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Synthesis and crystal structures of two polymeric cadmium(II) complexes containing skew–skew carboxylato-bridges

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Abstract—Two polymeric cadmium(II) complexes of betaine ($Me_3N^+CH_2CO_2^-$ = bet, $[Cd_3(bet)_4(H_2O)_2Cl_4]_n(ClO_4)_{2n}$ (**1**) and $[Cd(bet)_2(NO_3)]_n(ClO_4)_n$ (**2**), have been prepared and characterized by X-ray single-crystal structural analysis. Complex **1** has the metal atoms in two coordination geometries. One is coordinated in a distorted octahedral geometry, being surrounded by one aqua ligand, two chloro ligands and three carboxylate oxygen atoms, while the other is also in a distorted octahedral geometry, being surrounded by four chloro ligands and two carboxylate oxygen atoms. The aqua ligand acts as a terminal ligand [Cd—O = 2.368(2) Å], whereas the chloro and carboxylate ligands bridge in the μ_2-Cl and μ_2-carboxylato-*O,O′* bridging modes [Cd—Cl = 2.5828(7), 2.6405(7); Cd—O = 2.251(2), 2.291(2) Å]. In complex **2**, the metal atom is six-coordinate in a distorted octahedral geometry. The nitrate anion binds in an isobidentate η_2-chelate mode [Cd—O = 2.405(3) Å], while the carboxylate ligands bridge in the μ_2-carboxylato-*O,O′* bridging mode [Cd—O = 2.225(2), 2.315(2) Å]. The bet μ_2-carboxylato-*O,O′* groups in complexes **1** and **2** exhibit unusual skew–skew bridging fashions, with a pair of metal atom located either on the same side or on the opposite side of the carboxylate plane. © 1997 Elsevier Science Ltd

Keywords: cadmium(II); carboxylate; coordination mode; crystal structure.

Interest in the coordination chemistry of cadmium(II) carboxylate complexes derives from the coordination modes shown by the carboxylate groups. A number of cadmium(II) carboxylate complexes have been synthesized that upon crystal structure analyses have been shown to exist as polymeric compounds. In these complexes, the carboxylate group engages in monodentate binding [1–4], η_2-carboxylato-*O,O′* chelation [2,3,5–9], and μ_2-carboxylato-*O,O′* bridging [3,4,8–13], with the μ_2-carboxylato-*O,O′* bridging mode being the most common.

Betaine (IUPAC name: trimethylammonioacetate, $Me_3N^+CH_2CO_2^-$, designated as bet) and its derivatives are neutral analogues of common monocarboxylic acids and they are used to prepare metal complexes having other anionic ligands. They have been used in the synthesis of cadmium(II) halides and pseudohalides [1–3,7–10]. Cadmium(II) complexes of betaines that have been reported in the literature exhibit coordination *motifs* similar to those found in the complexes of cadmium(II) carboxylates. An earlier study of such cadmium complexes has documented an unusual trinuclear complex: pyridinioacetate coordinates to the cadmium atoms in a *syn*–skew bridging mode, so that one of the pair of cadmium atoms ligates to the carboxylate group in an out-of-plane manner [10]. Analogous skew ligation modes of carboxylate groups such as the skew monodentate [14,15], *syn*–skew bridging [16,17] and skew–skew bridging [17,18] modes have also been found in several zinc(II) and manganese(II) complexes of betaines. In addition, the carboxylate group in the zinc complex $[Zn(bipy)_2(MeCO_2)](ClO_4)_2 \cdot H_2O$ (bipy = 2,2′-bipyridine) engages in non-coplanar hydrogen bonding with water [19]. In this paper, we report the synthesis and crystal structures of two new polymeric cadmium(II) complexes, $[Cd_3(bet)_4(H_2O)_2Cl_4]_n(ClO_4)_{2n}$ and $[Cd(bet)_2(NO_3)]_n(ClO_4)_n$, in which the bet entities exhibit the unusual skew–skew coordination modes.

