Polyethylene glycol complexation of Cd^{2+}. Structures of triethylene glycol complexes of $CdCl_2$, $CdBr_2$ and CdI_2

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Abstract

The reactions of 1:1 molar quantities of triethylene glycol (EO3) and CdX_2 (X = Cl, Br, I) in 3:1 CH_3CN:CH_3OH produced three different complexes which have been structurally characterized. In $[Cd_2(EO3)_2(\mu\text{-}EO3)]Cl_4 \cdot 2H_2O$, one EO3 ligand coordinates exclusively to one metal ion, while a second type of glycol coordination features donor interactions with two different Cd^{2+} ions producing two six-coordinate metal centers in the dimer. $[Cd_2Br_4(EO3)_2]$ contains two seven-coordinate Cd^{2+} centers and is dimeric via two bridging bromide interactions. $[Cd(EO3)_2][CdI_4]$ consists of eight-coordinate Cd^{2+} complex cations hydrogen bonded to $[CdI_4]^{2-}$ anions.

Introduction

The structural chemistry of Cd^{2+} coordinated to a variety of open chain and macrocyclic polydentate ligands has been well investigated. Structures of cyclic and acyclic polyethers [1–5], polyamines [6–10] and O,N substituted aminoethers [11–14] have appeared in the literature. There are, however, no reports of polyethylene glycol (PEG) complexes of Cd^{2+} (although a tetraethylene glycol dimethyl ether adduct has been structurally characterized [5]). Our work investigating PEG complexation of the lanthanides [15, 16] and actinides [17] has recently been expanded to the environmentally toxic heavy metal ions Hg^{2+} [18], Pb^{2+} [19], Bi^{3+} [20, 21], and now Cd^{2+}.

Ready complexation of the PEGs with the metal ions we have studied has resulted from the flexibility of the acyclic PEG chain and the chelating nature of the donor interactions. In addition, the alcoholic termini of PEGs provide sites for hydrogen bonding which has proven to be an interesting facet of this ligand's coordination chemistry [15–21]. The supramolecular networks generated by hydrogen bonding to solvent molecules, anions and other PEG ligands add to the intricacy of the observed structures. The three structures reported here, $[Cd_2(EO3)_2(\mu\text{-}EO3)]Cl_4 \cdot 2H_2O$, $[Cd_2Br_4(EO3)_2]$ and $[Cd(EO3)_2][CdI_4]$, exemplify the flexibility and adaptability of PEGs as coordinating ligands.

Experimental

Preparation of complexes

$CdCl_2$, $CdBr_2$, CdI_2 and EO3 were used as purchased without further purification. CH_3CN and CH_3OH were distilled from CaH_2 and stored over 4 Å molecular sieves prior to use. All melting points are uncorrected.

$[Cd_2(EO3)_2(\mu\text{-}EO3)]Cl_4 \cdot 2H_2O$

EO3 (70 μl, 0.52 mmol) was added to $CdCl_2$ (0.0916 g, 0.50 mmol) in 3:1 CH_3CN:CH_3OH (5 ml). The solution was stirred at 60 °C for 1 h followed by centrifugation to remove a small quantity of precipitate. The supernatant was stored at 3 °C for 24 h followed by slow evaporation to produce colorless crystals. Melting range 145–150 °C. *Anal.* Calc. C, 25.34; H, 5.43. Found for precipitate: C, 10.34; H, 1.94. Found for crystals: C, 25.70; H, 4.94%.

$[Cd_2Br_4(EO3)_2]$

EO3 (0.13 ml, 0.97 mmol) was added to $CdBr_2$ (0.2722 g, 1.0 mmol) in 3:1 CH_3CN:CH_3OH (5 ml). The solution was then stirred at 60 °C for 1 h followed by storage at 5 and −10 °C for 24 h time periods. Slow evaporation produced colorless crystals. Melting point 139 °C. *Anal.* Calc. C, 17.06; H, 3.34. Found for crystals: C, 17.24; H, 3.54%.

$[Cd(EO3)_2][CdI_4]$

EO3 (0.13 ml, 0.97 mmol) was added to CdI_2 (0.3662 g, 1.0 mmol) in 3:1 CH_3CN:CH_3OH (5 ml). The solution was stirred at 60 °C for 1 h followed by storage at 5

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TABLE 1. Crystal data and summary of intensity data collection and structure refinement

