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FULL PAPER

Hydrogen-bonding interactions in the series of complexes $[M(C_4O_4)(OH_2)_2(dmf)_2]$ and $[M(C_4O_4)(OH_2)_4]$ (M = Mn, Co, Ni, Cu, Zn)

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Reaction of tetrabutylammonium aminosquarate (1-amino-2-methoxycyclobutenedionate) with $MCl_2 \cdot xH_2O$ (M = Mn, Co) and tetraethylammonium aminosquarate with $M(NO_3)_2 \cdot xH_2O$ (M = Ni, Cu, Zn) in *N*,*N*-dimethylformamide (dmf) afforded the series of complexes $M(C_4O_4)(OH_2)_2(dmf)_2$. The complexes are isomorphous and crystallise in the space group $P2_1/c$, with the exception of the copper analogue which crystallises in $P2_1/n$. They all have chain structures that are similar to the squarates $[M(C_4O_4)(OH_2)_4]$ and the complexes $[Zn(C_4O_4)(OH_2)_2(dmso)_2]$ and $[Ni(C_4O_4)(C_3N_2H_4)_2(OH_2)_2]$ and exhibit similar but subtly different hydrogen-bonding interactions to those observed in $[Zn(C_4O_4)(OH_2)_2(dmso)_2]$. Analysis of the hydrogen-bonding interactions in these complexes provides an insight into some additional factors that affect these interactions in transition metal squarates and their role in determining tertiary structure. The implications with respect to solid-state materials design are discussed.

Introduction

The importance of hydrogen-bonding in the design of organic and inorganic solid-state materials with extended networks is currently receiving considerable attention.[1–9] A complete understanding of its role in influencing tertiary structure or the ability to predict its behaviour in controlling solid state structure has remained somewhat elusive.[10–15] Some success in these transformations has been achieved over the last decade or so. For example, Yaghi *et al.*[4] were able to convert manganese(II) and zinc(II) squarates into three-dimensional cage networks using hydrogen-bonding to control the conversion. Whitesides and co-workers[2,3] have used hydrogen-bonded molecular "tapes" in the design of solid-state organic structures with different "tape" formats. Considerable research has also focussed on the role of hydrogen-bonding in self assembly, molecular recognition and other related phenomena.[16] The use of complementary hydrogen-bond interactions has proved an effective tool in molecular monolayer assembly, the formation of supramolecular aggregates and in crystal engineering.[17–23]

What is frequently not appreciated, however, is that apparently minor changes in, for example, the nature of a ligand in a metal complex, can produce major and sometimes even dramatic changes in the nature of the resulting engineered three-dimensional networks. One example of such ligand control in the context of the present studies is in the sheet structure of $Zn(C_4O_4)(OH_2)_2(dmso)_2$ synthesised by Yaghi *et al.*[4] compared with the network structure of $Ni(C_4O_4)(C_3N_2H_4)_2(OH_2)_2$ reported by van Ooijen *et al.*[24] It is clear that the key to controlling the three-dimensional structure is the ability to block/encourage different potential directions of hydrogen bond propagation. The blocking of three-dimensional propagation by dmso in the zinc complex may have been fortuitous as the sulfoxide oxygen atom could have acted as a hydrogen bond acceptor, though approach to this oxygen atom is hindered in one direction by the methyl groups and in another by the metal coordination sphere. If, on the other hand, dmf is used, though approach to the non-bonding *p*-orbitals of the nitrogen is possible, such interactions are not particularly common and would be expected to be weak. This was one of the considerations that prompted us to investigate the use of dmf instead of dmso as the solvent-based ligating agent with a view to determining the possible effects that such an apparently minor reduction in the potential for hydrogen bonding might have. Here, in addition to analysing the effects of changing the donor solvent from dmso to dmf, we also report the syntheses of a series of first row transition metal squarate complexes of formula $[M(C_4O_4)(OH_2)_2(dmf)_2]$ (M = Mn **1**, Co **2**, Ni **3**, Cu **4** and Zn **5**) and compare the hydrogen-bonding and structural features of these species with the series $[M(C_4O_4)(OH_2)_4]$[25,26] and the two related complexes $[Zn(C_4O_4)(OH_2)_2(dmso)_2]$[4] and $[Ni(C_4O_4)(C_3N_2H_4)_2(OH_2)_2]$.[24]

Experimental

Preparation of the ligand

1-Amino-2-methoxycyclobutenedione was first prepared according to the method of Cohen and Cohen.[27]

Tetraethylammonium aminosquarate. 17.7 ml (1.77×10^{-2} mol) of an aqueous solution of tetraethylammonium hydroxide (35 wt.%) was slowly added to 50 ml of an equimolar solution of 1-amino-2-methoxycyclobutenedione in water with constant stirring so that the pH of the mixture never exceeded 6.0. The mixture was then evaporated to dryness on a rotary evaporator and the crude product washed through a frit with acetonitrile in order to remove any squaric acid formed by hydrolysis. The filtrate was then evaporated to dryness on a rotary evaporator. Yield 99%. ^1H NMR [80 MHz, $(CD_3)_2SO$]: δ 1.15 (t, 12H), 3.20 (q, 8H), 4.20 (s, 2H).