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EXPERIMENTAL

Preparation

To an aqueous solution (10 cm^{-3}) containing bet (0.234 g, 2.0 mmol) was added $CdCl_2 \cdot 6H_2O$ (0.266 g, 1 mmol) and followed with the addition of $NaClO_4$ (0.150 g, 1 mmol). The resulting colourless solution was stirred for 20 min at 50°C. After slow evaporation of the solution at room temperature for a week, crystalline plates of complex **1** were obtained in *ca* 63% yield. IR data (cm^{-1}): 3388w, 3050w, 3022w, 2994w, 2952w, 1623vs, 1468m, 1426m, 1398s, 1335s, 1236w, 1145s, 1117vs, 1082vs, 983w, 962w, 927m, 906m, 737w, 632m, 603w, 547w.

Complex **2** was prepared by the above procedure with $Cd(NO_3)_2 \cdot 9H_2O$ (0.400 g, 1 mmol) instead of $CdCl_4 \cdot 6H_2O$. The yield was *ca* 58%. IR data (cm^{-1}): 3388m, 3057m, 3022m, 2994m, 2952m, 1644vs (br), 1475s, 1398vs(br), 1335vs, 1236w, 1145vs, 1117vs, 1082vs, 983m, 955m, 934s, 899s, 821w, 737m, 632s, 547w.

Crystallography

Diffraction intensities for both complexes **1** and **2** were collected at 25°C on an Enraf–Nonius CAD4 diffractometer using the ω-scan technique. Lp and absorption corrections were applied [20]. The detailed crystallographic parameters are given in Table 1. The structures were solved with direct methods of SIR92 [21] and refined with the full-matrix least-squares technique using the SHELXL-93 program [22]. Non-hydrogen atoms were refined anisotropically. The alkyl hydrogen atoms were generated geometrically (C—H = 0.96 Å); the aqua hydrogen atoms were located from difference maps and refined with isotropic temperature factors. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated [23]. The final discrepancy indices and other parameters at the conclusion of refinement are given in Table 1 and selected bond lengths and bond angles in Table 2. Supplementary materials including non-hydrogen and hydrogen atomic coordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

RESULTS AND DISCUSSION

The crystal structure of complex **1** comprises a packing of two-dimensional polymeric $[Cd_3(bet)_4(H_2O)_2Cl_4]_n^{2n+}$ cations and discrete perchlorate anions. In the polymeric cation, there are two crystallographically independent cadmium(II) atoms. As shown in Fig. 1, the Cd(1) atom is coordinated by three carboxylate oxygen atoms, one water molecule and two *cis*-related chloro ligands to result in a distorted octahedral environment about the Cd(1) atom.

Table 1. Crystallographic data

	Complex **1**	Complex **2**
Molecular formula	$C_{20}H_{48}Cl_6Cd_3N_4O_{18}$	$C_{10}H_{22}Cl_6CdN_3O_{11}$
Molecular weight	1182.52	508.16
Colour and habit	Colourless plate	Colourless block
System	Monoclinic	Orthorhombic
Space group	*P*2/*c* (No. 13)	*Pbcm* (No. 57)
Cell parameters	$a = 13.8717(12)$, $b = 11.6559(11)$ $c = 12.261(2)$ Å, $\beta = 93.202(10)°$ $V = 1979.4(4)$ Å^3	$a = 9.2832(5)$, $b = 7.5911(5)$ $c = 26.0452(12)$ Å $V = 1835.4(2)$ Å^3
Z	2	4
$F(000)$	1172	1024
Density (g cm^{-3})	1.984	1.839
Temperature (°C)	21	21
Radiation	Mo-K_α, $\lambda = 0.71073$ Å	Mo-K_α, $\lambda = 0.70173$ Å
Absorption coefficient (cm^{-1})	20.75	13.95
Crystal size (mm)	0.44 × 0.44 × 0.14	0.50 × 0.44 × 0.30
Collection range (°)	$1.47 \leqslant \theta \leqslant 27.47$	$1.56 \leqslant \theta \leqslant 29.97$
Transmission factors	1.0001/0.6600	0.9994/0.8140
Data collected	4731	2732
Unique data	4517 ($R_{int} = 0.0338$)	2732
Observed data [$I \geqslant 2\sigma(I)$]	4008	1942
Parameters refined	232	124
$R(R_w)$ value	0.0263 (0.0622)	0.0332 (0.0831)
Goodness-of-fit	1.060	1.060
Weighting scheme	$w = 1/[\sigma^2(F^2)+(0.0317P)^2+2.0554P]$, $P = (F_0^2+2F_c^2)/3$	$w = 1/[\sigma^2(F^2)+(0.0478P)^2+1.6884P]$, $P = (F_0^2+2F_c^2)/3$
$\Delta\rho_{max}/\Delta\rho_{max}$ (e Å^{-3})	0.781/−0.699	1.397/−0.692

