

structure: *Xtal3.4*. Program(s) used to refine structure: *Xtal3.4*. Molecular graphics: *Xtal3.4*. Software used to prepare material for publication: *Xtal3.4*.

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## A Star-Shaped Heptanuclear Tetramine Cadmium(II) Complex

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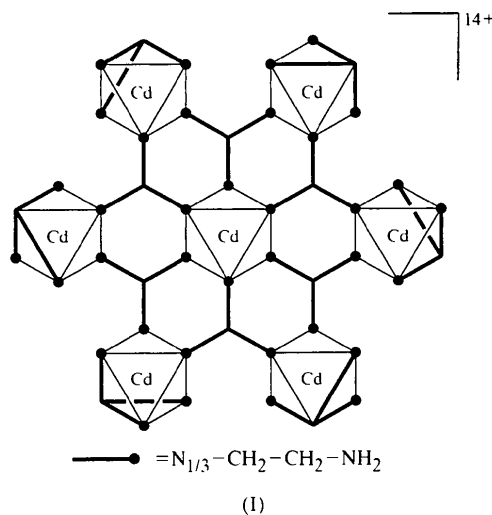
### Abstract

Colourless rhombohedral crystals of dodecakis[tris(2-aminoethyl)amine]heptacadmium(II) tetradecaperchlorate, [Cd<sub>7</sub>(tren)<sub>12</sub>](ClO<sub>4</sub>)<sub>14</sub> (tren = C<sub>6</sub>H<sub>18</sub>N<sub>4</sub>), form from

aqueous solutions of the cellulose solvent 'Cd-tren' on addition of perchloric acid. The heptanuclear cations are flat star-shaped disks and are composed of Cd(tren) moieties that are linked by further tren ligands, which exhibit the unusual  $\mu^3, \kappa^3 N, N', N''$  mode of coordination.

### Comment

Crystals of the perchlorate of the cation dodecakis[tris(2-aminoethyl)amine]heptacadmium(II) have been grown from aqueous solutions of cadmium oxide and tris(2-aminoethyl)amine (tren) in a molar ratio of about 1:1.2 on addition of perchloric acid. The rhombohedral crystals are composed of perchlorate anions and heptanuclear [Cd<sub>7</sub>(tren)<sub>12</sub>]<sup>14+</sup> cations, (I).



The star-shaped cations (Fig. 1) exhibit  $\bar{3}$  symmetry and may be regarded as having an octahedrally coordinated Cd atom as a nucleus, surrounded by six monohapto-bonded tren ligands with two pendant primary amino functions each. The latter assemble as six Cd(tren) moieties, the free coordination sites of which exactly match the number of available NH<sub>2</sub> functions. Thus, of the 12 tren molecules, six are each bound to an equal number of Cd atoms (Cd<sub>2</sub>) in the usual tetradentate mode of coordination towards a single central atom. The other six tetramine entities, however, coordinate through the primary amine functions exclusively, in the unusual tridentate  $\mu^3, \kappa^3 N, N', N''$  mode, thus giving rise to the star-shaped heptanuclear tetradecacationic structure. The molecular stars themselves are flat; their height is only about one third of their diameter. Accordingly, the crystal structure resembles a disk packing of cations, which may be regarded as a heavily [111]-compressed cubic closest packing of spheres. The anions are acceptors of hydrogen bonds, with the N—H functions of the cations acting as donors.

The bond distances are normal and narrowly distributed within the unordered perchlorate anions and the tren ligands [mean value  $\pm$  s.u. of the mean, mean

