O(1)—Pt(1)—O(1^i)	89.6 (2)	C(3)—C(2)—C(1)	109.7 (4)
C(1)—O(1)—Pt(1)	121.4 (3)	C(4)—C(2)—C(3)	108.6 (7)
O(2)—C(1)—O(1)	120.7 (5)	C(4)—C(2)—C(1)	107.0 (4)

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

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H$\cdots A$	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O3—H3$\cdots$O2^i	2.0 (1)	2.784 (7)	145 (4)
N1—H1$c\cdots$O3^{ii}	2.38 (9)	3.133 (7)	159 (4)

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

Table 4. *Torsion angles within the six-membered chelate ring (°)*

	Experimental	Model*
Pt(1)—O(1)—C(1)—C(2)	6	14
O(1)—C(1)—C(2)—C(1^i)	44	48
C(1)—C(2)—C(1^i)—O(1^i)	−44	48
C(2)—C(1^i)—O(1^i)—Pt(1)	−6	−14
C(1^i)—O(1^i)—Pt(1)—O(1)	41	59
O(1^i)—Pt(1)—O(1)—C(1)	−41	−59

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

* Values from model structure with bond lengths Pt—O 2.00, C—O 1.30 and C—C 1.52 Å, and bond angles O—Pt—O 90.0, Pt—O—C 109.5, O—C—C 109.5 and C—C—C 114.5°.

The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares techniques. All H atoms could be located from the difference Fourier maps and were refined with an overall isotropic displacement parameter.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXS*86. Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1135). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bréhin, P., Kozelka, J. & Bois, C. (1992). *Acta Cryst.* C**48**, 2094–2096.

Dong, Y.-H., Feng, J.-C., Huang, Z.-Y., Tang, W.-X., Dai, A.-B., Zhou, Z.-Y. & Yu, K.-B. (1990). *Sci. China Ser. B*, **33**, 1297–1303.

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Harrison, R. & McAuliffe, C. (1980). *Inorg. Chim. Acta*, **46**, L15–L16.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Larson, A. C. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 291–294. Copenhagen: Munksgaard.

Rochon, F. D., Melanson, R., Macquet, J. P., Bellanger-Gariepy, F. & Beauchamp, L. (1985). *Inorg. Chim. Acta*, **108**, 1–6.

Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

Watkin, D. J., Carruthers, J. R. & Betteridge, P. W. (1985). *CRYSTALS User Guide*. Chemical Crystallography Laboratory, University of Oxford, England.

Weiner, P. & Kollman, P. (1981). *J. Comput. Chem.* **2**, 287–303.

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Tetrahydrogen 1,2-Bis(1,4,7-triaza-1-cyclononyl)ethane Tetrachlorocadmate

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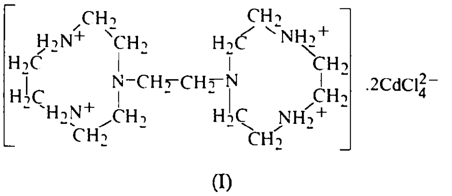
Abstract

The title salt, $C_{14}H_{36}N_6^{4+}.2CdCl_4^{2-}$ [1,2-bis(1-aza-4,7-diazonia-1-cyclononyl)ethane tetrachlorocadmate], has been structurally characterized. Hydrogen bonds are formed from protons of the secondary amine N atoms to the $CdCl_4^{2-}$ anions and the tertiary amine N atoms. This suggests that the secondary amines of the tetraprotonated cation are protonated in the crystal as they appear to be in aqueous solution.

Comment

Hexaprotonated salts of α,ω-bis(1,4,7-triaza-1-cyclononyl)alkanes are strong diprotic acids in aqueous solution. Trends in acidity within the series indicate that protons attached to the tertiary amines are most acidic (Zhang, Hsieh, Margulis & Zompa, 1995). In the course of metal complexation studies with 1,2-bis(1,4,7-triaza-1-cyclononyl)ethane, the title compound, (I), was isolated (see *Experimenatal*).



