O$, $[Pt(NH_3)_4][C_6H_5C_4O_3]_2 \cdot H_2O$, and $[Ni(H_2O)_6][(C_6H_5)_2NC_4O_3]_2 \cdot 2H_2O$.[1b,f,3] We assume that the enhanced stability of the tertiary structure because of the hydrogen-bonding interactions and the stability of $[M(H_2O)_6]^{2+}$ are major factors that contribute to the greater incidence of salt formation in this series.

Comparison of First-Row Transition-Metal Anisole- and Phenylsquarates. The pattern of bonding and extent of delocalization on the C_4 cycles in both the anisole- and phenylsquarate ligands are similar despite the presence of the electron-donating methoxy group in the former. The migration of the oxygen lone pairs on the methoxy group in the anisolesquarate ligand ($C_6-O_{methoxy}$, ca. 1.366 Å), which is significantly less than that observed in the methoxysquarate ligand ($C_4-O_{methoxy}$, ca. 1.305 Å), does not continue into the C_4 ring. However, despite this similarity, the phenylsquarate ligand forms complexes with Mn(II), Co(II), Ni(II), and Zn(II) ions (the Mn complex being a one-dimensional polymer and the Co(II), Ni(II), and Zn(II) complexes being isomorphous monomers), which is in contrast to the formation of the isomorphous salts when these metals were reacted with the anisolesquarate ligand. Thus, a minor change in the substituent on the monosubstituted squarate ligand (from phenyl to methoxyphenyl) results in differences in their complexing properties and in the formation of compounds of significantly different structural types.

Variable-Temperature Magnetochemical Analysis of $\{M(\mu\text{-}C_6H_5NHC_4O_3)_2(CH_3OH)_2\}_n$ [M = Mn (1) and Cu (4)] and Comparison with $\{Mn(\mu\text{-}C_6H_5C_4O_3)(C_6H_5C_4O_3)(H_2O)_3\}_n$ and $\{M[(\mu\text{-}(C_6H_5)_2NC_4O_3]_2[H_2O]_2\}_n$ [M = Mn and Cu]. Variable-temperature magnetochemical analysis between 2 and 300 K revealed a normal Curie behavior for **1** and a very weak ferromagnetic interaction for **4** (Figure 6). Although the ferromagnetic interaction in **4** is too small to be modeled, we suggest that it could possibly result from the almost orthogonal connections between the adjacent copper atoms in this complex, even though the intrachain Cu···Cu separations are large (7.38 Å compared to 5.21 Å in $[Cu_2(SalNEt_2)_2(H_2O)(C_4O_4)] \cdot H_2O$).[12]

Thus, contrary to our expectations, complex **1** shows a normal paramagnetic behavior similar to that of manganese(II) phenylsquarate, while manganese(II) diphenylaminosquarate exhibits a weak antiferromagnetic interaction which, however, is strong enough to be modeled.[3] The magnetic interaction shown by **4** is also weaker than we expected. It should be noted that the predicted increase in the electron density on the C_4 cycle of the anilinosquarate ligand relative to those of the phenyl- and diphenylaminosquarate ligands was observed, despite the unexpected noncoplanarity (27°) of the anilino and C_4 cycles, which would be expected to reduce the extent of conjugation and electron migration between these rings. Thus, the electron density on the C_4 cycle required to mediate any significant magnetic interactions is present in the anilinosquarate polymers **1** and **4**. However, unlike in the analogous phenyl- and diphenylaminosquarate complexes, where the respective C_4 cycles have approximately C_{2v} symmetry with two adjacent short and two adjacent long C−C bonds, in the anilinosquarate ligand in these complexes, the symmetry is lowered (here, the C_4 ring has one short, two intermediate, and one long C−C bonds). It should be noted that a significant antiferromagnetic interaction was observed in the μ-1,2-squarato-bridged dimeric complex $[Cu_2(SalNEt_2)_2(H_2O)(C_4O_4)] \cdot H_2O$, in which the squarate ligand is not distorted.[12,13] We therefore attribute the absence of any interaction in **1** and the weakness of the interaction in **4** to the distortion of the C_4 cycle in the anilinosquarate ligands in these complexes, which apparently affects the proper alignment of the magnetic orbitals.[12,13]

Conclusions

The series of isomorphous polymeric M(II) (M = Mn, Co, Cu, Zn) transition-metal anilinosquarate complexes provides another example of the influence of the steric demand of the substituent on the number of monosubstituted squarate ligands that the central metal atom can accommodate and the nature and structure of the polymer formed.[3,14] The less sterically demanding anilino substituent in the anilinosquarate ligand resulted in **1**, **2**, **4**, and **5** having the same number of anilinosquarate groups coordinated to each metal atom, while in the analogous diphenylaminosquarate complexes, the number of coordinated diphenylaminosquarate ligands paralleled the ionic size of the metal.[3] The noncoplanarity of the anilino substituent with the C_4 ring in the coordinated anilinosquarate ligands in complexes **1**−**5** is most likely a consequence of crystal packing forces. In ruthenium anilinosquarate complexes and a series of ionic lanthanide polymers (where the anilinosquarate ion exists as a counterbalancing ion),[15,16] the substituent and the C_4 ring are coplanar.

The polymeric first-row transition-metal complexes of the anilinosquarate ligand, quite unexpectedly, showed no sig-

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nificant magnetic interactions despite the presence of a mobile lone pair of electrons on the nitrogen atom of the anilino substituent and the enhanced electron density on the associated C_4 ring. We attribute this absence of magnetic interactions to an imperfect alignment of the magnetic orbitals resulting from the larger than usual distortion of the C_4 ring.

Thus, the anisole substituent is ineffective in influencing the extent of delocalization on the C_4 cycle in the monosubstituted anisolesquarate ligand when the atom with the mobile electron density is not attached directly to the C_4 cycle. Apparently, only substituents, e.g., anilino, diphenylamino, and methoxy, in which the atom with the mobile electron density is directly attached to the C_4 cycle in the monosubstituted squarate ligands are capable of changing the electron density on this cycle.

For the first-row transition metals, however, there are significant structural differences between the phenyl- and anisolesquarate compounds; complexation occurs in the former, while in the latter, only salt formation is achieved. This unexpected extensive salt formation, as exemplified by the formation of the compounds **6**−**9**, is apparently not effected by the predicted theoretical increase in resonance stabilization of the anisolesquarate but rather by the stability of the individual salts and of the overall tertiary, hydrogen-bonded structure.

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Supporting Information Available: Tables of X-ray data for the complexes in CIF format and thermal ellipsoid plots for all of the structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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