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Synthesis and Structures of Polymeric Mn, Co, Cu, and Zn Complexes of 3-Diphenylamino-4-hydroxycyclobut-3-ene-1,2-dione (Diphenylaminosquarate) and of the Salt $[Ni(H_2O)_6][(C_6H_5)_2NC_4O_3]_2{\cdot}2H_2O$

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Reaction of $M(NO_3)_2{\cdot}xH_2O$ (M = Mn, Co, Ni, Cu, Zn) with 3-diphenylamino-4-hydroxycyclobut-3-ene-1,2-dione (diphenylaminosquarate) produces the neutral polymeric species $\{M[\mu\text{-}(C_6H_5)_2NC_4O_3]_2[H_2O]_2\}_n$ [M = Mn (**1**), Cu (**2**)]; $\{M[\mu\text{-}(C_6H_5)_2NC_4O_3][(C_6H_5)_2NC_4O_3][H_2O]_3\}_n$ [M = Co (**3**), Zn (**4**)]; and in the case of Ni, the salt $[Ni(H_2O)_6][(C_6H_5)_2NC_4O_3]_2{\cdot}2H_2O$ (**5**). Complexes **1** and **2** are isomorphous and crystallize in the monoclinic space group $P2_1/c$ with, for **1**, $a = 13.138(1)$ Å, $b = 10.900(2)$ Å, $c = 9.269(2)$ Å, $\beta = 96.07(1)°$, and $Z = 2$. Complexes **3** and **4** are also isomorphous and crystallize in the space group $P2_1/c$ with, for **3**, $a = 13.211(1)$ Å, $b = 11.038(1)$ Å, $c = 18.748(1)$ Å, $\beta = 97.75(1)°$, and $Z = 4$. The nickel salt, **5**, crystallizes in the triclinic space group $P\bar{1}$ with $a = 6.181(1)$ Å, $b = 9.417(1)$ Å, $c = 15.486(1)$ Å, $\alpha = 101.37(1)°$, $\beta = 95.51(1)°$, $\gamma = 107.57(1)°$, and $Z = 1$. In **1** and **2**, the metal coordination is octahedral, comprising four μ−1,3-bridging diphenylaminosquarate ligands and two trans aqua ligands. In **3** and **4**, the metal coordination is again octahedral, comprising two μ−1,3-bridging and one pendant diphenylaminosquarate ligands, the octahedron being completed by three aqua ligands in a meridional configuration. In **5**, the hexaaquanickel(II) ion is linked by O−H···O hydrogen bonds to a pair of diphenylaminosquarate anions. These anion−cation units are linked via included water molecules to form hydrogen-bonded chains. The diphenylaminosquarate ligands in the polymeric complexes **1**−**4** display multiple-bond localization, a feature which is absent in **5**. Complex **1** exhibits weak antiferromagnetic coupling, whereas **2** shows no significant magnetic interactions.

Introduction

One of the major objectives of our investigations into the chemistry of monosubstituted squarate ligands is the development of a strategy for the synthesis of polymeric transition-metal and lanthanide complexes with the potential for exhibiting properties such as molecular magnetism.[1,2] Although we have synthesized several polymers, for example, $[M(\mu\text{-}CH_3C_4O_3)(H_2O)_4][NO_3]{\cdot}2H_2O$ (M = Co, Ni),[2] $[Mn(\mu\text{-}C_6H_5C_4O_3)(C_6H_5C_4O_3)(H_2O)_3]_n$,[3] and the lead(II) dialkylaminosquarates,[4] we have also produced monomers $[M(CH_3C_4O_3)_2(H_2O)_4]$ (M = Mn, Co, Cu, Zn),[2] $La[((C_6H_5)_2NC_4O_3)]_3[H_2O]_6{\cdot}5H_2O$,[5] and dimers $\{M[\mu\text{-}(C_6H_5)_2NC_4O_3][(C_6H_5)_2NC_4O_3][NO_3][H_2O]_4\}_2{\cdot}4H_2O$ (M = Eu, Gd, Tb)[5] under similar experimental conditions. We decided to extend our studies to include the synthesis of some selected first-row transition-metal diphenylaminosquarates in order to determine what role, if any, factors such as ionic size, coordination number of the metal, and steric bulk of the substituent on the ligand play in influencing polymer formation. Here we report the results of the syntheses of selected first-row transition-metal compounds of the diphenylaminosquarate ligand and present an analysis of their structures and physical properties.

Experimental Section

Preparation of the Ligand. 3-Diphenylamino-4-hydroxycyclobut-3-ene-1,2-dione (Diphenylaminosquarate). A total of 100 mL of a solution of diphenylamine (9.3 g, 0.055 mol) in propan-2-ol was added