(I)

The crystal is composed of discrete ions linked by hydrogen bonds between the secondary-amine groups and the tetrachlorocadmate ion. The closest nonbonded distances of the secondary-amine N atoms include: N2$\cdots$Cl2($-x, 1 - y, 2 - z$) 3.202 (6), N2$\cdots$Cl1 ($x - 1, y + 1, z$) 3.253 (6), and N3$\cdots$Cl2 ($x, y + 1, z$) 3.293 (6) Å. The shortest nonbonded contact to the tertiary amine N atom is N1$\cdots$Cl2 ($-x, 1 - y, 2 - z$) 3.448 (6) Å. This indicates that the protons of the tetracation are likely to be associated with the secondary amines. The Cd—Cl bond distances range from 2.429 (1) to 2.504 (1) Å. The Cl—Cd—Cl bond angles range from 99.48 (5) to 114.77 (5)°, indicating considerable distortion probably

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due to the different Cl^- environments. Similar parameters are observed for other chlorocadmates (Richardson, Franklin & Thompson, 1975). The observed trend is that the stronger the hydrogen-bonding interaction to Cl, the longer the Cd—Cl bond. The Cd—Cl2 bond is longest and is involved in two N—H···Cl attractions [H2*B*···Cl2($-x$, $1-y$, $2-z$) 2.32 (6) and H3*A*···Cl2 ($-x$, $1-y$, $2-z$) 2.48 (6) Å]. Intramolecular hydrogen bonding occurs between N1 and the two secondary-amine protons H2*B* and H3*A* [N1···H2*B* 2.50 (6) and N1···H3*A* 2.34 (6) Å]. Thus, H2*B* and H3*A* form bifurcated hydrogen bonds to both Cl2 and N1.

The conformation adopted by the tetraprotonated amine does not vary significantly from those observed for several binuclear metal complexes with similar ligands of this series or tridentate metal complexes of 1,4,7-triazacyclononane (Pletnev, 1994). The C atoms of the nine-membered rings are located on one side of the plane formed by the three N atoms of the ring. The C atom (C7) of the ethylenic chain is on the opposite side. The positions of the N atoms are fixed by the hydrogen bonds, resulting in a ring conformation similar to those found in tridentate metal complexes.

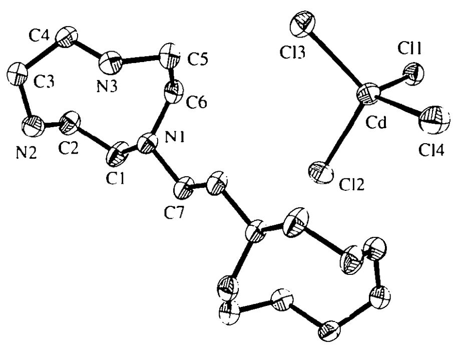

Fig. 1. Structure of (I) showing 50% probability displacement ellipsoids. H atoms are omitted for clarity.

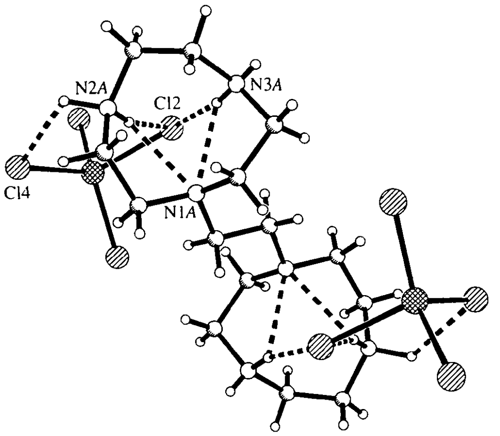

Fig. 2. Compound structure showing bifurcated hydrogen bonds. Projection is perpendicular to the plane formed by N1, N2 and N3. Some hydrogen bonds are omitted for clarity.

Experimental

The title compound was isolated from an aqueous solution at pH 6–7 containing the hydrochloride salt of 1,2-bis(1,4,7-tri-aza-1-cyclononyl)ethane and $Cd(NO_3)_2$ (1:2 molar ratio).