Table 2. Selected bond length (Å) and bond angles (°)

Complex 1			
Cd(1)—O(1)	2.251(2)	Cd(1)—O(3)	2.261(2)
Cd(1)—O(4a)	2.291(2)	Cd(1)—O(1w)	2.368(2)
Cd(1)—Cl(2b)	2.5828(7)	Cd(1)—Cl(1b)	2.6405(7)
Cd(2)—O(2)	2.370(2)	Cd(2)—Cl(1)	2.5928(7)
Cd(2)—Cl(2)	2.6418(7)	O(1)—C(1)	1.250(3)
O(2)—C(1)	1.251(3)	O(3)—C(6)	1.244(3)
O(4)—C(6)	1.251(3)		
O(1)—Cd(1)—O(3)	101.47(8)	O(1)—Cd(1)—O(4a)	92.13(7)
O(3)—Cd(1)—O(4a)	98.60(8)	O(1)—Cd(1)—O(1w)	85.97(7)
O(3)—Cd(1)—O(1w)	86.25(8)	O(4a)—Cd(1)—O(1w)	175.06(8)
O(1)—Cd(1)—Cl(2b)	168.92(6)	O(3)—Cd(1)—Cl(2b)	85.66(6)
O(4a)—Cd(1)—Cl(2b)	95.20(5)	O(1w)—Cd(1)—Cl(2b)	86.05(5)
O(1)—Cd(1)—Cl(1b)	86.72(6)	O(3)—Cd(1)—Cl(1b)	169.05(6)
O(4a)—Cd(1)—Cl(1b)	88.23(6)	O(1w)—Cd(1)—Cl(1b)	87.11(5)
Cl(2b)—Cd(1)—Cl(1b)	85.22(2)	O(2)—Cd(2)—Cl(1)	90.98(6)
Cl(1)—Cd(2)—Cl(2c)	95.01(2)	O(2)—Cd(2)—Cl(2)	96.07(5)
Cd(2)—Cl(1)—Cd(1d)	94.11(2)	Cd(1d)—Cl(2)—Cd(2)	94.32(2)
C(1)—O(1)—Cd(1)	127.2(2)	C(1)—O(2)—Cd(2)	134.0(2)
C(6)—O(3)—Cd(1)	127.3(2)	C(6)—O(4)—Cd(1a)	128.5(2)
O(1)—C(1)—O(2)	125.8(3)	O(3)—C(6)—O(4)	127.0(3)
Complex 2			
Cd(1)—O(1)	2.225(2)	Cd(1)—O(2a)	2.315(2)
Cd(1)—O(3)	2.405(3)	O(1)—C(1)	1.258(4)
O(2)—C(1)	1.242(4)	O(3)—N(2)	1.253(3)
O(4)—N(2)	1.229(5)		
O(1b)—Cd(1)—O(1)	114.86(13)	O(1)—Cd(1)—O(2c)	90.37(9)
O(1)—Cd(1)—O(2c)	96.90(8)	O(2a)—Cd(1)—O(2c)	166.49(13)
O(1b)—Cd(1)—O(3)	149.15(9)	O(1)—Cd(1)—O(3)	95.99(8)
O(2c)—Cd(1)—O(3)	81.57(8)	O(2a)—Cd(1)—O(3)	86.35(9)
O(3b)—Cd(1)—O(3)	53.18(11)	C(1)—O(2)—Cd(1a)	129.6(2)
N(2)—O(3)—Cd(1)	94.2(2)	C(1)—O(1)—Cd(1)	108.3(2)
O(4)—N(2)—O(3)	120.8(2)	O(4)—N(2)—O(3c)	120.8(2)
O(3)—N(2)—O(3c)	118.5(4)	O(2)—C(1)—O(1)	125.2(3)

