

Short Communication

Synthesis and Single-Crystal Structure of an Unusual Heptacoordinate Cadmium(II) Complex, [Cd(medien)(NO₃)₂] (medien = bis(2-aminoethyl)-methylamine)

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Molecular geometry and coordination number play the key role in exploring the chemistry of a coordination compound. Cadmium(II) usually possesses octahedral as well as tetrahedral geometry.¹ Pentacoordination in cadmium(II) is also described.^{1,2} However, heptacoordinate cadmium(II) complexes are not common,^{3–10} and most of them are examples of apparent seven-coordination forced by geometrical demand of polydentate ligands.^{3–7} The examples of truly seven-coordinate cadmium(II), i.e. in which the coordination of each atom is not forced by the geometry of the ligands, are very scant in the chemistry of cadmium(II).

The crystal structure characterization of many of the cadmium(II) complexes with chain triamines (L), such as bis(3-aminopropyl)amine (dpt), (2-aminoethyl)(3-aminopropyl)amine (aepn), and bis(2-aminoethyl)amine (dien) [L = H₂N¹–(CH₂)_n–N²H–(CH₂)_m–N³H₂ when n = m = 3, L = dpt; n = 3, m = 2, L = aepn; and n = m = 2, L = dien] have been reported by Cannas *et al.*^{2,11,12} but such characterization with N²-alkyl-substituted triamines has not yet been published. Here we report the synthesis and structural characterization of a rather unusual seven-coordinate cadmium(II) complex with bis(2-aminoethyl)methylamine(medien). This belongs to that rare family of seven-coordinate cadmium(II) where geometrical demands did not force it into such high coordination.

Experimental

Materials. High-purity (98%) bis(2-aminoethyl)methylamine(medien) was purchased from Aldrich Chemical Co. Inc. and used as received. All other chemicals used were of AR grade.

Physical measurements. Elemental analysis and recording of an IR spectrum (Nujol mull/KBr disc at 25 °C) were carried out on a Perkin–Elmer 2400 series (II) CHN analyser and a Perkin–Elmer 783 infrared spectrophotometer, respectively.

Preparation of the complex. The complex was prepared by adding medien (1 mmol) dropwise to cadmium(II) nitrate tetrahydrate (1 mmol) dissolved in a methanol–water (1 : 1) mixture (10 cm³) with stirring. The resulting colourless solution was kept in a CaCl₂ desiccator, and colourless diamond-shaped crystals separated out after a few days. They were washed with methanol and dried in a desiccator. Found: C, 17.0; H, 4.3; N, 20.0; Cd, 31.8. Calc. for C₅H₁₅N₅O₆Cd: C, 16.9; H, 4.2; N, 19.7; Cd, 31.7%. IR spectra (cm⁻¹): 3330(m), 3290(s), 3240(s) (νNH₂); 2980(w), 2970(s), 2920(w), 2880(m) (νCH₂); 1575(s) (δNH₂); 1320(m), 1300(m), 1275(m) (ρ_wCH₂).

Crystallography. The diffraction data were collected on a Nonius Mach3 diffractometer with graphite-monochromated radiation using the ω–2θ scan technique over the range 3 ≤ θ ≤ 25° (–9 ≤ h ≤ 8, 0 ≤ k ≤ 9, –12 ≤ l ≤ 12). The data were corrected for Lorentz and polarisation factors,

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and empirical absorption corrections were carried out using ψ -scan data from three reflections with $\chi=90^\circ$ using the NRCVAX¹³ suite of programs. Out of a total of 2151 unique reflections measured, 2032 were considered to be observed with $I > 2\sigma(I)$. Crystal data and data collection parameters are compiled in Table 1.

The structure was solved by the Patterson heavy-atom method and refined by a full-matrix least-squares method based on $|F_{\text{obs}}|^2$ with anisotropic thermal parameters for non-hydrogen atoms using program SHELXL93.¹⁴ All four main-chain carbon atoms were disordered and refined with partial occupancies. The 'major' component of the disordered carbon atoms has a partial occupancy of 0.669, while the 'minor' component has a partial occupancy of 0.331. The N–C–C–N chains in the two five-membered chelate rings formed by the tridentate ligand were 'restrained' to have similar interatomic distances. All hydrogen atoms were placed in calculated positions (with the methyl group staggered) and refined with the 'riding option' in SHELXL93. Final R for 'observed' reflections was 0.044 ('goodness of fit', $s=1.19$) and 0.046 ($s=1.17$) for all reflections. Maximum and minimum peak heights in the final Fourier difference map were 1.01 and -0.93 e \AA^{-3} . Atomic coordinates of non-hydrogen atoms are listed in Table 2, bond distances and angles in Table 3.

Table 1. Crystallographic data.

