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A Variable Ag–Cr–Oxalate Channel Lattice: $[M_xAg_{0.5-x}(H_2O)_3]@[Ag_{2.5}Cr(C_2O_4)_3]$, M = K, Cs, Ag

Philip A. W. Dean,*,† Don Craig,‡ Ian Dance,*,‡ Vanessa Russell,‡ and Marcia Scudder‡

Department of Chemistry, University of Western Ontario, London, Ontario N6A 5B7, Canada, and
School of Chemical Sciences, University of New South Wales, Sydney NSW 2052, Australia

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Reaction of aqueous $AgNO_3$ with aqueous $M_3[Cr(ox)_3]$ in ≥3:1 molar ratio causes the rapid growth of large, cherry-black, light-stable crystals which are not $Ag_3[Cr(ox)_3]$, but $[M_{0.5}(H_2O)_3]@[Ag_{2.5}Cr(ox)_3]$ (ox^{2-} = oxalate, $C_2O_4^{2-}$; M = Na, K, Cs, Ag, or mixtures of Ag and a group 1 element). The structure of these crystals contains an invariant channeled framework, with composition $\{[Ag_{2.5}Cr(ox)_3]^{-0.5}\}_\infty$, constructed with $[Cr(ox)_3]$ coordination units linked by Ag atoms through centrosymmetric $\{Cr–O_2C_2O_2–Ag\}_2$ double bridges. The framework composition $[Ag_{2.5}Cr(ox)_3]^{-0.5}$ occurs because one Ag is located on a 2-fold axis. Within the channels there is a well-defined and ordered set of six water molecules, strongly hydrogen bonded to each other and some of the oxalate O atoms. This invariant channel plus water structure accommodates group 1 cations, and/or Ag cations, in different locations and in variable proportions, but always coordinated by channel water and some oxalate O atoms. The general formulation of these crystals is therefore $[M_xAg_{0.5-x}(H_2O)_3]@[Ag_{2.5}Cr(ox)_3]$. Five different crystals with this structure are reported, with compositions **1** $Ag_{0.5}[Ag_{2.5}Cr(ox)_3](H_2O)_3$, **2** $Cs_{0.19}Ag_{0.31}[Ag_{2.5}Cr(ox)_3](H_2O)_3$, **3** $K_{0.28}Ag_{0.22}[Ag_{2.5}Cr(ox)_3](H_2O)_3$, **4** $Cs_{0.41}Ag_{0.09}[Ag_{2.5}Cr(ox)_3](H_2O)_3$, and **5** $Cs_{0.43}Ag_{0.07}$ $[Ag_{2.5}Cr(ox)_3](H_2O)_3$. All crystallize in space group *C*2/*c*, with $a \approx 18.4$, $b \approx 14.6$, $c \approx 12.3$ Å, $\beta \approx 113°$. Pure $Ag_3[Cr(ox)_3](H_2O)_3$, which has the same crystal structure (**1**), was obtained from water by treating $Li_3[Cr(ox)_3]$ with excess $AgNO_3$. Complete dehydration of all of these compounds occurs between 30 and 100 °C, with loss of diffraction, but rehydration by exposure to $H_2O(g)$ at ambient temperature leads to recovery of the original diffraction pattern. In single crystals, this reversible dehydration–hydration occurs without visually evident crystal change, but with loss of mechanical strength. We postulate a general mechanism for transport of water molecules along the channels, associated with local partial collapses of the channel framework, with concomitant bending but little breaking of the host Ag–O and Cr–O bonds, which is readily reversed.

Introduction

Oxalate ($C_2O_4^{2-}$, ox^{2-}) as a bridging ligand has enabled the construction of various nonmolecular coordination networks, with general formulas $[M_2^{II}(ox)_3]_n^{2n-}$, $[M_a^{I}M_b^{III}(ox)_3]_n^{2n-}$, and $[M_a^{II}M_b^{III}(ox)_3]_n^{n-}$.[1–3] The metal atoms in these are all coordinated by three bidentate ligands, and therefore the structures are built from 3-connecting metal sites with ditopic ligands. Two network types are known: one, with linked $M(ox)_3$ centers of alternating chirality, is a planar (6,3) network, while homochiral $M(ox)_3$ centers form a three-dimensional (10,3)-a chiral network.[3,4] These crystals, which are interesting for reasons of possible cooperativity of metal properties,[1,5] are usually templated by associated polyatomic cations, such as chiral $[M(2,2'\text{-bipyridyl})_3]^{2+}$ and $[M(1,10\text{-phenanthroline})_3]^{2+}$ complexes.

We have previously analyzed the cubic crystal structure of $(Ph_3MeP)_2[NaCr(ox)_3]$ which contains a (10,3)-a net of

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* Authors to whom correspondence should be addressed. E-mail: pawdean@uwo.ca (P.A.W.D.); I.Dance@unsw.edu.au (I.D.).

† University of Western Ontario.

‡ University of New South Wales.

