Ethylenediamine as a bridging ligand: structure solution of two cadmium(II)-based coordination polymers from powder diffraction data

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Structures of $[Cd(C_2H_8N_2)Cl_2]_n$ **(1)** and $[Cd(C_2H_8N_2)Br_2]_n$ **(2)** were solved from powder diffraction data. Compound **(1)** crystallizes in the space group *Pbam* (No. 55), $a = 9.9021(7)$ Å, $b = 7.8186(6)$ Å, $c = 4.0705(3)$ Å, $V = 315.13(3)$ Å^3, $Z = 2$. **(2)** is isostructural: space group *Pbam* (No. 55), $a = 10.405(2)$ Å, $b = 7.8634(8)$ Å, $c = 4.2079(5)$ Å, $V = 344.28(6)$ Å^3, $Z = 2$. The investigated compounds are examples of two-dimensional hybrid coordination polymers, in which neighboring metal centers are bridged via both organic and inorganic moieties: ethylenediamine molecules and halide anions. Both crystal structures were solved *ab initio* from powder data using direct methods. © *2013 International Centre for Diffraction Data.* [doi:10.1017/S0885715613000146]

Key words: cadmium(II) diamine complexes, coordination polymers, Rietveld method, powder diffraction, ethylenediamine

I. INTRODUCTION

Although predominantly occurring as a chelating agent, ethylenediamine (for simplicity, further denoted as **en**) has been observed to possess the capacity to act as a bridging ligand as well. Various coordination polymers have been reported so far with **en** linking neighboring metal centers such as: Co(II) (Lauchan *et al.*, 2008), Zn(II) (Pritchard *et al.*, 2001), or Ag(I) (Näther and Beck, 2004).

Cd(II) coordination arrays with extended structures formed via small anionic bridges are numerous (Zhou *et al.*, 2003; Xia *et al.*, 2004; Abu-Youssef, 2005). Examples of **en** connecting Cd(II) centers, whether exclusively or together with other types of bridging ligands present, are also known in the literature (Shen *et al.*, 2002; Yilmaz *et al.*, 2005).

Two polymeric compounds presented here, $[Cd(en)Cl_2]_n$ and $[Cd(en)Br_2]_n$, have already been synthesized and examined by means of thermogravimetry analysis, IR and Raman spectroscopy (Iwamoto and Shriver, 1971; De and Chaudhuri, 1984). Investigations revealed the presence of bridging *trans* **en** ligands. The authors, however, having assumed cubic, tetragonal, or hexagonal lattices, failed in their attempts to index the powder diffraction patterns they obtained (and therefore never submitted them for publication). To the best of our knowledge, no one else has successfully tried to solve the crystal structures of these polymers prior to this paper.

II. EXPERIMENTAL

A. Synthesis

Poly[cadmium(II)-di-µ-chloro-µ-(ethylenediamine-N,N')] **(1)** and poly[cadmium(II)-di-µ-bromo-µ-(ethylenediamine-N,N')] **(2)** were obtained from aqueous solutions of 8 mmol of CdX_2 (1.82 g $CdCl_2{\cdot}H_2O$ and 2.18 g $CdBr_2$, respectively). After heating to 60–70 °C, 8 mmol of ethylenediamine (0.53 ml) was added dropwise to each of the solutions. White precipitates were formed immediately and were collected after a few days (aging process), washed with 2-propanol and dried at 60 °C. They were air stable and not affected by moisture.

The same synthetic procedure was applied to obtain a CdI_2-based analogous polymer, but consecutive approaches yielded only bis[tris(ethylenediamine-*N*,*N*′)-cadmium] tetraiodocadmate diiodide complex, $[Cd(\mathbf{en})_3]_2[CdI_4]I_2$ (Wieczorrek and Tebbe, 1998). This is in agreement with the predictions of Iwamoto and Shriver (1971), who argued that **en** bridging in CdI_2 system would be energetically unfavorable.