Tetrabutylammonium aminosquarate. 150 ml of an aqueous solution of 1-amino-2-methoxycyclobutenedione (1.8 g, 1.4 ×

Table 1 Crystal data, data collection and refinement parameters for complexes **1**–**5**[a]

Data	**1**[b]	**2**	**3**	**4**	**5**
Formula	$C_{10}H_{18}N_2O_8Mn$	$C_{10}H_{18}N_2O_8Co$	$C_{10}H_{18}N_2O_8Ni$	$C_{10}H_{18}N_2O_8Cu$	$C_{10}H_{18}N_2O_8Zn$
Formula weight	349.2	353.2	353.0	357.8	359.6
Colour, habit	Clear needles	Pink square plates	Very pale blue plates	Yellow platy needles	Clear needles
Crystal size/mm	0.12 × 0.10 × 0.10	0.18 × 0.17 × 0.04	0.13 × 0.10 × 0.06	0.60 × 0.27 × 0.03	0.40 × 0.12 × 0.07
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group (no.)	$P2_1/c$ (14)	$P2_1/c$ (14)	$P2_1/c$ (14)	$P2_1/n$ (14)	$P2_1/c$ (14)
T/K	293	293	293	203	293
Cell dimensions					
a/Å	8.510(2)	8.413(1)	8.366(1)	8.632(1)	8.444(1)
b/Å	11.981(2)	11.903(1)	11.930(2)	7.718(1)	11.909(1)
c/Å	8.157(3)	8.007(1)	7.928(1)	11.220(2)	7.999(1)
β/°	112.57(2)	112.27(1)	112.24(1)	106.41(1)	112.51(1)
V/Å^3	768.0(4)	742.0(1)	732.4(1)	717.0(2)	743.1(1)
Z	2[c]	2[c]	2[c]	2[c]	2[c]
D_c/g cm^{-3}	1.510	1.581	1.601	1.657	1.607
F(000)	362	366	368	370	372
Radiation used	Cu-Kα[d]	Cu-Kα[d]	Cu-Kα[d]	Cu-Kα[d]	Cu-Kα
μ/mm^{-1}	7.37	9.46	2.31	2.56	2.69
θ range/°	5.6–60.0	5.7–60.0	5.7–60.0	5.8–57.2	5.7–60.0
No. of unique reflections					
measured	1143	1026	1082	977	1107
observed, $\|F_o\| > 4\sigma(\|F_o\|)$	864	774	1023	907	1037
Absorption correction	Semi-empirical	Semi-empirical	—	—	Semi-empirical
Max., min. transmission	0.66, 0.49	0.78, 0.42	—	—	0.92, 0.69
No. of variables	106	106	106	106	106
R_1[e]	0.050	0.052	0.036	0.034	0.044
wR_2[f]	0.114	0.113	0.090	0.094	0.116
Weighting factors a, b[g]	0.062, 0.165	0.046, 1.303	0.031, 0.943	0.059, 0.612	0.063, 0.851
Largest diff. peak, hole/ e Å^{-3}	0.30, −0.62	0.43, −0.57	0.26, −0.48	0.32, −0.78	0.78, −0.91

[a] Details in common: graphite monochromated radiation, ω-scans. Siemens P4 diffractometer, refinement based on F^2. [b] The unit cell dimensions at 203 K are $a = 8.499(1)$, $b = 11.983(1)$, $c = 8.139(1)$ Å, $\beta = 113.35(1)$°, $V = 761.1(1)$ Å^3. [c] The molecule has crystallographic C_i symmetry. [d] Rotating anode source. [e] $R_1 = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$. [f] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$. [g] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

10^{-2} mol) was left for 48 h in order to effect the hydrolysis of the methoxy group. This hydrolysis was monitored using pH and the reaction was assumed complete when there was no further change in pH. 14.20 ml of a 3 × 10^{-2} mol dm^{-3} methanolic solution of tetrabutylammonium hydroxide was slowly added to the hydrolysed ligand solution such that the pH of the mixture never exceeded 6.0. The solution was then evaporated on a rotary evaporator and the crude product obtained was recrystallised from acetonitrile. Yield, 99%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.95 (t, 12H), 1.35 (m, 8H), 1.60 (m, 8H), 3.20 (t, 8H), 4.5 (s, 2H).