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Table 1. Crystallographic Details

	1	2	3	4	5
formula	$C_{12}H_{12}Ag_6Cr_2O_{30}$	$C_{12}H_{12}Ag_{5.62}Cr_2Cs_{0.38}O_{30}$	$C_{12}H_{12}Ag_{5.44}Cr_2K_{0.56}O_{30}$	$C_{12}H_{12}Ag_{5.18}Cr_2Cs_{0.82}O_{30}$	$C_{12}H_{12}Ag_{5.14}Cr_2Cs_{0.86}O_{30}$
M	1387.4	1396.9	1348.9	1407.9	1408.9
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$C2/c$	$C2/c$	$C2/c$	$C2/c$	$C2/c$
a/Å	18.400(7)	18.382(3)	18.302(8)	18.338(9)	18.335(6)
b/Å	14.566(2)	14.599(1)	14.670(3)	14.619(3)	14.628(2)
c/Å	12.313(4)	12.313(2)	12.298(5)	12.379(4)	12.383(4)
β/deg	113.19(1)	113.12(1)	113.62(2)	113.00(2)	113.00(1)
V/Å^3	3033(2)	3038.9(8)	3025(2)	3055(2)	3057(1)
D_c/g cm^{-3}	3.04	3.05	2.96	3.06	3.06
Z	4	4	4	4	4
μ_{Mo}/ mm^{-1}	4.542	4.744	4.282	4.961	4.979
$2\theta_{max}$	50	50	50	50	50
crystal decay					5%
min transm factor	0.33	0.66	0.53	0.57	0.40
max transm factor	0.49	0.72	0.64	0.65	0.45
unique reflns	2659	2667	2655	2685	2689
obsd reflns	2356	2282	2257	2273	2441
R_{merge}	0.034	0.022	0.033	0.012	0.031
R^a	0.059	0.063	0.069	0.053	0.061
$R_w{}^b$	0.108	0.110	0.121	0.093	0.118

[a] $R = \sum^m|\Delta F|/\sum^m|F_o|$. [b] $R_w = [\sum^m w|\Delta F|^2/\sum^m w|F_o|^2]^{1/2}$.

[Cr(ox)$_3$] sites interpenetrated by another (10,3)-a net of Ph_3MeP^+ cations.[4] There are intermolecular homochiral embrace motifs between the 3-fold Ph_3MeP^+ cations and 3-fold [Cr(ox)$_3$] coordination complexes.[4] Crystals with the composition $(PhMe_3P)_5Na_2$[Cr(ox)$_3$]$_2$Cl$(H_2O)_5$ did not show this property.[6]

To develop this chemistry using other designed polyatomic cations, we attempted preparation of the compound Ag_3[Cr(ox)$_3$], to be used in cation metatheses by exchanging Ag^+. This led to discovery of a new set of crystalline compounds which contain a three-dimensional network with the composition [$Ag_{2.5}$Cr(ox)$_3$]$^{-0.5}$: this nonmolecular structure surrounds channels that contain well-positioned water molecules, and monatomic cations from group 1 (M^+), and Ag^+. The general formulation is [$M_xAg_{0.5-x}(H_2O)_3$]@[$Ag_{2.5}$Cr(ox)$_3$]. In this paper we describe the invariant and variable aspects of these crystal structures, together with the M-dependent crystallization phenomena, and the reversible small changes in structure that occur on dehydration and rehydration. Large crystals of these compounds are readily grown quickly, but were not mentioned in a previous report[7] involving similar reactions.

Results

Crystal Growth. Addition of aqueous $AgNO_3$ to aqueous K_3[Cr(ox)$_3$] in molar ratio 3, at room temperature and ca. 0.2 M concentration, leads to impressive immediate crystal growth. Cherry-black single crystals begin to grow almost immediately and can be collected within several hours as prisms, with the largest dimension of the order of mm. Elemental analysis and a subsequent crystal structure determination (described below) yielded a formula $K_{0.28}Ag_{2.72}$[Cr(ox)$_3$]$(H_2O)_3$. Increase in the molar ratio ($AgNO_3$/K_3[Cr(ox)$_3$]) to 10 caused similar crystals to grow at the same rate, but with the different composition $K_{0.08}Ag_{2.92}$[Cr(ox)$_3$]$(H_2O)_3$. These last crystals were obtained in a yield of 85%. Crystals of $K_{0.08}Ag_{2.92}$[Cr(ox)$_3$]$(H_2O)_3$ showed no evidence of decomposition after hours of exposure to fluorescent light: in sunlight the crystals develop a brown coating after several days, but diffraction measurements indicated that the bulk was unchanged.

Similar results were obtained with Na_3[Cr(ox)$_3$] as reactant. Remarkably, the presence of aqueous $NaNO_3$ (in ca. 10-fold molar proportion) suppressed all growth of these black crystals.

Crystallization using aqueous Li_3[Cr(ox)$_3$] and excess $AgNO_3$ (Ag/Cr = 12), yielded Ag_3[Cr(ox)$_3$]$(H_2O)_3$, characterized by single-crystal structure determination as described below. Crystallization experiments using aqueous $AgNO_3$ and aqueous Cs_3[Cr(ox)$_3$] in molar ratios (Ag/Cr) of 2.5, 3.0, 3.9, and 19, also grew large cherry-black crystals, with compositions ranging from $Cs_{0.43}Ag_{2.57}$[Cr(ox)$_3$]$(H_2O)_3$ to $Cs_{0.19}Ag_{2.81}$[Cr(ox)$_3$]$(H_2O)_3$.

Crystal Structure. All of the red-black crystals M_xAg_{3-x}[Cr(ox)$_3$]$(H_2O)_3$ have the same general powder X-ray diffraction pattern. Five single-crystal structure determinations have been made, **1**−**5**, all with space group $C2/c$, and very similar cell dimensions (see Table 1). At this point it is evident that a general structure type is being formed, with fixed and variable components. To understand how this occurs, and to provide the background for consideration of other properties of these systems, we next describe the crystal structure, starting with the invariant $Ag_{2.5}$Cr(ox)$_3$ framework. This composition for the framework occurs because it is generated by one [Cr(ox)$_3$] coordination unit plus two Ag atoms without crystallographic symmetry, and one Ag atom on a 2-fold axis.