B. Data collection

X-ray diffraction patterns of mortar-and-pestle-ground, back-loaded, pressed specimens were taken at room temperature using an X'Pert Pro MPD diffractometer (see details in Table I). Experiments were carried out in Bragg-Brentano geometry. Peak positions were determined with software from the PROSZKI package (Łasocha and Lewiński, 1994).

Program ITO-12 (Visser, 1969), included in the PROSZKI was used for indexing purposes. Structures were solved using

TABLE I. Parameters of X-ray powder diffraction measurements.

Diffractometer	X'Pert Pro mpd
Radiation	Cu*Kα*
Generator	40 kV, 30 mA
Monochromator	Graphite, on a secondary beam
Detector	PSD, PIXCEL
Geometry	Bragg-Brentano
Angular range	10 – 80 [°] 2θ
Step size (interpolated)	0.02 [°] 2θ
Incident and anti-scatter slits	Fixed, ¼ and ½ [°]

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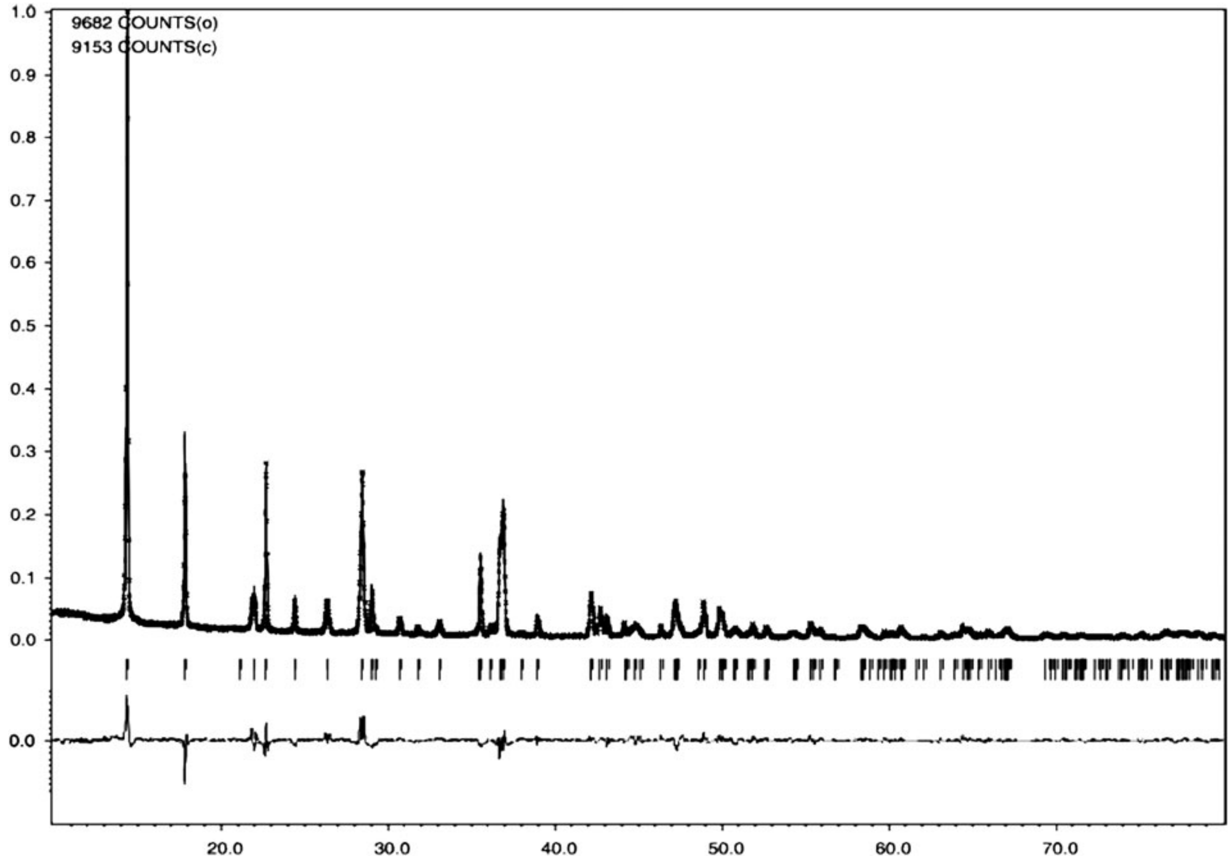

Figure 1. Observed (black, straight line), calculated (red, crosses), and difference (blue, straight line) Rietveld profiles for (**1**). Green (vertical) bars indicate the positions of Bragg reflections.

