Self-assembly of new three-dimensional molecular architectures of Cd(II) and Ag(I)–Na(I) using croconate as a building block

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Two new coordination polymers $[Cd(C_5O_5)(NH_3)_2]_n$ (**1**) and $[AgNa(C_5O_5)(H_2O)_2]_n$ (**2**) ($C_5O_5^{2-}$ = croconate dianion) have been synthesized and structurally characterized. Complex **1** is a one-dimensional coordination polymer of cadmium(II) bridging through the croconate dianion. In complex **1** each croconate chelates (O1 and O2) to a Cd centre, which is linked to another Cd centre by O1 through an oxo-bridge and the oxygen atom O5, neighbouring O1, binds to a third Cd centre and the remaining two oxygen atoms (O3 and O4) remain pendant. The 1D coordination polymer undergoes H-bonding interactions through $N–H(NH_3) \cdots O$ (pendant of C_5O_5) resulting in a 3D supramolecular network. Compound **2** is a heterometallic (Ag,Na) 3D coordination polymer. Here the croconate dianions interweave the alternately aligned and layered $–Na–(\mu–H_2O)_2–Na–(\mu–H_2O)_2–$ and $–Ag–Ag–Ag–$ chains. Two croconates chelate one Ag atom and two such Ag atoms from two neighbouring layers are bridged through croconate (O1, O2) and one oxygen of each croconate remains pendant (O3). The oxygen atom (O2) from every croconate binds a Na atom *via* an oxo-bridge. These types of tridentate and tetradentate linkage of croconate in complexes **1** and **2** are unprecedented. The thermal studies of the complexes corroborate that the ammonia molecules in **1** and the water molecules in **2** are involved in coordination together with strong H- bonding interactions.

Introduction

Over the past decade or so much research has been devoted to the synthesis and characterization of one- to three-dimensional functional organic–inorganic hybrid polymeric architectures.[1–8] The key factor to the design and synthesis of such networks is the choice of suitable organic or inorganic spacers and the metal ions, which allow a wide variety of geometries and coordination numbers. In attempting to prepare coordination polymers we were struck by the utility of avoiding the need for counter anions, like ClO_4^-, which must *inter alia* disrupt the solid state packing and give rise to additional cation–anion interactions, which might be difficult to control.[9,10] Accordingly we judiciously chose anions *i.e.* SCN^-, $SeCN^-$, fumarate, *etc.* which functioned as the essential element of the coordination polyhedra for synthesizing multifunctional networks.[6,7,11,12]

Therefore, we initiated a programme to explore the use of the benzenoid aromatic oxocarbons $C_nO_n^{2-}$ (n =3, deltate; n = 4, squarate; n = 5 croconate; n = 6, rhodizonate), with extensive delocalization of π-electrons all over the ring and the adjoining oxygen atoms.[13–15] The first synthesis of deltic acid was reported by Eggerding and West in 1976,[16] and since then its coordinating capability has remained unknown. The squarate ligand is well known and the crystal structures of squarate-containing copper(II), zinc(II), nickel(II), manganese(II), chromium(III), iron(III), cadmium(II), silver(I), alkaline-earth and rare earth cations have been reported exhibiting versatile bridging modes of the squarate ligand with different geometries.[13,17–21] Though croconate (C_5) and rhodizonate (C_6) oxocarbons were first synthesized more than 175 years ago,[22] and copper(II) croconate was first reported by Gmelin in 1841,[23] as far as the rhodizonate ligand is concerned, no report of structural work on any of its complexes can be found in the literature. In fact, rhodizonate solutions are rather unstable; thus the formation of single crystals by slow evaporation of solvent is unlikely.