Symmetry codes: for **1**, (a) $-x, 1-y, -z$; (b) $-x, 1/2+y, -1/2-z$; (c) $-x, 1-y, -1-z$; (d) $-x, -1/2+y, -1/2-z$. For **2**, (a) $1-x, 2-y, 1-z$; (b) $x, 3/2-y, 1-z$; (c) $1-x, -1/2+y, z$; (d) $1-x, 1/2+y, z$; (e) $x, 5/2-y, 1-z$; (f) $x, y, 1/2-z$.

The Cd(1)—O(carboxy) bond lengths range from 2.251(2) to 2.291(2) Å, which are slightly shorter than that of the Cd(1)—O(aqua) bond (2.368(2) Å). The Cd(1)—Cl bond lengths range from 2.5828(7) to 2.6405(7) Å. The Cd(2) atom, being located at an inversion centre, is surrounded by two *trans*-related carboxylate oxygen atoms and four chloro ligands in a distorted octahedral arrangement. The Cd(2)—O(carboxy) bond, i.e. Cd(2)—O(2), is 2.370(2) Å and is slightly longer than the Cd(1)—O(carboxy) bonds, whereas the Cd—Cl bond lengths which fall in the 2.5928(7)–2.6418(7) Å range are comparable with those found in cadmium(II) complexes containing μ_2-bridging chloro ligands [3,4,7–9,11–13]. The most distorted angles in the octahedra about the Cd(1) and Cd(2) atoms are O(1)—Cd(1)—O(3) [101.47(8)°] and O(2)—Cd(2)—Cl(2) [96.07(5)°]. Each pair of adjacent Cd(1) atoms is separated by 4.5130(5) Å, the atoms being bridged by a pair of μ_2-carboxylato-*O,O′* groups defined by O(1)—C(1)—O(2) (see Fig. 1); the Cd(2) atom is linked to the Cd(1) atom [Cd(1)...Cd(2) = 5.6832(8) Å] by a pair of μ_2-chloro bridges, extending the structure into a staircase-like one-dimensional chain in the lattice. These one-dimensional chains are further connected with each pair of adjacent Cd(1) and Cd(2) atoms by μ_2-carboxylato-*O,O′* groups to result in a two-dimensional network lattice, as illustrated in Fig. 2.

The most interesting feature of complex **1** is that both bet groups engage in skew–skew bridging, which contrasts with coplanar *syn–syn*, *syn–anti*, and *anti–anti* bridging (Fig. 3) that is commonly found in metal carboxylates [24,25]. In complex **1**, torsion angles of C(2)—C(1)—O(1)—Cd(1), C(2)—C(1)—O(2)—Cd(2), C(7)—C(6)—O(3)—Cd(1) and C(7)—C(6)—O(4)—Cd(1a) are 164.2(2), −7.5(4),