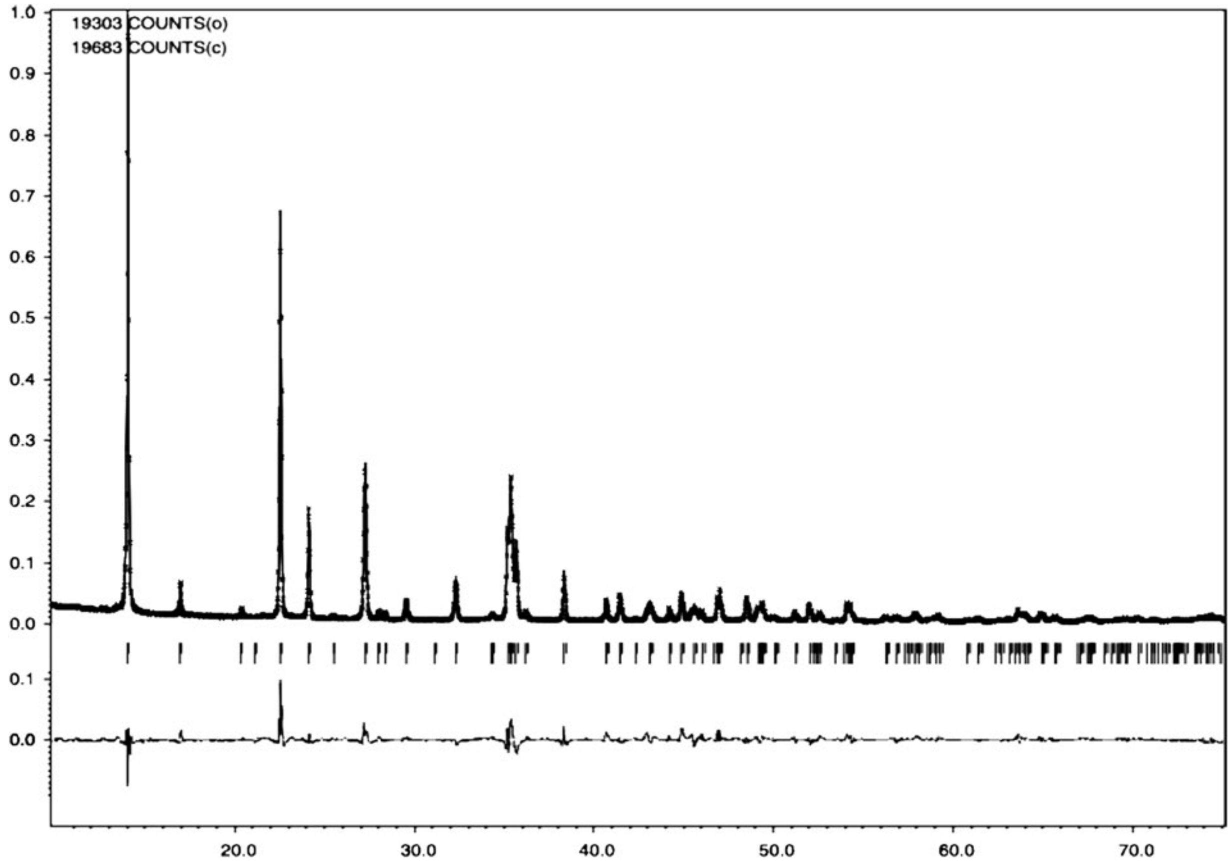

Figure 2. Observed (black, straight line), calculated (red, crosses), and difference (blue, straight line) Rietveld profiles for (**1**). Green (vertical) bars indicate the positions of Bragg reflections.