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

data	**1**	**2**	**3**	**4**	**5**
chemical formula	$C_{32}H_{24}N_2O_8Mn$	$C_{32}H_{24}N_2O_8Cu$	$C_{32}H_{26}N_2O_9Co$	$C_{32}H_{26}N_2O_9Zn$	$C_{32}H_{36}N_2O_{14}Ni$
F_w	619.5	628.1	641.5	647.9	731.3
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
T (°C)	−173	20	−123	−173	−173
a (Å)	13.138(1)	13.209(1)	13.211(1)	13.128(1)	6.181(1)
b (Å)	10.900(2)	10.898(1)	11.038(1)	10.988(1)	9.417(1)
c (Å)	9.269(2)	9.329(1)	18.748(1)	18.556(1)	15.486(1)
α (deg)					101.37(1)
β (deg)	96.07(1)	98.18(1)	97.75(1)	97.75(2)	95.51(1)
γ (deg)					107.57(1)
V (Å^3)	1319.9(4)	1329.3(1)	2709.1(3)	2652.2(2)	830.8(1)
Z	2^a	2^a	4	4	1^a
ρ_{calcd} (g·cm^{-3})	1.559	1.569	1.573	1.623	1.462
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
μ (cm^{-1})	5.61	8.82	6.98	9.92	6.57
$R_1{}^b$	0.066	0.035	0.051	0.074	0.031
$wR_2{}^c$	0.128	0.094	0.121	0.163	0.083

[a] The molecule has crystallographic C_i symmetry. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR_2 = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(F_o{}^2) + (aP)^2 + bP$.

to 200 mL of a solution of 3,4-diisopropoxycyclobut-3-ene-1,2-dione (10.0 g, 0.050 mol) in the same solvent. Concentrated hydrochloric acid (1 mL) was added to the mixture, which was then refluxed for approximately 3 h. The solvent was then removed on a rotary evaporator to give 9.8 g (63% yield) of 3-diphenylamino-4-isopropoxycyclobut-3-ene-1,2-dione. A 6.0 g (0.019 mol) portion of this product was dissolved in 200 mL of acetone, and 320 mL of 6 M HCl was added. This solution was stirred vigorously and refluxed for 5 h. The resulting red solution was pumped down on the rotary evaporator to give a green solid, which was redissolved in $CHCl_3$ and filtered to remove residual squaric acid. This filtrate was pumped down and the crude product recrystallized from hot water. Yield: 3.2 g (62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.4 (s, 1H), 7.2 (m, 5H), 7.4 (m, 5H). X-ray structural data for this ligand have already been reported.[5]

Preparation of the Metal Complexes. $\{M[\mu\text{-}(C_6H_5)_2NC_4O_3]_2[H_2O]_2\}_n$ [M = Mn (1), Cu (2)], $\{M[\mu\text{-}(C_6H_5)_2NC_4O_3][(C_6H_5)_2NC_4O_3][H_2O]_3\}_n$ [M = Co (3), Zn (4)], and $[Ni(H_2O)_6][(C_6H_5)_2NC_4O_3]_2\cdot 2H_2O$ (5). Diphenylaminosquarate (0.050 g, 1.90 × 10^{-4} mol) was dissolved in 40 mL of propan-2-ol. $M(NO_3)_2\cdot xH_2O$ (3.70 × 10^{-4} mol) [M = Mn, Ni, Cu, Zn] was dissolved in a similar volume of propan-2-ol and this solution slowly added to the ligand solution in each case. These mixtures were then left to stand at about 28 °C until crystallization was complete. A similar preparation was used for the Co complex except that methanol was used as the solvent.

$\{Mn[\mu\text{-}(C_6H_5)_2NC_4O_3]_2[H_2O]_2\}_n$ (1). Yield: 16%. Anal. Calcd for $C_{32}H_{24}MnN_2O_8\cdot H_2O$: C, 60.3; H, 3.8; N, 4.4; Mn, 8.6. Found: C, 60.2; H, 4.1; N, 4.3; Mn, 9.3.

$\{Co[\mu\text{-}(C_6H_5)_2NC_4O_3][(C_6H_5)_2NC_4O_3][H_2O]_3\}_n$ (3). Yield: 19%. Anal. Calcd for $C_{32}H_{26}CoN_2O_9\cdot H_2O$: C, 58.3; H, 4.0; N, 4.3; Co, 9.0. Found: C, 58.5; H, 4.2; N, 4.2; Co, 9.3.

$[Ni(H_2O)_6][(C_6H_5)_2NC_4O_3]_2\cdot 2H_2O$ (5). Yield: 18%. Anal. Calcd for $C_{32}H_{36}N_2NiO_{14}$: C, 52.6; H, 5.0; N, 3.8; Ni, 8.0. Found: C, 53.8; H, 5.0; N, 3.3; Ni, 8.3.

$\{Cu[\mu\text{-}(C_6H_5)_2NC_4O_3]_2[H_2O]_2\}_n$ (2). Yield: 70%. Anal. Calcd for $C_{32}H_{24}CuN_2O_8$: C, 61.2; H, 3.9; N, 4.5; Cu,10.1. Found: C, 61.0; H, 3.8; N, 4.4; Cu, 10.0.

$\{Zn[\mu\text{-}(C_6H_5)_2NC_4O_3][(C_6H_5)_2NC_4O_3][H_2O]_3\}_n$ (4). Yield: 16%. Anal. Calcd for $C_{32}H_{26}N_2O_9Zn\cdot H_2O$: C, 57.7; H, 3.9; N, 4.2; Zn, 9.8. Found: C, 57.5; H, 4.9; N, 4.2; Zn, 10.0.

Note: Complexes **1**, **3**, and **4** appear to be hygroscopic because, although no water of crystallization was located in their X-ray structures, elemental analyses were consistent with a formula that includes a molecule of water of crystallization.

