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μ-Nitrato-nitratobis[tris(2-aminoethyl)amine]dicadmium(II) dinitrate

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The two Cd atoms of the cation of the title compound, $[Cd_2(NO_3)_2(C_6H_{12}N_4)_2](NO_3)_2$, are both N,N',N'',N'''-chelated by the tren ligands, and both are also O,O'-chelated by the nitrato groups. Of these two nitro groups, one uses its third O atom to bind to the other Cd atom so that one Cd atom is six-coordinate whereas the other is seven-coordinate.

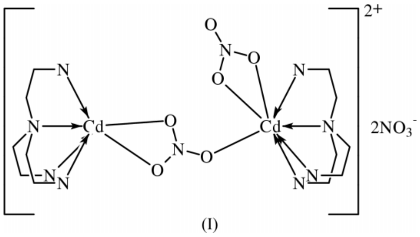
Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.009 Å
Disorder in solvent or counterion
R factor = 0.036
wR factor = 0.085
Data-to-parameter ratio = 17.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The tris(2-aminoethyl)amine (tren) ligand chelates to a plethora of metal ions; for Cd in particular, the $[(tren)Cd]^{2+}$ unit has been authenticated in, for example, the cadmium nitrate/1,10-phenanthroline monohydrate complex (Zhang *et al.*, 2000), in which the ligand binds to the metal atom through all four N atoms. The nitrate ions do not interact with the Cd atom but form hydrogen bonds to the amino H atoms instead. Another study on the complexes with the metalates, $[Fe(CN)_5(NO)]^{2-}$, $[Pd(CN)_4]^{2-}$ and $[Pt(CN)_6]^{2-}$, have shown that these anions bind directly to the $[(tren)Cd]^{2+}$ unit (Zhang *et al.*, 2002). The 2/2 adduct of tren with $Cd(NO_3)_2$ features bidentate and tridentate NO_3 groups (Fig. 1). Both Cd atoms are N,N',N'',N'''-chelated by the tren ligands and both are also O,O'-chelated by the nitrato groups [Cd1—O = 2.407 (4) and 2.534 (4) Å; Cd2—O 2.426 (5) and 2.593 (5) Å]. However, one of these nitrate groups engages in binding to the other Cd atom, the somewhat long interaction [Cd2—O3 = 2.654 (4) Å] raising the coordination number to seven. The packing is not compact, and the amino H atoms interact only weakly with the uncoordinated nitrato groups (Table 2). Such weak interactions have also been noted in the 7/12 cadmium diperchlorate adduct (Klüfers & Mayer, 1998).



(I)

Experimental

The compound was synthesized by the reaction of cadmium nitrate and tris(2-aminoethyl)amine (tren) on a millimolar scale. As the cadmium reagent had turned into a liquid from the absorption of water, it was not weighed. Several drops of the reagent were added to several drops of tren that were dissolved in ethanol (10 ml). A fine solid material formed immediately. The mixture was heated and more ethanol added to dissolve the compound. The light-brown solution was filtered and allowed to cool. The title compound separated from solution after several hours. The supernatant liquid was decanted and a specimen for the diffraction measurements was picked from the syrup that coated the crystals. The crystal was cleaned with vaseline to remove the syrup.

Crystal data

$[Cd_2(NO_3)_2(C_6H_{12}N_4)_2](NO_3)_2$
$M_r = 765.33$
Orthorhombic, $Pna2_1$
$a = 24.172\ (3)$ Å
$b = 13.365\ (1)$ Å
$c = 8.463\ (1)$ Å
$V = 2733.9\ (5)$ Å^3
$Z = 4$
$D_x = 1.859$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 954 reflections
$\theta = 2.9$–$23.0°$
$\mu = 1.63$ mm^{-1}
$T = 298\ (2)$ K
Parallelepiped, light yellow
$0.25 \times 0.13 \times 0.11$ mm

Data collection

Bruker SMART area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.654$, $T_{max} = 0.833$
23153 measured reflections
6164 independent reflections
4101 reflections with $I > 2\sigma(I)$
$R_{int} = 0.047$
$\theta_{max} = 27.4°$
$h = -31 \rightarrow 29$
$k = -17 \rightarrow 17$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.085$
$S = 1.01$
6164 reflections
361 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0369P)^2 + 0.7195P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.48$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}
Absolute structure: Flack (1983), 2850 Friedel pairs
Flack parameter = 0.00 (3)

Table 1
Selected geometric parameters (Å, °).