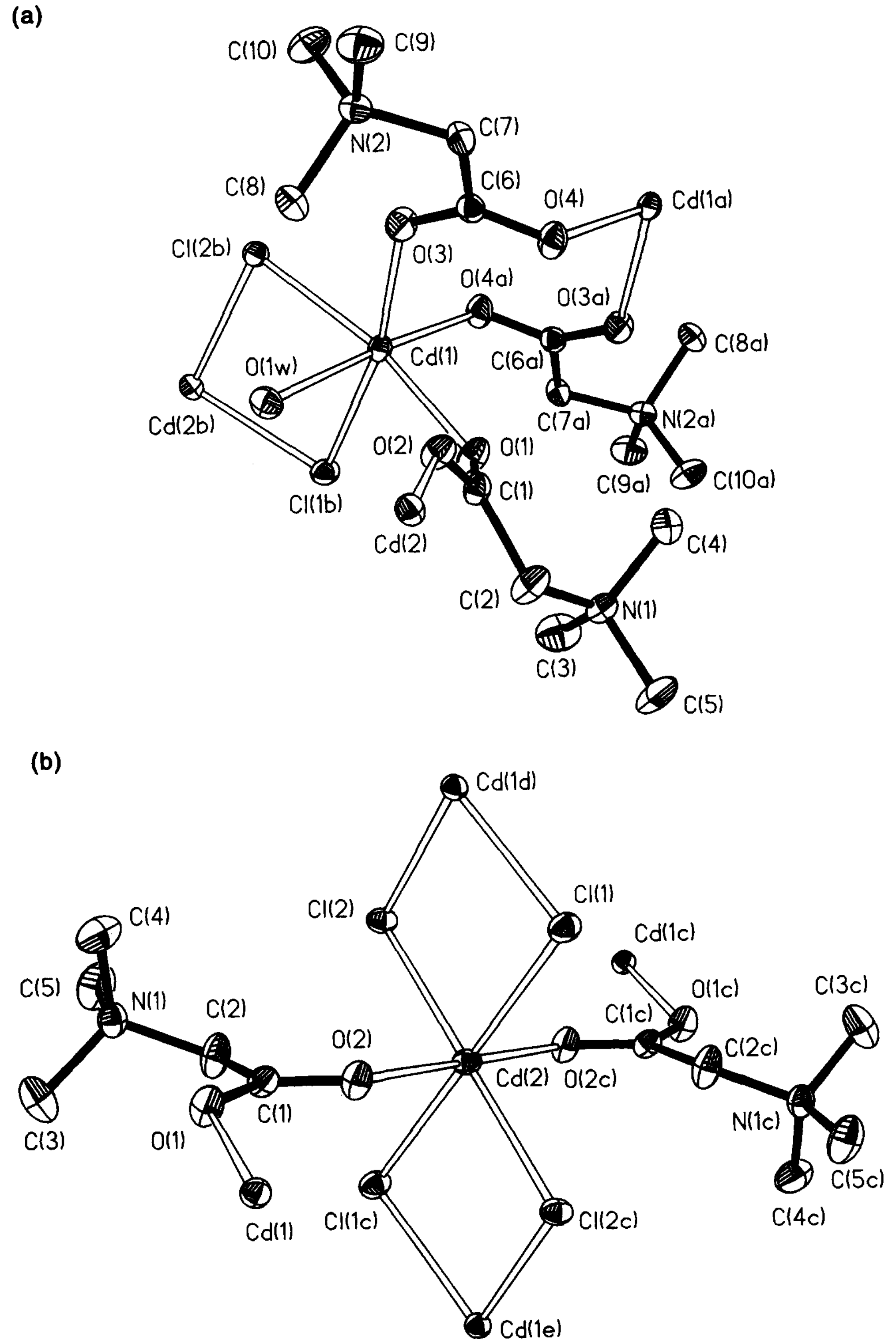


Fig. 1. *ORTEP* plot showing the coordination geometry about the cadmium(II) atoms in complex **1** and the atom-numbering scheme. The symmetry codes are given in Table 2.