Elemental Analyses. C, H, and N analyses were performed by MEDAC Limited, Brunel Science Centre, Egham, Surrey, 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 crystallographic data for compounds **1**−**5**. Data were collected on a Nonius KappaCCD diffractometer using graphite monochromated Mo Kα radiation. In each case, the data were corrected for Lorentz and polarization factors and for absorption. The structures were solved by direct methods, and the non-hydrogen atoms were refined anisotropically using full matrix least squares based on F^2. In all five structures, the C−H hydrogen atoms were placed in calculated positions, assigned isotropic thermal parameters, $U(H) = 1.2U_{eq}(C)$, and allowed to ride on their parent atoms. The O−H hydrogen atoms were located from ΔF maps and refined isotropically. All computations were carried out using the SHELXTL PC program system[6] (CCDC 146 304 to 146 308).

Variable-Temperature Magnetic Measurements. Variable-temperature magnetic data for **1** and **2** (2−300 K) were obtained using a Quantum Design MPMS5S Squid magnetometer operating in the range 0.01 to 1.0 T. Calibrations were carried out with a palladium standard cylinder and $[H_2TMEN][CuCl_4]$ ($H_2TMEN = (CH_3)_2HNCH_2CH_2NH(CH_3)_2{}^{2+}$).[7] The sample was placed in a gelatin capsule held within a drinking straw attached to the sample transport rod. Diamagnetic corrections for the sample holder assembly and compound were applied using established procedures.

Results and Discussion

Structure of $\{Mn[\mu\text{-}(C_6H_5)_2NC_4O_3]_2[H_2O]_2\}_n$ (1). The X-ray analysis of the manganese(II) complex formed with diphenylaminosquarate (dpas) shows the structure to be a sheet polymer (Figure 1). Each Mn atom lies on an inversion center and is bonded to two trans aqua ligands, and the ketonic oxygen atoms (syn to N) of four dpas ligands in a slightly distorted octahedral coordination geometry [cis angles in the range of 86.8(1)−93.2(1)°; Table 2 and Figure 2]. Each of the dpas ligands serves to bridge adjacent manganese(II) centers in a μ-1,3 fashion, creating the contiguous $Mn_4{-}L_4$ 24-membered macrocycles depicted in Figure 1. The overall conformation is stabilized by O−H···O hydrogen bonds between one of the axial aqua hydrogen atoms and the noncoordinated ketonic oxygen [O(2)] of one dpas ligand and by an O−H···π hydrogen bond

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

	1 [M = Mn]	**2** [M = Cu]		**1** [M = Mn]	**2** [M = Cu]
M−O	2.159(3)	1.951(2)	M−O′	2.159(3)	1.951(2)
M−O(1′)	2.177(3)	1.9842(14)	M−O(1″)	2.177(3)	1.9842(14)
M−O(3)	2.185(3)	2.438(2)	M−O(3′)	2.185(3)	2.438(2)
C(1)−O(1)	1.249(5)	1.259(2)	C(2)−O(2)	1.239(5)	1.228(3)
C(3)−O(3)	1.245(5)	1.229(3)	C(4)−N(4)	1.367(5)	1.357(3)
C(1)−C(2)	1.492(6)	1.481(3)	C(2)−C(3)	1.495(6)	1.493(3)
C(3)−C(4)	1.447(6)	1.455(3)	C(1)−C(4)	1.440(6)	1.434(3)
O−M−O′	180.0	180.0	O(3)−M−O(3′)	180.0	180.0
O−M−O(1″)	92.72(13)	95.13(6)	C(3)−O(3)−M	120.0(3)	114.67(14)
O−M−O(1′)	87.28(13)	84.87(6)	O(1′)−M−O(1″)	180.0	180.0
O−M−O(3″)	92.50(12)	92.62(7)	O(1″)−M−O(3)	93.16(10)	94.96(6)
O(1′)−M−O(3)	86.84(10)	85.04(6)	C(1)−O(1)−M′	128.2(3)	128.95(13)
O−M−O(3)	87.50(12)	87.38(7)			

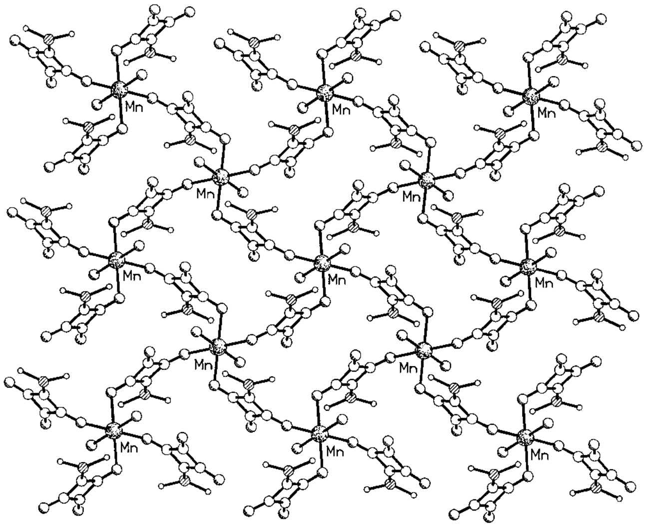

Figure 1. Part of one of the contiguous Mn dpas polymeric sheets in the structure of **1** (the phenyl rings have been omitted for clarity). The chain Mn⋯Mn separations are 7.15 Å (7.17 Å in **2**). The transannular C_4 ring centroid⋯centroid separations are 4.58 and 10.15 Å (4.67 and 10.04 Å in **2**).