Compound	$[Cd_2(EO3)_2(\mu\text{-}EO3)]Cl_4\ 2H_2O$	$[Cd_2Br_4(EO3)_2]$	$[Cd(EO3)_2][CdI_4]$
Color/shape	colorless/fragment	colorless/parallelepiped	colorless/parallelepiped
Formula weight	853.19	844.79	1032.8
Space group	$P\bar{1}$	$P\bar{1}$	$P2_12_12_1$
Temperature (°C)	20	23	20
Cell constants[a]			
a (Å)	8.855(6)	7.839(4)	9.578(2)
b (Å)	9.051(6)	11.418(7)	16.063(2)
c (Å)	10.758(5)	13.675(7)	17.720(4)
α (°)	90.59(5)	96.74(5)	
β (°)	92.58(5)	91.63(5)	
γ (°)	92.53(6)	104.36(5)	
Cell volume (Å^3)	860.4	1175	2726
Formula units/unit cell	1	2	4
D_{calc} (g cm^{-3})	1.65	2.39	2.52
μ_{calc} (cm^{-1})	15.9	90.4	61.7
Diffractometer/scan	Enraf-Nonius CAD-4/ω–2θ	Enraf-Nonius CAD-4/ω–2θ	Enraf-Nonius CAD-4/ω–2θ
Range of relative transmission factors (%)	52/100	57/100	82/100
Radiation, graphite monochromator	Mo Kα ($\lambda=0.71073$)	Mo Kα ($\lambda=0.71073$)	Mo Kα ($\lambda=0.71073$)
Max. crystal dimensions (mm)	0.25×0.38×0.40	0.15×0.15×0.45	0.30×0.30×0.40
Scan width	0.80+0.35tan θ	0.80+0.35tan θ	0.80+0.35tan θ
Standard reflections	400, 060, 007	500; 040, 008	800; 080; 0, 0, 12
Decay of standards (%)	±0.1	±1	±2
Reflections measured	3024	4140	2747
2θ Range (°)	$2\leqslant 2\theta\leqslant 50$	$2\leqslant 2\theta\leqslant 50$	$2\leqslant 2\theta\leqslant 50$
Range of h, k, l	+10, ±10, ±12	+9, ±13, ±16	+11, +19, +21
Reflections observed ($F_o\geqslant 5\sigma(F_o)$)[b]	2657	1836	2229
Computer programs[c]	SHELX [22]	SHELX [22]	SHELX [22]
Structure solution	SHELXS [23]	SHELXS [23]	SHELXS [23]
No. parameters varied	172	235	235
Weights	$[\sigma(F_o)^2+0.0065F_o^2]^{-1}$	$[\sigma(F_o)^2+0.0020F_o^2]^{-1}$	$[\sigma(F_o)^2+0.0005F_o^2]^{-1}$
GOF	0.84	2.16	0.90
$R=\Sigma\lVert F_o\rvert-\lvert F_c\rVert/\Sigma\lvert F_o\rvert$	0.055	0.076	0.030
R_w	0.075	0.094	0.040
R inverse configuration			0.032
Largest feature final difference map (e$^-$ Å^{-3})	1.65 within 0.96 Å of Cd	1.7 within 1 Å of Cd(1)	0.6

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections $\theta>16°$. [b] Corrections. Lorentz–polarization and absorption (empirical, psi scan). [c] Neutral scattering factors and anomalous dispersion corrections from ref. 24

and −10 °C for approximately 24 h time periods. Slow evaporation provided colorless crystals. Melting range 112–117.5 °C. *Anal.* Calc. C, 13.96; H, 2.73. Found for crystals: C, 14.39; H, 2.83%.

X-ray data collection, structure determination and refinement

Data collection was carried out on transparent single crystals mounted in thin-walled glass capillaries flushed with Ar. The space groups for the X = Cl and X = Br derivatives were determined to be either the centric $P\bar{1}$ or the acentric $P1$ with final refinements carried out in $P\bar{1}$. The X = I complex crystallized in the uniquely defined space group $P2_12_12_1$. A summary of data collection parameters is given in Table 1.

Geometrically constrained hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 Å^2. Aquo and alcoholic hydrogen atoms were not included in the final refinements. All non-hydrogen atoms were refined anisotropically. The final fractional coordinates are given in Tables 2 (X = Cl), 3 (X = Br) and 4 (X = I).

Results and discussion

$[Cd_2(EO3)_2(\mu\text{-}EO3)]Cl_4\cdot 2H_2O$

An ORTEP illustration of $[Cd_2(EO3)_2(\mu\text{-}EO3)]Cl_4\cdot 2H_2O$ is shown in Fig. 1. The dimeric cation resides

TABLE 2. Final fractional coordinates for $[Cd_2(EO3)_2(\mu\text{-}EO3)]Cl_4 \cdot 2H_2O$

Atom	x/a	y/b	z/c	B_{eq}[a]
Cd	0.22774(4)	0.23566(4)	0.33635(3)	1.57
Cl(1)	0.1345(2)	0.1773(2)	−0.0986(2)	3.39
Cl(2)	0.2874(2)	0.7121(2)	0.4784(2)	2.43
O(1)	0.2029(6)	0.0415(6)	0.1903(5)	3.05
O(2)	0.4778(6)	0.2194(6)	0.2477(5)	2.91
O(3)	0.2719(6)	0.4615(5)	0.2262(5)	3.00
O(4)	−0.0137(6)	0.3268(6)	0.3030(5)	3.19
O(5)	0.3461(6)	0.3541(5)	0.5158(4)	2.85
O(6)	0.2046(5)	0.0559(5)	0.5005(4)	2.30
O(7)	−0.1431(6)	0.1694(7)	0.0794(5)	3.65
C(1)	0.3539(7)	−0.0192(7)	0.1794(6)	2.41
C(2)	0.4667(7)	0.1032(8)	0.1496(6)	2.38
C(3)	0.5233(7)	0.3674(8)	0.2026(6)	2.63
C(4)	0.3937(8)	0.4455(8)	0.1410(7)	2.68
C(5)	0.1254(8)	0.4987(8)	0.1674(7)	2.84
C(6)	0.0027(8)	0.4829(7)	0.2595(7)	2.73
C(7)	0.3143(7)	0.2669(6)	0.6283(5)	2.10
C(8)	0.3183(6)	0.1061(6)	0.5998(5)	1.89
C(9)	0.0534(6)	0.0368(6)	0.5504(5)	1.79

