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Structural Relationship of Various Squarates

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Abstract

This work illustrates the structural relationship between three types of metal squarates as well as the ligand in its acid form and in its monoanion salt. Squaric acid, $H_2C_4O_4$, is known to have a polymeric layer structure with planar molecules connected through intermolecular hydrogen bonds. The interlayer distance is only 2.649 Å. The crystal of $H_2NMe_2[H_3(C_4O_4)_2]$ is found to contain columns of $[H_3(C_4O_4)_2{}^-]$ repeating units, again connected by intermolecular hydrogen bonds. Within the repeated unit, there is a symmetric hydrogen bond connected to two HC_4O_4 moieties. A new type of metal squarate with $M(HC_4O_4)_2(H_2O)_4$ [$M = \mathrm{Mn^{II}}$, $\mathrm{Fe^{II}}$ both belong to space group $P\bar{1}$, $Z = 1$, $a = 5.194(3)$, $b = 7.454(2)$, $c = 8.901(2)$ Å, $\alpha = 67.07(2)$, $\beta = 77.26(3)$, $\gamma = 74.46(4)°$, for $\mathrm{Mn^{II}}$] is shown to have a layer-type structure, where all $[HC_4O_4]$ units are bonded into infinite chains *via* symmetric hydrogen bonds, each $(HC_4O_4)_2^{2-}$ ligand bridging two metal ions (μ-2) in a *trans* fashion. The structurally most well understood metal squarate $M(C_4O_4)(H_2O)_4$ ($M = \mathrm{Mn^{II}}$, $\mathrm{Fe^{II}}$, $\mathrm{Co^{II}}$, $\mathrm{Ni^{II}}$ and $\mathrm{Zn^{II}}$, space group $C2/c$, $Z = 4$) is again a polymeric chain with $C_4O_4{}^{2-}$ serving as a bridging ligand between two metal ions (μ-2) in *trans* positions. A three-dimensional polymeric structure is found to have the formula $M(C_4O_4)(H_2O)_2$, where $C_4O_4^{2-}$ is a bridging ligand between four metal ions (μ-4). Due to the slight difference in packing, there are two structure types in this category: one is in space group $R\bar{3}$ [$M = \mathrm{Fe^{II}}$, $a = 11.440(2)$, $c = 14.504(3)$ Å, $Z = 9$], the other is in $Pn\bar{3}n$ [$M = \mathrm{Co^{II}}$, $a = 16.255(3)$ Å, $Z = 24$]. The structural relationship between all these structures relies heavily on the understanding of intra- and intermolecular hydrogen bonds. The interesting building blocks of each compound will be illustrated. There are tunnels of various sizes in all these structures.

1. Introduction

Supramolecular architecture out of soluble components is of intense interest (Yaghi & Li, 1995). A recent communication demonstrates that 4,4′-bpy is suitable to act as rods linking together metal centers to give an extended solid (Fujita, Kwon, Washizu & Ogura, 1994; Subramanian & Zaworotko, 1995). The squarate dianion $C_4O_4^{2-}$ is an interesting cyclic compound with aromaticity (Cohen, Lacher & Park, 1959; West, Niu & Ito, 1963; West & Powell, 1963; Haahs & Hegenberg, 1966; Ireland & Walton, 1967; MacDonald, 1968; Wang, Stucky & Williams, 1974; Wang & Stucky, 1974; Frankenbach *et al.*, 1992), with its symmetry likely to be D_{4h} (Ito & West, 1963). It is a potential bridging ligand with possible μ-2, μ-3 and μ-4 between metal ions. The anion could be served as a bidentate ligand, but it was only found in Ag complexes (Robl & Weiss, 1987). In addition, strong hydrogen bonds among dianions are often formed so that a polymeric chain, a flat sheet or even three-dimensional building blocks are easily formed. Squaric acid, 3,4-dihydroxy-3-cyclobutene-1,2-dione, $H_2C_4O_4$, is a flat sheet structure (Semmingsen, 1973; Wang, Stucky & Williams, 1974; Semmingsen, Hollander & Koetzle, 1977) with intermolecular hydrogen bonds formed between every hydroxyl group and ketone O atom. Hydro-bishydrosquarate $[H(HC_4O_4)_2]^-$ (Wang & Stucky, 1974) is no longer a planar structure, but a column structure of $[H_3(C_4O_4)_2]_n$ throughout the solid. There are symmetric and asymmetric hydrogen bonds in this solid (Wang & Stucky, 1974; Lin, Cheng & Wang, 1994) and detailed studies on its electron density distribution and electrostatic properties have been published recently (Lin, Cheng & Wang, 1994). The most well investigated metal squarate is $M(C_4O_4)(H_2O)_4$, with two bridging $C_4O_4^{2-}$ (μ-2) ligands at *trans* positions, which forms an infinite chain structure. Each metal ion is also bonded with four water molecules to form a distorted octahedral geometry. Such metals include $\mathrm{Mn^{II}}$, $\mathrm{Co^{II}}$, $\mathrm{Ni^{II}}$ (Weiss, Riegler, Alt, Bohme & Robl, 1986), $\mathrm{Fe^{II}}$ (Frankenbach *et al.*, 1992; Weiss, Riegler, Alt, Bohme & Robl, 1986), $\mathrm{Zn^{II}}$ (Weiss, Riegler, Alt, Bohme & Robl, 1986; Robl & Kuhs, 1988) and $\mathrm{Cu^{II}}$ (Frankenbach *et al.*, 1992). The former five are isomorphous, with the $\mathrm{Cu^{II}}$ complex having a slightly different relative orientation of the $C_4O_4^{2-}$ plane and the $M(H_2O)_4$ plane (Frankenbach *et al.*, 1992). Another type of metal squarate with the formula $M(C_4O_4)(H_2O)_2$ ($M = \mathrm{Fe^{II}}$, $\mathrm{Co^{II}}$, $\mathrm{Ni^{II}}$ and $\mathrm{Zn^{II}}$) was