1	$Ag_{0.5}$[$Ag_{2.5}$Cr(ox)$_3$]$(H_2O)_3$
2	$Cs_{0.19}Ag_{0.31}$[$Ag_{2.5}$Cr(ox)$_3$]$(H_2O)_3$
3	$K_{0.28}Ag_{0.22}$[$Ag_{2.5}$Cr(ox)$_3$]$(H_2O)_3$
4	$Cs_{0.41}Ag_{0.09}$[$Ag_{2.5}$Cr(ox)$_3$]$(H_2O)_3$
5	$Cs_{0.43}Ag_{0.07}$[$Ag_{2.5}$Cr(ox)$_3$]$(H_2O)_3$

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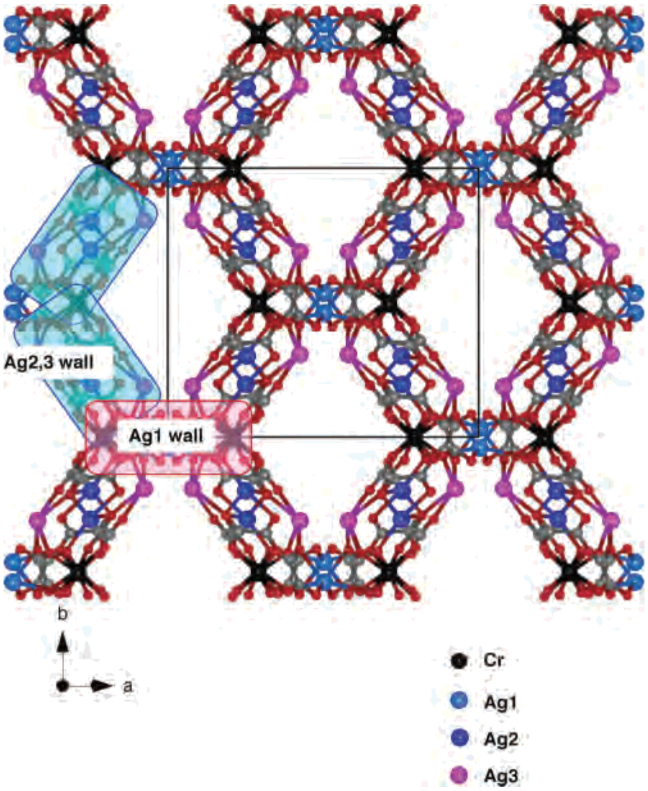
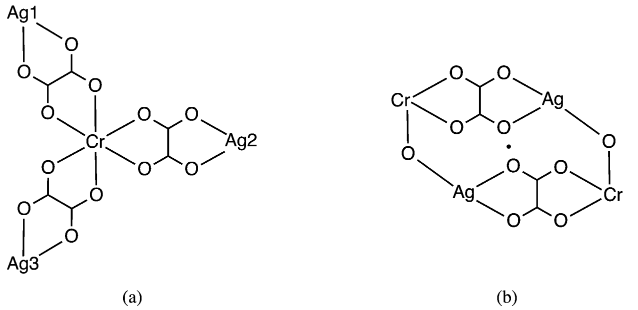


Figure 1. Projection of the net along the channels (space group $C2/c$, $a \approx 18.4$, $b \approx 14.6$, $c \approx 12.3$ Å, $\beta \approx 113°$). The Ag1 atoms (light blue) are located on 2-fold axes parallel to y at $x = 0, 0.5, 1$: Ag2 is dark blue, Ag3 magenta. The walls of the channels are composed of two types of double-oxalate-bridged segments, the Ag1 wall (red enclosure) and the Ag2,3 wall (blue enclosure). The wall segments are linked at $Cr(ox)_3$.



(a) (b)

Figure 2. The coordination that generates the walls of the network. Each of the three $Cr-O_2C_2O_2-Ag$ bridges in part a is doubled across a center of inversion, as shown in part b.

The $Ag_{2.5}Cr(ox)_3$ Framework. Figure 1 shows the $Ag_{2.5}Cr(ox)_3$ network, projected along the c axis, and the occurrence of channels separated by silver oxalate walls that connect Cr nodes. The asymmetric unit of the network contains one Cr, three oxalate ligands that bridge between Cr and Ag, and three different Ag atoms (which are color-differentiated in the figures). There are two types of channel wall, marked in Figure 1. One wall type, parallel to the [010] plane, contains the Ag1 atoms and is labeled the Ag1 wall. The other wall type, approximately parallel to the [110] and [$1\bar{1}0$] planes, contains the Ag2 atoms near its center and the Ag3 atoms, and is labeled the Ag2,3 wall. The Ag2 and Ag3 atoms (and the $[Cr(ox)_3]$ coordination unit) are located at general positions, while Ag1 atoms lie on 2-fold axes, and the framework is $(Ag1)_{0.5}(Ag2)(Ag3)[Cr(ox)_3]$.

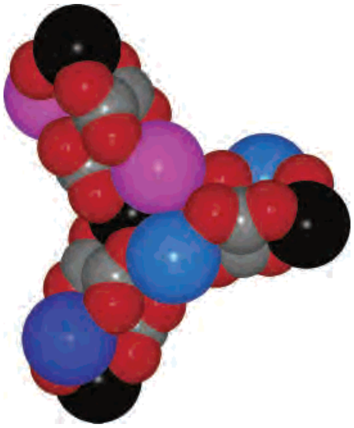


Figure 3. The three $\{Ag-O_2C_2O_2-Cr\}_2$ bridges connecting the central Cr atom (black) to three surrounding Ag atoms. The bridge to the right involves Ag1 and forms the Ag1 wall of the network, while the up and down bridges contribute to the Ag2,3 wall: colors as in Figure 1.

