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Metal–Betaine Interactions. XI.* Structure of *catena*-[μ-Dichloro-(triethylammonioacetato)cadmium(II)]

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Abstract. A new cadmium(II) complex of triethylammonioacetate [$(C_2H_5)_3N^+CH_2COO^-$, designated Et$_3$BET] has been prepared and characterized. $[Cd\{(C_2H_5)_3NCH_2COO\}(\mu\text{-}Cl)_2]_n$, $M_r = 342.55$, monoclinic, $C2/c$, $a = 18.097\,(4)$, $b = 9.714\,(2)$, $c = 13.845\,(1)$ Å, $\beta = 92.46\,(1)°$, $U = 2431.1\,(7)$ Å^3, $Z = 8$, $D_m = 1.862$, $D_x = 1.871$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 22.1$ cm^{-1}, $F(000) = 1360$, $T = 298\,(1)$ K, $R = 0.024$ for 2875 unique Mo $K\alpha$ observed data. Each Cd^{II} atom is in a distorted octahedral environment, surrounded by an uncommon symmetrical bidentate chelating carboxylato group and two pairs of bridging chloro ligands. Successive octahedra related by the c-glide share edges to generate a one-dimensional polymeric structure.

Introduction. Although the carboxylate group exhibits a number of coordination modes in the extensively studied crystal structures of its metal complexes, the symmetrical bidentate chelating mode is rarely observed. This has been correlated to the relief of steric constraints induced by the coordination mode resulting in the more appreciable unsymmetrical form of chelation (Oldham, 1987).

In our ongoing systematic investigation on the ligating properties of betaines, considered as neutral structural analogues of carboxylato ligands, we have found that the prototype betaine, $Me_3N^+CH_2COO^-$ (abbreviated as BET), and its derivatives exhibit a rich variety of bonding modes in their metal complexes (Huang, Lü, Chen & Mak, 1991), including the common bidentate *syn-syn* and *syn-anti* bridging modes and the tridentate bridging mode. Two very interesting variations have also been found, with pyridine betaine ($C_5H_5N^+CH_2COO^-$, pyBET) acting as an unusual *syn*-skew bridging ligand in $[Cd_3(pyBET)_4Cl_6]$ (Mak & Chen, 1991), and BET acting as an uncommon skew-skew bridging ligand in $[Mn(BET)_3]_n.nMnCl_4$ (Chen & Mak, 1991*a*). Owing to the fact that the O—C—O bond angle in betaine ligands is usually larger in comparison to that of the common carboxylates, the bidentate chelating mode is rarely observed in metal complexes of betaines. Even for zinc complexes, in which most carboxylates behave as bidentate chelates, the betaines still function as unidentate ligands in $[Zn(BET)_2Cl_2].H_2O$ and two other related zinc(II) complexes (Chen & Mak, 1991*b*). Hitherto the only example of an unsymmetrical chelating betaine

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* For Part X on silver(I) complexes of triethylammonioacetate, see Huang, Lü, Chen & Mak (1991).

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ligand is found in $[Cd(BET)(H_2O)(\mu\text{-}Cl)Cl]_2$ (Chen & Mak, 1991*c*). In the present paper, we report the preparation and crystal structure of a new cadmium(II) complex of triethylammonioacetate (conveniently referred to as triethyl betaine and designated as Et_3BET), namely dichloro(triethyl betaine)cadmium(II) $[Cd(Et_3BET)(\mu\text{-}Cl)_2]_n$, in which the organic ligand acts in a nearly symmetrical bidentate mode.

Experimental. Triethyl betaine was prepared as described previously (Huang *et al.*, 1991). The title complex was simply prepared by dissolving $CdCl_2.2.5H_2O$ (0.228 g, 1.0 mmol) and triethyl betaine (0.159 g, 1.0 mmol) in hot water (5 ml, 323 K). After evaporation at room temperature for a week, colorless polyhedral crystals suitable for X-ray work were obtained. D_m measured by flotation in $CCl_4/BrCH_2CH_2Br$.