Table 1. *Experimental details*

	Type (1)		Type (2)		Type (3)	
Crystal data						
Chemical formula	$[Co(C_4O_4)(H_2O)_4]$	$[Ni(C_4O_4)(H_2O)_4]$	$[Mn(HC_4O_4)_2(H_2O)_4]$	$[Fe(HC_4O_4)_2(H_2O)_4]$	$[Fe(C_4O_4)(H_2O)_2]$	$[Co(C_4O_4)(H_2O)_2].0.33H_2O$
Chemical formula weight	243.03	242.81	353.09	354.00	203.92	213.01
Cell setting	Monoclinic	Monoclinic	Triclinic	Triclinic	Trigonal	Cubic
Space group	$C2/c$	$C2/c$	$P\bar{1}$	$P\bar{1}$	$R\bar{3}$	$Pn\bar{3}n$
a (Å)	8.9667 (19)	8.9315 (16)	5.194 (3)	5.1577 (10)	11.4395 (19)	16.255 (3)
b (Å)	13.356 (3)	13.246 (3)	7.4537 (21)	7.4107 (13)	11.4395 (19)	
c (Å)	6.7119 (16)	6.6893 (18)	8.9007 (18)	8.7823 (13)	14.504 (3)	
α (°)			67.07 (2)	66.846 (12)		
β (°)	99.412 (2)	99.43 (2)	77.26 (3)	77.109 (15)		
γ (°)			74.46 (4)	74.748 (15)		
V (Å^3)	793.0 (3)	780.7 (3)	303.09 (21)	295.05 (9)	1643.7 (4)	4295.0 (8)
Z	4	4	1	1	9	24
D_x (Mg m^{-3})	2.036	2.066	1.935	1.992	1.854	1.977
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.7107	0.7107	0.7107	0.7107	0.7107	0.7107
No. of reflections for cell parameters	25	25	25	25	25	25
θ range (°)	10.50–25.34	11.39–18.81	9.56–19.46	9.29–16.82	7.47–12.70	9.39–13.81
μ (mm^{-1})	2.17	2.51	1.11	1.34	2.04	2.37
Temperature (K)	298	298	298	298	298	298
Crystal form	Rectangle	Rectangle	Square pyramid	Octahedron	Cube	Cube
Crystal size (mm)	0.40 × 0.20 × 0.20	0.20 × 0.15 × 0.15	0.40 × 0.40 × 0.20	0.50 × 0.30 × 0.27	0.20 × 0.15 × 0.15	0.20 × 0.20 × 0.20
Crystal color	Pale pink	Pale green	Pale violet	Pale yellow	Pale yellow	Pale pink
Data collection						
Diffractometer	Nonius CAD-4	Nonius CAD-4	Nonius CAD-4	Nonius CAD-4	Nonius CAD-4	Nonius CAD-4
Data collection method	$\theta/2\theta$ scans	$\theta/2\theta$ scans	$\theta/2\theta$ scans	$\theta/2\theta$ scans	$\theta/2\theta$ scans	$\theta/2\theta$ scans
2θ scan width (°)	$2(0.70 + 0.35\tan\theta)$	$2(0.70 + 0.35\tan\theta)$	$2(0.70 + 0.35\tan\theta)$	$2(0.70 + 0.35\tan\theta)$	$2(0.65 + 0.35\tan\theta)$	$2(0.90 + 0.35\tan\theta)$
Speed (° min^{-1})	2.06, 8.14	2.06, 8.14	2.06–8.24	2.06–8.24	2.06–8.24	4.0
Absorption correction	Gaussian integration	ψ scan (North, Phillips & Mathews, 1968)	ψ scan (North, Phillips & Mathews, 1968)	ψ scan (North, Phillips & Mathews, 1968)	ψ scan (North, Phillips & Mathews, 1968)	Gaussian integration
T_{min}	0.550	0.955	0.8834	0.92	0.9624	0.6375
T_{max}	0.693	1.00	1.00	1.00	0.9997	0.6723
No. of measured reflections	4351	693	1193	1369	574	4384
No. of independent reflections	4139	693	1064	1359	486	3798
No. of observed reflections	2425	574	1021	1287	435	657
Criterion for observed reflections	$I_{net} > 2.0\sigma(I_{net})$	$I_{net} > 2.0\sigma(I_{net})$	$I_{net} > 2.0\sigma(I_{net})$	$I_{net} > 2.0\sigma(I_{net})$	$I_{net} > 2.0\sigma(I_{net})$	$I_{net} > 2.0\sigma(I_{net})$
R_{int}	0.038	–	0.010	0.014	0.028	0.012
θ_{max} (°)	50.00	25.00	25.00	27.5	22.5	50.00
Range of h, k, l	$-19 \rightarrow h \rightarrow 19$ $0 \rightarrow k \rightarrow 28$ $0 \rightarrow l \rightarrow 14$	$-10 \rightarrow h \rightarrow 10$ $0 \rightarrow k \rightarrow 15$ $0 \rightarrow l \rightarrow 7$	$-5 \rightarrow h \rightarrow 6$ $0 \rightarrow k \rightarrow 8$ $-9 \rightarrow l \rightarrow 10$	$-6 \rightarrow h \rightarrow 6$ $0 \rightarrow k \rightarrow 9$ $-9 \rightarrow l \rightarrow 11$	$-9 \rightarrow h \rightarrow 10$ $0 \rightarrow k \rightarrow 12$ $0 \rightarrow l \rightarrow 15$	$1 \rightarrow h \rightarrow 35$ $0 \rightarrow k \rightarrow 24$ $0 \rightarrow l \rightarrow 20$
No. of standard reflections	3	3	3	3	3	3
Frequency of standard reflections (min)	60	60	60	60	60	60
Intensity decay (%)	1.0	None	None	None	None	2.0
Refinement						
Refinement on	F	F	F	F	F	F
R^*	0.032	0.026	0.023	0.028	0.028	0.055
wR^*	0.029	0.025	0.029	0.028	0.032	0.051
S^*	2.68	2.58	2.82	3.43	4.68	4.68
No. of reflections used in refinement	2425	574	1021	1287	435	657
No. of parameters used	66	66	104	104	55	59
H-atom treatment	H atoms placed in calculated positions	H atoms placed in calculated positions	H atoms placed in calculated positions	H atoms placed in calculated positions	H atoms placed in calculated positions	H atoms located from a difference Fourier map
Weighting scheme	$w = 1/\sigma^2(F)$	$w = 1/\sigma^2(F)$	$w = 1/[\sigma^2(F) + 0.00005F^2]$	$w = 1/\sigma^2(F)$	$w = 1/\sigma^2(F)$	$w = 1/[\sigma^2(F) + 0.00001F^2]$

Table 1 (*cont.*)

