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# Exploring control of cadmium halide coordination polymers via control of cadmium(II) coordination sites utilizing short multidentate ligands

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## Abstract

The goal of this project has been to determine the capability of a number of linear multidentate ligands to induce extended structures in cadmium halides. Metal salts of the form $CdX_2$ (X=Cl, Br, I), and for comparison $Cd(NO_3)_2$, were complexed with diethylene glycol (EO2), triethylene glycol monomethyl ether (EO3Me), triethylene glycol dimethyl ether (a glyme, EG3), diethylene triamine (EN2), and 1,3-propylenediamine (PN1). The crystal structures of 11 resulting complexes were structurally characterized including: $[Cd(EO2)_3][Cd_2I_6]$, $[Cd(EN2)_2]Cl_2\cdot H_2O$, $[Cd(EN2)_2]Br_2$, $[Cd(EN2)_2][CdI_4]$, $[CdCl_2(EO3Me)]_2$, $[CdBr_2(EO3Me)]_2$, $[Cd(NO_3)_2(EO3Me)]$, $[(CdCl_2)_2(EG3)]_n$, $[(CdBr_2)_2(EG3)]_n$, $[CdI_2(EG3)]$, and $[CdI_2(PN1)]_n$. While each structure is interesting in its own right, the continued observance of a wide variety of coordination modes for such similar ligands does little to help improve the predictability of simple $Cd^{2+}$ coordination compounds.

*Keywords:* Cadmium(II) halide; Coordination polymer; Polyethylene glycol; Glyme; Diethylene triamine

## 1. Introduction

We [1–4] and others [5–23] have explored the rich chemistry of cadmium(II) coordination polymers (a) via complexation of $Cd^{2+}$ salts with multifunctional ligands (e.g. bipyridyl, pyrimidine, pyrazine, tetrapyridylporphyrin, etc.) where the ligand is responsible for the extended structure, (b) via complexation of $CdX_2$ salts where halide bridges support the extended structures, and indeed (c) where both multifunctional ligand and halide are responsible for the coordination polymer. In previous work with crown ethers and one of its open chain linear analogs, triethylene glycol (EO3), we observed a variety of structures, many of which were unanticipated. The structural diversity observed included (a) monomers $[Cd(NO_3)_2(15\text{-crown-}5)]$ [2], $[Cd(NO_3)_2(18\text{-crown-}6)]$ [2], $[Cd(15\text{-crown-}5)(OHMe)(\mu\text{-}Br)CdBr_3]$ [3]; (b) dimers with halide bridges $[Cd(15\text{-crown-}5)(\mu\text{-}Br)_2CdBr(\mu\text{-}Br)]_2$ [3], $[Cd_2Br_4(EO3)_2]$ [4]; (c) dimers with hydrogen bonding $[Cd_2(EO3)_2(\mu\text{-}EO3)]Cl_4\cdot 2H_2O$ [4]; (d) coordination polymers via chloride bridging $[(CdCl_2)_2CdCl_2(15\text{-crown-}5)]_n$ [3]; (e) hydrogen bonded polymers $[CdI_2(OH_2)_2(THF)]\cdot$benzo-15-crown-5 [3], $[Cd(OH_2)_2(15\text{-crown-}5)][CdI_3(OH_2)]_2\cdot 2(15\text{-crown-}5)\cdot 2CH_3CN$ [3]; and even (f) charge separated ions (with or without hydrogen bonding) $[(NH_4)(\text{benzo-}15\text{-crown-}5)_2]_2[Cd_2I_6]$ [3], $[(NH_4)(\text{benzo-}15\text{-crown-}5)_2][Cd_2I_6]$ [4], $[Cd(EO3)_2][CdI_4]$ [4].

While crown ethers are in general limited in coordinative ability due to the formation of a cavity in which the metal ion may or may not fit, the open chain analogs are flexible enough to adapt to a variety of coordination geometries. Thus, ligands such as polyethylene glycols and their monomethyl or dimethyl ether derivatives may offer better control over the resulting $Cd^{2+}$ coordination sphere, by simply increasing or decreasing the chain length. These noncyclic ligands also have the possibility of coordination in a bridging mode where the polyether chelates one $Cd^{2+}$ metal ion and also bridges to an additional $Cd^{2+}$ ion resulting in dimers or polymers.

We were, thus, interested in whether by limiting the size of the polyethylene glycol chain, by varying the end groups between alcohols and ethers, or by changing the nature of the donor atoms, we could limit the number of $Cd^{2+}$ coordination sites utilized, and facilitate controlled coordination polymers

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via halide bridging. To this end, we reacted metal salts of the form $CdX_2$ (X = Cl, Br, I), and for comparison $Cd(NO_3)_2$, with diethylene glycol (EO2), triethylene glycol monomethyl ether (EO3Me), triethylene glycol dimethyl ether (a glyme, EG3), diethylene triamine (EN2), and 1,3-propylenediamine (PN1).