[a] $B_{eq} = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

TABLE 3. Final fractional coordinates for $[Cd_2Br_4(EO3)_2]$

Atom	x/a	y/b	z/c	B_{eq}
Cd(1)	0.0517(3)	0.0172(2)	0.2747(1)	1.71
Cd(2)	−0.1085(3)	0.3008(1)	0.2313(1)	1.89
Br(1)	0.0939(4)	0.2475(2)	0.3780(2)	2.25
Br(2)	−0.1631(4)	0.0682(2)	0.1419(2)	2.31
Br(3)	0.2548(4)	−0.0613(2)	0.3912(2)	2.56
Br(4)	−0.3110(4)	0.3767(2)	0.1159(2)	2.88
O(1)	0.309(2)	0.139(1)	0.194(1)	1.99
O(2)	0.139(3)	−0.100(1)	0.133(1)	2.65
O(3)	−0.135(2)	−0.201(1)	0.239(1)	1.91
O(4)	−0.215(3)	−0.024(2)	0.373(1)	3.49
O(5)	−0.379(2)	0.183(1)	0.320(1)	2.38
O(6)	−0.195(3)	0.423(1)	0.379(1)	2.49
O(7)	0.073(3)	0.515(1)	0.262(2)	2.87
O(8)	0.155(3)	0.332(2)	0.139(2)	3.53
C(1)	0.345(4)	0.071(2)	0.103(2)	2.67
C(2)	0.316(4)	−0.058(2)	0.112(2)	3.32
C(3)	0.069(4)	−0.230(2)	0.121(2)	2.75
C(4)	−0.122(3)	−0.255(2)	0.141(2)	1.74
C(5)	−0.309(3)	−0.214(3)	0.268(2)	2.86
C(6)	−0.299(4)	−0.151(2)	0.372(2)	2.77
C(7)	−0.409(4)	0.244(2)	0.412(2)	3.34
C(8)	−0.375(4)	0.380(2)	0.399(2)	2.58
C(9)	−0.131(6)	0.553(2)	0.369(2)	4.45
C(10)	0.053(6)	0.583(3)	0.356(3)	6.78
C(11)	0.244(5)	0.526(3)	0.239(3)	5.30
C(12)	0.251(4)	0.456(3)	0.136(3)	5.00

TABLE 4. Final fractional coordinates for $[Cd(EO3)_2][CdI_4]$

Atom	x/a	y/b	z/c	B_{eq}
Cd(1)	−0.37326(9)	−0.80864(5)	−0.25179(4)	2.12
Cd(2)	−0.92412(9)	−0.98406(6)	−0.46301(5)	2.66
I(1)	−0.6972(1)	−1.04645(6)	−0.53875(6)	3.56
I(2)	−1.0197(1)	−1.10246(7)	−0.36111(6)	3.90
I(3)	−0.8731(1)	−0.83987(5)	−0.37820(5)	3.04
I(4)	−1.1291(1)	−0.94198(6)	−0.56731(5)	3.34
O(1)	−0.498(1)	−0.9196(6)	−0.1987(5)	3.28
O(2)	−0.477(1)	−0.9000(5)	−0.3481(5)	2.71
O(3)	−0.293(1)	−0.7756(5)	−0.3771(4)	2.77
O(4)	−0.256(1)	−0.6788(6)	−0.2552(5)	3.32
O(5)	−0.5807(8)	−0.7493(5)	−0.2902(5)	2.78
O(6)	−0.4845(9)	−0.7324(5)	−0.1465(5)	2.79
O(7)	−0.2652(8)	−0.8330(5)	−0.1318(4)	2.57
O(8)	−0.1677(9)	−0.8852(6)	−0.2648(5)	3.45
C(1)	−0.579(1)	−0.9728(8)	−0.2482(8)	3.29
C(2)	−0.505(2)	−0.9799(9)	−0.3206(9)	4.33
C(3)	−0.404(2)	−0.8969(9)	−0.4191(7)	3.50
C(4)	−0.374(2)	−0.8084(8)	−0.4365(6)	3.13
C(5)	−0.252(2)	−0.6892(7)	−0.3859(7)	3.23
C(6)	−0.172(1)	−0.6645(8)	−0.3208(7)	3.26
C(7)	−0.650(1)	−0.6938(9)	−0.2392(7)	3.68
C(8)	−0.633(2)	−0.726(1)	−0.1578(7)	3.97
C(9)	−0.457(2)	−0.764(1)	−0.0733(8)	3.92
C(10)	−0.299(1)	−0.781(1)	−0.0683(8)	3.65
C(11)	−0.122(1)	−0.8581(9)	−0.1349(9)	3.75
C(12)	−0.105(2)	−0.921(1)	−0.1987(8)	4.47

on a crystallographic center of inversion. The six coordinate Cd^{2+} geometry is distorted, but closer to capped trigonal bipyramidal with O(3) and O(6) in axial sites and O(2) capping the O(1), O(3), O(5) triangular face, than to an octahedral geometry. The Cd–O_{eq} contacts (the three alcoholic positions) average 2.35(2) Å (Table 5), the Cd–O_{ax} distances average 2.41(1) Å, and the longest separation is to the capping atom, O(2), at 2.460(5) Å. The distortion from idealized geometry is clearly evident from the angles around cadmium: O(3)–Cd–O(6) = 162.7(2)° and the O_{ax}–Cd–O_{eq} angles range from 75.1(1) to 108.0(2)°. The smallest equatorial angle, 97.6(2)°, lies in between two adjacent alcoholic sites (O(1)–Cd–O(4)). The cadmium center resides 0.16 Å above the O(1), O(4), O(5) equatorial plane.