A crystal of size 0.20 × 0.22 × 0.30 mm was used to collect intensity data in the ω-scan mode on a Nicolet *R3m/V* diffractometer using graphite-monochromated Mo $K\alpha$ radiation; lattice parameters were refined from 25 reflections, $21 \leq 2\theta \leq 30°$; 3893 reflections were collected, $3 \leq 2\theta \leq 60°$, $0 \leq h \leq 25$, $0 \leq k \leq 13$, $-19 \leq l \leq 19$, two standards were checked after every 125 reflections, random deviation ($\leq 2\%$) only, Lp correction, empirical absorption correction based on ψ-scan data (transmission factors 0.455–0.636), after merging ($R_{\text{int}} = 0.015$) 3554 unique reflections, 2875 were considered observed with $I \geq 3\sigma(I)$; the structure was solved by Patterson superposition and subsequent difference Fourier synthesis and refined anisotropically. H atoms of the Et_3BET ligand were generated geometrically (C—H = 0.96 Å) and assigned the same isotropic thermal parameters of $U = 0.08$ Å^2. The quantity minimized was $\sum w(F_o - F_c)^2$, where $w = [\sigma^2(F_o) + 0.0002|F_o|^2]^{-1}$. Final $R = 0.024$, $wR = 0.031$ and $S = 1.358$ for 128 parameters and 2875 observed reflections; $(\Delta/\sigma)_{\max} = 0.0003$, $(\Delta\rho)_{\max} = 0.47$ e Å^{-3}.

All computations were performed on a DEC MicroVAX II computer with the *SHELXTL-Plus* program package (Sheldrick, 1982, 1985). Analytic expressions of neutral-atom scattering factors were employed (*International Tables for X-ray Crystallography*, 1974, Vol. IV, pp. 55, 99, 149).

Discussion. Atomic coordinates and thermal parameters are listed in Table 1,* and bond distances and angles in Table 2.

Table 1. *Atomic coordinates* ($\times 10^5$ *for* Cd, Cl; $\times 10^4$ *for others*) *and equivalent isotropic thermal parameters* (Å$^2 \times 10^4$ *for* Cd, Cl, O, N; $\times 10^3$ *for* C)

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

	x	*y*	*z*	U_{eq}
Cd(1)	2054 (1)	9493 (2)	38336 (1)	322 (1)
Cl(1)	−5913 (4)	13420 (7)	44382 (5)	429 (2)
Cl(2)	9577 (4)	6872 (8)	22679 (4)	420 (2)
O(1)	286 (1)	3420 (2)	3928 (1)	428 (6)
O(2)	1176 (1)	2255 (2)	4692 (2)	472 (6)
C(1)	816 (1)	3328 (3)	4527 (2)	36 (1)
C(2)	973 (1)	4651 (3)	5095 (2)	34 (1)
N(1)	1626 (1)	4688 (2)	5798 (2)	329 (6)
C(3)	1602 (2)	6104 (3)	6270 (2)	41 (1)
C(4)	2240 (2)	6416 (4)	6973 (3)	71 (1)
C(5)	1583 (2)	3567 (3)	6563 (2)	52 (1)
C(6)	885 (2)	3559 (5)	7122 (3)	77 (2)
C(7)	2343 (2)	4464 (3)	5289 (3)	53 (1)
C(8)	2504 (2)	5456 (5)	4520 (3)	79 (2)

Table 2. *Bond lengths* (Å) *and bond angles* (°)