Crystal data

$(C_{14}H_{36}N_6)[CdCl_4]_2$
$M_r = 796.9$
Triclinic
$P\overline{1}$
$a = 8.366\,(2)$ Å
$b = 9.430\,(2)$ Å
$c = 9.642\,(2)$ Å
$\alpha = 93.62\,(3)°$
$\beta = 103.22\,(3)°$
$\gamma = 91.24\,(3)°$
$V = 738.5\,(3)$ Å^3
$Z = 1$
$D_x = 1.792$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 24 reflections
$\theta = 15.41–20.20°$
$\mu = 2.178$ mm^{-1}
$T = 293\,(2)$ K
Block
0.35 × 0.20 × 0.20 mm
Colorless

Data collection

Syntex $P2_1$ diffractometer
$\theta–2\theta$ scans
Absorption correction: refined from ΔF (*SHELXA*90 in *SHELXL*93; Sheldrick, 1993)
$T_{min} = 0.435$, $T_{max} = 0.872$
5699 measured reflections
5381 independent reflections

4207 observed reflections [$I > 2\sigma(I)$]
$R_{int} = 0.018$
$\theta_{max} = 32.60°$
$h = 0 \rightarrow 12$
$k = -14 \rightarrow 14$
$l = -14 \rightarrow 14$
3 standard reflections monitored every 50 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0487$
$wR(F^2) = 0.1425$
$S = 1.084$
5380 reflections
148 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0657P)^2 + 1.3945P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.022$
$\Delta\rho_{max} = 1.031$ e Å^{-3}
$\Delta\rho_{min} = -1.516$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cd	0.33627 (4)	0.17426 (3)	0.78609 (3)	0.03464 (10)
Cl1	0.30554 (13)	−0.05009 (11)	0.63415 (11)	0.0356 (2)
Cl2	0.09828 (13)	0.14159 (12)	0.89968 (11)	0.0380 (2)
Cl3	0.29108 (15)	0.38161 (12)	0.64679 (12)	0.0403 (2)
Cl4	0.58861 (15)	0.18744 (16)	0.97410 (13)	0.0502 (3)

N1	−0.1494 (4)	0.5766 (3)	0.8466 (4)	0.0284 (6)
N2	−0.3474 (5)	0.8220 (4)	0.7930 (4)	0.0341 (7)
N3	0.0163 (4)	0.8071 (4)	0.7810 (4)	0.0298 (6)
C1	−0.3290 (5)	0.5602 (5)	0.7987 (5)	0.0400 (10)
C2	−0.4042 (5)	0.6807 (5)	0.7122 (5)	0.0362 (8)
C3	−0.2576 (5)	0.9261 (4)	0.7246 (5)	0.0343 (8)
C4	−0.1168 (5)	0.8662 (4)	0.6695 (4)	0.0315 (7)
C5	0.0717 (5)	0.6647 (4)	0.7359 (5)	0.0335 (8)
C6	−0.0647 (5)	0.5523 (4)	0.7288 (4)	0.0322 (7)
C7	−0.0908 (5)	0.4888 (4)	0.9671 (5)	0.0324 (8)

Table 2. *Selected geometric parameters (Å, °)*

Cd—Cl3	2.4293 (13)	N2—C2	1.510 (6)
Cd—Cl4	2.4430 (15)	N3—C5	1.501 (5)
Cd—Cl1	2.4700 (13)	N3—C4	1.503 (5)
Cd—Cl2	2.5044 (13)	C1—C2	1.515 (6)
N1—C7	1.468 (5)	C3—C4	1.505 (6)
N1—C1	1.469 (5)	C5—C6	1.527 (6)
N1—C6	1.480 (5)	C7—C7^{i}	1.511 (8)
N2—C3	1.497 (6)		
Cl3—Cd—Cl4	114.77 (5)	C3—N2—C2	118.1 (3)
Cl3—Cd—Cl1	112.36 (4)	C5—N3—C4	113.7 (3)
Cl4—Cd—Cl1	112.37 (5)	N1—C1—C2	112.8 (3)
Cl3—Cd—Cl2	108.37 (5)	N2—C2—C1	110.2 (4)
Cl4—Cd—Cl2	108.22 (5)	N2—C3—C4	114.8 (3)
Cl1—Cd—Cl2	99.48 (5)	N3—C4—C3	114.8 (3)
C7—N1—C1	109.9 (3)	N3—C5—C6	109.4 (3)
C7—N1—C6	113.6 (3)	N1—C6—C5	111.8 (3)
C1—N1—C6	112.8 (3)	N1—C7—C7^{i}	113.3 (4)

Symmetry code: (i) $-x, 1-y, 2-z$.