The two coordination modes of the EO3 ligands found in this complex have been observed previously. The O(1)–O(4) EO3 molecule mimics the coordination mode of its cyclic analog 12-crown-4. 12-Crown-4 has a cavity size too small to accommodate Cd^{2+}, as we have seen in $[Cd(12\text{-crown-}4)_2][CdX_4]$ (X = Br, I) [19], where the metal center resides out of the macrocycle cavity. In the title complex, the O(1)–O(4) donor atoms are planar to within 0.38 Å with Cd^{2+} residing 1.02 Å above the plane. The ability of certain metal ions to organize acyclic PEGs into conformations observed for out-of-cavity crown ether complexation has been previously reported for $[BiX_3(EO5)]$ (X = Cl, Br) [21] and $[BiI_2(EO5)][Bi_2I_7] \cdot 2MeOH$ [21]. The PEG ligands in these bismuth complexes coordinate in a fashion similar to the macrocyclic ethers in $[BiX_3(15\text{-crown-}5)]$

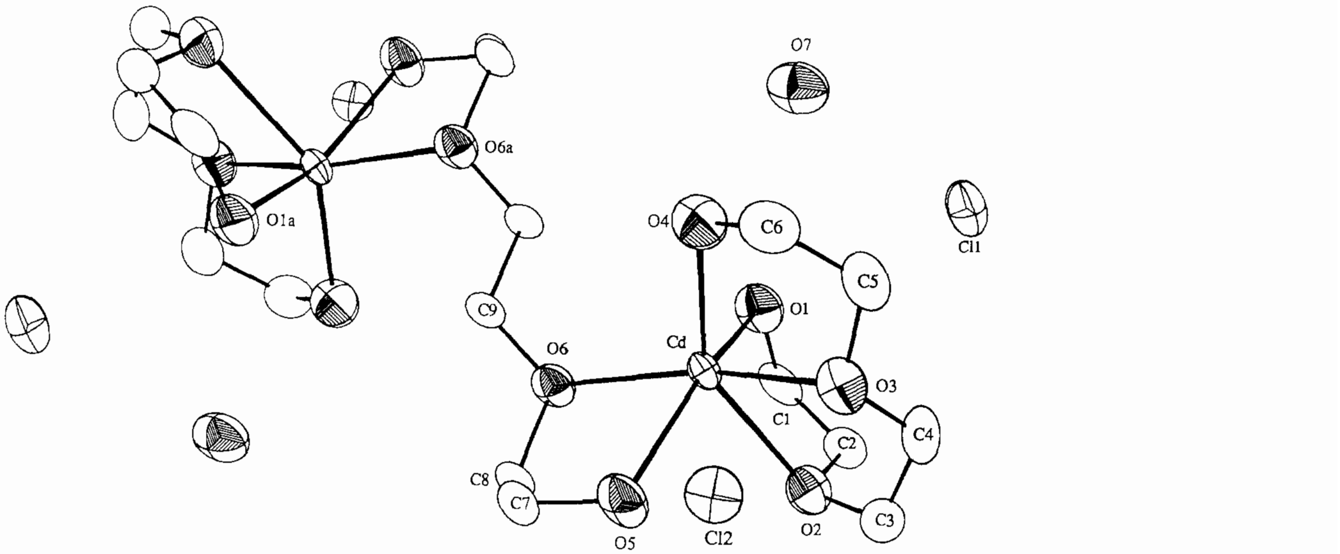

Fig 1 ORTEP diagram (50% probability ellipsoids) of [$Cd_2(EO3)_2(\mu\text{-}EO3)]Cl_4 \cdot 2H_2O$. H atoms have been omitted for clarity.

(X = Cl, Br) [21] and [$BiBr_2$(18-crown-6)][$BiBr_4$] [21].

The torsion angle sequence for the O(1)–O(4) glycol starting with O(1)–C(1)–C(2)–O(2) is $g^+(\sim 60°)a(\sim 180°)g^+g^+aag^-$. The set approaches the optimized sequence for the C_4 conformation of 12-crown-4 [25–27]. Average distances for the O(1)–O(4) EO3 ligand are $C\text{–}O_{alc} = 1.49(1)$, $C\text{–}O_{eth} = 1.471(9)$ and $C\text{–}C = 1.508(2)$ Å. The C–O–C, O_{alc}–C–C and O_{eth}–C–C angles average 114.6(6), 110.2(6) and 111(1)°, respectively.

The flexibility of the EO3 ligand is demonstrated by the second unique EO3 molecule (O(5)–O(6)) which chelates two Cd^{2+} centers in a bridging fashion. EO3 has previously been observed to bridge two or more metal centers [18], as have polyalkylamine chelates [8–10]. [$Ni_2(tren)_2(\mu\text{-trien})][ClO_4]_4$ [28] (tren = tris(2-aminoethyl)amine; trien = triethylenetetramine) has a bridging trien interaction that is identical to the bridging EO3 interaction in [$Cd_2(EO3)_2(\mu\text{-}EO3)]Cl_4 \cdot 2H_2O$.