Preparation of the metal complexes

$M(C_4O_4)(OH_2)_2(dmf)_2$ (M = Mn 1 and Co 2). 25 ml of a solution of tetrabutylammonium aminosquarate (0.10 g, 2.8 × 10^{-4} mol) in *N*,*N*-dimethylformamide (dmf) was mixed with 25 ml of an equimolar solution of the respective metal chloride in dmf. The mixture was filtered immediately and the filtrate left at room temperature until crystallisation was complete.

$M(C_4O_4)(OH_2)_2(dmf)_2$ (M = Ni 3, Cu 4 and Zn 5). 100 ml of a solution of tetraethylammonium aminosquarate (0.05 g, 2.1 × 10^{-4} mol) in *N*,*N*-dimethylformamide (dmf) was mixed with a 1.10 × 10^{-4} mol dm^{-3} solution of the respective metal nitrate in 100 ml of dmf. The mixtures were then left to evaporate at room temperature but had to be filtered on several occasions due to the repeated formation of fine precipitates, most likely produced by hydrolysis of the metal salts. When the formation of these precipitates ceased, the filtrates were left until crystal formation was complete. (Note: the repeated filtration resulted in low yields for complexes **3**–**5**.)

$Mn(C_4O_4)(OH_2)_2(dmf)_2$ 1. Clear needles (yield, 60%). Anal. Calc. for $C_{10}H_{18}N_2O_8Mn$: C, 34.40; H, 5.20; N, 8.02; Mn, 15.73. Found: C, 34.00; H, 5.16; N, 7.80; Mn, 15.26%.

$Co(C_4O_4)(OH_2)_2(dmf)_2$ 2. Pink, square plates (yield, 60%). Anal. Calc. for $C_{10}H_{18}N_2O_8Co$: C, 34.01; H, 5.14; N, 7.93; Co, 16.69. Found: C, 33.17; H, 5.45; N, 7.62; Co, 16.94%.

$Ni(C_4O_4)(OH_2)_2(dmf)_2$ 3. Very pale blue plates (yield, 21%). Anal. Calc. for $C_{10}H_{18}N_2O_8Ni$: C, 34.03; H, 5.14; N, 7.94; Ni, 16.63. Found: C, 33.65; H, 4.89; N, 7.24; Ni, 16.45%.

$Cu(C_4O_4)(OH_2)_2(dmf)_2$ 4. Yellow platy needles (yield, 16%). Anal. Calc. for $C_{10}H_{18}N_2O_8Cu$: C, 33.57; H, 5.07; N, 7.83; Cu, 17.76. Found: C, 33.21; H, 5.07; N, 7.75; Cu, 17.26%.

$Zn(C_4O_4)(OH_2)_2(dmf)_2$ 5. Clear needles (yield, 21%). Anal. Calc. for $C_{10}H_{18}N_2O_8Zn$: C, 33.40; H, 5.04; N, 7.79; Zn, 18.18. Found: C, 32.63; H, 4.82; N, 7.15; Zn, 18.02%.

Elemental analyses

C, H, N analyses were done by MEDAC Limited, Brunel University, Uxbridge, Middlesex, UK. The metal analyses were done by flame atomic absorption spectrophotometry using a Unicam 929 spectrophotometer.

NMR spectra

The NMR spectra were done on Bruker spectrometers (a WP 80 SY and a DRS 400).

Crystallographic analyses

Table 1 provides a summary of the crystal data, data collection and refinement parameters for complexes **1**–**5**. The structures were solved by direct methods and all of the non-hydrogen atoms were refined anisotropically by full matrix least-squares based on F^2. In each structure the single unique amide hydrogen atom was placed in a calculated position, assigned an isotropic thermal parameter, $U(H) = 1.2U_{eq}(C)$, and allowed to