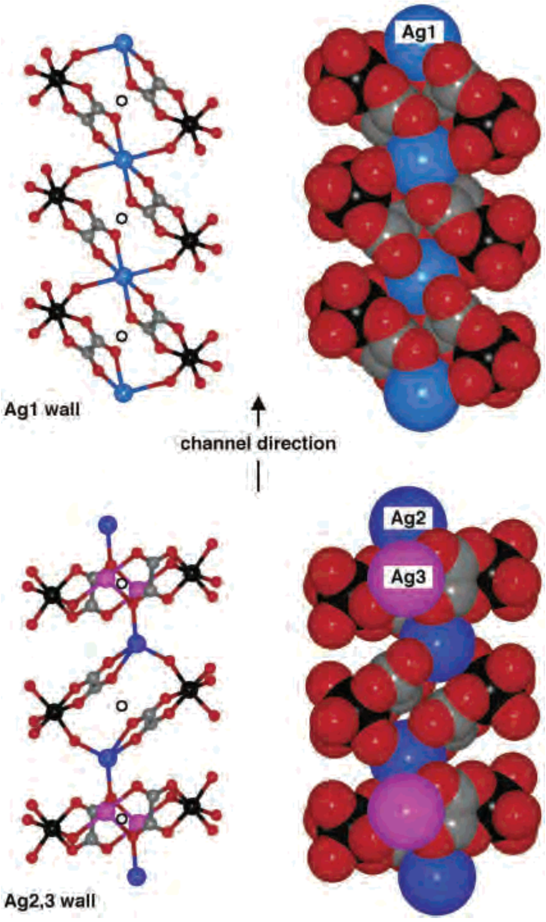


Figure 4. Skeletal and space-filling representations of the two types of channel wall segments, translated along the channel axis. The view direction is normal to the wall face. In the Ag1 wall (upper figures) the centers of inversion are marked as open circles, and there are 2-fold axes normal to the wall through the Ag1 atoms. Note that the $\{Ag-O_2C_2O_2-Cr\}_2$ double bridges cant alternately to left and right. The Ag2,3 wall (lower figures) contains centers of inversion (open circles), and double bridges involving Ag2 and Ag3 alternate along the wall. Note that Ag1 and Ag2 are inside their walls, with octahedral and tetrahedral coordination respectively, while Ag3 is on the edge of its wall.

It is helpful to appreciate the symmetry of this network. The array of channels is generated by the C-centering of the lattice; there are centers of inversion along the channels and at the midpoints of the Ag1 and Ag2,3 walls, and the propagation of the channels along the channel axes (*c*) is effected by c-glide operations.

The three oxalate ligands of the regular octahedral $[Cr(ox)_3]^{3-}$ complex bridge to the three crystallographically different Ag atoms Ag1, Ag2, and Ag3, as shown in Figure 2a, and each of these three blades of the coordination propellor around Cr is doubled by centrosymmetric pairing with another $Ag-O_2C_2O_2-Cr$ moiety, as illustrated for one ligand in Figure 2b. The doubling of the propellor blades in this way does not occur with pseudo-3-fold symmetry around Cr, but rather as shown in Figure 3. The significant aspect of this construction is that each centrosymmetric $\{Ag-O_2C_2O_2-Cr\}_2$ double blade is a well-formed offset-face-to-face motif.

Figure 4 shows more detail of the two walls and how they are constructed using the double bridges of Figure 3. Ag1 is octahedrally coordinated (Ag−O distances 2.37(×2), 2.55(×2), 2.61(×2) Å for **1**) by surrounding oxalate O atoms: Ag2 is tetrahedrally coordinated (Ag−O distances 2.33, 2.41, 2.42, 2.57 Å), with some longer Ag−O contacts not marked in Figure 4. Ag3 is coordinated by four oxalate O atoms (Ag−O distances 2.35, 2.43, 2.63, 2.68 Å) from both walls, in pyramidal stereochemistry. In addition, Ag3 is coordinated by one water molecule, as described next.

Contents of the Channels. The channels in the $Ag_{2.5}Cr(ox)_3$ network contain water molecules at invariant locations, with unambiguous hydrogen bonds. There are three independent water molecules, labeled W1, W2, W3, hydrogen bonded to each other and to surrounding oxalate O atoms. Figure 5 shows the water network and hydrogen bonds, viewed both in projection along the channels and as extended along the channels. Centrosymmetric sets of six water molecules are repeated along the channels: Figure 5c details the directions of the hydrogen bonds in this set. W1 is coordinated to Ag3 which protrudes from the channel walls.

Crystal structure determination was completed for five preparations, in which the channels contained differing additional cations in variable proportions: **1** $Ag_{0.5}$; **2** $Cs_{0.19}Ag_{0.31}$; **3** $K_{0.28}Ag_{0.22}$; **4** $Cs_{0.41}Ag_{0.09}$; **5** $Cs_{0.43}Ag_{0.07}$. The additional cations are disordered over several locations, which are illustrated in Figure 5 for **1** (Figure 5a) and **2** (Figure 5b). There are three locations for the additional Ag cations (green colorations in Figure 5) and one location for the group 1 cation (colored orange in Figure 5b). The positions for Ag^+ and the position for the group 1 cations Cs^+ or K^+ are differentiated by the size of the space within the surrounding coordinating O atoms from water and oxalate. The smaller spaces can be occupied by Ag^+, while Cs^+ or K^+ requires the one larger space, but only one of the four positions can be occupied at any locality in the crystal. Details of the positions and occupancies in each of the refined structures are presented in the Supporting Information. In Figure 5 the coordination of the additional cations by oxalate O is marked with black bonds, and the coordination by water with gray bonds. All bond distances and hydrogen bonding distances are normal and are tabulated in the Supporting Information.