	Type (1)		Type (2)		Type (3)	
$(\Delta/\sigma)_{\max}$	0.001	0.002	0.009	0.006	0.001	0.001
$\Delta\rho_{\max}$ (e Å^{-3})	0.59	0.38	0.42	0.40	0.39	1.12
$\Delta\rho_{\min}$ (e Å^{-3})	−0.92	−0.47	−0.32	−0.56	−0.24	−1.38
Extinction method	Secondary (Larson, 1970)	Secondary (Larson, 1970)	Secondary (Larson, 1970)	Secondary (Larson, 1970)	Secondary (Larson, 1970)	Secondary (Larson, 1970)
Extinction coefficient	0.344 (9) × 10^4	4.2 (3) × 10^4	0.57 (8) × 10^4	0.31 (2) × 10^4	0.3 (2) × 10^4	1.7 (1) × 10^4
Source of atomic scattering factors	*International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)	*International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)	*International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)	*International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)	*International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)	*International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)
Computer programs						
Data reduction	*NRCVAX DATRD2* (Gabe, Le Page, Charland, Lee & White, 1989)	*NRCVAX DATRD2* (Gabe, Le Page, Charland, Lee & White, 1989)	*NRCVAX DATRD2* (Gabe, Le Page, Charland, Lee & White, 1989)	*NRCVAX DATRD2* (Gabe, Le Page, Charland, Lee & White, 1989)	*NRCVAX DATRD2* (Gabe, Le Page, Charland, Lee & White, 1989)	*NRCVAX DATRD2* (Gabe, Le Page, Charland, Lee & White, 1989)
Structure solution	*NRCVAX SOLVER* (Gabe, Le Page, Charland, Lee & White, 1989)	*NRCVAX SOLVER* (Gabe, Le Page, Charland, Lee & White, 1989)	*NRCVAX SOLVER* (Gabe, Le Page, Charland, Lee & White, 1989)	*NRCVAX SOLVER* (Gabe, Le Page, Charland, Lee & White, 1989)	*NRCVAX SOLVER* (Gabe, Le Page, Charland, Lee & White, 1989)	*NRCVAX SOLVER* (Gabe, Le Page, Charland, Lee & White, 1989)
Structure refinement	*NRCVAX LSTSQ* (Gabe, Le Page, Charland, Lee & White, 1989)	*NRCVAX LSTSQ* (Gabe, Le Page, Charland, Lee & White, 1989)	*NRCVAX LSTSQ* (Gabe, Le Page, Charland, Lee & White, 1989)	*NRCVAX LSTSQ* (Gabe, Le Page, Charland, Lee & White, 1989)	*NRCVAX LSTSQ* (Gabe, Le Page, Charland, Lee & White, 1989)	*NRCVAX LSTSQ* (Gabe, Le Page, Charland, Lee & White, 1989)
Preparation of material for publication	*NRCVAX TABLES* (Gabe, Le Page, Charland, Lee & White, 1989)	*NRCVAX TABLES* (Gabe, Le Page, Charland, Lee & White, 1989)	*NRCVAX TABLES* (Gabe, Le Page, Charland, Lee & White, 1989)	*NRCVAX TABLES* (Gabe, Le Page, Charland, Lee & White, 1989)	*NRCVAX TABLES* (Gabe, Le Page, Charland, Lee & White, 1989)	*NRCVAX TABLES* (Gabe, Le Page, Charland, Lee & White, 1989)

* $R = \sum(F_o - F_c)/\sum F_o$.

Table 2. *Selected bond lengths (Å) with e.s.d.'s in parentheses for the structures of metal squarates: types (1), (2), (3) and* $H_2C_4O_4$ *and* $(H_2NMe_2)H_3(C_4O_4)_2$

Type (1) $M(C_4O_4)(H_2O)_4$; M = Fe,(a) Co, Ni, Cu,(a) Zn(b)

	M—O1$_{sq}$	M—O3$_w$	M—O4$_w$	O1—C1	O2—C2	C1—C2	C1—C2′
Fe	2.115 (2)	2.151 (2)	2.106 (2)	1.257 (2)	1.255 (3)	1.457 (3)	1.465 (1)
Co	2.0772 (9)	2.117 (1)	2.066 (1)	1.250 (1)	1.255 (2)	1.454 (2)	1.461 (2)
Ni	2.044 (2)	2.077 (2)	2.038 (3)	1.258 (4)	1.257 (4)	1.455 (4)	1.456 (5)
Cu	2.469 (2)	1.948 (2)	1.961 (3)	1.265 (4)	1.257 (2)	1.453 (5)	1.453 (5)
Zn	2.076 (1)	2.126 (1)	2.076 (1)	1.250 (1)	1.250 (1)	1.464 (1)	1.467 (1)

Type (2) $M(HC_4O_4)_2(H_2O)_4$; M = Mn, Fe; $H_2C_4O_4$,(c) $(H_2NMe_2)H_3(C_4O_4)_2$(d)

	M—O1$_{sq}$	M—O5$_w$	M—O6$_w$
Mn	2.150 (1)	2.141 (2)	2.219 (1)
Fe	2.100 (2)	2.061 (2)	2.182 (2)

	O1—C1	O2—C2	O3—C3	O4—C4	C1—C2	C1—C4	C2—C3	C3—C4
Mn	1.234 (2)	1.285 (2)	1.269 (2)	1.237 (2)	1.448 (2)	1.482 (2)	1.431 (2)	1.466 (2)
Fe	1.233 (3)	1.284 (3)	1.268 (2)	1.235 (3)	1.448 (3)	1.484 (3)	1.425 (3)	1.465 (3)
$H_2C_4O_4$	1.257 (2)	1.285 (2)	1.259 (2)	1.232 (2)	1.454 (3)	1.496 (3)	1.405 (3)	1.458 (3)
$H_3(C_4O_4)_2$	1.238 (2)	1.282 (2)	1.308 (2)	1.215 (2)	1.462 (2)	1.494 (2)	1.400 (2)	1.467 (2)

Type (3): $M(C_4O_4)(H_2O)_2$; M = Fe, Co, Ni,(e) Zn(f)

	M—O1$_{sq}$	M—O2$_{sq}$	M—O3$_w$	O1—C1	O2—C2	C1—C1*	C2—C2†
Fe	2.106 (4)	2.144 (4)	2.084 (4)	1.253 (7)	1.255 (7)	1.454 (7)	1.47 (1)
Co	2.074 (7)	2.138 (7)	2.040 (5)	1.290 (9)	1.20 (1)	1.42 (1)	1.52 (1)
Ni	2.060 (9)	—	2.09 (2)	1.22 (1)	—	1.49 (2)	—
Zn	2.096 (3)	2.132 (4)	2.053 (3)	1.26 (1)	1.227 (9)	1.46 (1)	1.47 (1)

(*a*) Frankenbach *et al.* (1992). (*b*) Robl & Kuhs (1988). (*c*) Wang, Stucky & Williams (1974). (*d*) Wang & Stucky (1974). (*e*) Habenschuss & Gerstein (1974). (*f*) Weiss, Riegler & Robl (1986*a*). *C1—C2 for Fe complex. †C1—C2′ for Fe complex.

found to be in cubic symmetry with cell length ~ 8 Å by powder X-ray diffraction (Habenschuss & Gerstein, 1974; West & Niu, 1963; Gerstein & Habenschuss, 1972), however, it was pointed out that such a cell might contain a disordered structure. Later a $[Zn(C_4O_4)(H_2O)_2](CH_3COOH)_{1/3}$ structure was determined to have a cubic structure with cell length a = 16.25 Å (Weiss, Riegler & Robl, 1986*a*,*b*).