Formula	C ₆ H ₁₅ N ₈ O ₆ Cd
Colour	Colourless
Formula weight	353.6
Crystal system	Triclinic
Space group	$P\bar{1}$
$a/\text{\AA}$	8.026(1)
$b/\text{\AA}$	8.113(1)
$c/\text{\AA}$	10.321(1)
$\alpha/^\circ$	90.449(8)
$\beta/^\circ$	89.862(8)
$\gamma/^\circ$	114.770(13)
$V/\text{\AA}^3$	610.2(2)
Z	2
Radiation, $\lambda/\text{\AA}$	MoK α (0.71073 \AA)
$F(000)$	352
μ/mm^{-1}	1.82
$D_c/\text{g cm}^{-3}$	1.925
$D_x/\text{g cm}^{-3}$	1.920
Crystal size/mm	0.50 \times 0.30 \times 0.20
θ -Range/ $^\circ$	$3 < \theta < 25$
Unique reflections	2151
Observed reflections [$I > 2\sigma(I)$]	2032
$R_1,^a wR_2^b$	0.0438, 0.1150
Weighting parameters (A, B) ^c	0.076, 0.7422
Goodness-of-fit, s^d	1.169
Maximum $\Delta/\text{e.s.d.}$	0.001
Final $\Delta\rho$, max/min/ e \AA^{-3}	+1.01/−0.93

$$^a R_1 = \sum \|F_o\| - |F_c| / \sum F_o$$

$$^b wR_2 = \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}$$

$$^c w = 1 / [\sigma^2(F_o^2) + (AP)^2 + BP], \text{ where } P = (F_o^2 + 2F_c^2) / 3$$

$$^d s = \{\sum [w(F_o^2 - F_c^2)^2] / (N - P)\}^{1/2}, \text{ where } N \text{ is the number of data and } P \text{ is the total number of parameters refined.}$$

Results and discussion

The medien molecule acts as a tridentate ligand, with the two terminal nitrogen atoms, N1 and N8, and the central nitrogen atom, N4, coordinating to the Cd ion, effectively forming two similar five-membered chelate rings (Cd–N1–C2–C3–N4 and Cd–N8–C7–C6–N4), both of which are disordered. The two oxygen atoms from each of the two nitrate groups also coordinate to the Cd ion to complete a seven-fold coordination (Fig. 1). The nitrogen atoms, N1, N4 and N8, together with one of the nitrate oxygen atoms, O13, form an approximate square plane [deviations from mean plane: N1 $-0.117(5)$, N4 $0.126(5)$, N8 $-0.115(5)$, O13 $0.094(5)$ \AA] with the Cd ion at a distance of $0.8454(4)$ \AA from this plane. The plane formed by the three nitrate oxygen atoms, O11, O15 and O16, lie on opposite sides of the Cd ion, with the latter at a distance of $1.8092(4)$ \AA from the this plane. The angle between the mean plane of N1, N4, N8 and O13 and the plane formed by O11, O15 and O16 is $163.6(1)^\circ$.

The Cd–N distances range from $2.232(5)$ to $2.460(4)$ \AA (Table 3) and are within the range of Cd–N bond distances in other similar complexes reported in the literature.^{4–6,10} The wider spread, from $2.348(4)$ to $2.617(4)$ \AA, in the distribution of the Cd–O distances is also observed in the latter.

The two disordered five-membered chelate rings are both in the twist conformation: the puckering parameters, q_2 and ϕ_2 ,¹⁵ for the rings of the 'major' component are $0.495(12)$ \AA and $-83.2(9)^\circ$ (ring Cd–N1–C2–C3–N4), $0.497(11)$ \AA and $97.1(8)^\circ$ (ring Cd–N8–C7–C6–N4); the corresponding parameters for the rings of the 'minor' component are $0.463(24)$ \AA and $85.4(16)^\circ$ (ring Cd–N1–C2'–C3'–N4) and $0.486(20)$ \AA and $-92.3(13)^\circ$ (ring Cd–N8–C7'–C6'–N4). Thus the pair of chelate rings are seen to flip between two twist conformations.

The coordination mode of NO_3^- was ascertained by several groups of workers^{16–18} using IR spectroscopy in the region $1700\text{--}1800 \text{ cm}^{-1}$, where a weak combination band of the ν_1 symmetric stretching and the doubly degenerate in-plane bending mode of NO_3^- ion in a metallic complex appears. In this region, the ionic nitrate, having D_{3h} symmetry, exhibits a single band. On coordination, the symmetry of the nitrate group reduces to C_{2v} and a splitting in the combination frequency occurs. The extent of splitting depends upon the distortion from the D_{3h} symmetry. In the monodentate complex, the separation between the peaks is smaller ($5\text{--}26 \text{ cm}^{-1}$) than that in the bidentate complexes ($20\text{--}66 \text{ cm}^{-1}$), indicating a greater distortion of the NO_3^- group from D_{3h} symmetry. In the present complex, two types of bidentate NO_3^- groups are present; one is almost symmetrically and the other is unsymmetrically coordinated. The deviation from D_{3h} symmetry in the latter should be comparable to that of the monodentate nitrate group. Consequently, a smaller separation is expected. The IR