On the other hand, the available information on the coordination chemistry of the croconate ligand is limited. Only a few structures of croconato complexes with first row transition metals, $[M(C_5O_5)(H_2O)_3]$ [M = Cu(II), Zn(II), Mn(II), Fe(II) and Co(II)][24–28] and also some complexes of croconate associated with another co-ligand such as imidazole,[29] histamine,[30] 2,2′-bipyridine,[31] bis(2-pyridylcarbonyl)amido anion,[32] *etc* are known. Available structural data dealing with the transition metal croconate complexes show that this ligand can act either as a terminal (Scheme 1, I)[29–32] or as a bridging ligand (Scheme 1, II and III).[24–28]
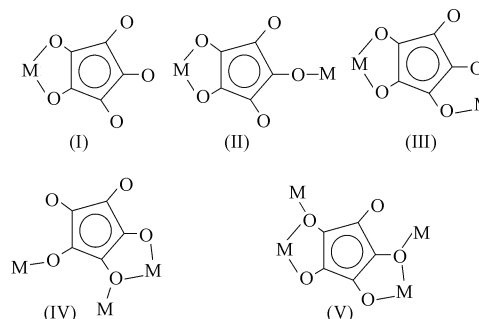
Scheme 1

In this paper we report the synthesis, single crystal structures and solid state thermal studies of two novel 3D architectures, $[Cd(C_5O_5)(NH_3)_2]_n$ (**1**) and $[AgNa(C_5O_5)(H_2O)_2]_n$ (**2**). In complex **1** croconate functions as a tridentate ligand (Scheme 1, IV) and in complex **2** as a tetradentate ligand (Scheme 1, V) and both bridging modes are new. To the best of our knowledge, complex **2** is the first 3D coordination polymer involving the croconate dianion.

Experimental

Materials and methods

The high purity (97%) disodium salt of croconic acid was purchased from Aldrich Chemical Company and used as received. All other reagents were of analytical grade.

Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin-Elmer 240C elemental analyzer. Infrared spectra (4000–400 cm^{-1}) were taken using a Nicolet Magna-IR 750 spectrometer, series-II, where KBr was used as the dispersal medium. Thermal analysis (TGA-DTA) was carried out on a Shimadzu DT-30 thermal analyzer under dinitrogen (flow rate: 30 cm^3 min^{-1}). The sample particle size was within 150–200 mesh.

Synthesis of [Cd(C$_5$O$_5$)(NH$_3$)$_2$]$_n$ (1)

Disodium croconate (1 mmol, 0.186 g) dissolved in water (10 cm^3) was added to an aqueous solution (15 cm^3) of cadmium nitrate tetrahydrate (1 mmol, 0.308 g) with continuos stirring. A deep yellow solid compound CdC$_5$O$_5$·2H$_2$O separated out which was filtered off and washed with water. The yellow solid was treated with water (10 cm^3) and stirred well to form a slurry. A dilute aqueous solution of ammonia (4 N) was slowly added to it dropwise until the solid just dissolved. The resulting deep yellow solution was filtered and the filtrate was kept in an open atmosphere and after 6–8 h deep yellow single crystals suitable for X-ray data collection were obtained. Yield 80%. Anal. calcd. for C$_5$H$_6$N$_2$O$_5$Cd: C, 20.94; H, 2.09; N, 9.77; Cd, 39.24%. Found: C, 20.91; H, 2.10, N, 9.80, Cd, 39. 31%.

Synthesis of [AgNa(C$_5$O$_5$)(H$_2$O)$_2$]$_n$ (2)

An aqueous solution (5 cm^3) of disodium croconate (1 mmol, 0.186 g) was added dropwise to an aqueous solution (15 cm^3) of silver(I) nitrate (1 mmol, 0.170 g) at room temperature. The resulting reaction mixture was stirred for 30 min and then filtered. The yellow filtrate was allowed to crystallize slowly in a CaCl$_2$ desiccator. After a few days shiny yellow single crystals suitable for X-ray diffraction were obtained. Yield 72%. Anal. found: C, 19.65; H, 1.20; N, 0.00; Ag, 35.02%. Calc. for C$_5$H$_4$AgNaO$_7$: C, 19.48; H, 1.29; N, 0.00; Ag, 34.85%.

