Synthesis, spectral, thermal, crystal structure, Hirschfeld analysis of [bis(triamine) Cadmium(II)][Cadmium(IV)tetra-bromide] complexes and their thermolysis to CdO nanoparticles

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Abstract

Background: The coordination chemistry of cadmium(II) with diamine ligands is of particular interest. The most common structure around cadmium(II) center in their complexes is tetrahedral, that is due the octet rule obeyed. Nevertheless, five and six-coordinated complexes are also well known. Now a day, many cadmium(II) complexes with chelate ligands were synthesized for their structural or applications properties. Antibacterial activities and DNA binding affinity of this class of cadmium complexes have attracted considerable interest.

Results: Cadmium(II) complexes in dicationic form with general formula [Cd(dien)₂]CdBr₄ complex 1 (dien = diethylenetriamine) and [Cd(dipn)₂]CdBr₄ complex 2 (dipn = diproylenetriamine) were prepared and elucidated there chemical structures by elemental analysis, UV–Vis, IR, TG and NMR, additionally complex 1 structure was solved by X-ray diffraction study. The Cd(II) cation is located in a slightly distorted octahedral geometry while Cd(IV) anion is in tetrahedral geometry. High stability of the synthesized complexes confirmed by TG. Thermolysis of complex 1 revealed the formation of pure cubic nanoparticles CdO which was deduced by spectral analysis. The average size of CdO nanoparticles was found to be ~60 nm.

Conclusions: Two new Cd(II) complexes of general formula [Cd(N₃)₂]CdBr₄ were made available. The structure of [Cd(dien)₂]CdBr₄ was confirmed by X-ray diffraction. Thermal, electro and spectral analysis were also investigated in this study. The direct thermolysis of such complexes formed a cubic CdO regular spherical nanoparticle with the ~60 nm average particle size.

Keywords: Cadmium(II) complexes, Triamine, XRD, CdO nanoparticles

Background

Cadmium(II) complexes with polydentate nitrogen ligands, mainly polyamines, have been studied for some time either because of their structural properties [1, 2] or their applications [3–7]. The synthesis and characterization of triamine complexes of transition and non-transition metals are of interest as they can potentially exist in three isomeric forms, i.e. mer and fac [8, 9]. The shape of cadmium(II) halide complex anions depending on the number of hydrogen bonds and the cations species [2–5]. There are variable shapes of the complex anions such as tetrahedral [10, 11], two-dimensional layered structures [12], and complex chain structures [13–15]. Cadmium complexes have attracted considerable interest due to...
pharmacological importance including anti-microbial agents [4], DNA binding affinity [3], and anticancer activities [5–7, 16, 17].

The design and development of novel functional materials utilizing non-covalent interactions in complexes have attracted considerable attention [17–20]. Various weak dispersive interactions, such as hydrogen bonding and other weak interactions involving π-cloud of the aromatic ring represents the backbone of self-assembly process to stabilize the crystals [22]. Hydrogen bonding interactions are the most reliable and widely used in building multidimensional supramolecular structures [21–23].

In the last decade, spherical shape metal oxide nanoparticles [24] composed of a mixed-ligand dinuclear and mononuclear cadmium(II) complexes building blocks [25–28]. We reported the synthesis and characterization of two new dicationic cadmium(II) complexes with general formula [Cd(N3)2]CdBr4. Complex I used as building block for preparation the CdO nanoparticles by direct open atmosphere thermolysis process.

**Results and discussion**

**Synthesis of the desired complexes**

Two new dicationic Cd(II) complexes with general formula [Cd(N3)2]CdBr4 have been prepared by mixing of excess of the tridentate free ligands with CdBr2*2.5H2O in EtOH under open ultrasonic atmosphere. The dicationic Cd(II) complexes were prepared in very good yield without side products, as seen in Scheme 1.

The X-ray single crystal diffraction technique used to confirm the structure of the target complex I and other spectral analysis including elemental analysis, IR, UV–vis, TG/DTA, CV and NMR. The isolated complexes are stable in air, soluble only in water, DMF and DMSO. The dicationic natural was supported by high water solubility (0.02 g/ml at RT) and molar conductance (\(\Lambda M = 190 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}\) of \(1 \times 10^{-3}\text{M}\) at RT) showed that the two complexes are electrolytic in their nature. The analytical data of the [Cd(dien)2]CdBr4 desired complex consisted with XRD analysis data. The TG-residue product of complex I revealed the formation of CdO cubic nanoparticle [23]. The genital heating with fixed heat of rate as well as the N-tridentate ligands may play the critical role in de-structure of the desired complexes to CdO nanoparticles.