TABLE II. Crystal data and structure refinement details for **(1)** and **(2)**.

	(1)	(2)
Formula	$[CdCl_2(C_2H_8N_2)]_n$	$[CdBr_2(C_2H_8N_2)]_n$
Molecular weight (g/mol)	235.35	324.25
System	Orthorhombic	Orthorhombic
Space group	*Pbam* (No. 55)	*Pbam* (No. 55)
a (Å)	9.9021(7)	10.405(2)
b (Å)	7.8186(6)	7.8634(8)
c (Å)	4.0705(3)	4.2079(8)
Volume (Å^3)	315.13(3)	344.28(5)
Z	2	2
F_N	$F_{30} = 140.1$ (0.005 77, 37) $M_{30} = 83.46$ (0.000 05, 37)	$F_{20} = 63.6$ (0.0115, 41) $F_{23} = 35.0$ (0.000 10, 41)
Number of atoms	6	6
Number of reflections	119	109
March–Dollase formula: [uvw], G	[110], 0.89	[110], 0.93
R_p (%), R_{wp} (%)	10.08, 13.13	10.60, 14.36
R_F (%)	4.79	7.46

TABLE III. Atomic coordinates and isotropic displacement parameters for **(1)**.

Atom	Position	x	y	z	U_{iso} [Å^2]
Cd	2c	1/2	0	0	0.024(3)
Cl	4h	0.6726(16)	−0.0688(16)	1/2	0.015(6)
C	4g	0.528(3)	−0.407(3)	0	0.112(19)
N	4g	0.420(4)	−0.294(4)	0	0.112(19)
H_C	8i	0.5814	−0.3895	0.1948	0.1348
H_N	8i	0.3704	−0.3113	0.1746	0.1348

TABLE IV. Atomic coordinates, occupancies, and isotropic displacement parameters for **(2)**.

Atom	Position	x	y	z	U_{iso} [Å^2]
Cd	2c	1/2	0	0.0	0.032(7)
Br	4h	0.6765(12)	0.065(2)	1/2	0.040(7)
C	4g	0.467(6)	−0.417(5)	0.0	0.04(4)
N	4g	0.558(7)	−0.279(7)	0.0	0.07(3)
H_N	8i	0.615	−0.2963	−0.1474	0.084
H_C	8i	0.413	−0.4086	−0.1854	0.048

TABLE V. Selected interatomic distances (Å) and angles (°) for **(1)**.

Cd–Cl	4 × 2.703(10)	Cd–N	2 × 2.43(3)
C–C^{iv}	1.55(3)	C–N	1.39(4)
Cl–Cd–Cl^{i}	96.8(4)	Cd–Cl–Cd^{iv}	96.8(5)
Cl–Cd–Cl^{ii}	180.0(5)	Cd–N–C	111(2)
Cl–Cd–N	91.1(6)	N–C–C^{iv}	109(3)
N–Cd–N^{iii}	180.0(5)		

Symmetry codes: (i) $x, y, z-1$, (ii) $-x+1, -y, z-1$, (iii) $-x+1, -y, z$, (iv) $-x+1, -y-1, z$

TABLE VI. Selected interatomic distances (Å) and angles (°) for **(2)**.

Cd–Br	4 × 2.837(7)	Cd–N	2 × 2.28(6)
C–C^{v}	1.48(6)	N–C	1.44(8)
Br–Cd–Br^{i}	95.1(2)	Cd–Br–Cd^{vi}	95.1(3)
Br–Cd–Br^{ii}	180.0(5)	Cd–N–C	123(5)
Br–Cd–N	90.1(13)	N–C–C^{v}	111(5)
N–Cd–N^{iii}	180.0(5)		

Symmetry codes: (i) $x, y, z-1$; (ii) $-x+1, -y, z-1$; (iii) $-x+1, -y, z$; (iv) $x, y, -z$; (v) $-x+1, -y-1, z$; (vi) $x, y, z+1$.