Crystal data collection and refinement

A suitable single crystal of complex **1** was mounted on a Bruker SMART CCD diffractometer equipped with graphite monochromated Mo-K$_\alpha$ (λ = 0.71073 Å) radiation. The intensity data were corrected for Lorentz and polarisation effects and an empirical absorption correction was also employed using the SAINT[33] program. A total of 4551 reflections [unique reflections, 1012, R_{int} = 0.081] were collected in the range 2.93 < θ < 28.30° and 755 were assumed observed applying the condition $I > 2\sigma(I)$. Whereas X-ray single crystal data collection of complex **2** was carried out on a Nonius DIP-1030H system with Mo-K$_\alpha$ (λ = 0.71073 Å) radiation and a total of 36 frames were collected, each with an exposure time of 12 min, over a half of reciprocal space with a rotation of 5° about φ, the detector being at a distance of 90 mm from the crystal. Data reduction and cell refinement was carried out using the program Mosflm.[34] A total 1886 [unique reflections, 959; R_{int} = 0.032] reflections were measured and 809 were assumed observed applying the condition $I > 2\sigma(I)$ for complex **2**. Both structures were solved by Patterson syntheses and followed by successive Fourier and difference Fourier syntheses. Full matrix least squares refinements on F^2 were carried out for both cases using SHELXL-97 with anisotropic displacement parameters for all non-hydrogen atoms. The refinement converged to residual indices R = 0.0639; wR = 0.1667 for complex **1**, and R = 0.0380; wR = 0.1049 for complex **2** with $I > 2\sigma(I)$. The final difference Fourier map showed maximum and minimum peak heights (3.64 and −0.74 e Å^{-3} and 0.85 and −0.90 e Å^{-3}) for complexes **1** and **2** respectively. The high difference peak of complex **1** being within 1 Å of the Cd(II) atom has no chemical significance. Complex neutral atom scattering factors[35] were used throughout. All calculations were carried out using SHELXS-

Table 1 Crystal data and details of the structure determination for [Cd(C$_5$O$_5$)(NH$_3$)$_2$]$_n$ (**1**) and [AgNa(C$_5$O$_5$)(H$_2$O)$_2$]$_n$ (**2**)

	1	**2**
Empirical formula	C$_5$H$_6$CdN$_2$O$_5$	C$_5$H$_4$AgNaO$_7$
Formula weight	286.53	306.94
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pnma*	*Pbcm*
a/Å	7.668(3)	8.890(4)
b/Å	7.668(3)	6.243(4)
c/Å	13.882(5)	14.452(5)
V/Å^3	816.2(5)	802.1(7)
Z	4	4
ρ/g cm^{-3}	2.332	2.542
$F(000)$	552	592
μ(Mo-Kα) / mm^{-1}	2.667	2.575
T /K	293(2)	293(2)
R	0.0639	0.0380
wR	0.1667	0.1049

97,[36] SHELXL-97,[37] PLATON-99,[38] ORTEP[39] programs and the WinGX System, Ver 1.64.[40] All crystallographic data and refinement parameters for both complexes are summarized in Table 1. Selected bond lengths and angles and H-bonding parameters are displayed in Tables 2 and 3 for complex **1** and Tables 4 and 5 for complex **2**.

CCDC reference numbers 183156 and 183157.

See http://www.rsc.org/suppdata/dt/b2/b208933p/ for crystallographic data in CIF or other electronic format.

Results and discussion

Synthesis

Reactions of disodium croconate with cadmium(II) nitrate tetrahydrate in aqueous medium results in a yellow compound with composition Cd(C$_5$O$_5$)·2H$_2$O. It does not dissolve in any common organic solvents. But in an aqueous solution of ammonia (4 N) it dissolves and yields single crystals with composition [Cd(C$_5$O$_5$)(NH$_3$)$_2$]$_n$ **1**, replacing the water molecules with NH$_3$. Reaction of disodium croconate with silver nitrate in aqueous medium produces the complex **2**.

IR spectroscopy

The IR spectra of complex **1** show a broad and split band in the region 3000–3200 cm^{-1} which can be assigned to the stretching vibration, ν(N–H), of the NH$_3$ ligand and complex **2** shows a broad band in the region 3300–3500 cm^{-1}, which can be assigned to the stretching vibration, ν(O–H) of the water molecules. The most relevant IR features of complexes **1** and **2** are those associated with the chelating croconate ligand. Our spectra are in agreement with the West and Niu analysis.[41] The peaks at 1770 cm^{-1}, 1740 cm^{-1} for complex **1** and 1725 cm^{-1} for complex **2** are assigned to the uncoordinated carbonyl groups, which exhibit a strong double bond character. The coordinated CO groups are characterised by medium absorptions at 1668 cm^{-1}, 1660 cm^{-1} and 1590 cm^{-1} for complex **1**, and 1666 cm^{-1} and 1560 cm^{-1} for complex **2**. A very strong and broad peak centred at 1508 cm^{-1} for complex **1** and 1528 cm^{-1} for complex **2** is attributed to the vibrational modes representing mixtures of C–O and C–C stretching motions. This absorption is characteristic of the salts of C$_n$O$_n$$^{2-}$ ions.