Dehydration and Rehydration. The water in the channel can be removed by heating, or by very high vacuum. After 4 days at a pressure of ca. 6×10^{-6} bar, the crystalline compound with composition $K_{0.08}Ag_{2.92}Cr(ox)_3(H_2O)_3$ lost 7.4% mass: calculated mass for $3H_2O$ is 7.8%. Thermogravimetric analysis of samples with composition $Cs_{0.42}Ag_{0.08}[Ag_{2.5}Cr(ox)_3]\ (H_2O)_3$ shows that water loss commences at relatively low temperatures of ca. 30 °C, and is complete by 100 °C within 2 h.

During dehydration, diffraction is lost, indicating lack of long range order. However, on subsequent exposure to water vapor there is rehydration, with recovery of sharp diffraction showing the same pattern as the original sample. Representative data are presented in Figure 6. Rehydration occurs on a time scale of 24 h at ambient temperature and 100% humidity for typical microcrystalline samples.

It is possible to observe the dehydration and rehydration cycle in a single crystal. Single-crystal diffraction data were measured for a crystal prepared with Na^+ as the group 1 cation. The mounted crystal was heated at 100 °C for 2h, after which there was no measurable diffraction. This mounted crystal was then rehydrated for ca. 18 h with ca. 30 mm $H_2O(g)$ at room temperature, and its diffraction remeasured, revealing recovery of the single crystal diffraction pattern at about 10% of the original intensity. There was no visually observable degradation of single crystals after dehydration (photographs are provided in the Supporting Information), but mechanical strength is degraded.

Attempts to reabsorb CH_2Cl_2, MeCN, MeOH into dehydrated crystals did not regenerate crystalline material, and there is no evidence that these small molecules absorb in preference to water.

Discussion

Crystalline $Ag_3Cr(ox)_3(H_2O)_3$ has a structure which is not simply a network of $[Cr(ox)_3]^{3-}$ entities linked by Ag^+ through Cr−ox−Ag bridges, as might have been expected. In fact, 5/6 of the Ag ions are bridged in this fashion, and generate a fully bridged three-dimensional lattice which contains parallel channels. The remaining 1/6 of the Ag^+ are located in these channels, and are coordinated by the water molecules that occupy the channel in a well-defined hydrogen bonding array. The 1/6 of Ag^+ ions in the channels are disordered over three positions, unlike the network Ag^+ ions which are fixed. The crystals are therefore better formulated as $[Ag_{0.5}(H_2O)_3]@[Ag_{2.5}Cr(ox)_3]$. The $[Ag_{2.5}Cr(ox)_3]$ host lattice is built from Cr−ox−Ag bridges, which are doubled across a center of inversion: these are the only fundamental moieties for the network. The formulation $[Ag_{2.5}Cr(ox)_3]$ for a lattice network built entirely from $\{Cr-ox-Ag\}_2$ bridges is accounted for because one of the lattice Ag^+ lies on a 2-fold axis.

The channel domain in this $[Ag_{2.5}Cr(ox)_3]$ can also accommodate group 1 cations, $M^+ = Na^+$ to Cs^+, and, if these M^+ cations are present in the crystallization solution (from the common precursors $M_3[Cr(ox)_3]$), they are included in the channels, forming crystals with the general composition $[M_xAg_{0.5-x}(H_2O)_3]@[Ag_{2.5}Cr(ox)_3]$. The structures of four of