the direct methods program EXPO2004 (Altomare *et al.*, 2004). Crystal structure refinement was carried out by using the JANA2006 (Petricek *et al.*, 2006) program. The pseudo-Voigt function was used to generate the line shape of the diffraction peaks. A total of 43 parameters were refined, including scale factor, background, zero point, unit-cell parameters, and fractional coordinates as well as those describing peak shape, width, and peak asymmetry. C–C and C–N distances in **en** molecules were weakly restrained to 1.54(±0.02) and 1.44(±0.04) Å, respectively. Hydrogen atoms were placed in idealized positions (by JANA2006 program assuming sp^3 hybridization) and not refined.

Tabulated powder diffraction data have been sent to the International Centre for Diffraction Data (ICCD), where they have been accepted and assigned PDF numbers 00-061-11059 and 00-061-11058, respectively.

III. RESULTS AND DISCUSSION

Figures 1 and 2 show the powder diffraction patterns of the investigated compounds together with the results of

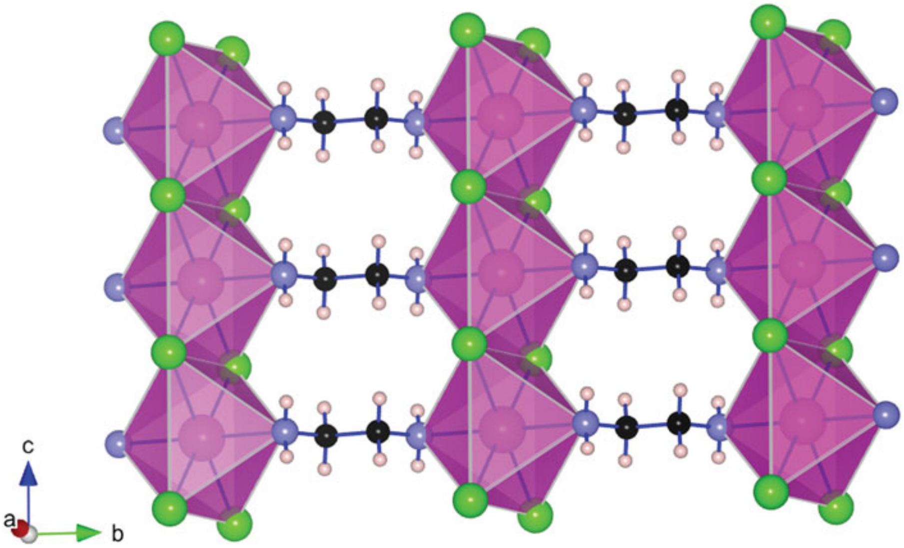

Figure 3. Hybrid organic–inorganic layer of **(1)** showing octahedral coordination environment of Cd^{2+} ions. Cd = pink(octahedron centre), Cl = green (vertices), N = gray (medium), and C = black (small). The smallest circles represent hydrogen atoms.

Rietveld analysis (peak positions, calculated, and difference curves). In both cases, Bragg reflections were indexed based on an orthorhombic unit cell; obtained unit-cell parameters and figures of merit F_N (Smith and Snyder, 1979) are given in Table II. Both compounds were found to be isostructural, crystallizing in the space group *Pbam* (No. 55). There are two formula units in one unit cell of each compound. The refined structural parameters are listed in Tables III and IV and selected interatomic distances and angles in Tables V and VI.

X-ray structural analysis of **(1)** reveals a neutral polymeric coordination compound. As shown in Figure 3, the coordination environment of each Cd(II) center consists of two N-donor atoms from **en** molecules in *trans* coordination and four chloride anions to constitute a distorted octahedron. Adjacent Cd coordination octahedra share Cl–Cl (or Br–Br) edges, thus forming one-dimensional chains spreading infinitely along the *c*-direction. Two **en** molecules interconnect Cd centers on alternate sides of these chains; as a result, two-dimensional sheets are created (see Figures 3 and 4).