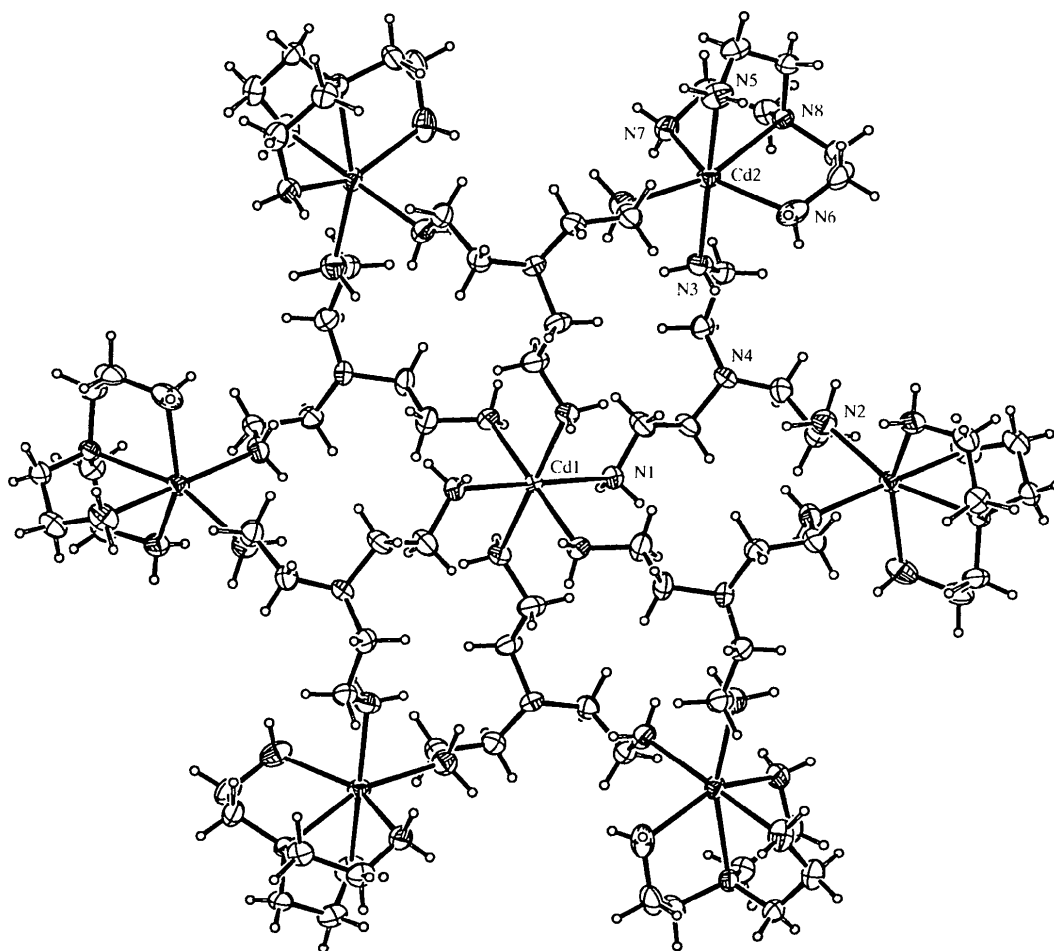


Fig. 1. The structure of the cation (I), with 60% probability ellipsoids and H atom as spheres of arbitrary radii.

s.u. in parentheses, in Å: Cl—O  $1.439(4) \pm 0.009$ , C—N  $1.474(4) \pm 0.008$  and C—C  $1.530(5) \pm 0.003$ . Each Cd1 atom forms the centre of an almost regular  $N_6$  octahedron; the distortions from right angles are within  $5^\circ$ . The coordination about each Cd2 atom is more irregular owing to the tren ligand being too small to fit into a regular octahedron around the large  $Cd^{2+}$  ions (*cf.* the N—Cd—N angles given in Table 2, which are the bond angles in the five-ring chelates). The mean Cd—N distances in the Cd(tren) moieties of  $2.405(3) \pm 0.028$  Å resemble those in the same entities incorporated in two diolato complexes ( $2.423 \pm 0.075$  and  $2.396 \pm 0.137$  Å; Klüfers & Mayer, 1998), without showing the larger deviation from the mean observed therein, which results from a larger distance of the central metal to the tertiary N atom in the diolates.

The title compound was crystallized in an attempt to investigate the solution species of 'Cd-tren' at various pH values. Cd-tren is the short symbol [*cf.* Burger *et al.* (1997) for a suggested nomenclature of metal-based polysaccharide solvents] for an aqueous solution of Cd(tren)(OH)<sub>2</sub>, which is a coordinating solvent for cellulose, *i.e.* a solvent that acts upon cellulose

through diolato complex formation (Klüfers & Mayer, 1998). In the course of its preparation from CdO and aqueous tren, a ~20% excess of tren was used to enhance cadmium oxide dissolution. The assumption was made that an excess of tren would not cause the formation of  $CdN_6$  species, since the coordination of a second tren ligand to a central Cd atom in the sense of further five-ring chelate formation would give rise to two pendant aminoethyl arms of the ligand, but instead bonding which involves only one  $NH_2$  group and the unfavourably ligating tertiary amine function. However, the unexpected formation of the title compound exemplifies the propensity of cadmium for nitrogen-ligand binding, which has to be taken into account in the formulation of agents for complexation of further chelating ligands, like the carbohydrates in our work.