Table 2 Selected bond lengths (Å) and angles (°) for complexes **1**–**5**

	1 (M = Mn)	**2** (M = Co)	**3** (M = Ni)	**4** (M = Cu)	**5** (M = Zn)
M–O(1)	2.176(3)	2.111(3)	2.063(2)	1.975(2)	2.103(2)
M–O(5)	2.208(4)	2.131(4)	2.090(2)	2.413(2)	2.151(2)
M–O(10)	2.160(3)	2.064(4)	2.042(2)	1.973(2)	2.054(2)
O(1)–C(2)	1.251(6)	1.253(6)	1.253(3)	1.253(3)	1.249(4)
C(2)–C(3)	1.458(6)	1.472(7)	1.460(4)	1.473(4)	1.463(5)
C(2)–C(3A)	1.462(6)	1.447(7)	1.456(4)	1.463(4)	1.459(5)
C(3)–O(4)	1.251(6)	1.254(6)	1.256(3)	1.249(3)	1.255(4)
O(5)–C(6)	1.225(7)	1.220(7)	1.224(4)	1.236(4)	1.229(5)
C(6)–N(7)	1.303(7)	1.292(8)	1.315(4)	1.323(4)	1.311(5)
N(7)–C(8)	1.432(9)	1.446(10)	1.434(5)	1.456(4)	1.443(6)
N(7)–C(9)	1.465(9)	1.466(8)	1.463(5)	1.462(4)	1.459(6)
O(1)–M–O(1B)	180.0	180.0	180.0	180.0	180.0
O(1)–M–O(5)	91.3(2)	91.1(2)	90.87(8)	85.07(7)	90.92(10)
O(1)–M–O(5A)	88.7(2)	88.9(2)	89.13(8)	94.93(7)	89.08(10)
O(1)–M–O(10)	93.38(13)	94.72(14)	94.84(7)	85.21(8)	94.45(9)
O(1)–M–O(10A)	86.62(13)	85.28(14)	85.16(7)	94.79(8)	85.55(9)
O(5)–M–O(10)	90.3(2)	88.8(2)	87.77(8)	91.16(7)	88.43(10)
O(5)–M–O(5A)	180.0	180.0	180.0	180.0	180.0
O(5A)–M–O(10)	89.7(2)	91.2(2)	92.23(8)	88.84(7)	91.57(10)
O(10)–M–O(10A)	180.0	180.0	180.0	180.0	180.0

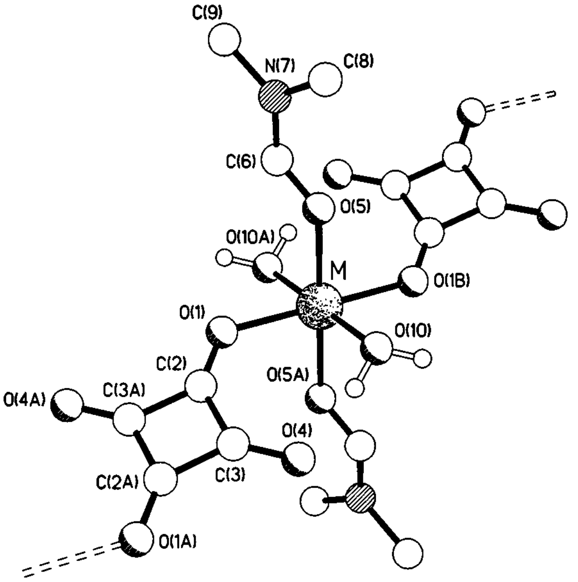

Fig. 1 The metal environment in the polymer complexes **1**–**5**.

ride on the parent atom. The methyl hydrogen atoms were located from ΔF maps, optimised, assigned isotropic thermal parameters, $U(\mathrm{H}) = 1.5U_{\mathrm{eq}}(\mathrm{C})$, and allowed to ride on their parent atoms. In all five structures the hydrogen atoms of the aqua ligands were located from ΔF maps and refined isotropically subject to an O–H distance constraint. Computations were carried out using the SHELXTL PC program system.[28]

CCDC reference number 186/1165.

See http://www.rsc.org/suppdata/dt/1998/3845/ for crystallographic files in .cif format.

Results and discussion

From previous experience we were aware that the amino group in the tetraalkylammonium aminosquarate ligands has a tendency to hydrolyse during the preparation of first row transition metal complexes.[29] Here we utilise this hydrolysis to our advantage in the synthesis of a series of transition metal squarate complexes, since X-ray quality crystals are more easily obtained with the tetraalkylammonium amino ligands than with neat squaric acid. Using this approach the complexes $[\mathrm{M(C_4O_4)(OH_2)_2(dmf)_2}]$ (M = Mn **1**, Co **2**, Ni **3**, Cu **4** and Zn **5**), which exist as polymeric chains similar to those in the complexes $[\mathrm{M(C_4O_4)(OH_2)_4}]$,[25,26] $[\mathrm{Zn(C_4O_4)(OH_2)_2(dmso)_2}]$[4] and $\mathrm{Ni(C_4O_4)(C_3N_2H_4)_2(OH_2)_2}$,[24] were produced.