**X-ray crystal structure of complex 1**

An asymmetric unit cell consists of two Cd\(^{2+}\) ions of which one is a cation and the other counter ion, two dien fully coordinated to the Cadmium cation center. An N6 coordinated complex is formed. The Cd(II) cation are

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**Scheme 1** Synthesis of the desired complexes
located in a slightly distorted octahedral geometry while Cd(IV) counter anion are in tetrahedral geometry seen in Fig. 1. The bond length between the Cd(IV) anions and the bromine atoms are in the expected range except for the elongation of Br3 atom which is actively involved in the hydrogen bonding as seen in Fig. 2. This type of hydrogen bonding helps in the better stabilization of the crystal structure. A study of torsion angles, asymmetric parameters and least-square plane calculations reveals that one of the four five membered ring the ring adopts an envelope conformation with the atoms N10 and N13 deviating 0.230 (3) and −0.109 (3) Å respectively from the Cremer and Pople plane [29]. This is confirmed by the puckering parameters \( Q = 0.472 (3) \) Å and \( \phi = 255.5 (3) \) Å. The other three five membered rings adopts a twisted conformation on the bonds C8–C9, C15–C16 and C18–C19 respectively. The structure exhibits both inter and intramolecular hydrogen bonds of the N–H…Br and C—H…Br which helps in stabilizing the crystal structure [14, 15]. Packing of the molecules when viewed down along the \( a \) axis indicates that the molecules exhibit layered stacking and several hydrogen bonds as seen in Fig. 3. The crystal data deposited and can be retrieved via CCDC 1404033.

IR spectrum

The IR spectrum of complex 1 is depicted in Fig. 4. Complex 1 revealed three main characteristic absorptions peaks in the range 3180–3300, 2780–2850 and 650–450 \( \text{cm}^{-1} \), which was assigned to N–H, C–H alkyl and Cd–N stretching vibrations, respectively [25–27]. No water was recorded in the structures of the complexes. The chemical shifts of N–H functional groups of dipen coordinated to the Cd(II) center in the complexes was shifted down filed by ~60 \( \text{cm}^{-1} \) compared by the free one, this support the tridentate ligand full coordination to the Cd(II) center.

UV–Vis spectral study

The UV–Vis absorption spectra of the complex 1 and complex 2 in water solvent presented one sharp dominant bands at 270 and 280 nm respectively, no other bands were detected elsewhere, as seen in Fig. 5. The cadmium centers showed only the charge transfer transitions which can be assigned to charge transfer from the metal to ligand and vice versa (d—σ* electron transfer), no absorption resonated to \( \pi–\pi^* \) electron transfer (dien and dipn ligands are saturated) or d–d transition are expected for d10 Cd(II) complexes [30, 31].

NMR investigation

The \(^1\)H and \(^{13}\)C\(^{[\text{1}]}\)H NMR spectra of the synthesized complexes were carried out in \(d^6\)-DMSO solvent to confirm the binding of the dien ligands to the cadmium(II) in 2:1 ratio respectively. The \(^1\)H and \(^{13}\)C\(^{[\text{1}]}\)H NMR spectra corroborate the structure of the desired complexes as well as the XRD; only three functional groups, \(^1\)H NMR (\(d^6\)-DMSO): d (ppm) 2.55 and 2.62 (2 br, 16H, 8CH\(_2\)), 2.85 (br, 8H, 4NH\(_2\)), 3.35 (br, 2H, 2NH), signals belonging to the CH\(_2\)CH\(_2\) and NH\(_2\) of dien ligand coordinated with CdBr\(_2\) were recorded, as depicted in Fig. 6.

TG analysis

The TG of the complex was carried out in the range of 0–800 °C and 10 °C/min heating rate, typical thermal TG curve are given in Fig. 7 which shows that there is no coordinated or uncoordinated water in the range 0–180 °C. Also organic and inorganic contents were destructured away (to CO\(_2\), NO\(_x\) gas product) from the Cd(II) metal center in one step decomposition in range 290–500 °C with ~80 % weight loss. The final product (20 % residue) was confirmed to be CdO by IR [32–34].

CdO nanoparticle formed by direct thermolysis of complex 1

The phase information and composition of the TG final residue produced through open atmosphere thermolysis of complex 1 was deduced by FT-IR, X-ray powder diffraction (XRD), EDX, SEM and TEM. The product was characterized as CdO nanoparticles.