The unique torsion angle sequence in the O(5)–O(6) EO3 molecule is g^-g^-aa. The linear portion of the glycol chain is generated by four consecutive anti angles. The average bond lengths of $C\text{–}O_{alc} = 1.483(8)$, $C\text{–}O_{eth} = 1.478(9)$ and $C\text{–}C = 1.51(2)$ Å, and average angles of $C\text{–}O\text{–}C = 110.9(4)$, $O_{alc}\text{–}C\text{–}C = 110.1(5)$ and $O_{eth}\text{–}C\text{–}C = 111(2)°$, compare well with those observed for the pseudocyclic EO3 (O(1)–O(4)).

The contact geometries suggest several hydrogen bonding possibilities which combine to form a three-dimensional network. O(4) may donate a hydrogen bond to either O(7) or Cl(2)^b (b = symmetry code $-x$, $1-y$, $1-z$), O(7) may donate to O(4) while forming a bifurcated interaction with Cl(1) and Cl(1)^d (d = $-x$, $-y$, $-z$), or O(7) may accept an interaction from O(4) and form two direct interactions with Cl(1) and Cl(1)^d. In addition, O(1) interacts with Cl(1) and O(5) hydrogen bonds directly to either Cl(2) or Cl(2)^c (c = $1-x$, $1-y$, $1-z$), or forms a bifurcated interaction to each.

[$Cd_2Br_4(EO3)_2$]

[$Cd_2Br_4(EO3)_2$] (Fig. 2) crystallizes as a halide bridged dimer with two seven-coordinate pentagonal bipyramidal Cd^{2+} sites. The bridging Br(2) and terminal Br(3) reside in axial sites about Cd(1) with the equatorial pentagonal plane of Br(1), O(1)–O(4) planar to within 0.09 Å and Cd(1) 0.15 Å out of this plane. The bridging Br(1) and terminal Br(4) are the axial ligands around Cd(2), and the pentagonal plane of Br(2), O(5)–O(8) is planar to 0.15 Å with Cd(2) 0.18 Å out of this plane. Several cadmium compounds in the literature possess a similar array of halogens and chelating ligands [7, 29–31] but [$Cd_2Br_4(EO3)_2$] appears to be the only example utilizing an all oxygen donor chelating ligand.

Both Cd(1) and Cd(2) have one short (O(2), 2.44(2) Å; O(7), 2.49(2) Å) and one longer (O(3), 2.54(2) Å; O(6), 2.53(2) Å) etheric interaction. Hydrogen bonding to and from the four alcoholic positions results in a large range (2.43(2)–2.62(2) Å) in $Cd\text{–}O_{alc}$ separations, but the mean values for the two metals are nearly identical at 2.50(2) Å for Cd(1) and 2.5(1) Å for Cd(2). The terminal Cd–Br contacts are both similar, although a slight lengthening is observed for the Cd(1)–Br(3) interaction due to hydrogen bonding. Hydrogen bonding interactions also contribute to a significant lengthening of the mean bridging Cd–Br(1) separation of 2.76(2) Å, compared to 2.68(3) Å for Cd–Br(2).

The coordination mode of the EO3 ligand differs from either of those found in the previous complex. The ligands wrap around equatorial planes in a more traditional template fashion [18–20] and exhibit torsion

TABLE 5. Bond distances (Å) and angles (°)