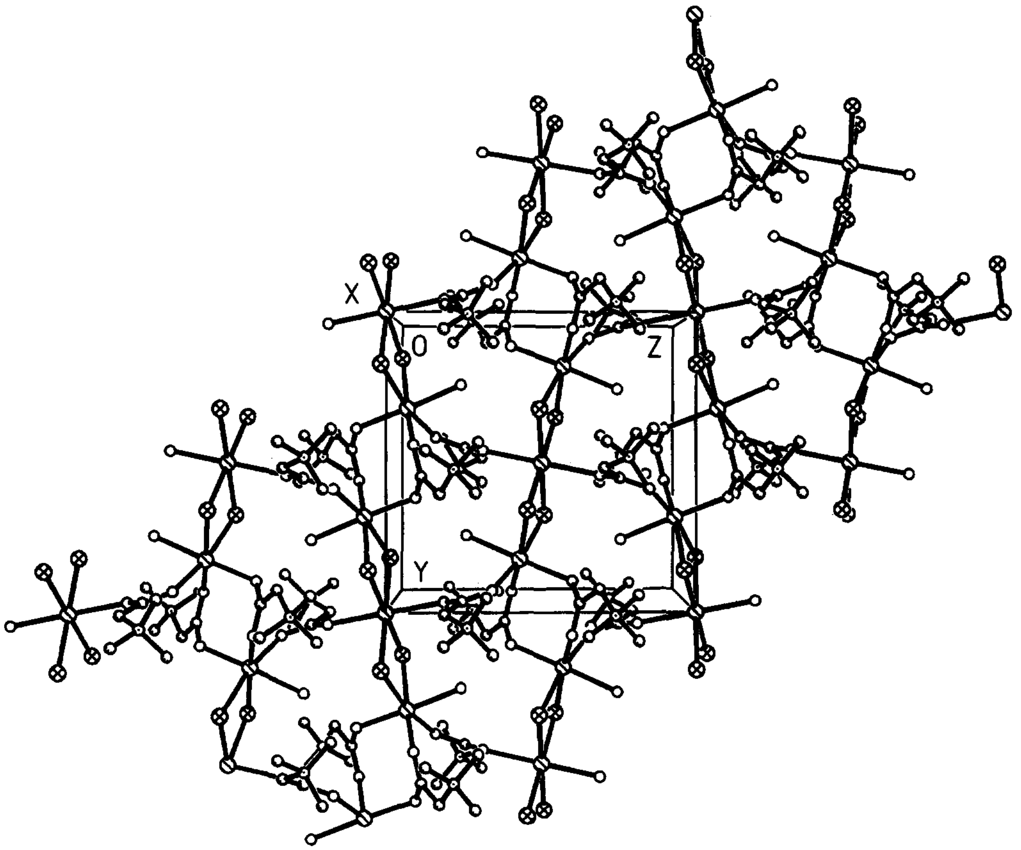
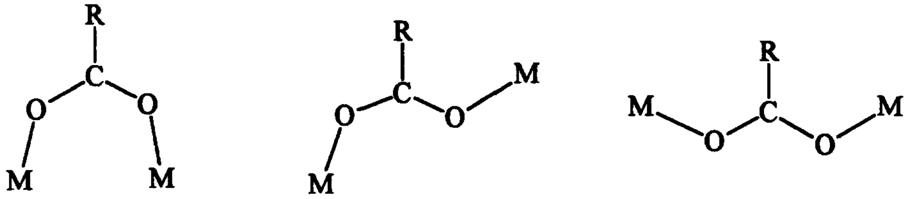


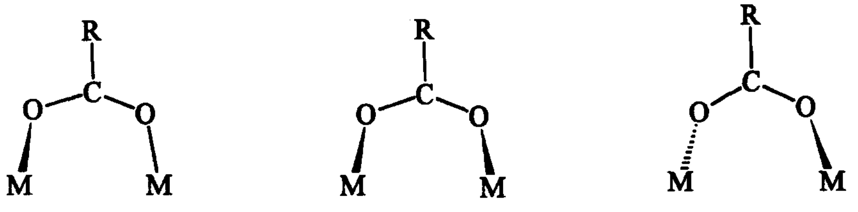
Fig. 2. Structure of the two-dimensional network of the $[Cd_3(bet)_4(H_2O)_2Cl_4]_n^{2n+}$ cation view along the *a* axis.



a) *syn-syn* coplanar
(180, 180)

b) *syn-anti* coplanar
(180, 0)

c) *anti-anti* coplanar
(0, 0)



d) *syn*-skew non-planar
(180, -90)

e) skew-skew non-planar
(90, -90)

f) skew-skew non-planar
(90, 90)

Fig. 3. Six idealized μ_2-carboxylato-bridging modes. Enclosed in the parentheses are the numerical values of the pair of C—C—O—M torsion angles (°) for each type of geometry.