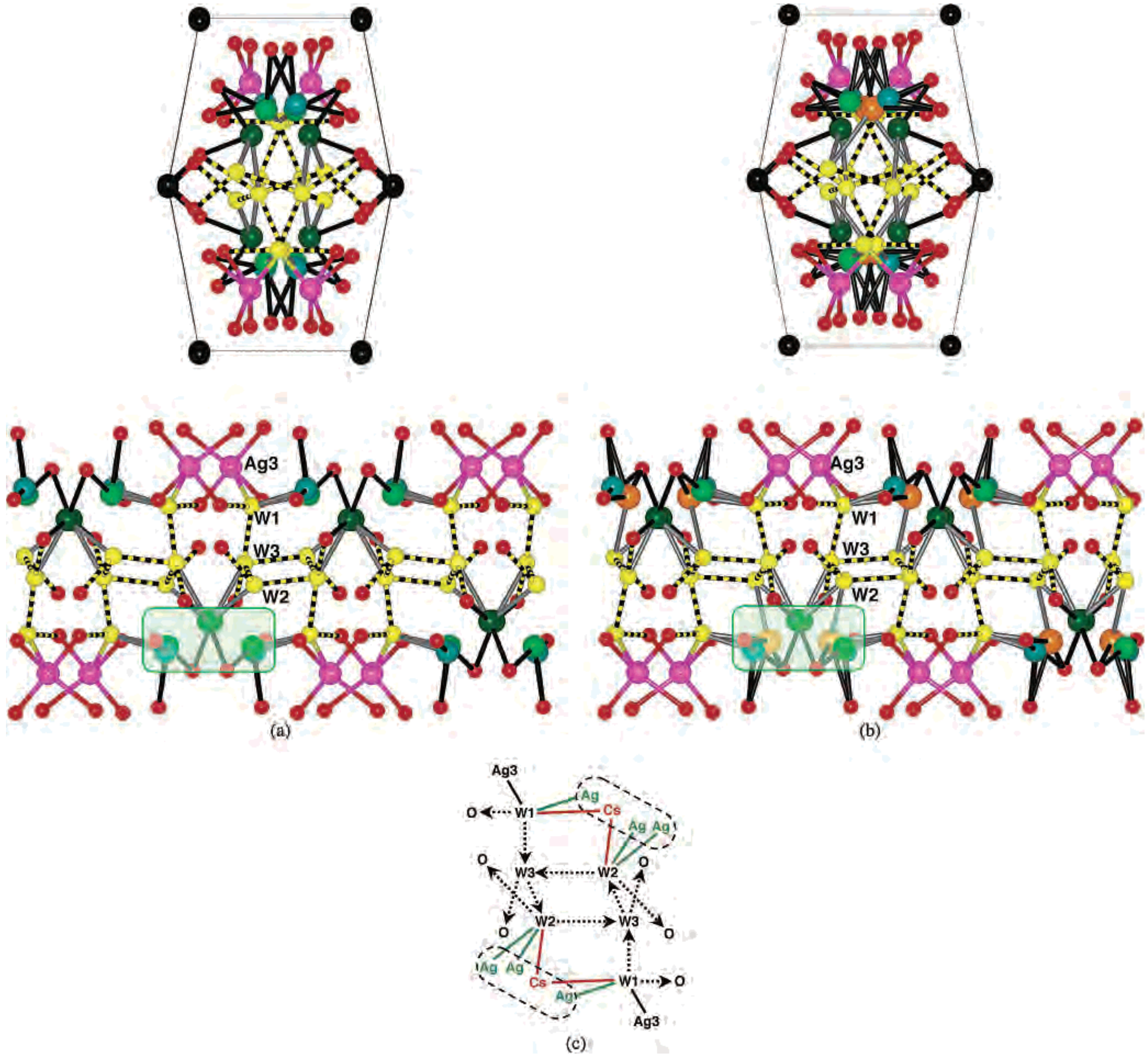


Figure 5. The water molecules (yellow) and additional M^+ cations as they occur in the channels of the $Ag_{2.5}Cr(ox)_3$ network. Part a shows crystal **1**, part b shows crystal **2**, and part c gives details of the metal coordination and hydrogen bonding (OH → O) of the water molecules, W1, W2, and W3. The upper parts of parts a and b present projections of the channel contents along the channel (outlined by six Cr atoms, black), and the lower parts are cutaway views of the channel contents as they recur along the channel. The orientation of diagram c is the same as that of the lower views in parts a and b. Oxalate O atoms are restricted to those bonding the channel contents, and Ag3 is included because it is coordinated by W1. The channel Ag^+ locations are identified by three different green colors, and the M^+ location is orange. The green enclosures draw attention to the region where one of the four possible positions can be occupied by a group 1 cation or a Ag^+ ion. Channel cations are coordinated by oxalate O atoms (black bonds) and by W1, W2 molecules (gray bonds).

these crystals, and the variable locations of the channel M and Ag, have been described. The M^+ in the crystallization solutions compete with Ag^+ for the channel domains, and an $Ag^+/[M_3Cr(ox)_3]$ ratio of 12 for M = Li and more than 19 for M = Cs in the crystallization solution is required to suppress crystal inclusion of M^+ in the channel, and yield $Ag_3Cr(ox)_3(H_2O)_3$. The highest ratio of M^+ over Ag^+ in the channels was 0.43/0.07, in $Cs_{0.43}Ag_{0.07}[Ag_{2.5}Cr(ox)_3](H_2O)_3$ which occurred for crystallization of 2.5 $AgNO_3$ with 1 $Cs_3[Cr(ox)_3]$. Similar results have been obtained for $[Co(ox)_3]^{3-}$. Avoidance of M^+ contamination of the channels of $Ag_3Cr(ox)_3(H_2O)_3$ can be achieved by use of $(NH_4)_3[Cr(ox)_3]$ as precursor.

The variable occurrence of M^+ and Ag^+ in the channels is supported by the invariant domain of hydrogen bonded water molecules in the channels: these water molecules provide coordination for M^+ and Ag^+, as do some of the oxalate O atoms. All metal coordination is normal.

The compounds $[M_xAg_{0.5-x}(H_2O)_3]@[Ag_{2.5}Cr(ox)_3]$ manifest impressive crystal growth, with single crystals of mm dimensions growing in a few hours. The water in the channels can be removed by heating or with high vacuum, and reintroduced by exposure to water vapor at ca. 30 mm. The large crystals do not change their external morphology during their dehydration. However single crystals and polycrystalline samples do lose most of their diffraction

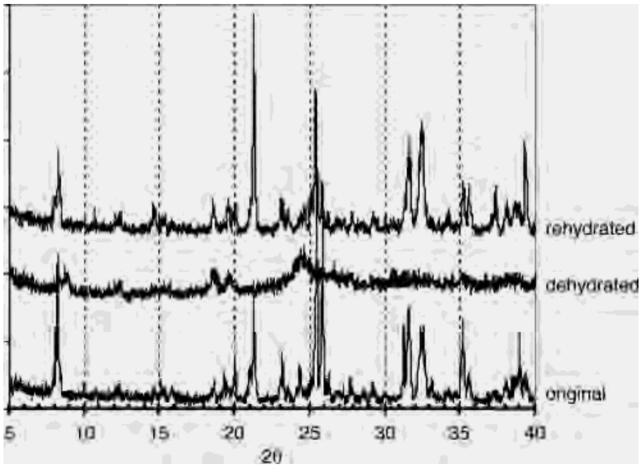


Figure 6. X-ray diffraction patterns of a polycrystalline sample of $Cs_{0.43}Ag_{0.07}[Ag_{2.5}Cr(ox)_3](H_2O)_3$ **5** (lower trace), and the same sample after heating at 100 °C for 2h (middle trace) and then after rehydration by exposure to 100% humidity at ambient temperature for 24 h (upper trace).

intensity during dehydration. Remarkably, during rehydration some of the original diffraction intensity is recovered, and shows that the original hydrated crystal structure is regenerated. Large single crystals, while showing no external morphological change during dehydration/rehydration and concomitant loss and recovery of diffraction, do lose mechanical strength during this cycle.