Cd1—N1	2.447 (4)	Cd2—N7	2.280 (6)
Cd1—N2	2.263 (5)	Cd2—N8	2.294 (6)
Cd1—N3	2.257 (5)	Cd2—N9	2.274 (6)
Cd1—N4	2.268 (6)	Cd2—O3	2.654 (4)
Cd1—O1	2.407 (4)	Cd2—O4	2.593 (5)
Cd1—O2	2.534 (4)	Cd2—O5	2.426 (5)
Cd2—N6	2.442 (4)		
N1—Cd1—N2	76.1 (2)	N6—Cd2—O3	124.3 (1)
N1—Cd1—N3	76.3 (2)	N6—Cd2—O4	149.0 (2)
N1—Cd1—N4	75.7 (2)	N6—Cd2—O5	155.6 (2)
N1—Cd1—O1	162.5 (1)	N7—Cd2—N8	102.2 (3)
N1—Cd1—O2	145.0 (1)	N7—Cd2—N9	127.0 (2)
N2—Cd1—N3	112.5 (2)	N7—Cd2—O3	82.5 (2)
N2—Cd1—N4	114.5 (2)	N7—Cd2—O4	136.7 (2)
N2—Cd1—O1	89.1 (2)	N7—Cd2—O5	90.4 (2)
N2—Cd1—O2	138.7 (2)	N8—Cd2—N9	111.0 (3)
N3—Cd1—N4	116.0 (3)	N8—Cd2—O3	160.1 (2)
N3—Cd1—O1	118.8 (2)	N8—Cd2—O4	95.3 (2)
N3—Cd1—O2	83.1 (2)	N8—Cd2—O5	89.9 (2)
N4—Cd1—O1	102.9 (3)	N9—Cd2—O3	79.8 (2)
N4—Cd1—O2	88.7 (2)	N9—Cd2—O4	80.6 (2)
O1—Cd1—O2	51.3 (1)	N9—Cd2—O5	128.4 (2)
N6—Cd2—N7	74.2 (2)	O3—Cd2—O4	69.3 (2)
N6—Cd2—N8	75.4 (2)	O3—Cd2—O5	70.6 (2)
N6—Cd2—N9	75.7 (2)	O4—Cd2—O5	50.0 (1)