−153.8(2) and −112.6(2)°. Both the Cd(1)—O(1) and Cd(1)—O(2) bonds rotate out the O(1)—C(1)—O(2) carboxylate plane toward one side of the carboxylate plane, which is different from the *syn*–skew mode found for the trinuclear cadmium(II) complex [10]. In this tricadmium complex, only one metal atom is not co-planar with the carboxylate group [Fig. 3(d)]. A similar skew–skew coordination mode with the pair of metal atoms lie on the same side of the carboxylate group [Fig. 3(e)] has been documented in a polymeric manganese(II) complex of bet [17] and a dinuclear manganese(II) complex containing a betaine derivative [18], but these appear to be the only example in the literature to date. The pair of metal atoms Cd(1) and Cd(1a) are located at the opposite sides of the O(3)—C(6)—O(4) carboxylate plane. Such an arrangement of two metal atoms about the bridging carboxylate group, although shown to be theoretically possible [17], has not been reported. Complex **1** therefore, shows a carboxylate coordination mode that is new in metal carboxylate chemistry.

The crystal structure of complex **2** is composed of a packing of one-dimensional polymeric chain-like $[Cd(bet)_2(NO_3)]_n^{n+}$ cations and discrete perchlorate anions. In the polymeric chain, each cadmium atom, being located at a two-fold axis, is coordinated by four carboxylate oxygen atoms and a chelating nitrate groups, as depicted in Fig. 4. The Cd(1)—O(carboxy) bond lengths are in range 2.225(2)–2.315(2) Å and are significantly shorter than the Cd(1)—O(nitrato) bond length of 2.405(3) Å. The Cd—O(nitrato) bond length is compatible with those found for cadmium(II) nitrate complexes [26]. Owing to isobidentate chelation by the nitrate group, the six oxygens ligating the cadmium(II) atom surround it in an irregular octahedral arrangement, as implied by the angles of O(3)—Cd(1)—O(3b) and O(1b)—Cd(1)—O(3) of 53.18(8) and 149.15(9)°, respectively. Each pair of adjacent cadmium atoms, being separated at 4.3551(3) Å, are bridged by a pair of μ_2-carboxylato-*O,O′* groups into a one-dimensional chain running along the *b*-axis, as shown in Fig. 5.

The bet carboxylate group in complex **2** also coordinates in a skew–skew bridging mode. The O(1) coordinates the Cd(1) atom in a slightly out-of-plane fashion with a torsion angle of C(2)—C(1)—O(1)—Cd(1) = 168.1(2)°, while the Cd(1a)—O(2) bond rotates out of the carboxylate plane by a much greater extent with torsion angle of C(2)—C(1)—O(2)—Cd(1a) = −80.7(3)°. The Cd(1) and Cd(1a) atoms lie at the same side of the carboxylate plane, an arrangement that is similar to those found in the manganese(II) complexes of betaines [17,18].

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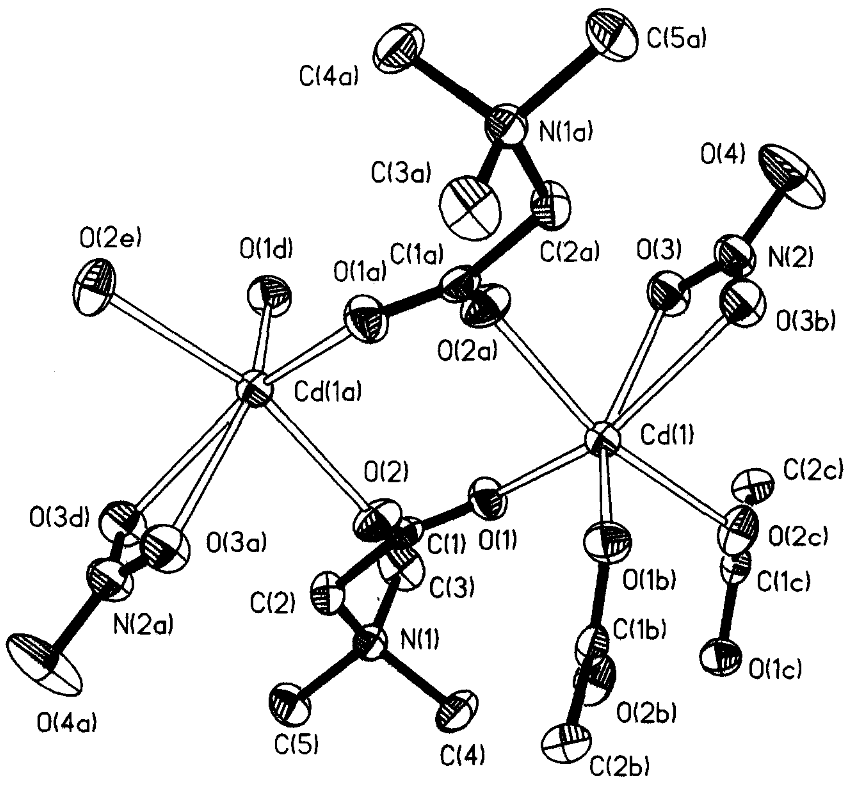