The unobstructed channel structure, evident in the projection views of Figure 5, suggests a straightforward mechanism for dehydration and rehydration, by water transport along the channels. Our interpretation of the observations of morphology and diffraction during dehydration is that some but not all of the channels undergo partial collapse, so that crystal form can be retained, but long range order within the crystal is not. During this process the already partly disordered M^+ and Ag^+ cations in the channels probably become more disordered in rearranging to use only oxalate O atoms as ligands. Rehydration is postulated to reconstruct the collapsed channel regions, with recovery of the ordered host channel structure. We suggest that local partial collapses of the channel framework cause bending but little breaking of the host Ag−O and Cr−O bonds (involving shearing of metal coordination polyhedra), thereby facilitating the reconstruction of the channel framework upon rehydration. The well-defined order of the water molecules and their hydrogen bonds is likely to be a thermodynamic advantage for the reconstruction of the host lattice, and the open channel structure is expected to provide kinetic facility for dehydration and rehydration.

The dehydration and rehydration property of the $[M_xAg_{0.5-x}(H_2O)_3]@[Ag_{2.5}Cr(ox)_3]$ system described here is intermediate between that of zeolitic nonmolecular lattices, which are usually rigid, and robust molecular frameworks such as $Ni_2(4,4'\text{-bipyridine})_3(NO_3)^4$ which undergo flexible intermolecular scissoring during sorption and desorption of guest molecules.[8,9] This latter system also retains crystal mosaicity during guest loss.[8]

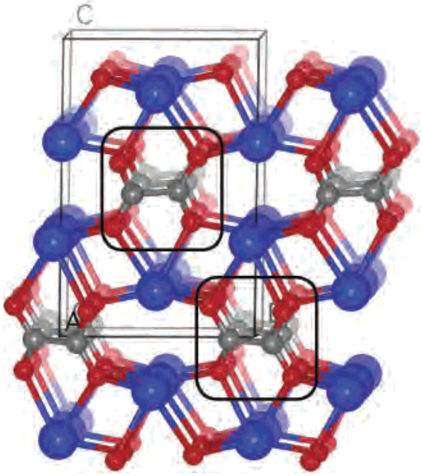


Figure 7. The crystal structure of silver oxalate, Ag_2ox (CSD code AGOXAL02), emphasizing the stacks of offset-face-to-face oxalate groups. The two stacks outlined are inclined oppositely to the projection direction, and the separation between oxalate planes is 2.95 Å.

We make two further points about the crystallization phenomena. First, the compounds $[M_xAg_{0.5-x}(H_2O)_3]@[Ag_{2.5}Cr(ox)_3]$ crystallize readily from water in good yield (up to 85% for $K_{0.08}Ag_{2.92}[Cr(ox)_3](H_2O)_3$), but crystallization of $[Na_xAg_{0.5-x}(H_2O)_3]@[Ag_{2.5}Cr(ox)_3]$ was suppressed with additional Na^+ in solution. We suggest that this is due to the prevalence of species $[Cr(-ox-Na_{aq})_3]$ in solution,[10] relative to $[Cr(-ox-Ag_{aq})_3]$, and thereby reduced bridging Cr−ox−Ag−ox−Cr through Ag^+ as required to form the host lattice. This is a manifestation of M^+/Ag^+ competition for the channel host component of the crystals, analogous to the observed M^+/Ag^+ competition for location in the channels. Second, among the compounds that form the $\{[M'M''(ox)_3]^{2-}\}$ three-dimensional (10,3)-a net there is one with $M', M'' = Ag, Cr$, namely $[Fe(bipy)_3][AgCr(ox)_3]$,[7] in which all connections are Cr−ox−Ag and the local metal coordination is $Cr(ox)_3$ and $Ag(ox)_3$. This compound was apparently crystallized from a mixture that contained $K_3[Cr(ox)_3](H_2O)_3$ and Ag^+ in an aqueous silicate gel.[1,7] It is significant that crystals of $[K_xAg_{0.5-x}(H_2O)_3]@[Ag_{2.5}Cr(ox)_3]$ which we observe were not formed in the mixtures in silica gel.

Finally, we note that the $\{Ag-O_2C_2O_2-Cr\}_2$ double-bridge (Figures 2b, 3), a key component of the $[Ag_{2.5}Cr(ox)_3]$ framework structures in $[M_xAg_{0.5-x}(H_2O)_3]@[Ag_{2.5}Cr(ox)_3]$, has offset-face-to-face oxalate groups that are also characteristic of the crystal structure of silver oxalate, Ag_2ox.[11] Figure 7 shows that the Ag_2ox structure has stacks of offset-face-to-face oxalate groups. The $\{Ag-O_2C_2O_2-Cr\}_2$ double-bridge occurs also in the structure of $\{AgCr(2,2'\text{-bipyidine})(\mu\text{-ox})_2(H_2O)\}_2$.[12]