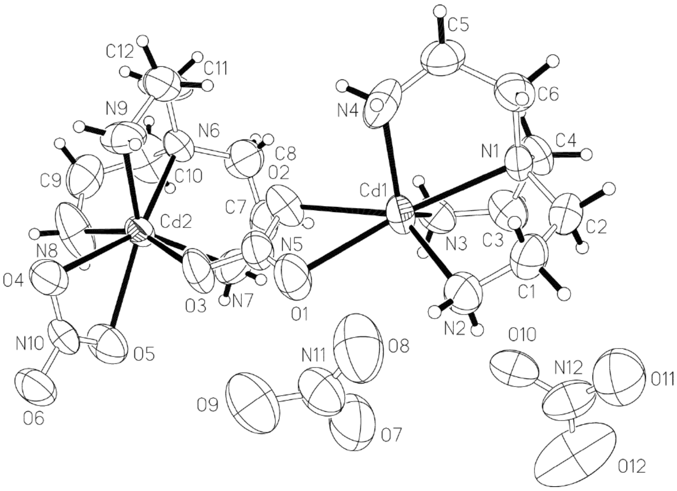


Figure 1
*ORTEP*II (Johnson, 1976) plot of (I), with displacement ellipsoids drawn at the 50% probability level. H atoms are drawn as spheres of arbitrary radii. Only one component of the disordered anions is shown.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H2n1$\cdots$O7	0.90	2.25	2.91 (3)	130
N2—H2n1$\cdots$O8	0.90	2.36	3.25 (4)	172
N2—H2n1$\cdots$O7′	0.90	2.60	3.30 (3)	135
N2—H2n1$\cdots$O8′	0.90	2.21	3.10 (4)	171
N2—H2n2$\cdots$O10	0.90	2.18	3.00 (3)	151
N2—H2n2$\cdots$O10′	0.90	2.29	3.16 (3)	162
N3—H3n1$\cdots$O6^{i}	0.90	2.24	3.11 (1)	165
N3—H3n2$\cdots$O11^{ii}	0.90	2.40	3.23 (3)	153
N3—H3n2$\cdots$O11$'^{ii}$	0.90	2.57	3.36 (3)	146
N3—H3n2$\cdots$O12^{ii}	0.90	2.41	3.11 (3)	136
N3—H3n2$\cdots$O12$'^{ii}$	0.90	2.39	3.19 (3)	149
N4—H4n1$\cdots$O6^{iii}	0.90	2.40	3.16 (1)	143
N4—H4n2$\cdots$O10^{iv}	0.90	2.64	3.48 (4)	155
N4—H4n2$\cdots$O10$'^{iv}$	0.90	2.61	3.49 (4)	163
N4—H4n2$\cdots$O12^{iv}	0.90	2.45	3.27 (3)	151
N4—H4n2$\cdots$O12$'^{iv}$	0.90	2.26	3.02 (3)	141
N7—H7n1$\cdots$O2	0.90	2.62	3.18 (1)	122
N7—H7n2$\cdots$O3^{i}	0.90	2.55	3.16 (1)	126
N7—H7n1$\cdots$O4^{i}	0.90	2.60	3.44 (1)	154
N8—H8n1$\cdots$O8$'^{i}$	0.90	2.34	3.18 (5)	155
N8—H8n2$\cdots$O10$'^{iii}$	0.90	2.33	3.13 (2)	148
N9—H9n1$\cdots$O7^{iii}	0.90	2.74	3.52 (5)	146
N9—H9n2$\cdots$O3^{iii}	0.90	2.64	3.22 (1)	124
N9—H9n1$\cdots$O9$'^{iii}$	0.90	2.72	3.44 (5)	138

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

The uncoordinated nitrate groups are disordered, and each was refined as two half-occupancy NO_3 entities sharing a common N atom. The N—O distances of the two disordered groups were restrained to be within 0.01 Å of each other, as were the non-bonded O$\cdots$O distances. The entities were restrained to be planar; the unprimed and primed O atoms (Table 2) were constrained to have the same displacement parameters. Some of the bond distances in the two tren ligands were somewhat short and and others long, which is an indication of possible disorder. The six C—C distances were restrained to be within 0.01 Å of each other, as were the six $N_{tertiary}$—C and six $N_{primary}$—C distances. H atoms were positioned geometrically (C—H = 0.97 Å and N—H = 0.90 Å), and were given displacement parameters 1.2 times $U_{\rm eq}$ of the parent atom. These were included in the refinement in the riding-model approximation.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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References

Bruker (1998). *SAINT* and *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

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

Klüfers, P. & Mayer, P. (1998). *Acta Cryst.* C**54**, 722–725.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Zhang, H., Cai, J., Feng, X. L., Sang, H. Y., Liu, J. Z., Li, X. Y. & Ji, L. N. (2002). *Polyhedron*, **21**, 721–728.

Zhang, H., Cai, J., Yang, G., Xue, G. Q. & Ji, L. N. (2000). *Acta Cryst.* C**56**, e562–e563.