Structures of $\mathrm{M(C_4O_4)(OH_2)_2(dmf)_2}$ (M = Mn 1, Co 2, Ni 3, Cu 4 and Zn 5)

The X-ray analyses of the products of the reactions between $\mathrm{MCl_2{\cdot}6H_2O}$ (M = Co, Mn) and $\mathrm{M(NO_3)_2{\cdot}6H_2O}$ (M = Ni, Cu, Zn) and dialkylammonium aminosquarates in *N*,*N*-dimethylformamide (dmf) reveal the formation of two types of polymer structure. The Mn, Co, Ni and Zn complexes are isomorphous and constitute one type whereas the Cu constitutes the other. In all cases the squarate ligands are μ-1,3-bridging and are coordinated *trans* to form an extended polymer chain (Fig. 1). The other metal coordination sites are occupied by *trans* aqua and *trans* dmf ligands respectively. In all the complexes except the Cu one there are only small distortions from octahedral geometry, the largest deviations from 90° for the *cis* coordinated ligands being in the Ni complex where these angles range between 85.16(7) to 94.84(7)° (Table 2). Similarly the largest variation in coordination distances also occurs in the Ni complex where the Ni–O distances range between 2.042(2) and 2.090(2) Å. The Cu complex exhibits the expected Jahn–Teller distortion with equatorial Cu–O distances of 1.973(2) and 1.975(2) Å and an axial bond length to the dmf ligands of 2.413(2) Å. In all the complexes the equivalent bond lengths within the squarate ligand do not differ significantly and are comparable to those previously reported in the literature.[25,26,30] In all but the Cu complex the polymer chains extend along the crystallographic *c* direction, the metal atoms and the squarate rings each being positioned on and about independent inversion centres respectively. The metal · · · metal separations within the polymer chains range between 7.928(1) Å in the Ni complex to 8.157(3) Å in the Mn complex, the latter being accompanied by the largest M–O–C(squarate) angle of 131.6(3)°. In the Cu polymer, chain propagation occurs along the crystallographic *b* direction with a Cu · · · Cu separation of 7.718(1) Å and an associated contraction of the Cu–O–C(squarate) angle of 128.6(2)°.

Within the polymer chains the conformation is stabilised *via* pairs of intramolecular O–H · · · O hydrogen bonds between one of the hydrogen atoms of each *trans* aqua ligand and the *trans* non-coordinated squarate oxygen atoms (**a** in Figs. 2 and 3). To accommodate this pattern of hydrogen-bonding the

Table 3 Hydrogen bonding geometries, in-chain angle at the coordinated oxygen atom O(1) and the ligand/coordination plane inclinations for complexes **1**–**5**[a]

	a in Fig. 2/3			**b** in Fig. 2/3					
	O···O/Å	H···O/Å	O–H···O/°	O···O/Å	H···O/Å	O–H···O/°	Angle at O(1)/°	A/°	B/°
1 (M = Mn)	2.67	1.79	163	2.69	1.80	172	131.6(3)	24	19
2 (M = Co)	2.65	1.76	171	2.70	1.82	166	130.5(3)	25	19
3 (M = Ni)	2.64	1.75	171	2.72	1.83	171	130.5(2)	25	19
4 (M = Cu)	2.67	1.78	170	2.74	1.86	165	128.6(2)	33	23
5 (M = Zn)	2.65	1.75	174	2.71	1.81	174	130.6(2)	25	19

[a] All O–H bonds normalised to 0.90 Å. A: inclination of C_4O_4 plane to equatorial coordination plane. B: inclination of dmf plane to axial coordination plane.

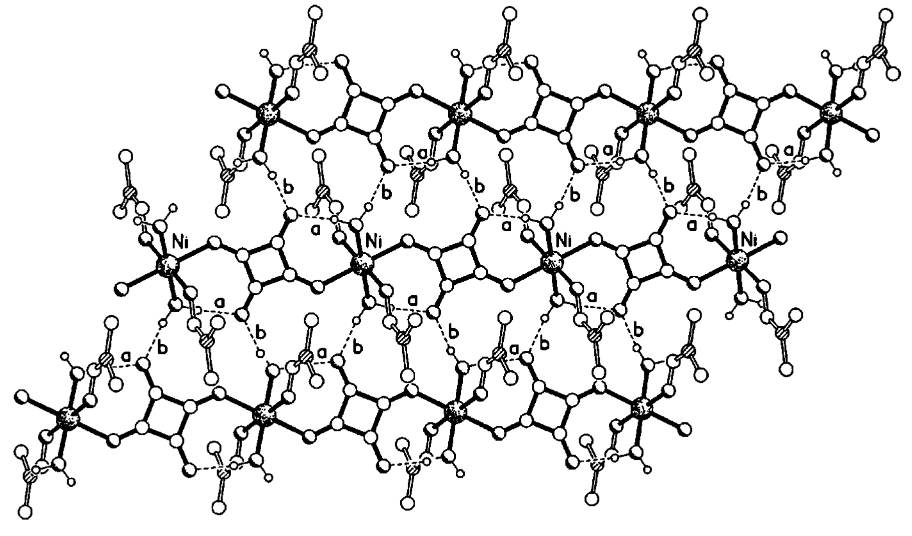

Fig. 2 The cross-linked polymer chains present in complexes **1**, **2**, **3** and **5** [the nickel complex **3** is illustrated, the others being isomorphous].