Cd(1)—Cl(1)	2.727 (1)	Cd(1)—Cl(2)	2.621 (1)
Cd(1)—O(1)	2.407 (2)	Cd(1)—O(2)	2.435 (2)
Cd(1)—Cl(1*a*)	2.529 (1)	Cd(1)—Cl(2*b*)	2.558 (1)
O(1)—C(1)	1.245 (3)	O(2)—C(1)	1.245 (3)
C(1)—C(2)	1.527 (4)	C(2)—N(1)	1.499 (3)
N(1)—C(3)	1.524 (3)	N(1)—C(5)	1.523 (4)
N(1)—C(7)	1.519 (4)	C(3)—C(4)	1.508 (5)
C(5)—C(6)	1.509 (5)	C(7)—C(8)	1.474 (5)
Cl(1)—Cd(1)—Cl(2)	177.4 (1)	Cl(1)—Cd(1)—O(1)	81.3 (1)
Cl(2)—Cd(1)—O(1)	96.3 (1)	Cl(1)—Cd(1)—O(2)	85.7 (1)
Cl(2)—Cd(1)—O(2)	93.7 (1)	O(1)—Cd(1)—O(2)	54.1 (1)
Cl(1)—Cd(1)—Cl(1*a*)	86.8 (1)	Cl(2)—Cd(1)—Cl(1*a*)	95.7 (1)
O(1)—Cd(1)—Cl(1*a*)	147.2 (1)	O(2)—Cd(1)—Cl(1*a*)	94.7 (1)
Cl(1)—Cd(1)—Cl(2*b*)	92.8 (1)	Cl(2)—Cd(1)—Cl(2*b*)	86.6 (1)
O(1)—Cd(1)—Cl(2*b*)	100.2 (1)	O(2)—Cd(1)—Cl(2*b*)	154.3 (1)
Cl(1*a*)—Cd(1)—Cl(2*b*)	110.9 (1)	Cd(1)—Cl(1)—Cd(1*a*)	93.2 (1)
Cd(1)—Cl(2)—Cd(1*b*)	92.3 (1)	Cd(1)—O(1)—C(1)	90.4 (2)
Cd(1)—O(2)—C(1)	89.2 (2)		
O(1)—C(1)—O(2)	124.4 (2)	O(1)—C(1)—C(2)	113.8 (2)
O(2)—C(1)—C(2)	121.7 (2)	C(1)—C(2)—N(1)	118.6 (2)
C(2)—N(1)—C(3)	105.3 (2)	C(2)—N(1)—C(5)	111.8 (2)
C(3)—N(1)—C(5)	110.1 (2)	C(2)—N(1)—C(7)	111.1 (2)
C(3)—N(1)—C(7)	111.6 (2)	C(5)—N(1)—C(7)	106.9 (2)
N(1)—C(3)—C(4)	115.0 (2)	N(1)—C(5)—C(6)	115.4 (3)
N(1)—C(7)—C(8)	116.2 (3)		

Symmetry transformation: (*a*) $-x, -y, 1-z$; (*b*) $-x, y, \frac{1}{2}-z$.

As illustrated in Fig. 1, the Cd$^{\text{II}}$ atom is in an elongated octahedral environment, being coordinated by two *trans*-related chloro ligands [Cd(1)—Cl(1) = 2.727 (1), Cd(1)—Cl(2) = 2.621 (1) Å] and two *cis*-related chloro ligands [Cd(1)—Cl(1*a*) = 2.529 (1), Cd(1)—Cl(2*b*) = 2.558 (1) Å], as well as a chelating Et_3BET ligand [Cd—O = 2.407 (2), 2.435 (2) Å]. The most distorted angle of the octahedron is O(1)—Cd(1)—O(2) at 54.1 (1)°. Neighboring Cd$^{\text{II}}$ atoms are linked by two pairs of bridging chloro ligands [Cd—Cl—Cd = 92.3 (1), 93.2 (1)°] to build up a one-dimensional polymer running parallel to the *c* axis (see Fig. 2). The closest Cd···Cd contact of

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54451 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS0497]

3.735 (1) Å is much larger than that (2.98 Å) in the metal. The structure of the present complex is different from those of the polymeric Cd^{II} complexes of analogous ligands, namely $[Cd(BET)Cl_2]_n$ (Chen & Mak, 1991*c*), $[Cd(4\text{-hydroxy-L-proline})Cl_2]_n$ (Yukawa, Inomata, Takeuchi, Shimoi & Ouchi, 1982) and $[Cd(proline)Cl_2]_n.nH_2O$, (Yukawa, Inomata & Takeuchi, 1983), which are all one-dimensional polymeric species with each pair of Cd^{II} atoms bridged by two chloro ligands and a *syn-syn* bridging carboxylato group. In the latter two cases, the amino acids function as zwitterions and only their carboxylate groups participate in coordination.