### Experimental

The cellulose solvent Cd-tren ( $0.8 \text{ mol l}^{-1}$ , 20% tren excess) was prepared according to Klüfers & Mayer (1998). 0.2 ml of 20% perchloric acid was added to 4 ml of the solvent,

yielding a colourless precipitate, which redissolved on heating. On cooling to room temperature, small needles formed, which converted to fewer but larger crystals over a period of several weeks.

#### Crystal data

[Cd <sub>7</sub> (C <sub>6</sub> H <sub>18</sub> N <sub>4</sub> ) <sub>12</sub> ](ClO <sub>4</sub> ) <sub>14</sub>	Mo K $\alpha$ radiation
$M_r = 3933.99$	$\lambda = 0.71069 \text{ \AA}$
Trigonal	Cell parameters from 5000 reflections
$R\bar{3}$	$\theta = 2.1\text{--}27.9^\circ$
$a = 24.580 (2) \text{ \AA}$	$\mu = 1.316 \text{ mm}^{-1}$
$c = 21.5609 (11) \text{ \AA}$	$T = 210 (3) \text{ K}$
$V = 11\,281.4 (12) \text{ \AA}^3$	Irregular
$Z = 3$	$0.33 \times 0.20 \times 0.11 \text{ mm}$
$D_x = 1.7372 (2) \text{ Mg m}^{-3}$	Colourless
$D_m$ not measured	

#### Data collection

Stoe IPDS diffractometer	4696 reflections with $I > 2\sigma(I)$
Area-detector scans	$R_{\text{int}} = 0.029$
Absorption correction: numerical (Stoe, 1997)	$\theta_{\text{max}} = 27.88^\circ$
$T_{\text{min}} = 0.705$ , $T_{\text{max}} = 0.817$	$h = -32 \rightarrow 32$
49 405 measured reflections	$k = -32 \rightarrow 32$
5649 independent reflections	$l = -25 \rightarrow 25$

#### Refinement

Refinement on $F^2$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.037$	$\Delta\rho_{\text{max}} = 2.125 \text{ e \AA}^{-3}$
$wR(F^2) = 0.098$	$(0.746 \text{ \AA from Cd2})$
$S = 1.049$	$\Delta\rho_{\text{min}} = -1.016 \text{ e \AA}^{-3}$
5649 reflections	Extinction correction: none
346 parameters	Scattering factors from <i>International Tables for Crystallography</i> (Vol. C)
H atoms constrained	
$w = 1/[\sigma^2(F_o^2) + (0.0525P)^2 + 54.9603P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

		$U_{\text{eq}} = (1/3)\sum_i U^{ij}a'_i a'_j$			
Occupancy		x	y	z	$U_{\text{eq}}$
Cd1	1	1/3	2/3	1/6	0.01764 (11)
Cd2	1	0.206457 (10)	0.277005 (10)	0.166004 (10)	0.02308 (8)
N1	1	0.24782 (12)	0.60342 (12)	0.09703 (14)	0.0261 (5)
N2	1	0.02949 (13)	0.40143 (13)	0.11934 (14)	0.0325 (6)
N3	1	0.19766 (13)	0.35720 (12)	0.10942 (14)	0.0304 (6)
N4	1	0.14584 (12)	0.43448 (11)	0.04548 (13)	0.0226 (5)
C1	1	0.08210 (14)	0.40452 (15)	0.0195 (2)	0.0298 (7)
C2	1	0.18176 (14)	0.40833 (14)	0.0156 (2)	0.0260 (6)
C3	1	0.1772 (2)	0.50357 (13)	0.0400 (2)	0.0287 (7)
C4	1	0.2270 (2)	0.53612 (14)	0.0901 (2)	0.0318 (7)
C5	1	0.17103 (15)	0.34762 (14)	0.0468 (2)	0.0278 (6)
C6	1	0.03446 (15)	0.4165 (2)	0.0536 (2)	0.0317 (7)
N5	1	0.21387 (15)	0.20170 (14)	0.23244 (15)	0.0350 (6)
N6	1	0.10731 (14)	0.24568 (15)	0.2113 (2)	0.0366 (7)
N7	1	0.26249 (13)	0.26592 (13)	0.08047 (14)	0.0303 (6)
N8	1	0.13718 (11)	0.17258 (11)	0.12210 (12)	0.0221 (5)
C7	1	0.14389 (14)	0.12306 (14)	0.1549 (2)	0.0281 (7)
C8	1	0.15579 (15)	0.1786 (2)	0.0565 (2)	0.0290 (7)
C9	1	0.2039 (2)	0.1482 (2)	0.1935 (2)	0.0337 (7)
C10	1	0.0629 (2)	0.1792 (2)	0.1964 (2)	0.0365 (8)
C11	1	0.2263 (2)	0.2044 (2)	0.0492 (2)	0.0297 (7)
C12	1	0.07316 (14)	0.1634 (2)	0.1304 (2)	0.0314 (7)
C13	1	0.27285 (3)	0.04548 (4)	0.11238 (4)	0.0300 (2)