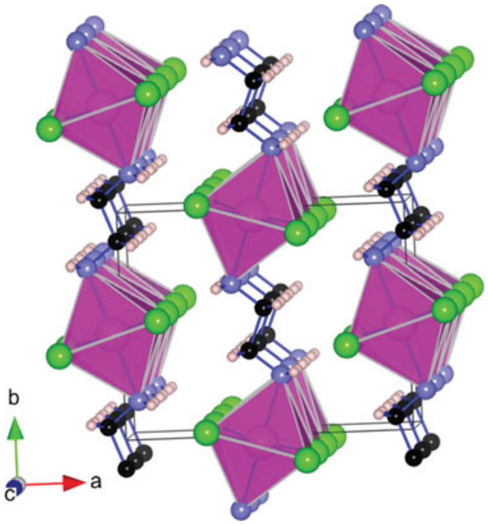

Figure 4. Packing of 2D layers in **(1)**. Notations of atoms are the same as in Figure 3.

It has already been stated that the chloride and bromide polymers are isostructural. Distances between neighboring Cd centers were found to be 4.042 Å in **(1)** and 4.185 Å in **(2)**, more than the sum of their van der Waals radii ($r_{vdW\_Cd} = 1.58$ Å), thus excluding metal–metal interactions. Cd–Cl bonds of 2.703(10) Å agree well with data on Cd–halide complexes gathered by Bailey and Pennington (1997), whereas Cd–Br bonds of 2.837(7) Å are a little bit longer [$Cd–Cl_{range}$: 2.576(7)–2.731(2) Å; $Cd–Br_{range}$: 2.691 (1) – 2.819(2) Å]. For both polymers, Cd–N bonds of 2.43 (6) Å in **(1)** and 2.28 (6) Å in **(2)** fit within the range found in similar compounds by Strasdeit *et al.* (1988) [$Cd–N_{aliphatic}$ range: 2.25(1) – 2.44(1) Å].

The substitution of Cl by Br in **(2)** is responsible for lengthening of Cd–halide and slight contraction of Cd–N bonds. Similar trends were observed and reported for a series of cadmium halide complexes with other N-coordinating ligands (Strasdeit *et al.*, 1988). These changes could indicate a tendency to lower the coordination number of cadmium from 6 to 4 because of steric hindrance, with the greater size of the anion when moving down the series, accompanied by the softer character of the heavier halide, resulting in increased electronic density at the metal centre. This chain of arguments serves, then, as another explanation of our unsuccessful attempts to obtain $[Cd(en)I_2]_n$.

IV. CONCLUSION

It is worth noting that the crystal structure solution of **(1)** and **(2)** from powder diffraction data corroborates the structural model of Iwamoto and Shriver (1971) of cadmium (II) halide polymers with bridging **en** ligands in *trans* coordination and illustrates in an elegant manner the complementary character of solid state investigation methods. By contemporary powder diffraction methods, interesting but quite old scientific problems concerning crystal structure of cadmium (II) diamine complexes (described so far by IR, RS, and TGA methods only), could be easily solved.

Crystal structure data have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 911610 {**1**} and 911611 {**2**}, and can be obtained on request.

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Abu-Youssef, A. M. A. (**2005**). "Two new 1D cadmium(II) azido complexes: *catina*-poly[di-$\mu_{1,1}$-azido(2,2′-bipyridyl)cadmium(II)] and a new polymorph of *catina*-poly[di-$\mu_{1,1}$-azido (2-acetylpyridine)cadmium(II)]," J. Coord. Chem. **58**, 1377–1386.

Altomare, A., Caliandro, R., Camalli, M., Cuocci, C., Giacovazzo, C., Moliterni, A. G. G., and Rizzi, R. (**2004**). "Automatic structure determination from powder data with *EXPO2004*," J. Appl. Crystallogr. **37**, 1025–1028.

Bailey, R. D. and Pennington, W. T. (**1997**). "Cadmium(II) halide complexes of pyrazine," Polyhedron **16**, 417–422.

De, G. and Chaudhuri, N. R. (**1984**). "Thermal investigations of cadmium(II) diamine complexes in the solid phase," Thermochim. Acta **77**, 1–11.