It is noteworthy that the carboxylato group of the Et_3BET ligand in the present complex partakes in an uncommon symmetrical chelating mode with two equivalent C—O bonds at 1.245 (2) Å and a small difference in Cd—O bond lengths [Δ(Cd—O) = 0.028 Å], in contrast to the unsymmetrical chelating mode [C—O = 1.233 (5), 1.259 (4) Å; Δ(Cd—O) = 0.148 Å] as found in $[Cd(BET)(H_2O)(\mu\text{-}Cl)Cl]_2$ (Chen & Mak, 1991*c*). The O—C—O angle [124.4 (2)°] in the present complex, being similar to that [123.9 (3)°] in $[Cd(BET)(H_2O)(\mu\text{-}Cl)Cl]_2$, is significantly smaller than that [126.2 (4)°] of the *syn-syn* bridging Et_3BET ligand in $[Ag_2(Et_3BET)_2(NO_3)_2]$ (Chen & Mak, 1991*a*). This smaller O—C—O angle arises as a consequence of the chelating coordination mode of the carboxylato group (Oldham, 1987). Nevertheless, the O—C—O angle of Et_3BET in the present complex is still significantly larger than that of the symmetrical chelating acetate found in $[Ru(CH_3COO)H(Ph_3P)_3]$ [115 (1)°] (Skapski & Stephens, 1974), and those of the unsymmetrical chelating acetate found in $[Cd(CH_3COO)_2.2H_2O]$ [119.7 (4), 121.0 (5)°] (Harrison & Trotter, 1972) and diaquabis(phenoxyacetato)cadmium(II) [121.1 (5)°] (Mak, Yip, O'Reilly, Smith & Kennard, 1985). Reasonably, this may be attributed to the inductive effect of the positively charged N atom in betaine ligands and is likely to account for the fact that the bidentate chelating mode rarely occurs in the betaine complexes unless the metal ion has an appropriate covalent radius.

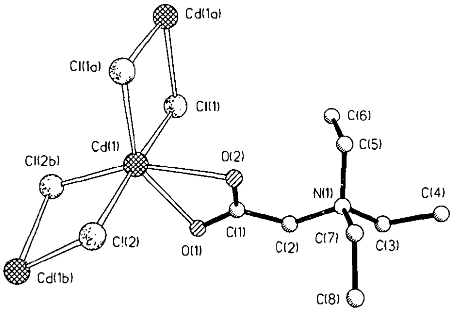

Fig. 1. Perspective view showing the coordination geometry of the metal atom in $[Cd(Et_3BET)(\mu\text{-}Cl)_2]_n$ and the atom-numbering scheme. Symmetry codes are given in Table 2.

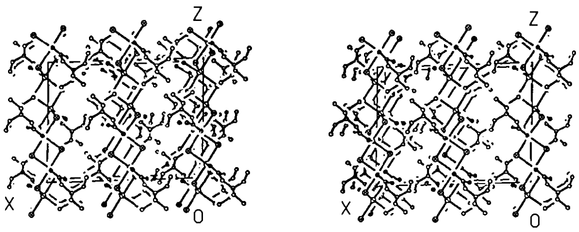

Fig. 2. Stereoview of the crystal structure of $[Cd(Et_3BET)(\mu\text{-}Cl)_2]_n$. The origin of the unit cell lies at the upper left corner, with **a** pointing from left to right, **b** towards the reader and **c** downwards.

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