Figure 8 shows the IR spectrum product CdO nanoparticle, the formation of CdO nanoparticle was supported by two signs vibration at 420 and 560 cm\(^{-1}\) belongs to Cd=O bond, it could be useful in understanding the bonding between the Cd–O atoms [32]. All the other vibration assigned to the starting complexes was disappeared due to the thermal digestion of all organic contents.
The (111), (200) and (220) reflections are closely match the reference CdO prepared with JCPDS file No. 05-0640, the formation of CdO cubic crystal nanoparticle was confirmed, see Fig. 9. The particles were found in polycrystalline structure and that the nanostructure grew in a random orientation which confirmed by sharp peaks from XRD data [32–36].

The size and morphology of these particles were determined by Scanning Electron Microscopy (SEM) before and after calcination, as seen in Fig. 10a, b, respectively. SEM image for complex 1, particles were irregular before calcination, while after calcination regular spherical particles were collected, which confirmed that tridentate organic ligands play de-structure role during thermolysis process [30–36]. According to this micrograph, nanoparticles with less than 100 nm in diameter were produced.

Also, TEM was carried out for the CdO nanoparticles corresponding to the same sample above was illustrated in Fig. 11. From TEM image, the average size of the nanoparticles found to be around 60 nm. The particles are spherical in shape, not unlike those reported by Dong et al. [34].

**Hirshfeld surface analysis for complex 1**

Crystal structure analysis of complex 1 using the cif file was generated by Hirshfeld Surface, to analysis the intermolecular interactions then illustrated the fingerprint map of atoms inside/atom outside interactions of molecules. The Hirshfeld surfaces of complex 1 is displayed in Fig. 12, showing surfaces that have been mapped over a d_norp', d_e and d_i [37, 38]. “For each point on that isosurface two distances are determined: one is d_e represents the distance from the point to the nearest nucleus external to the surface and second one is d_i represents the distance to the nearest nucleus internal to the surface. The dark-red spots on the d_norp surface arise as a result of the short interatomic contacts, i.e. strong hydrogen bonds, while the other intermolecular interactions appear as light-red spots [18–22].”

The surface here in this work represents the circular depressions (deep red) visible on the Hirshfeld surface indicative of strong hydrogen bonding contacts of types N–H…Br and C—H…..Br.

The two-dimensional fingerprint plots over the Hirshfeld surfaces of complex 1 illustrate the significant differences between the intermolecular interaction patterns. H…all (64.6 %), Br…all (34.4 %), Cd…all (0.6 %) and all…all (Fig. 13) and Table 1.

Table 1 illustrate the detail fingerprints intermolecular interaction between inside and outside atoms in both neighbor molecules.

**Experimental section**

**Material and instrumentation**

“Dien, dipn ligands and CdBr₂•2.5H₂O were purchased from Fluka. Elemental analyses were carried out on an
Fig. 3 A crystal packing of complex 1 exhibiting layered stacking when viewed (perspective) along the crystallographic a axis. The dotted lines indicate hydrogen bonds.

Fig. 4 IR-KBr disk spectra of the complex 1

Fig. 5 UV–Vis spectrum of the complex 1 in water at RT
Elementar Vario EL analyzer. The IR spectra for samples were recorded using (Perkin Elmer Spectrum 1000 FT-IR Spectrometer). The UV–visible spectra were measured by using a TU-1901 double-beam UV–visible spectrophotometer. TG/DTA spectra were measured by using a TGA-7 Perkin-Elmer thermogravimetric analyzer. The obtained nanoparticles were examined by a Bruker D/MAX 2500 X-ray diffractometer with Cu K radiation (λ = 1.54 Å), and the operation voltage and current were maintained at 40 kV and 250 mA, respectively. The transmission electron microscopy was (TEM, 1001 JEOL Japan). The scanning electron microscopy (SEM, JSM-6360 ASEM, JEOL Japan). The Hirshfeld surfaces analysis of complex 1 was carried out using the program CRYSTAL EXPLORER 3.1 [39].

General procedure for the preparation of the desired complexes

In an ultrasonic open atmosphere media, a mixture of CdBr₂•2.5H₂O (2.0 mmol) in distilled ethanol (15 mL) and the free ligand was added in excess (6.0 mmol). The reaction mixture was subjected to ultrasonic vibration until the product complex appeared as white precipitate after ~20 min. The product was filtered and washed several times with ethanol. The product was only soluble in water, DMF and DMSO. Single crystals suitable for X-ray diffraction experiments were obtained by slow evaporation of water from complex solution.