The crystallographic results to date are mixed and consistent control of these coordination complexes is still elusive. This will be illustrated herein with 11 coordination complexes including: $[Cd(EO2)_3][Cd_2I_6]$, $[Cd(EN2)_2]Cl_2 \cdot H_2O$, $[Cd(EN2)_2]Br_2$, $[Cd(EN2)_2][CdI_4]$, $[CdCl_2(EO3Me)]_2$, $[CdBr_2(EO3Me)]_2$, $[Cd(NO_3)_2(EO3Me)]$, $[(CdCl_2)_2(EG3)]_n$, $[(CdBr_2)_2(EG3)]_n$, $[CdI_2(EG3)]$, and $[CdI_2(PN1)]_n$.

## 2. Experimental

### 2.1. General synthetic scheme and X-ray data collection

Unless otherwise noted, 0.50 mmol of each $Cd^{2+}$ salt was dissolved in 5 mL of a 3:1 $CH_3CN:CH_3OH$ mixture followed by the addition of the ligand in a 1:1 metal:ligand molar ratio. The solutions were then stirred at 60 °C for 1 h followed by centrifugation to remove any precipitate. The supernatants were decanted and stored at 3 °C for 24 h followed by slow evaporation at ambient temperature to yield crystals suitable for single crystal X-ray diffraction. Slight variations in this protocol are noted below as appropriate.

Diffraction data for $[Cd(EN2)_2]Cl_2 \cdot H_2O$ and $[CdI(EN2)_2][CdI_4]$ were collected with a Siemens CCD area detector-equipped diffractometer with Mo Kα graphite monochromated radiation. Data collection for all other complexes was obtained with an Enraf-Nonius CAD4 diffractometer also using Mo Kα graphite monochromated radiation. All data were treated for absorption using empirical psi-scan data. The space groups assigned were determined by systematic absences and, in those cases where multiple space group possibilities existed, by successful solution and refinement of the structures. The structures were solved by direct methods and refined using the SHELXTL v.5.03 software package unless otherwise noted.

All non-hydrogen atoms were, absent of notation otherwise, anisotropically refined and the geometrically constrained hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon and allowed to ride on that atom. When present, the methyl hydrogen atoms were included as a rigid group with rotational freedom at the bonded carbon atom (C–H = 0.95 Å). Features, such as disorder, specific to each crystallographic study are noted below and a summary of all data collection and refinement parameters are provided in Table 1.

### 2.2. $[Cd(EO2)_3][Cd_2I_6]$

After mixing, the solution was stirred at 60 °C for 1 h followed by storage for ca. 14 h, producing crystalline material. The EO2 ligand, which resides on a twofold axis was found to be disordered with alternate positions for the ethylene carbon atoms. C5 and C6 were refined in two alternate positions, each with 50% occupancy, along with the fixed associated hydrogen atoms. The terminal alcoholic hydrogen atoms were not included in the final refinement.

### 2.3. $[Cd(EN2)_2]Cl_2 \cdot H_2O$

The hydrogen atoms bonded to the carbon atoms, terminal nitrogen atoms, and to the water molecule were located from a difference Fourier map and allowed to ride on the bonded atom with a thermal parameter 1.2 times that of the bonded atom.

### 2.4. $[Cd(EN2)_2]Br_2$

After mixing, the solution was stirred at 60 °C for 1 h followed by storage for ca. 14 h, producing crystalline material. The amine hydrogen atoms were not included in the final refinement.

### 2.5. $[Cd(EN2)_2][CdI_4]$

After mixing, the solution was stirred at 60 °C for 1 h followed by storage for ca. 14 h, producing crystalline material. The space group was determined to be either the centric I4/*mmm* or the acentric *I*422, *I*4*mm*, *I*-42*m*, or *I*-4*m*2 from systematic absences. The subsequent refinement and solution was carried out in the acentric space group *I*-4*m*2.

Both ions reside on crystallographic −42m sites, however, the cation is disordered, while the anion is ordered. In the cation, N1 resides on a mirror plane and is present at 100% occupancy. N2 also resides on a mirror site, but is fractionally disordered across an mm site and is present at 50% occupancy. The ethyl groups are also fractionally disordered and present at 50% occupancy. The ethyl group disorder manifests itself as ± gauche disorder in the N–C–C–N torsion angles.

Despite resolution of the disorder models, the thermal ellipsoids for the C atoms and especially for N2 are elongated. The disorder model appears to account for most, but possibly not all of the disorder present. Due to this severe disorder, the hydrogen atoms were not included in the final refinement, but all non-hydrogen atoms were successfully anisotropically refined.

### 2.6. $[CdX_2(EO3Me)]_2$ (X = Cl and Br) and $[Cd(NO_3)_2(EO3Me)]$

The terminal alcoholic hydrogen atom in each case was located from a difference Fourier map and allowed to ride on the bonded atom with a thermal parameter tied to that of the bonded atom.

### 2.7. $[(CdX_2)_2(EG3)]_n$ (X = Cl, Br)

The glyme resides on a center of inversion and the C1–C2 ethyl group is disordered 61%/39% into alternate positions. The hydrogen atoms on the disordered carbon atoms were not included in the final refinement.