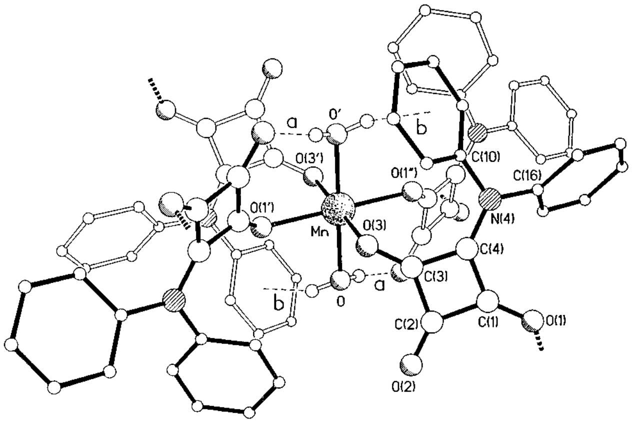

Figure 2. Coordination environment in the Mn diphenylaminosquarate complex **1**. The dashed bonds indicate the linkage to adjacent Mn centers. The H-bonding geometries are as follows: (a) O⋯O, 2.70 Å; H⋯O, 1.80 Å; O−H⋯O, 171°; (b) H⋯π, 2.41 Å; O−H⋯π, 144°.

between the other aqua hydrogen atom and the π system of the C(10) phenyl ring of another dpas ligand (interactions **a** and **b** in Figure 2).

The Mn−O(aqua) bonds [2.159(3) Å] are significantly shorter than those to the dpas oxygen atoms (av 2.181 Å), a pattern that was also observed in the complex formed between manganese(II) and the methylsquarate ligand.[2] The bonding within the C_4 cycle exhibits the usual "two long and two short" C−C linkages. The Δ(C−C) value is 0.05 Å, a value that is the same as that observed in the first-row transition-metal complexes of the methoxysquarate ligand[8] but again significantly less than that observed [Δ(C−C) = 0.09 Å] in the analogous methylsquarate complexes,[2] phenylsquarate complexes,[3] and squarate complexes $[Cu_2(SalNEt_2)_2(H_2O)(C_4O_4)]\cdot H_2O$[11] and $NH_4[V_2O_2(OH)(C_4O_4)_2(H_2O)_3]\cdot H_2O$.[1o] This pattern of bonding in **1** coupled with a slight lengthening of the C(1)−O(2) and C(3)−O(3) bonds [cf. C(2)−O(2)] is consistent with a partially delocalized system that extends from one manganese center, via the carbon atom [C(4)] which contains the diphenylamino substituent, to the next in each polymer chain.

The amino nitrogen N(4) is slightly pyramidalized with the N atom lying 0.061 Å out of the plane of its substituents. The two phenyl rings are rotated by circa 35° [C(10) ring] and 41° [C(16) ring] out of this plane; values within the range are observed in the lanthanide dpas complexes.[5] The N(4)−C(4) linkage [1.367(5) Å] clearly retains some partial double-bond character and is only marginally longer than that observed in the free ligand [1.348(3) Å].[5] The rotation of the diphenylamino group out of the plane of the C_4-cycle (ca. 24°) lies just outside the range (15−21°) observed in the lanthanide complexes,[5] a difference that is unlikely to have any major effect on the C(1)−C(4) and C(3)−C(4) bond lengths.

Adjacent sheets are closely packed and held together by C−H⋯π interactions between one of the meta hydrogen atoms of the C(16) rings in one sheet and the faces of the C(10) rings of the next (the H⋯π distance is 2.90 Å with a C−H⋯π angle of 149°).

Structure of $\{Cu[\mu\text{-}(C_6H_5)_2NC_4O_3]_2[H_2O]_2\}_n$ (2). The copper(II) dpas complex **2** is isomorphous with **1**. The most significant difference between the two structures is the expected tetragonal Jahn−Teller distortion of the copper octahedron in **2**. The cis angles at copper are in the range of 85.04(6)−95.13(6)°, a range slightly greater than that in **1**. The Cu−O(aqua) bond lengths [1.951(2) Å] are significantly shorter than their corresponding distances to Mn [2.159(3) Å] in **1**, and the two M−O(dpas) distances (which are the same in **1**) differ by 0.45 Å [Cu−O(3) 2.438(2) Å, cf. Cu−O(1″) 1.984(1) Å]. Surprisingly, despite the significant differences in the M−O(ligand) bonds in the Cu complex (cf. those in **1**), the M⋯M separations within the network differ only slightly, being 7.15 Å in **1** compared to 7.17 Å in **2**. The conformational features of the dpas ligand are essentially the same as those observed in **1**: the nitrogen atom lying 0.055 Å out of plane, the phenyl rings being inclined by 37 and 41°, and the torsional twist about the N(4)−C_4-cycle bond being circa 21°. The intramolecular hydrogen bond (a) has O⋯O and H⋯O distances of 2.60 and

