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Sodium copper(II) trimesate, $[NaCu\{C_6H_3(COO)_3\}(H_2O)_4]\cdot 2H_2O$, a double-sheet coordination polymer with bridging aqua ligands

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Abstract

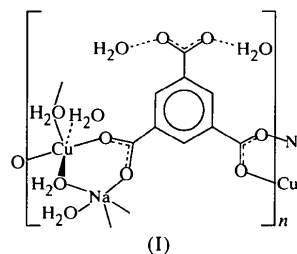
The title compound, poly[[[μ -aqua-diaquasodium(I)copper(II)]- μ -aqua- μ -trimesate(3-)] dihydrate], contains one-dimensional zigzag polymer strands of trimesate and Cu^{2+} ions, which are connected into a two-dimensional double-sheet network *via* sodium ions and bridging aqua ligands.

Comment

There has been much recent interest in the synthesis of metal coordination polymers (Yaghi & Li, 1995) due to their possible application as microporous hosts for absorption or even as catalysts. Trimesic acid or 1,3,5-benzenetricarboxylic acid (TMA- H_3) has been of

particular interest since it is capable of articulating polymer networks, and serves as a useful model system for studying coordination polymer formation. We have studied its coordination chemistry in aqueous solution with a wide variety of divalent metal ions (Ca, Sr, Ba, Zn, Cd and Pb) and found a wide variety of coordination modes and polymer arrangements and topologies. These are both metal and pH dependent (Chui & Williams, 1999).

For copper, a one-dimensional $[Cu(TMA-H)(H_2O)_3]$ coordination polymer containing square-pyramidal Cu^{2+} centres and monoprotonated trimesate dianions has been reported from neutral solution (Pech & Pickardt, 1988). We were curious to see the effect of pH on this system and the polymer formed from basic conditions. We report herein the formation of $[NaCu(TMA)(H_2O)_4]\cdot 2H_2O$, (I), which has one-dimensional zigzag polymer strands similar to the monoprotonated form, but now consisting of Cu and TMA^{3-} trianions. The asymmetric



unit is shown with the labelling scheme in Fig. 1. Each Cu^{2+} ion is square pyramidal with two monodentate carboxylates which are stabilized by four hydrogen bonds to aqua ligands of adjacent strands or to extra-framework water molecules. The two O atoms of

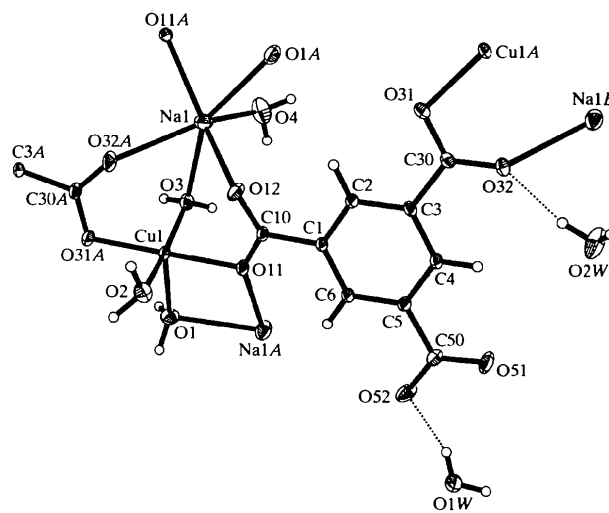


Fig. 1. The molecular structure of the title compound showing 40% probability displacement ellipsoids for non-H atoms. H atoms are shown as spheres of arbitrary radii.

TMA³⁻ coordinated to copper are related by a pseudo-threefold rotation, which means the trimesate introduces alternating $\pm 60^\circ$ kinks into the linearly articulated chain.

In contrast to the protonated analogue, two of the three coordinated waters on copper, one basal and the axial aqua ligand, are now involved in bridging to the Na⁺ cations. These, together with additional coordination of the sodium to carboxylate O atoms, effectively serve as crosslinks to other parallel strands of [Cu(TMA)] and 'anti-parallel' strands in a neighbouring layer to form what can be described overall as a two-dimensional double-sheet network (Fig. 2).