The H atoms on all C atoms were located on Fourier difference maps, but were fixed at ideal positions (0.96 Å) with common isotropic displacement parameters ($U_{\rm iso}$ = 0.08 Å) and refined using a riding model. The four amino H atoms were found in difference maps and refined with fixed isotropic displacement parameters ($U_{\rm iso}$ = 0.08 Å); N—H distances varied from 0.79–0.99 Å with an average e.s.d. of 0.08 Å. The largest peaks and holes in these maps were located near Cd.

Data collection: *P3/PC* (Siemens, 1989*a*). Cell refinement: *P3/PC*. Data reduction: *XDISK* (Siemens, 1989*b*). Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1194). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Pletnev, I. V. (1994). *Can. J. Chem.* **72**, 1404–1411.

Richardson, M. F., Franklin, K. & Thompson, D. M. (1975). *J. Am. Chem. Soc.* **97**, 3204–3209.

Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Siemens (1989*a*). *P3/PC Diffractometer Program*. Version 3.13. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1989*b*). *XDISK. Data Reduction Program*. Version 3.11. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Zhang, X., Hsieh, W. Y., Margulis, T. N. & Zompa L. J. (1995). *Inorg. Chem.* **34**, 2883–2888.

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The β Form of the Macrocyclic Complex $[Eu(NCS)_3(C_{22}H_{26}N_6)]$

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Abstract

In the β form of tris(thiocyanato-*N*)[2,7,13,18-tetramethyl-3,6,14,17,23,24-hexaazatricyclo[17.3.1.1^{8,12}]-tetracosa-1(23),2,6,8(24),9,11,13,17,19,21-decaene-N^3,N^6,N^{14},N^{17},N^{23},N^{24}]europium, the nine-coordinate Eu^{III} ion is bound to the N atoms of three monodentate isothiocyanate ligands and to the six N atoms of the macrocyclic ligand *L* ($C_{22}H_{26}N_6$), which has an 18-membered six-N-atom donor cavity, with a coordination geometry analogous to that of the α form.

Comment

Lanthanide(III) complexes of the 18-membered six-N-atom donor macrocyclic ligand *L* ($C_{22}H_{26}N_6$) have been synthesized by the metal-templated cyclic Schiff base condensation of 2,6-diacetylpyridine and 1,2-diaminoethane (De Cola, Smailes & Vallarino, 1986). A representative selection of these complexes has been characterized by single-crystal X-ray diffraction analysis, as well as by infrared (IR) and nuclear magnetic resonance (NMR) spectra (Fonda, Smailes, Vallarino, Bombieri, Benetollo, Polo & De Cola, 1993). All these complexes have, as a common feature, the presence of a highly inert metal–macrocycle entity accompanied by two or three labile exocyclic ligands, linked to the central metal ion on opposite sides of the macrocycle. Most of these complexes were initially isolated as acetates or nitrates, as these coordinating oxygen-donor anions greatly facilitated the metal-template synthesis of the macrocycle. Once the cationic metal macrocycle was formed, salts of other non-coordinating or coordinating counterions were obtained simply by anion metathesis (Bombieri, Benetollo, Polo, De Cola, Smailes & Vallarino, 1986; Bombieri, Benetollo, Polo, Fonda & Vallarino, 1991).

We have previously reported the crystal structures of the tris(isothiocyanato) complexes of the $\{Eu^{III}L\}$ and $\{Y^{III}L\}$ macrocycles, obtained from the corre-

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