In addition to the aforementioned metal squarates, we have found two new types of structures: $M(HC_4O_4)_2(H_2O)_4$ [M = Fe^{II}, Mn^{II}* (Yaghi, Li & Groy, 1995)] and $Fe(C_4O_4)(H_2O)_2$. The former can be considered as a two-dimensional network built by $(HC_4O_4)_2$ and $M(H_2O)_4$ units. The latter is in a trigonal space group $R\bar{3}$ (Fe case) in addition to the cubic (Co case) structure. The structural relationship between all these structures are worthy of investigation.

2. Results and discussion

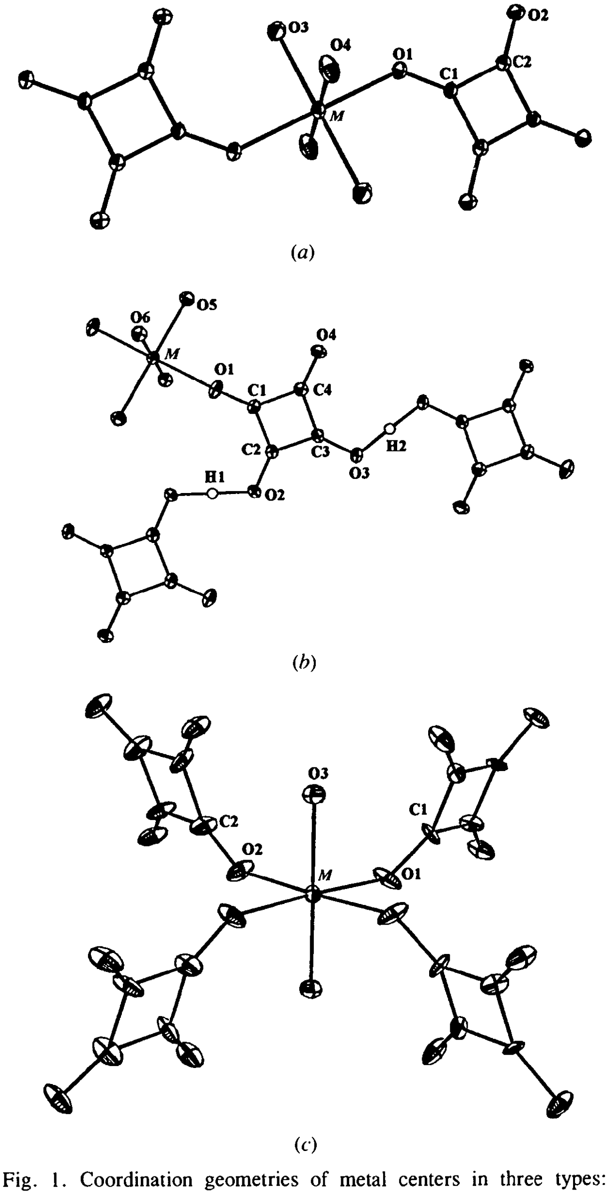
2.1. *Structures*

There are three types of compounds in this report: (1) [$M(C_4O_4)(H_2O)_4$], (2) [$M(HC_4O_4)_2(H_2O)_4$] and (3) [$M(C_4O_4)(H_2O)_2$]. Type (1) compounds are isostructural and in space group $C2/c$, $Z = 4$. There is a symmetry (1) at M, when M = Mn, Fe (Frankenbach *et al.*, 1992), Co, Ni and Zn (Weiss, Riegler, Alt, Bohme & Robl, 1986). However, the Cu complex crystallizes in a different space group, $P2_1/c$ (Frankenbach *et al.*, 1992). For type (2) compounds we herein report two complexes, M = Mn and Fe, which both belong to $P\bar{1}$, $Z = 1$, and again the metal ion is located at $\bar{1}$. For type (3) compounds we find two structural types: when M = Fe, the compound crystallizes in $R\bar{3}$, $Z = 9$, and the site symmetry of Fe is also $\bar{1}$; when M = Co, it crystallizes in $Pn\bar{3}n$, $Z = 24$, the site symmetry of Co is on a twofold axis, which bisects the O1—Co—O1′ angle. These two structures are very similar, however, they are different in packing. Crystal data for all three types are given in Table 1.†

2.1.1. *Coordination sphere of metal center.* The coordination sphere of metal centers in all three types (1), (2) and (3) is distorted octahedron. The geometries at the metal centers for these three types of compounds are illustrated in Fig. 1. In structures of types (1) and (2) there are four coordination sites occupied by O atoms of water molecules (O_w) and two coordination sites occupied by O atoms from squarates (O_{sq}). However, in type (3) structures there are only two O atoms from the water molecules and four O atoms from squarates in the coordination sphere. The M—O distances for three types are listed in Table 2. It is worth noticing that $M—O_{sq}$ is shorter than one of the $M—O_w$ bonds, but longer than the other $M—O_w$ bond in both types (1) and (2).

One exception is the Cu complex in type (1) (Frankenbach *et al.*, 1992), where the bond length of $Cu—O_{sq}$ is much longer than both bond lengths of $Cu—O_w$, which may be due to the strong Jahn–Teller distortion of Cu^{II} ions.

2.1.2. *Ligand squarate.* According to the formula, the squarate ion in types (1) and (3) should be the $C_4O_4^{2-}$ dianion and is likely to be in D_{4h} symmetry with C—C and C—O distances of 1.46 and 1.26 Å, respectively. The exact symmetry of this dianion in the crystal is $\bar{1}$ in type (1) structures and the Fe complex of type (3). In the case of the Co complex of type (3), the two independent squarate rings are of 4 and $\bar{4}$ symmetries. The squarates in type (2) are, however, close to a 1,2-dione type, similar to those in $H_2C_4O_4$ (Semmingsen, 1973; Wang, Stucky & Williams, 1974; Semmingsen,



(*a*)

(*b*)

(*c*)

Fig. 1. Coordination geometries of metal centers in three types: (*a*) type (1); (*b*) type (2); (*c*) type (3).

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* While preparing this work, the Mn complex was published independently by Yaghi, Li & Groy (1995).

† Lists of atomic coordinates, anisotropic displacement parameters, complete geometry and structure factors have been deposited with the IUCr (Reference: OA0002). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Hollander & Koetzle, 1977) and $H_3(C_4O_4)_2^-$ (Wang & Stucky, 1974). A comparison of the C—C and C—O distances on various metal squarates, $H_2C_4O_4$ and $H_3(C_4O_4)_2^-$, is also given in Table 2. Each squarate ring here is more like a 1,2-dione type. The H atom in the ligand is at $\bar{1}$ symmetry. In addition, the IR spectra of the Fe complexes [types (1) and (3)] are consistent with the $C_4O_4^{2-}$ dianion (Ito & West, 1963; West & Niu, 1963; Long, 1978). However, additional absorption bands for C═C and C═O are observed in the IR spectra of the Fe complex in type (2), which are consistent with $H_2C_4O_4$ (Wang, Stucky & Williams, 1974) and the Fe squarate complex, although the predicted structure of the Fe complex was then incorrect (Wrobleski & Brown, 1978). The best way of describing the relative orientation of the squarate plane in various complexes is by the torsional angle of the C—C vector in the squarate plane and the vector of M—O_{sq}.