Structural description of [Cd(C$_5$O$_5$)(NH$_3$)$_2$]$_n$ (1)

The structure determination reveals that complex **1** is an infinite one-dimensional coordination chain of cadmium(II) bridged by croconate ligands. An ORTEP view with atom numbering scheme of the coordination chain lying along the crystallographic a-direction is shown in Fig. 1. In the structure, the cadmium atom along with the croconate moiety occupies a

Table 2 Selected bond lengths (Å) and angles (°) for [Cd(C$_5$O$_5$)-(NH$_3$)$_2$]$_n$ (**1**)

Cd–O1	2.439(8)	Cd–O2	2.459(7)
Cd–N	2.181(8)	Cd–O5^b	2.502(8)
Cd–O1^a	2.396(7)		
O1–Cd–O2	71.5(2)	O1–Cd–N	91.83(14)
O1–Cd–O5^b	168.0(3)	O1–Cd–O1^a	123.5(2)
O1–Cd–N^c	91.83(14)	O2–Cd–N	90.31(18)
O2–Cd–O5^b	96.6(3)	O1^a–Cd–O2	165.1(2)
O2–Cd–N^c	90.31(18)	O5^b–Cd–N	88.15(15)
O1^a–Cd–N	89.23(17)	N–Cd–N^c	176.3(2)
O1^a–Cd–O5^b	68.5(3)	O5^b–Cd–N^c	88.15(15)
O1^d–Cd–N^c	89.23(17)	Cd–O1–Cd^d	127.8(3)

Symmetry code: a = 1/2 + x, 1/2 − y, 1/2 − z. b = 1 + x, y, z. c = x, 1/2 − y, z. d = −1/2 + x, 1/2 − y, 1/2 − z.

Table 3 Hydrogen bonds (Å /°) for [Cd(C$_5$O$_5$)(NH$_3$)$_2$]$_n$ (**1**)

D–H ⋯ A	D–H	H ⋯ A	D ⋯ A	D–H ⋯ A
N–H1A ⋯ O3^i	0.89	2.249	3.064(10)	151.92
N–H1A ⋯ O3^{ii}	0.89	2.249	3.064(10)	151.92
N–H2B ⋯ O4^{iii}	0.89	2.204	3.054(10)	159.65
N–H2B ⋯ O4^{iv}	0.89	2.204	3.054(10)	159.65
N–H3C ⋯ O3^v	0.89	2.374	3.193(10)	153.02
N–H3C ⋯ O3^{vi}	0.89	2.374	3.193(10)	153.02

Symmetry code: i = 3/2 − x, −y, −1/2 + z. ii = 3/2 − x, −1/2 + y, −1/2 + z. iii = 1 − x, −1/2 + y, 1 − z. iv = 1 − x, −y, 1 − z. v = 2 − x, −1/2 + y, 1 − z. vi = 2 − x, −y, 1 − z.
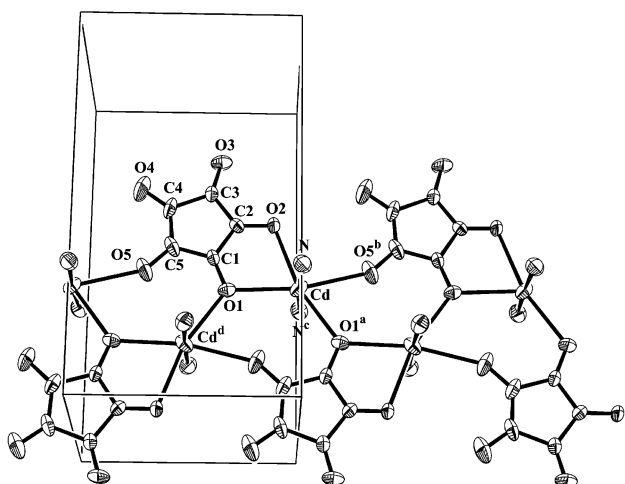