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Experimental Section

Literature preparations were followed for $K_3Cr(ox)_3(H_2O)_3$.[13] $Na_3Cr(ox)_3(H_2O)_5$ was prepared similarly, but using NaOH, $Na_2C_2O_4$, $H_2C_2O_4{\cdot}2H_2O$, and CrO_3 as reactants; its authenticity was confirmed by comparison of the powder XRD pattern with that expected from the literature crystal structure (refcode SOXCRP).[14] $Cs_3Cr(ox)_3(H_2O)_3$[15] was prepared similarly, but from Cs_2CO_3, $H_2C_2O_4.2H_2O$, and CrO_3. $Li_3Cr(ox)_3$, prepared in solution from LiOH, $H_2C_2O_4{\cdot}2H_2O$, and CrO_3, proved difficult to isolate by crystallization from EtOH:H_2O. Therefore, after filtration to remove a small amount of insoluble matter, it was isolated by removal of the solvent at 60 °C. Anal. Found: Cr, 13.8; Li, 5.5%. Calcd for $Li_3[Cr(ox)_3](H_2O)_2$: Cr, 13.9; Li, 5.6%. The hexahydrate $Li_3[Cr(ox)_3]$ is known to undergo ready partial dehydration.[16]

All mixtures containing Ag^+ and $[Cr(ox)_3]^{3-}$ were kept in the dark.

Representative Crystallization Procedure for $[M_xAg_{0.5-x}(H_2O)_3]@[Ag_{2.5}Cr(ox)_3]$. A solution of $AgNO_3$ (0.508 g, 2.97 mmol, in 6 mL water) at ambient temperature was added slowly down the side of a tilted vial containing a solution of $K_3Cr(ox)_3(H_2O)_3$ (0.485 g, 0.996 mmol, in 6 mL water), with minimal stirring. Crystallization of cherry-black blocks commenced immediately. After 2 h these crystals were separated by decantation, washed with cold water, water−methanol, and then methanol, and then dried briefly under low vacuum. Yield 0.313 g: a further 0.040 g was obtained from the mother liquor after 24 h. After several days some preparative solutions showed evidence of a white film, probably silver oxalate.

$K_{0.08}Ag_{2.92}Cr(ox)_3(H_2O)_3$. A solution of $AgNO_3$ (1.694 g, 9.97 mmol, in 6 mL water) was added with minimal mixing to a solution of $K_3Cr(ox)_3(H_2O)_3$ (0.488 g, 1.00 mmol, in 6 mL water) at ambient temperature. After crystallization for 1 h the mother liquor was almost colorless. The crystals were separated by decantation and washed with small amounts of cold water and methanol. Yield: 0.582 g. Analysis: Cr 7.6% (calcd 7.6%), Ag 46.1% (calcd 45.8%), K 0.45% (calcd 0.45%). A sample kept in the ultrahigh vacuum chamber (6×10^{-6} bar) of a mass spectrometer lost 7.4% mass (calcd 7.8%).

Crystallization of $Ag_3Cr(ox)_3(H_2O)_3$, 1. A solution of $AgNO_3$ (0.359 g, 2.10 mmol, in 1 mL of water) was slowly added without mixing to a solution of $Li_3Cr(ox)_3(H_2O)_5$ (0.067 g, 0.17 mmol, in 1 mL water). Crystallization began immediately, and after 30 min there was a mixture of black crystals and red solid. The black crystals were separated, washed with cold water, and characterized by single-crystal diffraction.

Crystallization of $Cs_{0.43}Ag_{0.07}[Ag_{2.5}Cr(ox)_3](H_2O)_3$, 5. A solution of $AgNO_3$ (0.425 g, 2.50 mmol, in 6 mL water) was added with minimal mixing to a solution of $Cs_3Cr(ox)_3(H_2O)_3$ (0.769 g, 1.00 mmol, in 6 mL water). The dark crystals were collected after 2.5 h (yield 0.338 g), washed and dried, and characterized by crystal diffraction.

Experiment with Excess Na^+. When a solution of 0.071 g (0.42 mmol) of $AgNO_3$ in 1 mL of water was mixed with a solution containing 0.073 g (0.15 mmol) of $Na_3Cr(ox)_3(H_2O)_5$ in 1 mL of water, crystals of $[Na_xAg_{0.5-x}(H_2O)_3]@[Ag_{2.5}Cr(ox)_3]$ formed when the mixture was allowed to stand overnight at room temperature. When a solution containing 0.072 g (0.15 mmol) of $Na_3Cr(ox)_3(H_2O)_5$ and 0.12 g (1.4 mmol) of $NaNO_3$ in 1 mL of water was added to a solution of $AgNO_3$ (0.071 g, 0.42 mmol) and $NaNO_3$ (0.12 g, 1.4 mmol) in 1 mL of water, there was no crystallization of Ag−$Cr(ox)_3$ compounds after 5 days at room temperature. At this time, a white film, possibly $Ag_2C_2O_4$, was apparent.

Thermogravimetric measurements were made using heating rates of 0.2, 1, and 2 deg min^{-1}, from 20 °C to 200 °C.

Elemental analyses: ICP was used to determine Ag and Cr, and alkali metals were determined by AA.

Powder XRD data were measured at room temperature on samples that had been (a) ground only, (b) ground and heated to 100 °C for various times, and (c) heated then, at ambient temperature, rehydrated at 100% humidity for various times (by allowing the dehydrated sample, in a small open vial, to sit in a large sealed vial with water in the annulus).

Crystallography

X-ray data for all five structures were collected at ambient temperature (294 K) using a Nonius CAD4 diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.7107$ Å). Data were corrected for absorption[17] and were considered observed for $I > 2\sigma(I)$. The structures were refined anisotropically,[18] with identical thermal motion being used to describe some of the minor components of the cations. Details of data collection and refinement are given in Table 1. The crystal packing figures were constructed with CrystalMaker.[19]

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Supporting Information Available: Crystallographic data in CIF format. Comparative details of atom positions, bond distances, and photos of crystals before and after dehydration. This material is available free of charge via the Internet at http://pubs.acs.org.

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