$[Cd_2(EO3)_2(\mu\text{-}EO3)]Cl_4 \cdot 2H_2O$			
Cd–O(1)	2.341(5)	Cd–O(2)	2.460(5)
Cd–O(3)	2.400(5)	Cd–O(4)	2.339(5)
Cd–O(5)	2.377(4)	Cd–O(6)	2.423(4)
O(1)–Cd–O(2)	74.2(2)	O(1)–Cd–O(3)	108.0(2)
O(2)–Cd–O(3)	73.7(2)	O(1)–Cd–O(4)	97.6(2)
O(2)–Cd–O(4)	144.0(2)	O(3)–Cd–O(4)	75.9(2)
O(1)–Cd–O(5)	151.9(2)	O(2)–Cd–O(5)	89.1(2)
O(3)–Cd–O(5)	88.0(2)	O(4)–Cd–O(5)	108.9(2)
O(1)–Cd–O(6)	88.9(2)	O(2)–Cd–O(6)	109.0(2)
O(3)–Cd–O(6)	162.7(2)	O(4)–Cd–O(6)	105.8(2)
O(5)–Cd–O(6)	75.1(1)		
$[Cd_2Br_4(EO3)_2]$			
Cd(1)–Br(1)	2.772(3)	Cd(1)–Br(2)	2.652(3)
Cd(1)–Br(3)	2.603(3)	Cd(1)–O(1)	2.52(2)
Cd(1)–O(2)	2.44(2)	Cd(1)–O(3)	2.54(2)
Cd(1)–O(4)	2.49(2)	Cd(2)–Br(1)	2.738(3)
Cd(2)–Br(2)	2.716(3)	Cd(2)–Br(4)	2.573(4)
Cd(2)–O(5)	2.62(2)	Cd(2)–O(6)	2.53(2)
Cd(2)–O(7)	2.49(2)	Cd(2)–O(8)	2.43(2)
Br(1)–Cd(1)–Br(2)	90.0(1)	Br(1)–Cd(1)–Br(3)	97.7(1)
Br(2)–Cd(1)–Br(3)	172.3(1)	Br(1)–Cd(1)–O(1)	78.5(3)
Br(2)–Cd(1)–O(1)	88.9(4)	Br(3)–Cd(1)–O(1)	92.8(4)
Br(1)–Cd(1)–O(2)	145.4(4)	Br(2)–Cd(1)–O(2)	83.7(4)
Br(3)–Cd(1)–O(2)	90.1(4)	O(1)–Cd(1)–O(2)	67.4(5)
Br(1)–Cd(1)–O(3)	147.3(4)	Br(2)–Cd(1)–O(3)	85.9(4)
Br(3)–Cd(1)–O(3)	87.5(4)	O(1)–Cd(1)–O(3)	133.7(5)
O(2)–Cd(1)–O(3)	66.3(5)	Br(1)–Cd(1)–O(4)	80.9(4)
Br(2)–Cd(1)–O(4)	84.1(5)	Br(3)–Cd(1)–O(4)	96.9(5)
O(1)–Cd(1)–O(4)	158.2(5)	O(2)–Cd(1)–O(4)	131.8(6)
O(3)–Cd(1)–O(4)	66.4(6)	Br(1)–Cd(2)–Br(2)	89.35(9)
Br(1)–Cd(2)–Br(4)	170.4(1)	Br(2)–Cd(2)–Br(4)	99.0(1)
Br(1)–Cd(2)–O(5)	85.6(4)	Br(2)–Cd(2)–O(5)	77.2(4)
Br(4)–Cd(2)–O(5)	91.6(4)	Br(1)–Cd(2)–O(6)	79.6(4)
Br(2)–Cd(2)–O(6)	141.2(4)	Br(4)–Cd(2)–O(6)	90.9(4)
O(5)–Cd(2)–O(6)	65.1(5)	Br(1)–Cd(2)–O(7)	88.2(4)
Br(2)–Cd(2)–O(7)	150.5(5)	Br(4)–Cd(2)–O(7)	86.8(4)
O(5)–Cd(2)–O(7)	131.8(6)	O(6)–Cd(2)–O(7)	66.8(6)
Br(1)–Cd(2)–O(8)	86.0(5)	Br(2)–Cd(2)–O(8)	82.9(5)
Br(4)–Cd(2)–O(8)	99.6(5)	O(5)–Cd(2)–O(8)	158.4(6)
O(6)–Cd(2)–O(8)	132.4(6)	O(7)–Cd(2)–O(8)	67.7(7)
Cd(1)–Br(1)–Cd(2)	88.71(9)	Cd(1)–Br(2)–Cd(2)	91.7(1)
$[Cd(EO3)_2][CdI_4]$			
Cd(1)–O(1)	2.341(9)	Cd(1)–O(2)	2.460(8)
Cd(1)–O(3)	2.409(8)	Cd(1)–O(4)	2.370(9)
Cd(1)–O(5)	2.306(8)	Cd(1)–O(6)	2.472(8)
Cd(1)–O(7)	2.398(8)	Cd(1)–O(8)	2.333(8)
Cd(2)–I(1)	2.744(1)	Cd(2)–I(2)	2.778(1)
Cd(2)–I(3)	2.804(1)	Cd(2)–I(4)	2.780(1)
O(1)–Cd(1)–O(2)	67.6(3)	O(1)–Cd(1)–O(3)	134.5(3)
O(2)–Cd(1)–O(3)	67.7(3)	O(1)–Cd(1)–O(4)	157.2(3)
O(2)–Cd(1)–O(4)	134.3(3)	O(3)–Cd(1)–O(4)	68.3(3)
O(1)–Cd(1)–O(5)	89.7(3)	O(2)–Cd(1)–O(5)	72.2(3)
O(3)–Cd(1)–O(5)	85.0(3)	O(4)–Cd(1)–O(5)	92.1(3)
O(1)–Cd(1)–O(6)	81.6(3)	O(2)–Cd(1)–O(6)	130.2(3)
O(3)–Cd(1)–O(6)	136.4(3)	O(4)–Cd(1)–O(6)	77.8(3)
O(5)–Cd(1)–O(6)	69.3(3)	O(1)–Cd(1)–O(7)	74.9(3)
O(2)–Cd(1)–O(7)	133.8(3)	O(3)–Cd(1)–O(7)	135.6(3)
O(4)–Cd(1)–O(7)	87.8(3)	O(5)–Cd(1)–O(7)	134.5(3)
O(6)–Cd(1)–O(7)	66.3(3)	O(1)–Cd(1)–O(8)	93.9(3)
O(2)–Cd(1)–O(8)	87.5(3)	O(3)–Cd(1)–O(8)	75.8(3)
O(4)–Cd(1)–O(8)	93.5(4)	O(5)–Cd(1)–O(8)	156.3(3)
O(6)–Cd(1)–O(8)	134.4(3)	O(7)–Cd(1)–O(8)	68.7(3)
I(1)–Cd(2)–I(2)	109.21(4)	I(1)–Cd(2)–I(3)	115.21(4)
I(2)–Cd(2)–I(3)	105.94(5)	I(1)–Cd(2)–I(4)	108.86(4)
I(2)–Cd(2)–I(4)	111.44(4)	I(3)–Cd(2)–I(4)	106.17(4)

angle sequences of $g^+aag^-aag^+$ about Cd(1) and $g^-aag^+aag^-$ about Cd(2). (These torsion angle sequences are similar to those observed for the D_{3d} form of complexed 18-crown-6.) Average distances and angles within the glycols are: $C\text{–}O_{alc} = 1.44(1)$, $C\text{–}O_{eth} = 1.42(3)$, $C\text{–}C = 1.50(5)$ Å; $C\text{–}O\text{–}C = 115(1)$, $O_{alc}\text{–}C\text{–}C = 108(2)$, $O_{eth}\text{–}C\text{–}C = 108(2)$°.