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$).^a

Atoms	x	y	z	U(eq) ^a
Cd	1710(1)	3180(1)	1043(1)	43(1)
N(1)	3457(7)	6075(6)	1548(4)	53(1)
C(2)	3957(16)	6250(13)	2935(9)	63(3)
C(3)	2330(16)	5147(12)	3755(8)	56(3)
N(4)	1728(6)	3201(6)	3435(4)	56(1)
C(2')	3138(34)	6435(19)	2909(14)	63(6)
C(3')	3191(30)	5021(18)	3793(14)	55(6)
N(8)	-1241(6)	1573(7)	1553(4)	54(1)
C(7)	-1418(15)	1102(16)	2931(9)	64(3)
C(6)	-249(12)	2690(16)	3761(8)	57(3)
C(7')	-1542(18)	1935(34)	2917(14)	61(6)
C(6')	-136(18)	1774(28)	3783(13)	58(5)
C(5)	2632(14)	2231(13)	4063(6)	88(2)
N(9)	1420(7)	3489(7)	-1735(4)	51(1)
N(10)	3811(7)	1031(6)	1275(5)	54(1)
O(11)	2263(6)	2709(6)	-1133(3)	53(1)
O(12)	1395(10)	3514(10)	-2909(4)	93(2)
O(13)	649(6)	4249(6)	-1060(4)	58(1)
O(14)	4591(9)	43(8)	1488(10)	126(3)
O(15)	2120(6)	354(6)	1170(4)	62(1)
O(16)	4670(6)	2700(5)	1190(4)	63(1)

^aU(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected bond distances (in \AA) and angles (in $^\circ$).

Cd-N(1)	2.232(5)	Cd-N(4)	2.469(4)
Cd-N(8)	2.236(4)	Cd-O(16)	2.568(5)
Cd-O(11)	2.348(4)	Cd-O(13)	2.617(4)
Cd-O(15)	2.453(4)		
N(1)-Cd-N(8)	127.2(2)	N(8)-Cd-O(16)	135.9(2)
N(1)-Cd-O(11)	108.0(2)	O(11)-Cd-O(16)	77.6(1)
N(8)-Cd-O(11)	111.0(2)	O(15)-Cd-O(16)	50.2(1)
N(1)-Cd-O(15)	134.3(2)	N(4)-Cd-O(16)	86.3(2)
N(8)-Cd-O(15)	88.0(2)	N(1)-Cd-O(13)	89.3(2)
O(11)-Cd-O(15)	78.3(1)	N(8)-Cd-O(13)	88.8(2)
N(1)-Cd-N(4)	76.5(2)	O(11)-Cd-O(13)	50.8(1)
N(8)-Cd-N(4)	76.6(2)	O(15)-Cd-O(13)	123.4(1)
O(11)-Cd-N(4)	162.8(2)	N(4)-Cd-O(13)	146.4(2)
O(15)-Cd-N(4)	86.7(2)	O(16)-Cd-O(13)	123.5(1)
N(1)-Cd-O(16)	86.1(2)		

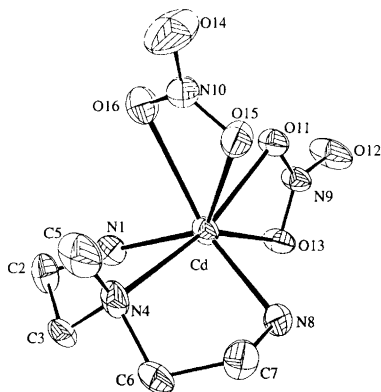


Fig. 1. ORTEP diagram of $[\text{Cd}(\text{medien})(\text{NO}_3)_2]$ with thermal ellipsoids at the 30% probability level.

spectra of the complex in the region $1700\text{--}1800\text{ cm}^{-1}$ show four peaks at 1755 , 1735 , 1715 and 1705 cm^{-1} . The large separation (50 cm^{-1}) between the first (1755 cm^{-1}) and the last peaks (1705 cm^{-1}) are attributable to the symmetrically coordinated nitrate ion, while the other two peaks and their small separation corresponds to the unsymmetrically coordinated one.

The present compound joins the very small family of seven-coordinate Cd^{II} species in which the coordination of each atom is not forced by the geometrical demands of the other coordinating atom.⁸⁻¹⁰ It is interesting to note that in all members of this special family the common ligands are either bidentate nitrate ions or bidentate carboxylate ions. Since the angles made by the coordinated oxygens of these bidentate anionic ligands at the Cd atom are restricted by their geometry to values of ca. $50\text{--}55^\circ$, there is enough space for the other ligands to coordinate cadmium without facing much steric hindrance (to complete the seven-coordination).

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