Table 3. *Torsional angles (°) for C—C—O_{sq}—M*

	Mn	Fe	Co	Ni	Cu	Zn
$M(C_4O_4)(H_2O)_4$		3.4	2.9	2.7	79.8	2.9
$M(HC_4O_4)_2(H_2O)_4$	82.7	80.1				
$M(C_4O_4)(H_2O)_2$		5.9	8.2			

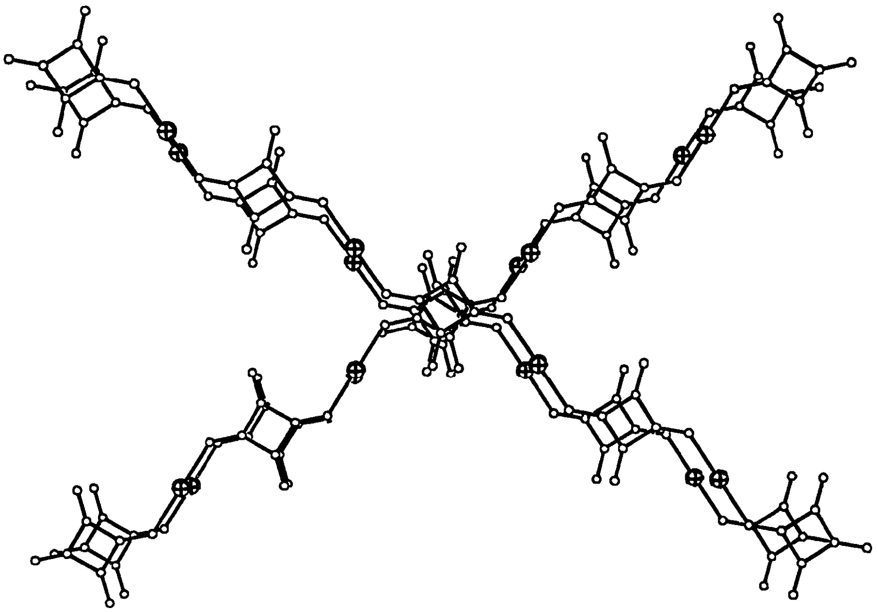

Fig. 2. Chain structure of type (1); water molecules are omitted for clarity, shaded sphere is M.

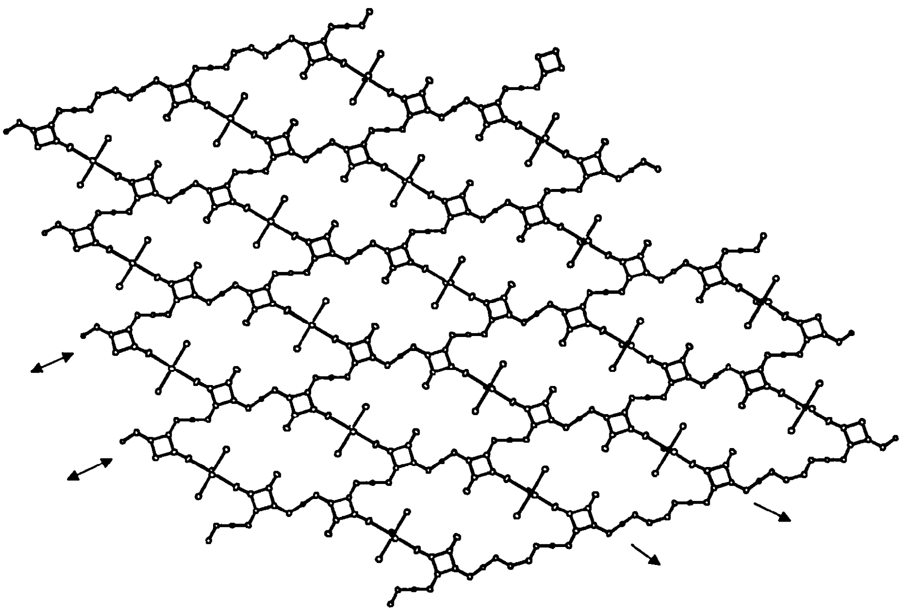

Fig. 3. Sheet structure of type (2).

Such an angle can determine whether $M—O_{sq}$ is coplanar with the squarate plane. This angle is listed in Table 3 for all three types of compounds. It is interesting to notice that in type (1) compounds all are coplanar (~ 3°), except the Cu complex which is approximately perpendicular (~ 80°). However, in

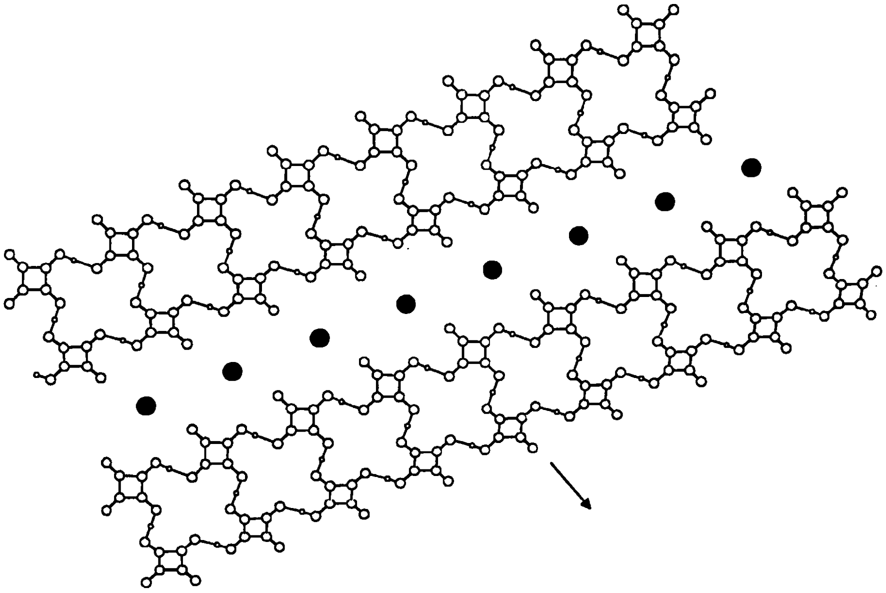

Fig. 4. Structure of (H_2NMe_2)-$[H_3(C_4O_4)_2]$ in the *b*-axis projection; the cation is simplified to a solid sphere for clarity.