Fig. 1 ORTEP plot of the 1D coordination chain of [Cd(C$_5$O$_5$)(NH$_3$)$_2$]$_n$ (**1**) at 40% thermal ellipsoids (symmetry code: a = 1/2 + x, 1/2 − y, 1/2 − z; b = 1 + x, y, z; c = x, 1/2 − y, z).

special position as they lie on a mirror plane. Each cadmium atom is linked to two neighbouring symmetry related counterparts by bridging croconate ligands. Consequently, two neighbouring cadmium(II) ions are separated by a croconate ion with an intrachain Cd ⋯ Cd distance of 4.355 Å. The geometry around each cadmium atom is best described as a distorted octahedron with a CdO$_4$N$_2$ chromophore. Two oxygen atoms (bridging O1 and O2) of one chelated croconate, one bridging oxygen (O1^a) of a second croconate and one single oxygen (O5^b) from a third croconate define the equatorial plane around each cadmium atom while the nitrogen atoms (N and N^c) of the ammonia ligands occupy the *trans* axial positions. The cadmium atom and croconate ring are strictly planar being located on a mirror plane. The equatorial Cd–O distances are asymmetric (Cd–O1 2.439(8), Cd–O2 2.459(7), Cd–O1^a 2.396(7), Cd–O5^b 2.502(8) Å). The difference observed between the Cd–O1 and Cd–O2 distances confirms the intrinsic tendency

of croconate to coordinate as an asymmetric bidentate ligand similar to other metal–croconate complexes. The bridging (Cd–O1–Cd^d) and the ligand bite (O1–Cd–O2) angles are 127.8(3)° and 71.5(2)° respectively. The five C–O bond distances in a free delocalized croconate ring are expected to be identical, C–O, 1.244 Å but in this complex the non-coordinated oxygens (O3 and O4) show shorter "ketonic" bond distances (C3–O3 1.223 (12), C4–O4 1.219(14) Å) compared to the C–O distances (C1–O1, 1.275(12); C2–O2, 1.262(12); C5–O5, 1.257(15) Å) of the metal-coordinated oxygens due to a partial localization of the π-electrons upon complexation. These uncoordinated oxygens, O3 and O4, of the croconate ligand interact with the ammonia ligands through N–H ⋯ O hydrogen bonding (Table 3). These H-bonding interactions facilitate the formation of Cd–croconate sheets in the *ab* plane (Fig. 2). It is interesting
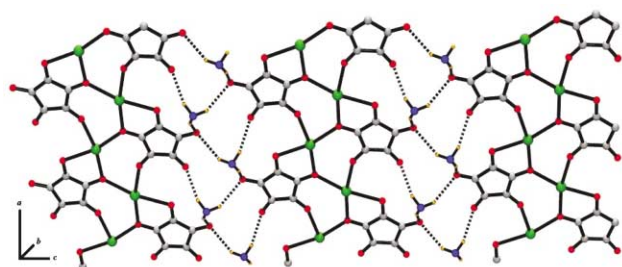
Fig. 2 H-Bonding motifs of the ammonia ligand generating infinite 2D sheets of Cd–croconate in the *ac* plane (for clarity only the upper side of the ammonia ligands is shown. Dotted lines represent the hydrogen bonding interactions.). Colour code: green Cd; gray C; red O; blue N; orange H.

to note that every pendant ammonia above and below the plane interacts with three croconates, two from one chain and one from a neighbouring chain, through H-bonding encouraging the Cd–croconate 1D chains to lie in a plane (Fig. 2). These interactions, finally, generate an infinite 3D supramolecular network (Fig. 3). The distance between the two cadmium centres among such adjacent sheets is 3.834 Å.
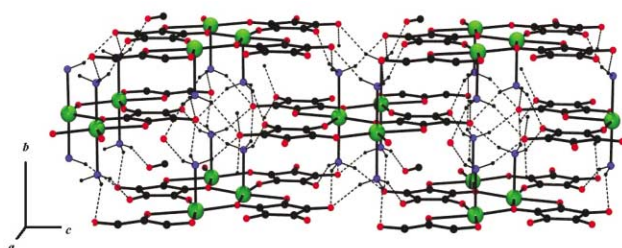
Fig. 3 3D supramolecular network of [Cd(C$_5$O$_5$)(NH$_3$)$_2$]$_n$ (**1**) viewed along the [100] direction. Dotted lines represent the hydrogen bonding interactions. Colour code: green Cd; gray C; red O; blue N; orange H.