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

	3 [M = Co]	**4** [M = Zn]		**3** [M = Co]	**4** [M = Zn]
M−O(1)	2.130(2)	2.091(7)	M−O(5)	2.093(2)	2.049(7)
M−O(7′)	2.076(2)	2.087(6)	M−O(9)	2.057(2)	2.049(6)
M−O(10)	2.058(3)	2.027(6)	M−O(11)	2.103(2)	2.104(6)
O(1)−C(1)	1.263(4)	1.239(12)	O(2)−C(2)	1.228(4)	1.217(9)
O(3)−C(3)	1.240(4)	1.214(11)	N(4)−C(4)	1.356(4)	1.351(9)
O(5)−C(5)	1.248(4)	1.251(11)	O(6)−C(6)	1.228(4)	1.221(8)
O(7)−C(7)	1.250(4)	1.251(11)	N(8)−C(8)	1.351(4)	1.346(9)
C(1)−C(2)	1.471(5)	1.500(13)	C(2)−C(3)	1.481(5)	1.516(14)
C(3)−C(4)	1.453(5)	1.461(13)	C(1)−C(4)	1.451(4)	1.468(13)
C(5)−C(6)	1.490(5)	1.487(13)	C(6)−C(7)	1.494(5)	1.489(13)
C(7)−C(8)	1.446(5)	1.442(12)	C(5)−C(8)	1.443(5)	1.437(12)
O(5)−M−O(1)	176.54(9)	175.9(3)	O(7′)−M−O(1)	91.79(9)	92.3(3)
O(9)−M−O(1)	91.16(9)	90.8(2)	O(10)−M−O(1)	96.63(9)	97.3(3)
O(11)−M−O(1)	83.36(9)	82.5(3)	O(7′)−M−O(5)	88.98(9)	88.3(2)
O(9)−M−O(5)	88.06(9)	88.4(2)	O(10)−M−O(5)	86.76(9)	86.8(2)
O(5)−M−O(11)	93.25(9)	93.4(3)	O(9)−M−O(7′)	177.04(9)	176.6(3)
O(10)−M−O(7′)	88.96(10)	88.1(2)	O(7′)−M−O(11)	91.10(9)	91.2(2)
O(9)−M−O(10)	91.04(11)	92.7(2)	O(9)−M−O(11)	88.89(10)	88.0(2)
O(10)−M−O(11)	179.93(11)	179.3(2)	C(1)−O(1)−M	131.8(2)	132.0(6)
C(5)−O(5)−M	127.9(2)	127.9(6)	C(7)−O(7)−M′	122.5(2)	121.7(6)

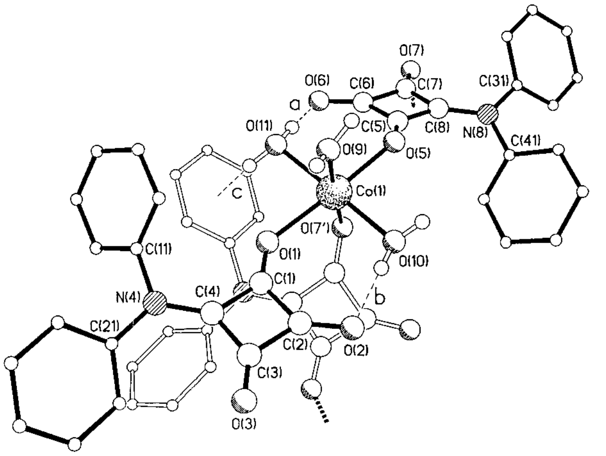

Figure 3. Coordination environment in Co diphenylaminosquarate (**3**). The H-bonding geometries for O···O (Å), H···O (Å), and O−H···O (deg) are (a) 2.67, 1.77, and 173 and (b) 2.61, 1.72, and 172. The H···π distance and O−H···π angle (c) are 2.57 Å and 133°.

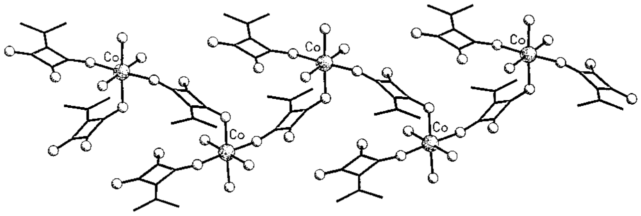

Figure 4. Part of one of the zigzag polymer chains present in the structure of **3**.

1.70 Å, respectively, and an O−H···O angle of 173°. The O−H···π interaction is weaker, with H···π = 2.65 Å and O−H···π = 129°. The intersheet C−H···π interactions in **2** are also weaker, with H···π = 2.99 Å and C−H···π = 151°.

Structures of $\{M[\mu\text{-}(C_6H_5)_2NC_4O_3][(C_6H_5)_2NC_4O_3][H_2O]_3\}_n$ **[M = Co (3), Zn (4)].** In the cobalt complex **3**, the pattern of coordination is different, comprising three dpas and three aqua ligands in a mer configuration about the metal center. Two of the dpas ligands are independent, one adopting a μ−1,3-bridging role analogous to that seen in the manganese and copper complexes, **1** and **2**, whereas the other is pendant (Figure 3). The departures from octahedral coordination geometry are small, the cis angles ranging between 83.4(1) and 96.9(1)°. The Co−O(aqua) bonds, which vary between 2.058(3) and 2.103(2) Å, are very similar to the Co−dpas linkages, which range between 2.076(2) and 2.130(2) Å, the longest bond being associated with the pendant ligand [O(1)] trans to O(5). The Δ(C−C) in the bridging dpas ligand is 0.05 Å (the same as in **1** and **2**), whereas in the pendant ligand, Δ(C−C) is smaller at circa 0.03 Å. Both amino nitrogen atoms are slightly pyramidalized, N(4) by 0.073 Å and N(8) by 0.054 Å. We conjecture that the smaller torsional twist about the N−C_4 bond (12° in the pendant ligand compared to 24° in the μ-1,3-bridging ligands) provides a better overlap between the nitrogen pπ orbitals and their counterparts on the C_4 cycle, resulting in greater electron migration and consequent reduction in Δ(C−C). The phenyl rings are rotated out of the plane of the amino groups by 51 and 33° for the pendant ligand and by 39° for both rings in the bridging ligand.