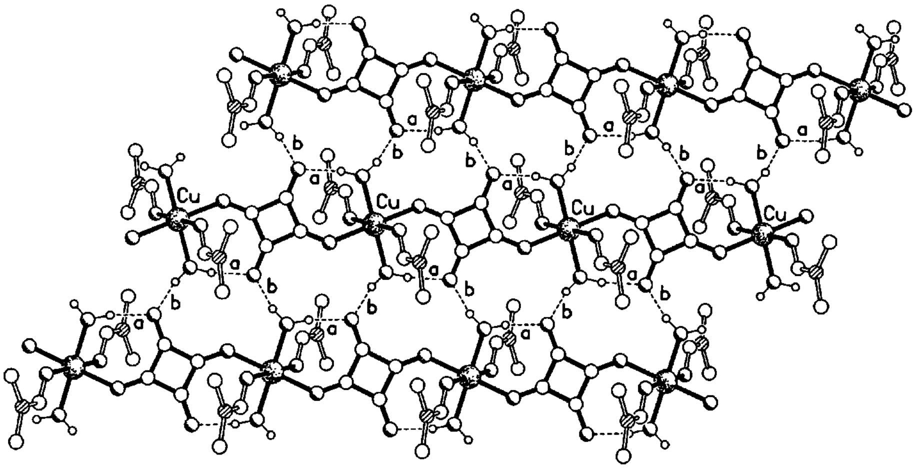

Fig. 3 The cross-linked polymer chains present in the copper complex (**4**) showing the subtle difference in the relative orientations of adjacent chains *cf.* Fig. 2.

planes of the squarate rings are tilted by 25° out of the equatorial coordination plane† (Table 3). The dmf ligands are inclined by 19° to the axial coordination plane. In the Cu complex, however, these tilt angles are significantly different with the squarate ring being inclined by 33° and the dmf ligand by 23° to their respective coordination planes. In the related $[Zn(C_4O_4)(OH_2)_2(dmso)_2]$ complex reported by Yaghi *et al.*, where chain propagation also occurs along the *b* direction in a monoclinic cell (which contains two independent molecules), the Zn···Zn repeat is 8.116(4) Å, similar to that in our Mn complex. However, the angle at the ligating squarate O atom is noticeably larger at 135° and the C_4-ring plane is essentially coplanar with the equatorial coordination plane (inclined by 1°) in one of the independent molecules whereas in the other the angle at O is 132° and the C_4-ring is inclined by 27°.

In all five complexes, including the Cu, adjacent polymer chains are crosslinked *via* O–H···O hydrogen bonds utilising the other *trans* aqua hydrogen atoms as donors and the *trans* ketonic oxygen atoms already involved in intra-chain H-bonding as acceptors (**b** in Figs. 2 and 3). In the Mn, Co, Ni and Zn complexes the linking of adjacent chains produces (when viewed down the chain direction) corrugated sheets, the dmf ligands in one chain overlaying those in the next in a zigzag fashion with N···N separations of 4.02 Å (Fig. 4). Adjacent

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† The average e.s.d. in the tilt angles in structures **1**–**5** is *ca.* 1°.

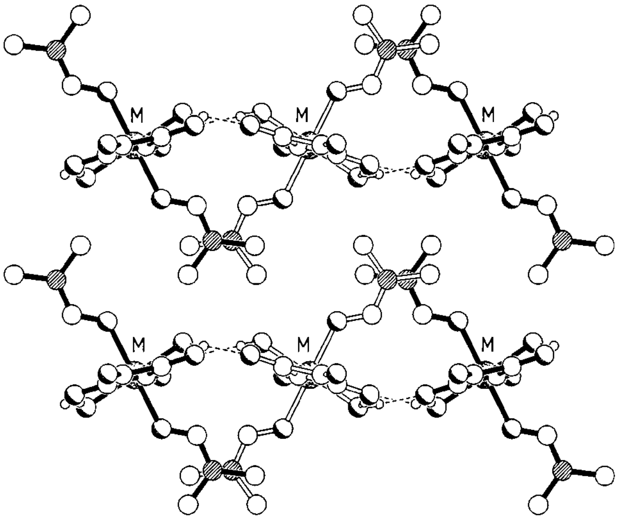

Fig. 4 View down the polymer chains (the crystallographic *c* direction) in complexes **1**, **2**, **3** and **5** showing the zigzag pattern and overlapping dmf ligands.