Structural description of [AgNa(C$_5$O$_5$)(H$_2$O)$_2$]$_n$ (2)

The crystal structure of **2** consists of metal–metal chains of silver and water bridged chains of sodium, interwoven by croconate ions to form a 3D coordination-polymeric network. A perspective view showing the connectivity of the ligand with the metal is given in Fig. 4. The silver atoms align along the *b*-direction to form –Ag–Ag–Ag– infinite zigzag chains with a Ag–Ag distance of 3.170(2) Å, which is shorter than twice the van der Waal radius (3.44 Å for Ag), indicating the presence of metal–metal interactions. The Ag–Ag contacts are unsupported by bridging ligands and the distances lie within the range observed for other argentophilic bonds in the literature.[42–45] The sodium centres are bridged by water molecules and are also aligned along the *b* direction. The –Ag–Ag–Ag– and –Na–(μ-H$_2$O)$_2$–Na–(μ-H$_2$O)$_2$– chains line up alternately and strictly in the *ab* plane. In the *ab* plane alternate metal atom pairs (Ag,

Table 4 Selected bond lengths (Å) and angles (°) for [AgNa(C$_5$O$_5$)-(H$_2$O)$_2$]$_n$ (**2**)

Ag–O1	2.339(3)	Ag–O2	2.615(3)
Na–O1W	2.414(3)	Na–O2	2.434(4)
Ag–Ag^h	3.170(2)		
O1–Ag–O2	70.69(7)	O1^a–Ag–O2	140.12(7)
O2–Ag–O2^a	73.47(8)	Ag–O2–Na	103.29(9)
O1^a–Ag–O2^a	70.69(7)	O1–Ag–O1^a	148.38(7)
O1–Ag–O2^a	140.12(7)	Ag^g–Ag–Ag^h	159.85(2)
Ag^h–Ag–O2	102.80(6)		
O1W^d–Na–O2^a	88.35(10)	O1W^c–Na–O2^a	90.56(10)
O1W^a–Na–O1W^d	87.02(9)	O1W^a–Na–O1W^c	93.89(10)
Na–O1W–Na^c	92.98(10)	O1W^c–Na–O1W^d	178.58(15)
O1W–Na–O2	90.09(8)	O1W–Na–O1W^a	99.93(13)
O1W–Na–O2^a	169.83(12)	O1W–Na–O1W^c	87.02(9)
O1W–Na–O1W^d	93.89(10)	O1W^a–Na–O2	169.83(12)
O2–Na–O2^a	79.96(12)	O1W^c–Na–O2	88.35(10)
O1W^d–Na–O2	90.56(10)	O1W^a–Na–O2^a	90.09(8)

Symmetry code: a x, 3/2 − y, 1 − z. b x, y, 1/2 − z. c 1−x, 1 − y, 1 − z. d 1−x, 1/2 + y, z. g 2 − x, 1 − y, 1 − z. h 2 − x, 2 − y, 1 − z.

Table 5 Hydrogen bonds (Å,°) for [AgNa(C$_5$O$_5$)(H$_2$O)$_2$]$_n$ (**2**)

D–H ⋯ A	D–H	H ⋯ A	D ⋯ A	D–H ⋯ A
O1W–H1 ⋯ O1^i	0.98	1.89(3)	2.860(4)	166(4)
O1W–H2 ⋯ O3	0.99	1.78(3)	2.766(4)	173(4)

Symmetry code: i = −1 + x, y, z.

Scheme 2

Fig. 5 A perspective view showing the connectivity of –Ag–Ag–Ag– and –Na–(μ–H$_2$O)$_2$–Na–(μ–H$_2$O)$_2$– chains in the *ab* plane. Colour code: green Ag; red O; blue Na; pink O1w.