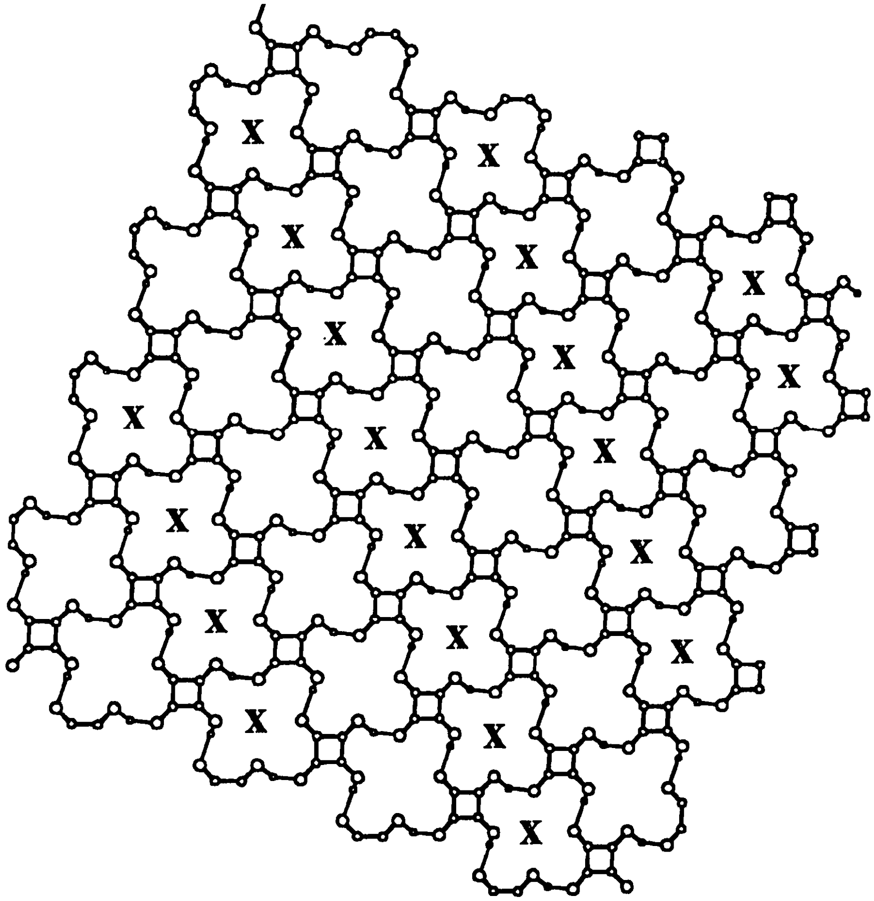

Fig. 5. Sheet structure of $H_2C_4O_4$; X's are marked for interpretation.

Table 4. *O···O distances (Å) and ∠O—H···O angle (°) for hydrogen bonds*

(*a*) Type (1): O1, O2 = O_{sq}; O3, O4 = O_w

	Fe[a]	Co	Ni	Zn[b]
O3···O2	2.71	2.697 (2)	2.710 (3)	2.716 (1)
∠O3—H1···O2	166	166	169	163
O3···O2	2.99	2.977 (2)	2.966 (4)	2.986 (1)
∠O3—H2···O2	151	134	145	146
O4···O1	2.82	2.800 (2)	2.784 (3)	2.806 (2)
∠O4—H3···O1	164	166	157	166
O4···O2	2.80	2.780 (2)	2.776 (3)	2.787 (2)
∠O4—H4···O2	176	168	171	178

(*b*) Type (2): O1—O4 = O_{sq}; O5, O6 = O_w

	Mn	Fe	$H_2(C_4O_4)$[c]		$H_3(C_4O_4)_2^-$[d]	
O2···O2	2.463 (3)	2.458 (3)	O3···O1	2.544 (1)	O2···O2	2.435 (2)
∠O2···H1···O2	180	180	∠O3—H3···O1	151	∠O2···H2···O2	180
O3···O3	2.483 (3)	2.470 (3)	O2···O4	2.545 (1)	O3···O1	2.582 (2)
∠O3···H2···O3	180	180	∠O2—H4···O4	180	∠O3—H1···O1	169
O5···O2	2.745 (2)	2.726 (2)				
∠O5—H3···O2	177	174				
O5···O6	2.754 (2)	2.720 (2)				
∠O5—H4···O6	177	166				
O6···O4	2.709 (2)	2.699 (2)				
∠O6—H5···O4	179	173				
O6···O4	2.747 (3)	2.763 (2)				
∠O6—H6···O4	152	147				

(*c*) Type (3): O1, O2 = O_{sq}; O3 = O_w

	Co	Fe
O2···O3	2.74 (1)	2.757 (5)
∠O2—H1···O3	135	178
O1···O3	2.73 (1)	2.738 (8)
∠O1—U2···O3	153	165

(*a*) Frankenbach *et al.* (1992). (*b*) Robl & Kuhs (1988). (*c*) Wang, Stucky & Williams (1974). (*d*) Wang & Stucky (1974).

type (2) both structures are perpendicular (~ 80°). In type (3) both are roughly coplanar (~ 6°).

3. Intra- and intermolecular hydrogen bonds

Hydrogen bonds are very interesting and do play an important role in all the aforementioned compounds. The varieties of squarate forms from $H_2C_4O_4$ to $HC_4O_4^-$ to $C_4O_4^{2-}$ are found in these structures. A polymeric column of $(HC_4O_4)_n$ or $(H_3(C_4O_4)_2)_n$ (Wang & Stucky, 1974; Lin, Cheng & Wang, 1994) actually exists through strong hydrogen bonds in these structures. Even when the ligand is in its acid form, $H_2C_4O_4$ (Wang, Stucky & Williams, 1974; Semmingsen, 1973; Semmingsen, Hollander & Koetzle 1977), it forms sheets in the solid state *via* intermolecular hydrogen bonds. Apparently there are symmetric and asymmetric hydrogen bonds commonly observed in these structures.

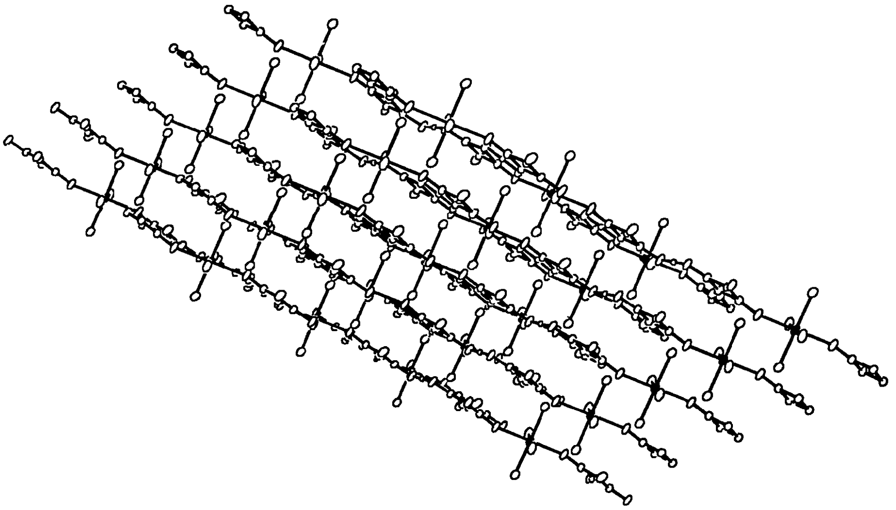

Fig. 6. Layers of type (2) structure.