The cis coordination of the bridging ligands gives rise to the formation of zigzag polymer chains (Figure 4). Two of the aqua ligands are involved in intrachain hydrogen bonding (interactions **a**−**c** in Figure 3), two of these being conventional O−H···O interactions whereas the third is an O−H···π interaction analogous to that seen in the structures of **1** and **2**. The remaining aqua hydrogen atoms [those on O(9)] link adjacent polymer chains, with one of them forming a strong O−H···O hydrogen bond to O(3) [O···O, 2.62 Å; H···O, 1.74 Å; O−H···O, 167°], and the other forming a much longer linkage to O(11) of another chain [O···O, 3.02 Å; H···O, 2.28 Å; O−H···O, 140°], producing hydrogen-bonded sheets. In common with **1** and **2**, these sheets have their upper and lower surfaces bounded by the diphenylamino phenyl ring systems and are weakly cross-linked by C−H···π interactions [H···π, 2.90 Å; C−H···π, 154°] between C_i-related pendant ligand groups.

The zinc complex **4** is isomorphous with **3**, there being no significant differences in either the bond lengths or conformational angles (Table 3).

Structure of $[Ni(H_2O)_6][(C_6H_5)_2NC_4O_3]_2{\cdot}2H_2O$ **(5).** The X-ray analysis of what was intended to be a nickel(II) complex with dpas showed that instead the C_i symmetric salt $[Ni^{II}(H_2O)_6][dpas^{-1}]_2{\cdot}2H_2O$ had been formed (Figure 5).

The geometry of the hexaaquanickel(II) ion is virtually identical to that observed in the $[Ni(H_2O)_6][HC_4O_4]_2{\cdot}2H_2O$ salt.[9] The cis angles at nickel in both compounds are, within statistical significance, the same. However, it is interesting to note that, whereas in **5** the Ni−O distances lie within the narrow range

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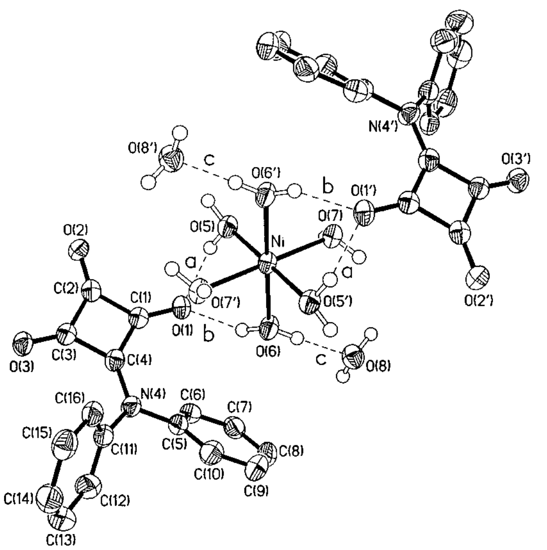

Figure 5. Structure of the $[Ni(H_2O)_6][dpas]_2{\cdot}2H_2O$ complex showing the anion−cation and the cation−water hydrogen bonding (90% probability ellipsoids). The H-bonding geometries for O···O (Å), H···O (Å), O−H···O (deg) are (a) 2.74, 1.85, and 163; (b) 2.81, 1.97, and 156; and (c) 2.72, 1.82, and 179.

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

Ni−O(5)	2.0529(11)	Ni−O(5′)	2.0529(11)
Ni−O(6)	2.0482(12)	Ni−O(6′)	2.0482(12)
Ni−O(7)	2.0562(12)	Ni−O(7′)	2.0562(12)
O(1)−C(1)	1.257(2)	O(2)−C(2)	1.2357(19)
O(3)−C(3)	1.232(2)	N(4)−C(4)	1.349(2)
C(2)−C(1)	1.471(2)	C(2)−C(3)	1.501(2)
C(4)−C(3)	1.460(2)	C(1)−C(4)	1.437(2)
O(5′)−Ni−O(5)	180.0	O(6)−Ni−O(5)	91.21(5)
O(5)−Ni−O(7′)	91.71(5)	O(6)−Ni−O(5′)	88.79(5)
O(5′)−Ni−O(7′)	88.29(5)	O(5)−Ni−O(7)	88.29(5)
O(6)−Ni−O(7)	92.26(5)	O(6)−Ni−O(6′)	180.0
O(7)−Ni−O(7′)	180.0	O(6)−Ni−O(7′)	87.74(5)

of 2.048(1)−2.056(1) Å, in the squarate salt[10] the spread of values is much greater, ranging between 2.029(1) and 2.066(1) Å. The geometry of the dpas anion in **5** is very similar to that of the free ligand,[5] the only notable differences being (i) an expected decrease in the length of the bond to the deprotonated oxygen atom O(1) [1.257(2) Å compared to 1.309(3) Å], which is accompanied by a marked increase in the C(1)−C(4) bond length from 1.398(3) Å in the free ligand to 1.437(2) Å in the salt, and (ii) a slight increase in the torsional twist about the C(4)−N(4) bond (19° compared to 11° in the free ligand).