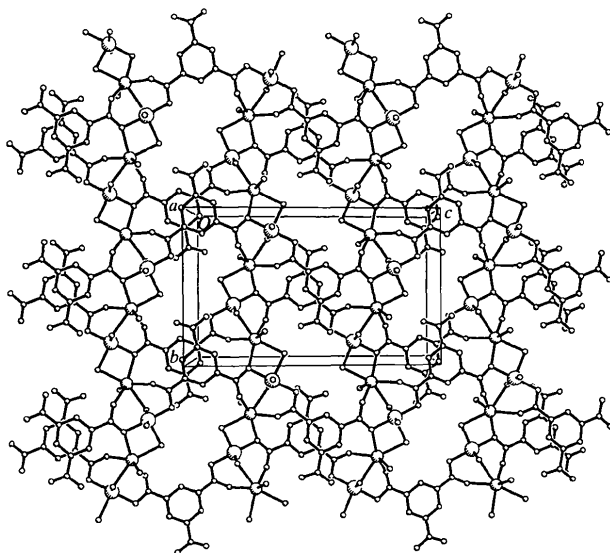


Fig. 2. Plan view of the double sheet viewed along [100].

Bridging aqua ligands between transition metals and sodium ions are well established, though not common. They are not as acidic as μ -aqua ligands between two transition metals (Ye *et al.*, 1997), but still require stabilization by serving as hydrogen-bond donors. This effect is also seen in some related compounds, for example [NaZn(TMA)(H₂O)₄].1.5H₂O, which also has some topological similarity to the title compound, despite trigonal bipyramidal coordination at zinc (Robl, 1988). Six compounds containing sodium, copper and aqua ligands were found in the Cambridge Structural Database (1997), including one (Codon: GADWOX) which showed clear μ -aqua bridging between the Na⁺ and Cu²⁺ ions (Guerriero *et al.*, 1988). Another compound, CEWBAH, had a shorter Na⁺··Cu contact distance (3.201 Å), but bridging was *via* another oxygen-based ligand, glycinate (Khodashova *et al.*, 1984).

Further studies in this system to form [Cu₃(TMA)₂] polymer networks are in progress.

Experimental

The title compound was synthesized by dissolving copper nitrate trihydrate (0.48 g, 2.0 mmol) in 5 ml of water and layering it with a mixture of a methanolic solution of trimesic acid (0.5 g, 2.0 mmol) and 5 ml of 2 M sodium hydroxide. Large turquoise crystals grew over a period of two weeks by layer diffusion.

Crystal data

[NaCu(C₉H₃O₆)-
(H₂O)₄].2H₂O
M_r = 401.74
Monoclinic
*I*2/a
a = 13.524 (2) Å
b = 11.221 (1) Å
c = 18.410 (2) Å
 β = 96.06 (1)°
V = 2778.2 (6) Å³
Z = 8
D_x = 1.921 Mg m⁻³
D_m not measured

Mo K α radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 2.50–17.25°

μ = 1.670 mm⁻¹

T = 293 (2) K

Prism

0.60 × 0.35 × 0.20 mm

Turquoise

Data collection

Siemens P4-RA diffractometer

$\theta/2\theta$ scans

Absorption correction:

ψ scan (XEMP in

XSCANS; Siemens, 1994a)

T_{min} = 0.559, *T_{max}* = 0.716

4085 measured reflections

4008 independent reflections

3482 reflections with

$I > 2\sigma(I)$

R_{int} = 0.016

θ_{\max} = 30°

h = -18 → 18

k = 0 → 15

l = 0 → 25

3 standard reflections

every 150 reflections

intensity decay: none

Refinement

Refinement on *F*²

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.085$

S = 1.064

4000 reflections

212 parameters

H atoms constrained

$w = 1/[\sigma^2(F_o^2) + (0.0369P)^2 + 3.6563P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = -0.003$

$\Delta\rho_{\max} = 0.518 \text{ e } \text{Å}^{-3}$

$\Delta\rho_{\min} = -0.474 \text{ e } \text{Å}^{-3}$

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Cu1—O2'	1.94 (2)	Na1—O11 ⁱⁱ	2.425 (2)
Cu1—O31 ⁱ	1.964 (1)	Na1—O1 ⁱⁱ	2.440 (2)
Cu1—O11	1.980 (1)	Na1—O3	2.469 (2)
Cu1—O2	1.987 (2)	Na1—O12	2.482 (2)
Cu1—O3	1.988 (1)	Na1—O4	2.484 (2)
Cu1—O1	2.324 (1)	Na1—O32 ⁱ	2.560 (2)
Cu1—Na1	3.391 (1)		
O31 ⁱ —Cu1—O11	178.67 (6)	O3—Cu1—O1	87.90 (6)
O2—Cu1—O3	166.08 (6)	O11 ⁱⁱ —Na1—O1 ⁱⁱ	76.35 (5)
O31 ⁱ —Cu1—O1	92.95 (6)	O11 ⁱⁱ —Na1—O4	84.82 (7)
O11—Cu1—O1	88.25 (5)	O1 ⁱⁱ —Na1—O4	76.53 (7)
O2—Cu1—O1	105.93 (6)		

Symmetry codes: (i) $x, \frac{3}{2} - y, z - \frac{1}{2}$; (ii) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$.