Fig. 4 ORTEP plot of [AgNa(C$_5$O$_5$)(H$_2$O)$_2$]$_n$ (**2**) showing the metal coordination spheres at 40% thermal ellipsoids (symmetry code: a x, 3/2 − y, 1 − z; b x, y, 1/2 − z; c 1 − x, 1 − y, −z; d 1 − x, 1/2 + y, z; e 1 − x, 2 − y, −z; f x, y, −1/2 − z; g 2 − x, 1 − y, 1 − z; h 2 − x, 2 − y, 1 − z).

Fig. 6 Crystal packing diagram of [AgNa(C$_5$O$_5$)(H$_2$O)$_2$]$_n$ (**2**) showing the connectivity in the undulating ribbon of croconate and –Ag–Ag–Ag– chains generating a 3D network. Colour code: green Ag; red O; blue Na; black C.

Na) of adjacent chains are linked by O2 atoms of the croconate ligand, to form a AgNaO$_2$ four remembered ring (Scheme 2, Fig. 5). The croconate oxygens O1 and O2, act as bridging donors towards the Ag atoms from adjacent layers to give rise to a 3D network (Fig. 6) of undulating ribbons which are organised in between the *ab* planes.

In this structure, the Ag, Na, O3 and C3 atoms occupy special positions, and the Ag and Na atoms lie on a two-fold axis whereas the O3 and C3 atoms are in a mirror plane. The coordination environment around each Na atom presents a slightly distorted octahedron through two croconate oxygens (μ-O2) and four water molecules (μ-O1w) (only one crystallo-graphically independent). The Na–O distances (Na–O1w 2.414(3) Å and Na–O2 2.434(4) Å) have typical values for this ion (Table 4).[46] Each silver atom is coordinated to four oxygens

of two bridging chelated croconate ligands with asymmetric bond distances (Ag–O1 2.339(3); Ag–O2 2.615(3) Å) as usual where the distance Ag–O2 could be indicative of an interac-

tion more ionic in character, as the O2 atom represents a compromise in order to allow this oxygen to interact, as bridging donor, also with sodium. Each croconate functions as a tetradentate ligand with a new kind of bridging mode (Scheme 1(V)). The bridging (Na–O1w–Na^c, Na^c–O2^d–Ag^g) angles are 92.98(10)° and 103.29(9)° respectively. The ligand bite (O1–Ag–O2) angle is 70.69(7)°, which is slightly smaller than that found in complex **1**. The Ag^g–Ag–Ag^h angle is 159.85(2)°. It may be noted that the difference between coordinated and uncoordinated "ketonic" bond distances is not evidenced in structure **2**. The overall structure is reinforced by an ordered H-bonding between the water molecule and the croconate oxygens (O1w ··· O3 2.766 Å; O1w ··· O1 2.860 Å) (Table 5) which is responsible for the overall stability of the crystal packing.

Thermal investigation

Complex [Cd(C$_5$O$_5$)(NH$_3$)$_2$] (**1**) upon heating loses two molecules of NH$_3$ in two steps overlapping with each other at temperatures *ca.* 210 °C corroborating the fact that the NH$_3$ molecules are involved in coordination as well as being involved in strong H-bonding interactions. It is worth mentioning that the compound, Cd(C$_5$O$_5$)·2H$_2$O loses two water molecules at ≈180 °C suggesting also that the water molecules are involved in strong H-bonding interactions other than coordination. The deaminated compound remains stable up to 340 °C but upon further heating it decomposes to unidentified products. The deaminated product can be stored in a dessicator or in an open humid atmosphere (RH ≈60%). To characterize it properly we tried to grow single crystals but our attempts were unsuccessful due to insolubility in common organic solvents.

The complex [AgNa(C$_5$O$_5$)(H$_2$O)$_2$] (**2**) upon heating loses two molecules of water at ≈140 °C suggesting that the water molecules are involved in strong H-bonding interactions other than coordination. The dehydrated compound remains stable up to ≈280 °C but upon further heating it begins to decompose. This dehydrated compound is rehydrated on exposure to a humid atmosphere (RH ≈60%) for several hours.

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