The anions, cation, and included water molecules are intimately linked by a network of O−H···O hydrogen bonds which utilize all of the donor hydrogen atoms, forming two-dimensional hydrogen-bonded sheets bounded on their upper and lower surfaces by the phenyl rings of the diphenylamino groups (Figure 6). In contrast to the pattern of C−H···π interactions seen in structures **1**−**4**, here there is only minimal parallel $\pi\cdots\pi$ overlap [centroid···centroid separation, 4.76 Å; mean interplanar separation, 3.92 Å].

This compound represents only the second example of a first-row transition-metal salt of a monosubstituted squarate ligand. It is possible that the Ni^{2+} ion cannot form a stable complex with the sterically demanding diphenylaminosquarate groups because of its small size (ionic radius = 0.83 Å), vide infra, and therefore opts for the formation of a simple salt consisting of the stable hexaaquanickel(II) ion and the resonance-stabilized diphenylaminosquarate ion. The hexaaquanickel(II) ion in **5** is only very slightly distorted when compared with the severe distortion resulting from the hydrogen-bonding interactions observed in the hexaaquamanganese(II) ion in the salt $[Mn(H_2O)_6][C_4O_3NH_2]_2{\cdot}2H_2O$.[10] The multiple-bond localization observed in the diphenylaminosquarate ligands in complexes **1**−**4** and in the aminosquarate anion in $[Mn(H_2O)_6][C_4O_3NH_2]_2{\cdot}2H_2O$[10] is absent in **5**, in which there are two C−C bonds of approximately the same length [C(1)−C(2) = 1.471(2) Å and C(3)−C(4) = 1.460(2) Å], the other two bonds being significantly different in length [C(2)−C(3) = 1.501(2) Å and C(1)−C(4) = 1.437(2) Å]. The increased electron density on the C_4 ring in the $(C_4O_3NH_2)^-$ ion facilitated by the near coplanar amino substituent is responsible for the multiple-bond localization in this ion. However, in $[(C_6H_5)_2NC_4O_3]^-$ migration of the nitrogen lone pair to the C_4-ring is hampered by the out-of-plane diphenylamino substituent, and hence, there is an absence of multiple-bond localization.

Effects of Substituent Size on Coordination and Structure. The reduction in the number of coordinated diphenylaminosquarate ligand groups per metal atom from four in the Mn^{2+} (ionic radius = 0.97 Å) complex (**1**) to three in the cobalt and zinc complexes (**3** and **4**) can be attributed to the effect of increased steric hindrance around the smaller Co^{2+} (ionic radius = 0.89 Å) and Zn^{2+} (ionic radius = 0.88 Å) ions. However, despite the smaller size of the Cu^{2+} ion (ionic radius = 0.87 Å), the long Cu−O bonds resulting from the severe tetragonal (Jahn−Teller) distortion in complex **2** reduce the steric effect sufficiently to allow the Cu to coordinate four diphenylaminosquarate groups. We conclude that the meridional configuration adopted by complexes **3** and **4** is to minimize the steric demands of the bulky diphenylamino substituent. In manganese(II) phenylsquarate $[Mn(\mu\text{-}C_6H_5C_4O_3)(C_6H_5C_4O_3)(H_2O)_3]_n$[3] however, where the steric bulk of the ligand is less, a facial configuration is adopted.

Variable-Temperature Magnetic Determinations. (i) $\{Mn[\mu\text{-}(C_6H_5)_2NC_4O_3]_2[H_2O]_2\}_n$ (1). The variable-temperature (2−300 K) magnetic data for **1**, expressed as χ ($cm^3{\cdot}mol^{-1}$), are shown in Figure 7. The moment is essentially constant down to ~100 K and then drops to 2.5 μ_B at 2 K, indicative of very weak antiferromagnetic exchange. The two-dimensional grid structure of **1** (Figure 1) can be envisaged as an array of intersecting one-dimensional chains, with essentially equal spacing between the chains. This geometry presents a significant problem in terms of a complete two-dimensional exchange equation, and so the data were fitted using a nonlinear regression analysis to a one-dimensional uniform Heisenberg chain expression,[11−13] adapted for interchain interaction by a first-order molecular field correction, and show very small intrachain (J) and interchain (J') exchange integrals. Using this model, a good fit was obtained, and the best-fit line shown in Figure 7 was calculated for $g = 2.000$, $J = -0.27(5)$ cm^{-1}, $J' = -0.40(5)$ cm^{-1}, and TIP = 0 emu ($10^2R = 0.21$, $R = [\sum(\chi_{obs} - \chi_{calc})^2/\sum\chi_{obs}^2]^{1/2}$). The very weak antiferromagnetic coupling situation is consistent with the structure of **1**, which has a two-dimensional arrangement of intersecting manganese chains with long, six-bond connections between the metal centers. The structurally similar two-dimensional manganese(II) carboxylato polymer