Iwamoto, T. and Shriver, D. F. (**1971**). "Vibrational spectra of *catena*-μ-ethylenediamine complexes of zinc(II), cadmium(II) and mercury(II) with the formula M(en)X_2," Inorg. Chem. **10**, 2428–2432.

Łasocha, W. and Lewiński, K. (**1994**). "Proszki – a system of programs for powder diffraction data analysis," J. Appl. Cryst. **27**, 437–438.

Lauchan, S., Prior, T. J., Meansiri, S., and Rujiwatra, A. (**2008**). "Cobalt(ethylenediamine) sulfate: a pillared layered coordination polymer," J. Inorg. Organomet. Polym. **18**, 352–357.

Näther, C. and Beck, A. (**2004**). "Synthesis, crystal structure and thermal properties of silver(I) bromide ethylenediamine coordination polymers," Z. Naturforsch. **59b**, 992–998.

Petricek, V., Dusek, M., and Palatinus, L. (**2006**). *JANA2006. Structure Determination Software Programs* (Institute of Physics, Praha, Czech Republic).

Pritchard, R. G., Eaton, N., McDonald, S., and Strickland, P. (**2001**). "Catena-poly[dibromozinc(II)-μ-ethylenediamine-N:N']: resolution of structural anomalies resulting from the interpretation of vibrational spectra," Acta Cryst. **C57**, 672–673.

Shen, L., Xu, D., Liu, J., and Xu, Y. (**2002**). "Synthesis and crystal structure of a polymeric heteronuclear complex of cadmium(II) and silver(I)," J. Coord. Chem. **55**, 301–307.

Smith, G. S. and Snyder, R. L. (**1979**). "F_N: a criterion for rating powder diffraction patterns and evaluating the reliability of powder-pattern indexing," J. Appl. Crystallogr. **12**, 60–65.

Strasdeit, H., Saak, W., Pohl, S., Driessen, W. D., and Reedijk, J. (**1988**). "Synthetic and structural studies on the novel nitrogen ligand 2,5,8,10,13,16-hexaazapentacyclo[8.6.1.1^{2,5}.0^{9,18}.0^{13,17}] octadecane and its reaction products with methanolic cadmium halogenide solutions: C_i-$C_{12}H_{22}N_6$, [CdX_2(C_2-$C_{12}H_{22}N_6$)] (X = Cl, Br, I), and [$CdI_2(C_{12}H_{23}N_6OCH_3)$]]," Inorg. Chem. **27**, 1557–1563.

Visser, J. W. (**1969**). "A fully automatic program for finding the unit cell from powder data," J. Appl. Cryst. **2**, 89–95.

Wieczorrek, C. and Tebbe, K. -F. (**1998**). "Bis[tris(1,2-ethandiamin) cadmium]-tetraiodocadmat-diiodid," Acta Cryst. **C54**, 1804–1807.

Xia, S. -Q., Hu, S. -M., Dai, J. -C., Wu, X. -T., Fu, Z. -Y., Zhang, J. -J., and Du, W. -X. (**2004**). "Syntheses and structures of 1D, 2D, 3D cadmium(II) coordination polymers with oxalate and aromatic co-ligands," Polyhedron **23**, 1003–1009.

Yilmaz, F., Yilmaz, V. T., and Kazak, C. (**2005**). "Bis-(5,5'-diethylbarbiturato) copper(II) and cadmium(II) complexes with ethylenediamine. Synthesis, crystal structures, spectroscopic and thermal characterization of *cis*-[Cu(barb)$_2$(en)] and {[Cd (barb)$_2$(μ-en)]·2H_2O}$_n$," Z. Anorg. Allg. Chem. **631**, 1536–1540.

Zhou, Y. -F., Xu, Y., Yuan, D. -Q., and Hong, M. -C. (**2003**). "The chain structure of catena-poly-[[(2,2'-bipyridine)cadmium(II)]-di-μ-chloro]," Acta Cryst. **E59**, m821–m823.