O1	1	0.22271 (12)	0.05626 (14)	0.0956 (2)	0.0454 (7)
O2	1	0.31608 (13)	0.06117 (15)	0.06115 (14)	0.0483 (7)
O3	1	0.3042 (2)	0.0791 (2)	0.1669 (2)	0.0660 (10)
O4	1	0.24671 (14)	-0.02137 (13)	0.1231 (2)	0.0554 (8)
Cl2	1	0	0	0.27305 (7)	0.0311 (3)
O5	1	0	0	0.2065 (2)	0.0424 (11)
O6	1	0.05815 (14)	0.05138 (14)	0.2961 (2)	0.0536 (8)
Cl3	1	0.19067 (4)	0.24016 (4)	0.40447 (4)	0.0397 (2)
O71	0.44 (2)	0.1826 (8)	0.1871 (4)	0.4419 (6)	0.0499 (8)
O72	0.17 (2)	0.1673 (16)	0.1752 (6)	0.4233 (19)	0.0499 (8)
O73	0.128 (12)	0.1910 (15)	0.1811 (8)	0.4088 (17)	0.0499 (8)
O74	0.053 (7)	0.160 (3)	0.1800 (13)	0.372 (2)	0.0499 (8)
O75	0.093 (9)	0.1405 (10)	0.213 (2)	0.4505 (11)	0.0499 (8)
O81	0.56 (2)	0.1586 (4)	0.2334 (10)	0.3457 (2)	0.0499 (8)
O82	0.17 (2)	0.1645 (9)	0.2587 (15)	0.3534 (9)	0.0499 (8)
O83	0.28 (2)	0.1515 (6)	0.2092 (12)	0.3505 (6)	0.0499 (8)
O91	0.518 (8)	0.2514 (2)	0.2514 (3)	0.3817 (3)	0.0499 (8)
O92	0.251 (8)	0.1765 (8)	0.2805 (7)	0.4427 (6)	0.0499 (8)
O93	0.271 (8)	0.2447 (5)	0.2999 (3)	0.4229 (6)	0.0499 (8)
O94	0.16 (2)	0.1620 (16)	0.1882 (10)	0.4485 (11)	0.0499 (8)
O95	0.221 (8)	0.25896 (14)	0.2792 (7)	0.4050 (8)	0.0499 (8)
O96	0.313 (9)	0.1446 (4)	0.2418 (7)	0.4461 (4)	0.0499 (8)
O97	0.204 (11)	0.2132 (10)	0.2972 (6)	0.4413 (9)	0.0499 (8)
O98	0.178 (11)	0.1997 (10)	0.3024 (4)	0.4172 (12)	0.0499 (8)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Cd1—N1	2.413 (3)	Cd2—N3	2.418 (3)
Cd2—N6	2.369 (3)	Cd2—N5	2.418 (3)
Cd2—N2'	2.377 (3)	Cd2—N8	2.452 (2)
Cd2—N7	2.397 (3)		
N6—Cd2—N8	75.88 (10)	N5—Cd2—N8	72.91 (9)
N7—Cd2—N8	73.85 (9)		

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

The perchlorate ion incorporating Cl3 is heavily affected by rotational disorder, which was handled by allowing for 16 partially-occupied O-atom positions. For these positions, one common  $U_{\text{iso}}$  was refined, all distances from Cl3 to disordered O atoms were fixed at one common restrained value, and the sum of the population parameters was restricted to 4. H atoms were placed in geometrically idealized positions with the C—H and N—H distances, but not the angles, of each different C or N atom being allowed to refine freely. A common overall isotropic displacement parameter was refined for the H atoms.