Table 2. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
O1—H1...O5 ⁱ	0.850	1.933	2.681 (2)	146.2
O1—H2...O1W ⁱⁱ	0.850	2.005	2.852 (2)	174.4
O2—H4...O12 ⁱⁱⁱ	0.850	1.951	2.739 (2)	153.8
O2—H3...O1W ^{iv}	0.850	1.824	2.627 (2)	156.9
O3—H5...O5 ⁱⁱ	0.850	1.766	2.601 (2)	167.2
O3—H6...O2W ^v	0.850	1.826	2.666 (3)	169.4
O4—H7...O5 ^{iv}	0.850	2.132	2.852 (3)	142.2
O4—H8...O2W ^v	0.850	2.452	2.994 (3)	122.3
O1W—H1W...O31 ^{vi}	0.850	2.124	2.910 (2)	153.6
O1W—H2W...O5 ⁱⁱ	0.850	1.829	2.643 (3)	159.7
O2W—H3W...O2 ^{vii}	0.850	2.118	2.887 (3)	150.2
O2W—H4W...O3 ⁱⁱ	0.850	1.848	2.682 (3)	166.6

Symmetry codes: (i) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (ii) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $\frac{1}{2} - x, \frac{3}{2} - y, \frac{1}{2} - z$; (iv) $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} - z$; (v) $1 - x, 1 - y, 1 - z$; (vi) $x, y - 1, z$; (vii) $\frac{1}{2} - x, y, 1 - z$.

H atoms were found in difference Fourier maps and then placed in geometrically optimized positions with $d(\text{O—H}) = 0.85 \text{ \AA}$ and $d(\text{C—H}) = 0.96 \text{ \AA}$. They were then allowed to ride with isotropic displacement parameters 20% greater than those of the atoms to which they were attached. A final difference map revealed the largest residual peak of $+1.1 \text{ e \AA}^{-3}$ to be located *ca* 0.9 \AA from O2, the terminal aqua ligand of the Cu atom. This could be refined using disordered positions for this atom with an improvement of *ca* 0.2% in discrepancy indices. The minor component of O2, labelled O2', forms a different hydrogen-bond arrangement. It still occupies a geometrically reasonable position about the square-pyramidal Cu^{II} since it has different deviations from orthogonality to the other ligands than does O2. Using common linked displacement parameters, the occupancy factors of O2 and O2' refined to 92.5 and 7.5%, respectively. These were then fixed and O2 refined anisotropically and O2' isotropically without restraints.

Data collection: XSCANS (Siemens, 1994a). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: XP (Siemens, 1994b).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1164). Services for accessing these data are described at the back of the journal.

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The homoleptic lithium complex

[Li(CH₃CN)₄]ClO₄

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Abstract

The homoleptic lithium acetonitrile complex tetra(acetonitrile-*N*)lithium perchlorate, [Li(CH₃CN)₄]ClO₄, was synthesized by the reaction of LiClO₄ and acetonitrile. The structural measurements are more regular than those of two homoleptic analogues reported previously by others.

Comment

A large number of homoleptic [M(CH₃CN)_m] cationic complexes ($m = 2-6$) are known for both monovalent and divalent metals. Anions for such complexes have included Cl⁻, I⁻, [MCl₄]⁻ ($M = \text{B, Al, Ga, In, Tl, Fe}$), [MBr₄]⁻ ($M = \text{Al, Fe, In, Tl}$), [MF₄]⁻ ($M = \text{Sb, Sn}$), [MF₆]^{x-} ($M = \text{Bi, Sb}$), ClO₄⁻, [WF₇]⁻, [Sn(NCS)₆]²⁻, [Cu₂I₃]⁻, [W₄N₄CCl₁₄]⁻, and [Bi₄Cl₁₆]⁴⁻. Cationic complexes of transition metals of the form [M₂(CH₃CN)₁₀]⁴⁺ have also been synthesized wherein the counter-ion is [BF₄]⁻ (Brokaar *et al.*, 1970; Reedijk & Groeneveld, 1968; Zuur & Groeneveld, 1967). Among the Li complexes reported to date, only two have been characterized by X-ray crystal structure analysis, namely, [Li(CH₃CN)₄]I (Raston *et al.*, 1989), which diffracted poorly, was disordered and gave limited data, and [Li(CH₃CN)₄][Cu₂I₃] (Hoyer & Hartl, 1992). During the course of investigating the