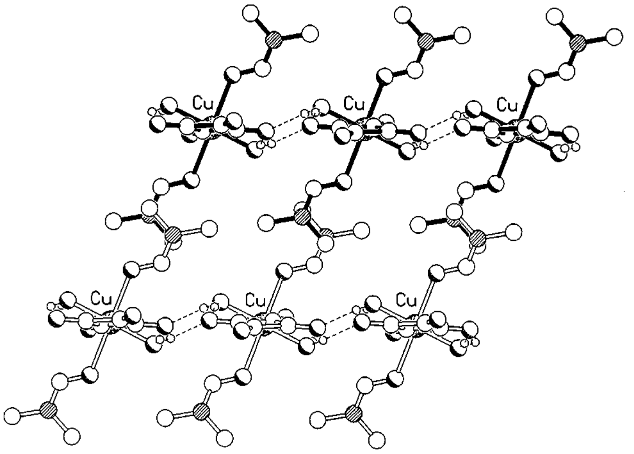

Fig. 5 View down the polymer chains (the crystallographic *b* direction) in the copper complex (**4**) showing the retention of an overlap of the dmf ligands, but an absence of the zigzag motif *cf.* Fig. 4.

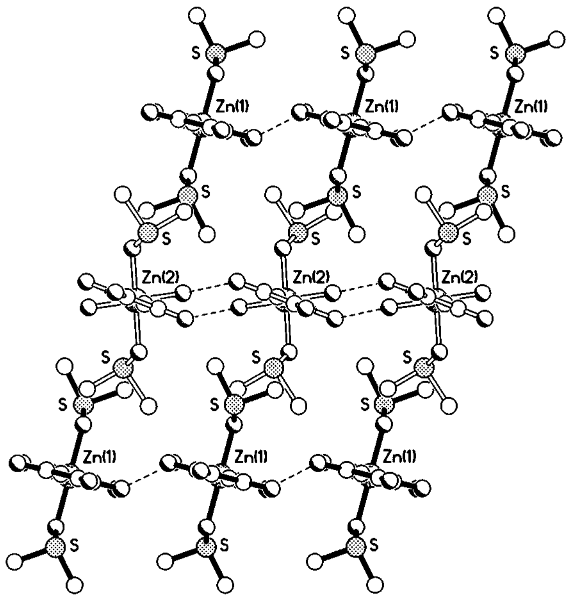

Fig. 6 The very similar packing motif present for the two independent molecules in the related polymeric zinc–dmso complex *cf.* Fig. 5.[4]

sheets stack crest in trough and *vice versa*. In the case of the Cu complex the cross-linking between polymer chains, although being between equivalent donor and acceptor atoms as in the Mn, Co, Ni and Zn complexes, produces instead a stepped sheet without the overlap of dmf groups in adjacent sheet chains (Fig. 5). However, adjacent sheets are oriented such that the axial dmf ligands are again overlapping, the shortest ligand · · · ligand contact being significantly reduced, the closest distance between the amido nitrogen in one sheet and a methyl carbon in the next being only 3.47 Å. The sheet structure and packing that we observe in the Cu complex—the odd one out—is very similar to that seen in the [Zn(C_4O_4)(OH_2)$_2$(dmso)$_2$] complex reported by Yaghi *et al.* (Fig. 6) though in the latter the steric bulk of the non-planar dmso ligands necessitates the presence of two crystallographically independent slightly differing polymer chains to achieve this packing motif. It is possible that, although small, the differences between the axial and equatorial coordination distances in the copper complex, due to the Jahn–Teller effect, are sufficient to cause the subtle, but marked, differences in supramolecular structure. In order to ascertain whether the dramatic differences in the structure of the copper complex could have been due to a phase change having occurred at the reduced temperature at which the structure was determined (*cf.* the remainder of the complexes) the structure of the manganese complex was redetermined at the same reduced temperature. Apart from small changes in the unit cell parameters (detailed in the footnote to Table 1) the overall structure and superstructure are unchanged and there are no statistically significant differences in either the bond lengths or the bond angles. The dramatic structural differences described are thus not a function of temperature.

Comparison of H-bonding interactions in 1–5 with [M(C_4O_4)(OH_2)$_4$] and [M(HC_4O_4)$_2$(OH_2)$_4$]

The transition metal squarates [M(C_4O_4)(OH_2)$_4$] (M = Mn, Fe, Co, Ni and Zn) synthesised by Weiss *et al.*[25] consist of chain molecules similar to **1**–**5**. The copper analogue [Cu(C_4O_4)(OH_2)$_4$] synthesised by Frankenbach *et al.*[26] also has a similar structure. All the tetrahydrates have both inter- and intra-chain hydrogen-bonds. The intra-chain hydrogen-bonding interactions occur between each of two *trans* aqua ligands and a non-coordinated ketonic oxygen atom on separate neighbouring squarate ligands. The interchain H-bonding occurs between the other pair of *trans* aqua ligands as follows: each of these two aqua ligands is simultaneously hydrogen-bonded to two non-coordinated ketonic oxygen atoms from two different neighbouring squarate ligands in the same chain. Each of these same aqua ligands is also hydrogen-bonded to one of the aqua ligands involved in intra-chain hydrogen bonding.