A typical symmetric hydrogen bond is very strong with an $O\cdots O$ distance of less than 2.5 Å (Maurin, Les & Winnicka-Maurin, 1995; Kubicki, Borowiak & Antkowiak, 1995; Lin, Cheng & Wang, 1994; Alcock, 1990; Semmingsen, 1976; Macintyre & Werkema, 1964). There are two symmetric hydrogen bonds in type (2) compounds between squarate ions ($O\cdots O$ distances of 2.464 and 2.472 Å). Weaker hydrogen bonds existed between water molecules in the coordination sphere and the O atoms of squarate ions in all these structures. The corresponding $O\cdots O$ distances and $O—H\cdots O$ angles for these compounds are listed in Table 4.

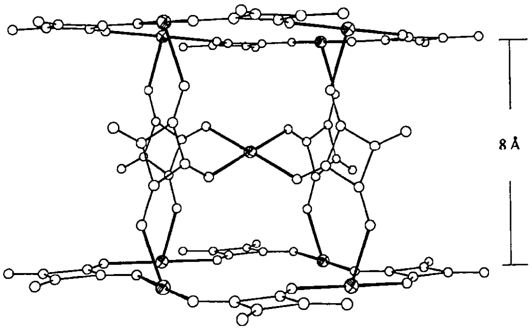

Fig. 7. The three-dimensional building block of type (3); M = Fe, shaded sphere is Fe, water molecules are omitted for clarity.

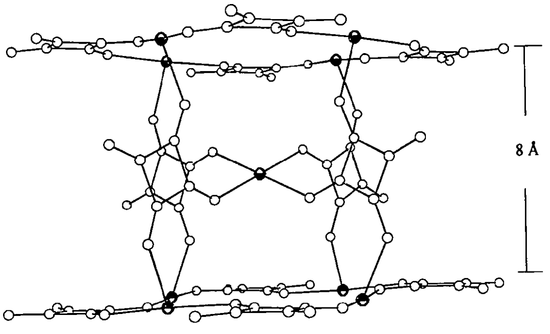

Fig. 8. The three-dimensional building block of type (3); M = Co, shaded sphere is Co, water molecules are omitted for clarity.

4. Structural relationship

Polymeric chains, sheets and three-dimensional building blocks are characteristics of metal squarates. We will start with the chain structure type (1) [$M(C_4O_4)(H_2O)_4$], which is quite well known for nearly all the transition metal complexes (Frankenbach *et al.*, 1992; Weiss, Riegler, Alt, Bohme & Robl, 1986; Robl & Kuhs, 1988). The chain directions are along (1$\bar{1}$0) and (110), and the plane of squarate is perpendicular to the $M(H_2O)_4$ plane (Fig. 1), as described earlier (West & Powell, 1963; Frankenbach *et al.*, 1992; Weiss, Riegler, Alt, Bohme & Robl,

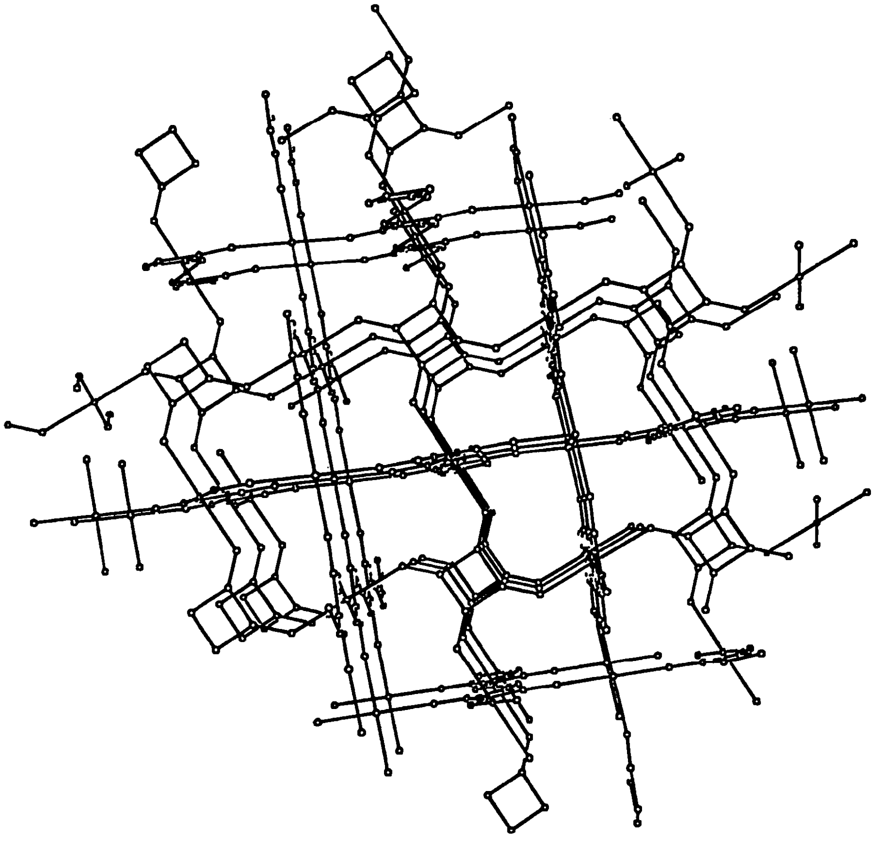

Fig. 9. Packing diagram of type (3); M = Fe, top view of Fig. 7.

1986), where $C_4O_4^{2-}$ is stacked along the *c* axis with an interplanar distance of ~ 3.4 Å. The torsion angle of C—O vectors between successive pairs in the stack is 115°. Such intersecting chains are displayed in Fig. 2. Each chain is built by a $C_4O_4^{2-}$ anion bridging between two metal centers in a *trans* fashion. The same feature occurs for $M = \mathrm{Cu}$, however, the plane of squarate is parallel to that of $\mathrm{Cu(H_2O)_4}$ (Frankenbach *et al.*, 1992).