Fig. 4. *ORTEP* plot showing the coordination geometry about the cadmium(II) atoms in complex **2** and the atom-numbering scheme. The symmetry codes are given in Table 2.

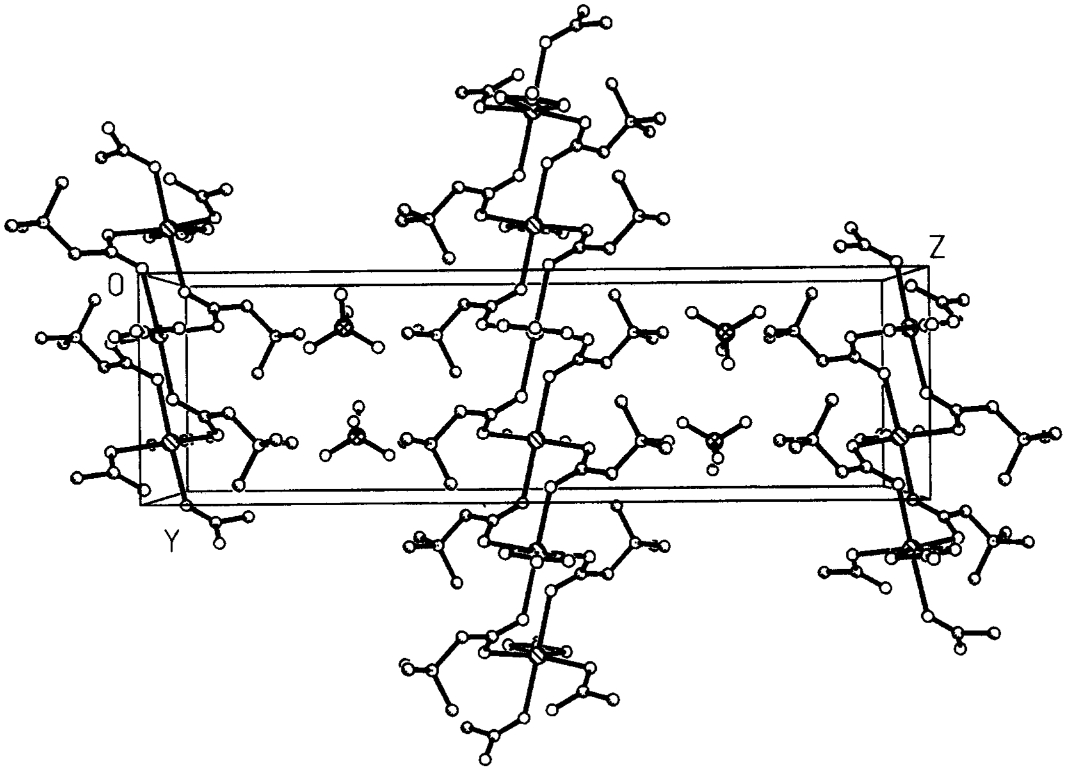

Fig. 5. Molecular packing of complex **2** viewed along the *a* axis.

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