In the tetrahydrate [Mn(HC_4O_4)$_2$(OH_2)$_4$] synthesised by Yaghi *et al.*[4] there are also both inter- and intra-chain hydrogen-bonding interactions but there are significant differences between these interactions and the ones observed in the tetrahydrates [M(C_4O_4)(OH_2)$_4$]. In [Mn(HC_4O_4)$_2$(OH_2)$_4$] the intra-chain hydrogen bonds only serve to link monomers consisting of octahedral Mn^{2+} coordinated to two *trans* squarate and four aqua ligands. These linking hydrogen-bonds are formed between the hydroxy group on one ligand in one monomeric unit and one of the non-coordinated ketonic oxygen atoms on a neighbouring monomeric unit. The interchain hydrogen bonds occur between aqua ligands and squarate ketonic oxygen atoms.

An important structural difference between complexes **1**–**5**, [M(C_4O_4)(OH_2)$_4$] and [Mn(HC_4O_4)$_2$(OH_2)$_4$], is that whereas **1**–**5** consist of continuous chains, in [M(C_4O_4)(OH_2)$_4$] there are finite chain lengths, and [Mn(HC_4O_4)$_2$(OH_2)$_4$] consists of H-bonded linked monomers. The finite chain lengths in [M(C_4O_4)(OH_2)$_4$] allow hydrogen-bond formation between an aqua ligand and a ketonic oxygen atom on each of two terminal squarate ligand groups in the same plane. This type of hydrogen-bond formation cannot occur in a system comprising continuous chains. In [Mn(HC_4O_4)$_2$(OH_2)$_4$] the monomers are linked end-to-end *via* hydrogen bonds. Again this type of hydrogen-bonding cannot occur in **1**–**5** which contain continuous, covalently linked polymeric chains. The presence of only two aqua ligands in **1**–**5** also causes a significant reduction in the extent of hydrogen bonding when compared with [M(C_4O_4)(OH_2)$_4$] and [Mn(HC_4O_4)$_2$(OH_2)$_4$] all of which have four aqua ligands.

In [Ni(C_4O_4)($C_3N_2H_4$)$_2$(OH_2)$_2$] there are a wide variety of both inter- and intra-chain hydrogen bonds involving the aqua, squarato and imidazole ligands.[24] Hydrogen bonds occur between non-coordinating squarate oxygens and aqua ligands within the chains and intersheet hydrogen bonds occur between imidazole hydrogens and coordinating squarate oxygens.

Conclusions

All the complexes discussed in this paper exhibit similar intra-chain hydrogen-bonding interactions involving an aqua ligand and a non-coordinated ketonic oxygen on an adjacent squarate group. This occurs in the tetraaqua complexes because there always exists at least one aqua ligand which lies close to a squarate ligand plane. Even in the case of complexes **1**–**5** and in [Zn(C_4O_4)(OH_2)$_2$(dmso)$_2$] where two of the four coordinated H_2O groups are replaced by dmf and dmso groups respectively, this type of hydrogen bonding still occurs because the two remaining aqua ligands lie near to the plane of the squarate moieties whilst the coordinated dmf and dmso groups are directed essentially orthogonally to this plane. As with [Zn(C_4O_4)(OH_2)$_2$(dmso)$_2$], complexes **1**–**5** do not show intersheet hydrogen bonding.

Although hydrogen bonding to the dmf ligands is theoretically possible (*vide supra*) no such interactions are observed in complexes **1**–**5**. Likewise the dmso molecules in [Zn(C_4O_4)(OH_2)$_2$(dmso)$_2$] do not participate in hydrogen-bond formation. However, the coordinated imidazole ligands in [Ni(C_4O_4)($C_3N_2H_4$)$_2$(OH_2)$_2$] do participate in hydrogen-bond formation and thus increase the complexity of the hydrogen bonding in this particular complex.

Although the differences in hydrogen bonding interactions seen between (i) **1**, **2**, **3** and **5** and (ii) **4** (which is similar to [Zn(C_4O_4)(OH_2)$_2$(dmso)$_2$][4]) are subtle, they are nevertheless important. The changing of the ligating solvent from dmso to dmf is seen in some complexes to significantly alter the nature of the supramolecular structure, whereas in others it is little affected. Indeed, the difficulties in predicting extended structure are exemplified by the unexpected differences observed between the copper complex (**4**) and the other members of the dmf-coordinated series. The above results provide a salutary object lesson in the need to consider even the most apparently trivial details when embarking upon the design of engineered solid state materials.

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