The type (2) squarate [$M(\mathrm{HC_4O_4})_2(\mathrm{H_2O})_4$, $M = \mathrm{Mn}$ (Yaghi, Li & Groy, 1995), Fe] is a sheet structure, as shown in Fig. 3. Within the sheet it is apparent that in one direction (→) the linking unit is $(\mathrm{HC_4O_4})_2$ bridging between two metal centers in a *trans* position, however, in the other direction (↔) it is a $(\mathrm{HC_4O_4})_n$ column linking between the squarate ions in a *cis* position, where all the H atoms in the column are symmetrically bonded between two squarates. Therefore, the sheet structure can be described as columns of $(\mathrm{HC_4O_4})_n$ interlinked by metal centers. It forms a grid-like parallelogram with size 6 × 17 Å. This is very similar to that of $(\mathrm{H_2NMe_2})[\mathrm{H_3(C_4O_4)_2}]$ (Wang & Stucky, 1974), where columns of $\mathrm{H_3(C_4O_4)_2^-}$ are separated by the $\mathrm{H_2NMe_2^+}$ ion, as shown in Fig. 4. However, in the structure of $(\mathrm{H_2NMe_2})[\mathrm{H_3(C_4O_4)_2}]$, the columns are no longer planar, but making an angle of 26.5° at the symmetric H position (Wang & Stucky, 1974; Lin, Cheng & Wang, 1994). The sheet structure of type (2) [$M(\mathrm{HC_4O_4})_2(\mathrm{H_2O})_4$] can then be related with the structure of $(\mathrm{H_2NMe_2})[\mathrm{H_3(C_4O_4)_2}]$ by breaking the two asymmetric hydrogen bonds in the $(\mathrm{HC_4O_4})_n$ column and making a shift along the direction [indicated as (→) in Fig. 4] at every other row, so that it forms another symmetric hydrogen bond between squarate units. Another sheet structure is found in the network of squaric acid shown in Fig. 5, where a cavity (grid size) of 6 × 6 Å is found between four squaric acid molecules. The structural relationship between this $\mathrm{H_2C_4O_4}$ and $(\mathrm{H_2NMe_2})[\mathrm{H_3(C_4O_4)_2}]$ compounds is such that when every other row of cavities in the acid, as indicated by an 'X' in Fig. 5, is completed with $\mathrm{H_2NMe_2^+}$ in accompanying the breaking of intermolecular hydrogen bonds, the angular anion columns $[\mathrm{H(HC_4O_4)_2}]_n$ are formed between a row of cations, as shown in Fig. 4. Therefore, the structures of $\mathrm{H_2C_4O_4}$, $(\mathrm{H_2NMe_2})[\mathrm{H_3(C_4O_4)_2}]$ and [$M(\mathrm{HC_4O_4})_2(\mathrm{H_2O})_4$] type (2) are indeed closely related to one another. The interlayer distances for these three structures are 2.65 (Wang, Stucky & Williams, 1974), 2.71 (Wang & Stucky, 1974) and 3.12 Å, respectively.

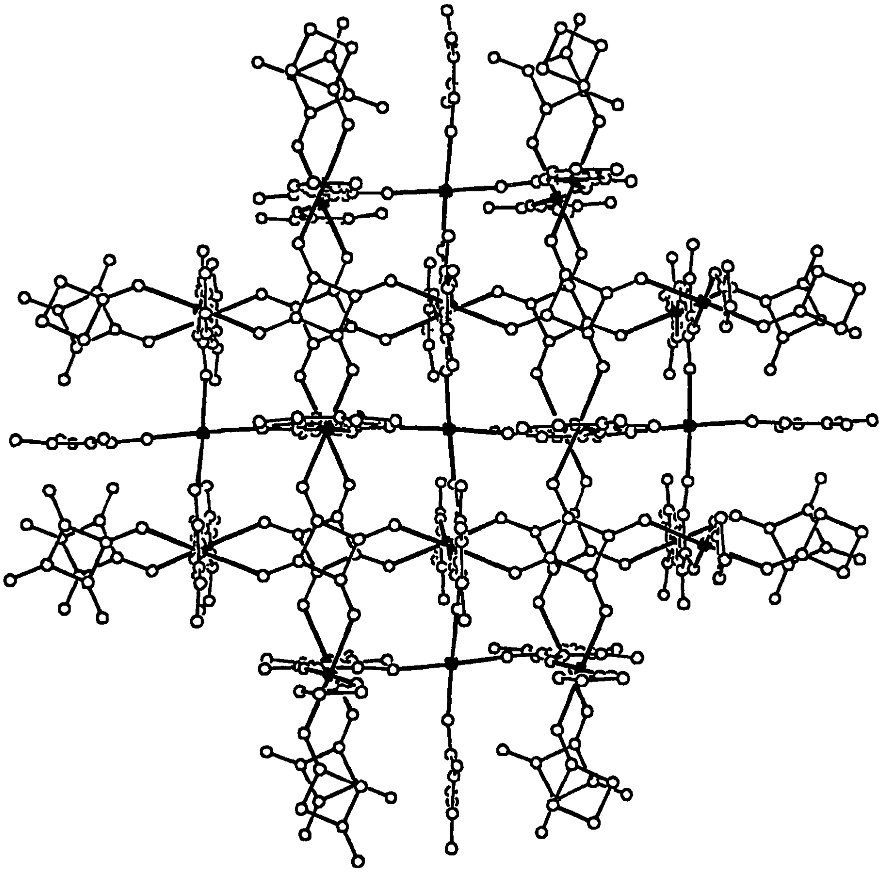

Fig. 10. Packing diagram of type (3); $M = \mathrm{Co}$, top view of Fig. 8.

The layer-like architecture of $[M(HC_4O_4)_2(H_2O)_4]$ is depicted in Fig. 6.

Lastly, the three-dimensional building blocks of the type (3) squarates $[M(C_4O_4)(H_2O)_2]$ are formed in two space groups. Unlike the aforementioned structures, where each metal center is bonded to four water molecules, the metal center here is bonded to only two water molecules, the rest are bonded to four squarates and the dianion $C_4O_4^{2-}$ here is a μ-4 ligand. The building blocks of two structures are illustrated in Figs. 7 and 8 for $M = \mathrm{Fe}$ and Co, respectively. The dimensions of these building blocks are $8 \times 8 \times 8$ Å in both cases. It is clear that these two building blocks are very similar, the only significant difference being the relative orientation of the squarates between the successive layers. The packing of the building blocks in $R\bar{3}$ (Fe case) is such that the linking $C_4O_4^{2-}$ units are stacked in the same orientation between the successive layers, which gives rise to a repeat distance of 8 Å, as shown in Fig. 9. However, in the Co case, the relative orientation of such units in successive layers (Fig. 10) differs by ~45°, so that the repeat distance is twice larger (16 Å).

In summary, the structures of all three types of metal squarate complexes are closely related to one another. They are also related to the acid $H_2C_4O_4$ and bishydrosquarate monoanion form, $H_3(C_4O_4)_2^-$. The structural relationship is best demonstrated in the packing diagrams.

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