Data collection: *IPDS Software Manual* (Stoe, 1997). Cell refinement: *IPDS Software Manual*. Data reduction: *IPDS Software Manual*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL92* (Sheldrick, 1992). Molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *SCHAKAL* (Keller, 1995). Software used to prepare material for publication: *PLATON95* (Spek, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1016). Services for accessing these data are described at the back of the journal.

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## [2,3-Bis(salicylideneamino-*O,N*)pyridinato]-nickel(II)

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### Abstract

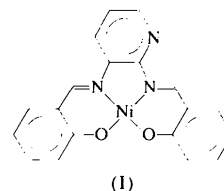
The coordination around the Ni atom in the title compound, {2,2'-[2,3-pyridinediylbis(iminomethyl-*N*)]diphenolato-*O,O'*}nickel(II), [Ni(C<sub>19</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub>)], is slightly distorted from square planar. Within the coordination square, the bond angles are in the range 83.8(1)–94.8(2)°. The Ni–N and Ni–O distances are equal within experimental error, with average values of 1.854(2) and 1.835(2) Å, respectively. Comparison of bond lengths in free and nickel-coordinated ligands indicates a shortening of the C–O bonds due to packing effects. On complex formation, the whole molecule assumes a more planar form, which brings the Ni atoms of neighbouring molecules as close as 3.1908(10) Å to each other.

### Comment

Schiff bases derived from salicylaldehyde and aminopyridines are of interest because of their metal-complexing behaviour. The structure of the Schiff base 2,3-bis(salicylideneamino)pyridine (bimorphous) has been determined previously (Cimerman *et al.*, 1992). Both forms of the molecule have the imine structure and there was no evidence of tautomerism with the ketamine isomer. 2-Salicylideneaminopyridine has potential use as an anti-inflammatory agent and the corresponding complex with Co<sup>II</sup> has been reported (Parashar *et al.*, 1988). The thermochromic and photochromic properties of a

series of 2-, 3- and 4-salicylideneaminopyridines have been observed and reported by Hadjoudis (1981).

The structure of the title compound, (I), was determined to find out whether it has the imine or the ketamine tautomeric form. As can be seen from Fig. 1, the Ni<sup>II</sup> ion has slightly distorted square-planar coordination. The displacement of the Ni<sup>II</sup> ion from the best plane through the donor atoms O1, O2, N1 and N3 is 0.0081(6) Å. The coordination bond angles have values between 83.8(1) (O1–Ni–O2) and 94.8(2)° (O1–Ni–N1), their sum being 360.0(1)°. The Ni–O distances [1.834(3) and 1.837(3) Å], as well as the Ni–N distances [1.853(4) and 1.856(4) Å], are equal within experimental error. The free ligand molecule, 2,3-bis(salicylideneamino)pyridine, which is not planar (Cimerman *et al.*, 1992), seems to assume a more planar form on coordination to nickel. For instance, the dihedral angles between the pyridine and two benzene rings in the free ligand are 5.7(4) and 51.1(4)°, while the corresponding angles in the title complex are equal within experimental error, with a mean value of 5(1)°. The molecule as a whole is practically planar. The planarity of the molecule permits parallel packing in the unit cell so that the closest intermolecular Ni···Ni distance is 3.1908(10) Å.



A comparison of the bond lengths reported for the free Schiff base with those observed here indicates that on complex formation the C–O bond lengths are shortened [average value 1.35(1) versus 1.293(4) Å],

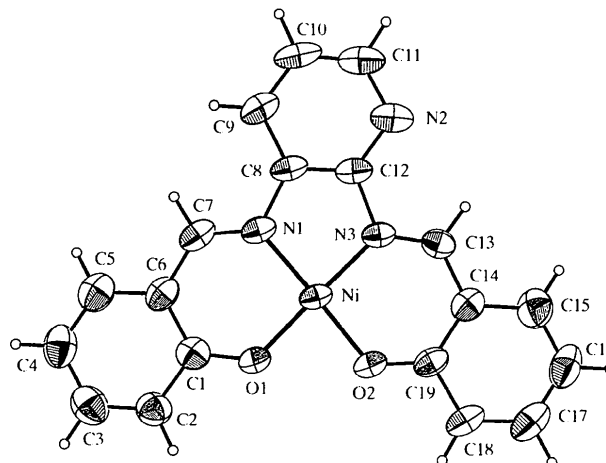


Fig. 1. The title compound with the atomic numbering scheme and displacement ellipsoids at the 50% probability level. H atoms are shown as small circles of arbitrary radii.