O(1) accepts a hydrogen bond from $O(5)^c$ ($c = 1+x, y, z$) and donates to O(8), which (through a lengthy 3.53(2) Å interaction) donates to Br(1). O(4) and O(5) donate hydrogen bonds to $Br(3)^a$ ($a = -x, -y, 1-z$) and $O(1)^b$ ($b = x-1, y, z$), respectively, resulting in a zigzag hydrogen bonded polymer propagating along unit cell direction *b*.

[Cd(EO3)₂][CdI₄]

In $[Cd(EO3)_2][CdI_4]$, the cation (Fig. 3) has an eight-coordinate dodecahedral geometry with etheric donors in the A sites and alcoholic oxygen atoms occupying the B sites. The donors O(1)–O(4) are planar to within 0.18 Å, and O(5)–O(8) are planar to 0.15 Å. The angle between the two planes is 88.8°. Average metal to ligand distances are $Cd\text{–}O_{alc} = 2.34(2)$ Å (B sites) and $Cd\text{–}O_{eth} = 2.43(3)$ Å (A sites). A similar dodecahedral 2/1 $EO3/M^{2+}$ cation was observed in the Ca^{2+} complex $[Ca(EO3)_2]Cl_2 \cdot 4H_2O$ [32].

A comparison of the average bonding parameters within the two EO3 ligands shows little difference between alcoholic and etheric oxygen atoms: $C\text{–}O_{alc} = 1.438(8)$, $C\text{–}O_{eth} = 1.43(2)$, $C\text{–}C = 1.50(4)$ Å; $C\text{–}O\text{–}C = 114(2)$, $O_{alc}\text{–}C\text{–}C = 108.0(7)$, $O_{eth}\text{–}C\text{–}C = 108(1)$°. The sequences of torsion angles for the EO3 ligands are $g^-aag^+aag^-$ (O(1)–O(4)) and $g^+aag^-aag^+$ (O(5)–O(8)) and match those observed in $[Cd_2Br_4(EO3)_2]$ where similar equatorial wrapping is observed.

The tetrahedral $[CdI_4]^{2-}$ anion (depicted in Fig. 4 in its hydrogen bonding environment) has I–Cd–I angles ranging from 105.94(5) to 115.21(4)° and a mean Cd–I separation of 2.78(2) Å which is not significantly lengthened despite having four hydrogen bonding contacts [33, 34]. The I···O hydrogen bonded contacts range from 3.441(9) Å ($O(1)^a\text{–}I(4)$, $a = -\frac{3}{2}-x, -2-y, -\frac{1}{2}+z$) to 3.567(9) Å ($O(4)^b\text{–}I(2)$, $b = -1-x, -\frac{1}{2}+y, -\frac{1}{2}-z$). The hydrogen bonding forms zigzag chains perpendicular to *a*.

The reaction of the cyclic analog of EO3, 12-crown-4, with CdX_2 (X = Br, I) results in similar ion paired complexes. $[Cd(12\text{-crown-}4)_2][CdX_4]$ [19] is comprised of a disordered eight-coordinate sandwich cation and a tetrahedral $[CdX_4]^{2-}$ anion.