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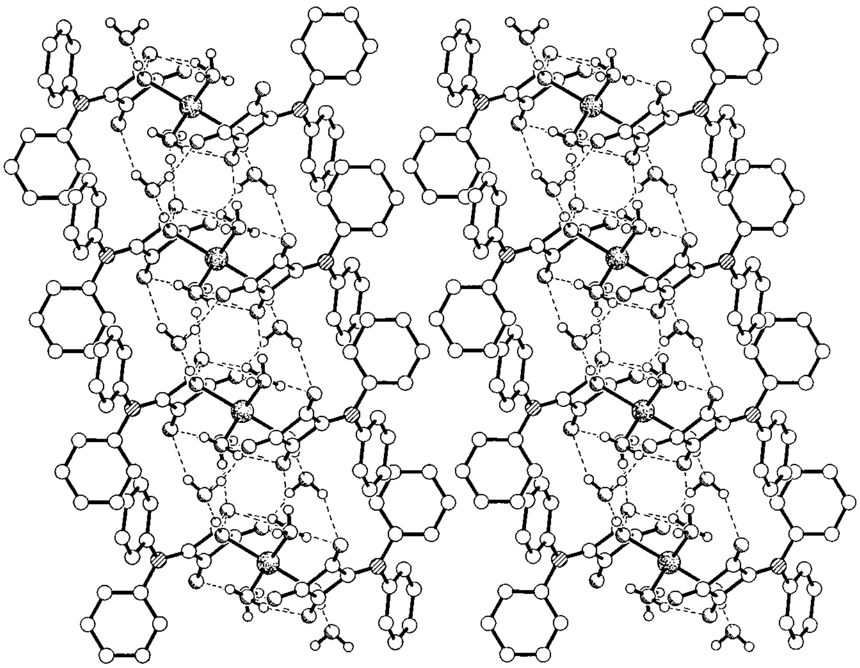

Figure 6. Packing of the H-bonded anions and cations in the structure of **5**.

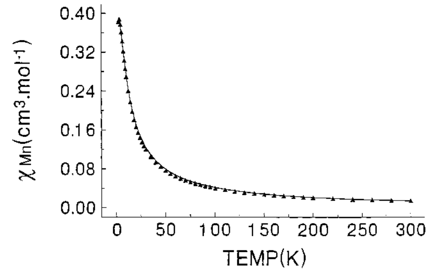

Figure 7. Graph of χ_{Mn} (cm^3·mol^{-1}) versus temperature (K) for **1**.

$[Mn(MCPA)_2(H_2O)_2]_n$ (MCPA = 2-methyl-4-chlorophenoxyacetic acid) reported by Tangoulis et al.[14] contains bridging carboxylate groups and shows magnetochemistry similar to that of **1**. It should be noted that within the same temperature range the magnetic moment for manganese(II) phenylsquarate $[Mn(\mu\text{-}C_6H_5C_4O_3)(C_6H_5C_4O_3)(H_2O)_3]_n$[3] only varied from 5.8 to 5.6 μ_B, indicating that the manganese(II) centers in this complex are uncoupled. It is assumed that the weak coupling in manganese(II) diphenylaminosquarate **1** is due to the symmetrically oriented $\mu-1,3$-bridging ligands, and the additional electron density on the ligand C_4-cycle is due to the migration of the nitrogen lone pair in this complex, a feature which is absent in $[Mn(\mu\text{-}C_6H_5C_4O_3)(C_6H_5C_4O_3)(H_2O)_3]_n$.

(ii) $\{Cu[\mu\text{-}(C_6H_5)_2NC_4O_3]_2[H_2O]_2\}_n$ (2). Variable-temperature magnetic susceptibility data were collected for **2** at 0.01 and 1.0 T from 2 to 300 K. No maximum in χ_M was observed down to 2 K, and plots of μ versus temperature show straight line behavior down to ~2.5 K, followed by a very slight increase at lower temperatures. Fitting of the magnetic data to a one-dimentional ferromagnetic chain expression[15] indicates that if this model is realistic, the intrachain coupling constant is <0.1 cm^{-1} and indicative of no significant effect. Although both the Mn and Cu complexes are isostructural, with the chains linking the metal centers oriented approximately orthogonally to each other (80.7° in Mn compared to 81.1° in Cu), in the Cu complex, coordination involves both axial and equatorial sites on the metal, whereas in the Mn complex, only equatorial sites are utilized. Thus in the Cu complex, both the d_{z^2} and $d_{x^2-y^2}$ orbitals are involved in bridging, whereas in the Mn complex, only the $d_{x^2-y^2}$ is employed and, hence, exchange between the metal centers is weak.

Conclusions

This series of first-row transition-metal compounds of the diphenylaminosquarate ligand illustrates clearly that the number of monosubstituted squarate ligands coordinated to the metal atom is dependent on the ionic size of the metal and steric bulk of the substituent on the ligand. As a result, these factors will (i) influence the potential for polymer formation in the synthesis of transition-metal and lanthanide complexes and (ii) help determine whether neutral or ionic polymers will be produced. The electron density on the C_4-ring in monosubstituted squarate ligands also seems to be important with respect to the mediation of coupling interactions.

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Supporting Information Available: X-ray crystallographic files, in CIF format, containing data for the structures of **1**−**5**. X-ray crystallographic data for complexes **1**−**5**: (1) $\{M[\mu\text{-}(C_6H_5)_2NC_4O_3]_2[H_2O]_2\}_n$ [M = Mn (**1**) (50% thermal ellipsoids), Cu (**2**) (50% thermal ellipsoids)], (2) $\{M[\mu\text{-}(C_6H_5)_2NC_4O_3][(C_6H_5)_2NC_4O_3][H_2O]_3\}_n$ [M = Co (**3**) (90% thermal ellipsoids), Zn (**4**) (50% thermal ellipsoids)], (3) $[Ni(H_2O)_6][(C_6H_5)_2C_4O_3]_2\cdot 2H_2O$ (**5**) (80% thermal ellipsoids). This material is available free of charge via the Internet at http://pubs.acs.org.

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