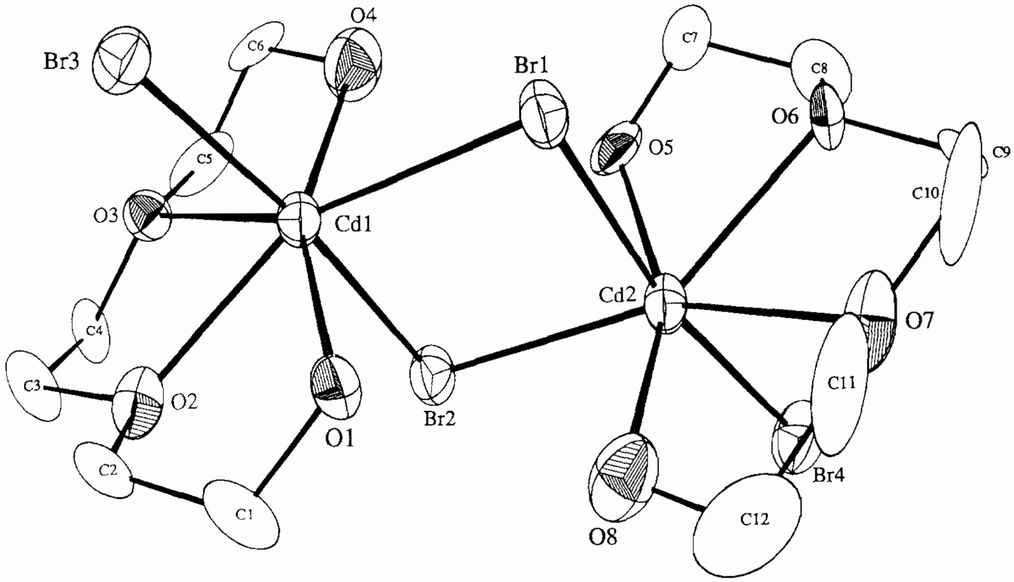

Fig. 2 $[Cd_2Br_4(EO3)_2]$

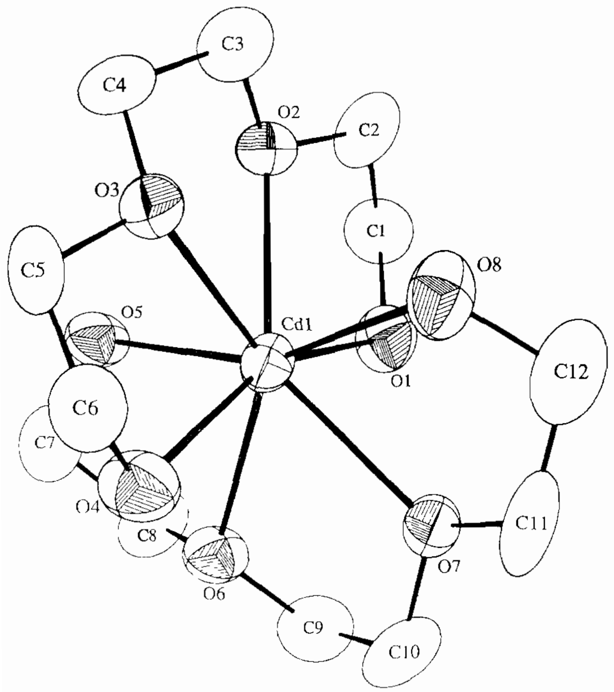

Fig. 3. The $[Cd(EO3)_2]^{2+}$ cation in $[Cd(EO3)_2][CdI_4]$.

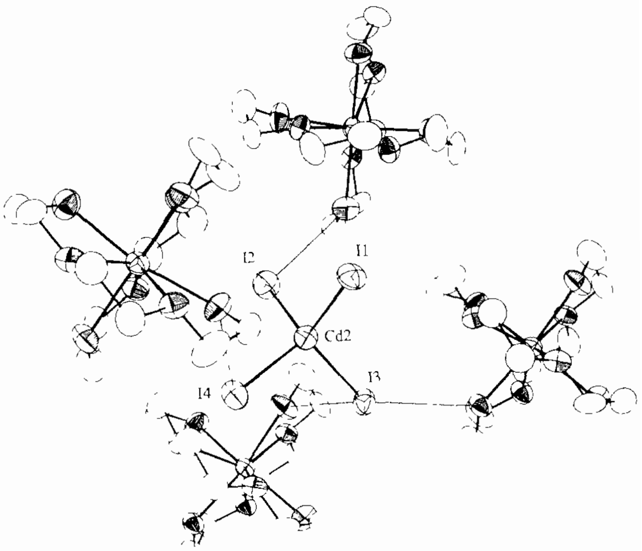

Fig. 4 The $[CdI_4]^{2-}$ anion and its hydrogen bonding contacts

Conclusions

The title complexes exemplify the range in coordination number shown by Cd^{2+}. The differences in coordination geometries observed here are a function of the halide ion, the inherent flexibility of the PEG ligand, and the hydrogen bonding. These structures demonstrate the ability of the EO3 ligand to pseudocyclize and mimic out-of-cavity crown ether coordination or to adopt nearly planar donor arrays reminiscent of in-cavity crown ether coordination. A survey of the three primary coordination modes we have found for PEG ligands reveals that helical wrapping is most commonly observed for the hard oxophilic cations Y^{3+}, La^{3+}, and the lanthanides [15, 16], while a pseudo-planar template arrangement is commonly observed in Pb^{2+} [19] and Hg^{2+} [18] complexes, and out-of-cavity cyclization closely resembling out-of-cavity crown ether coordination is prominent for Bi^{3+} [20, 21].

The hydrogen bonding capabilities of EO3 and the choice of halide ion also play important roles in the crystallization of these complexes. The chloride ion is supported in a hydrogen bonded network by the alcoholic and aquo oxygen atoms, thus the X = Cl complex contains no tight ion pairs and instead glycol bridged cationic dimers are formed. The X = Br derivative crystallizes as the more common neutral halide bridged dimer. Hydrogen bonding to the bromine atoms is weak at best. The use of the soft I^- anion allows the isolation of monomeric cations and complex anions. In these complexes the hydrogen bonding serves to separate the ions and is exclusively to iodine atoms in the anions.

Increasing the glycol chain length from the four donor EO3 to the five donor EO4 ligand should preclude the formation of coordinatively saturated complexes similar to those observed here for X = Br and I, and should lead to a new series of structures. We are currently investigating these reactions, as well as complexation studies of EO5–EO7 ligands which may lead to interesting polynuclear species.

Supplementary material

Tables listing bond distances and angles for all non-hydrogen atoms, hydrogen bonding contact geometries, least-squares planes results, torsion angles, thermal parameters, H atom coordinates, and observed and calculated structure factors are available from the authors upon request (37 pages).

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