**Complex 1**

Yield: (91 %). Anal. Calc. for C₈H₂₆Br₄Cd₂N₆: C, 12.80; H, 3.49; N, 11.19 %. Found. C, 12.53; H, 3.61; N, 11.28 %. MS [M+2] = 320.0 [theoretical = 320.2 m/z]. UV–Vis bands in water 275 nm. m.p 340 °C. Conductivity in DMF: 18.3 (µS/cm). ¹H NMR (d⁶-DMSO): d (ppm) 2.55 and 2.62 (2br, 16H, 8CH₂), 2.85 (br, 8H, 4NH₂), 3.35 (br, 2H, 2NH), ¹³C[^¹H] NMR (d⁶-DMSO):d (ppm) 25.2 (s, 4C, CH₂), 34.5 (s, 4C, CH₂).
Complex 2
Yield: (88 %). Anal. Calc. for C₁₂H₃₄Br₄Cd₂N₆: C, 17.86; H, 4.25; N, 10.42 %. Found. C, 17.48; H, 4.21; N, 10.38 %. MS [M⁺²] = 376.0 [theoretical = 376.19 m/z]. UV–Vis bands in water 285 nm. m.p 320 °C. Conductivity in DMF: 22.3 (µS/cm). ¹H NMR (d₆-DMSO): δ (ppm) 1.85 (br, 8H, 4CH₂), 2.62 and 2.82 (2 br, 16H, 8CH₂), 2.88 (br, 8H, 4NH₂), 3.38 (br, 2H, 2NH), 13C[¹H] NMR (d₆-DMSO):δ (ppm) 20.0 (s, 4C, CH₂), 25.8 (s, 4C, CH₂), 34.9 (s, 4C, CH₂).

Crystallography
A colourless prism shaped single crystal of dimensions 0.35 × 0.23 × 0.19 mm of the title compound was chosen for an X-ray diffraction study. The X-ray intensity Data were collected on a Bruker APEX-II CCD area diffractometer and equipped with graphite monochromatic MoKα radiation of wavelength 0.71073 Å at 100 (2) K. Cell refinement and data reduction were carried out using SAINT PLUS [24]. The structure was solved by direct methods and refined by full-matrix least
squares method on $I^2$ using SHELXS and SHELXL programs [40]. All the non-hydrogen atoms were revealed in the first difference Fourier map itself. All the hydrogen atoms were positioned geometrically and refined using a riding model. After ten cycles of refinement, the final difference Fourier map showed peaks of no chemical significance and the residuals saturated to 0.0237. The geometrical calculations were carried out using the program PLATON [41]. The molecular and packing diagrams were generated using the software MERCURY [42]. The details of the crystal structure and data refinement are given in Table 2. The list of bond lengths and bond angles of the non-hydrogen atoms are given in Table 3. Figure 6 represents the ORTEP of the molecule with thermal ellipsoids drawn at 50% probability.
Conclusions

For the first time, two new complexes [Cd(dien)₂]CdBr₄ and [Cd(dipn)₂]CdBr₄ were synthesized in good yield. The chemical structure of [Cd(dien)₂]CdBr₄ was confirmed by X-ray diffraction. The Cd(II) cation center is located in a slightly distorted octahedral geometry while Cd(IV) anion are in tetrahedral and in high stability. Thermolysis of the complexes revealed the formation of CdO cubic nanoparticle, which was deduced by XRD, FT-IR, TEM and SEM, the average size of CdO nanoparticles found to be 60 nm.

Table 1 Inside/outside intermolecular interaction percentage by atoms

|          | Hᵢ𝐧ₛᵢᵈᵉ | Brᵢ𝐧ₛᵢᵈᵉ | Cdᵢ𝐧ₛᵢᵈᵉ | Nᵢ𝐧ₛᵢᵈᵉ | Cᵢ𝐧ₛᵢᵈᵉ |
|----------|-----------|-----------|-----------|-----------|-----------|
| Hᵢ𝐧ₛᵢᵈᵉ | 41.7      | 32.7      | 0         | 0         | 0         |
| Brᵢ𝐧ₛᵢᵈᵉ | 22.4      | 0.8       | 0         | 0         | 0         |
| Cdᵢ𝐧ₛᵢᵈᵉ | 0.2       | 0         | 0         | 0         | 0         |
| Nᵢ𝐧ₛᵢᵈᵉ | 0         | 0         | 0         | 0         | 0         |
| Cᵢ𝐧ₛᵢᵈᵉ | 0         | 0         | 0         | 0         | 0         |

Table 2 Crystal data and structure refinement for Ligand and complex 1

| Parameter                          | Value                  |
|------------------------------------|------------------------|
| Empirical formula                  | C₈H₂₆Br₄Cd₂N₆          |
| Formula weight                     | 750.79                 |
| Temperature                        | 100 (2) K              |
| Wavelength                         | 0.71073 Å              |
| Crystal system, space group        | Monoclinic, P2₁/n      |
| Unit cell dimensions               |                        |
| a                                  | 9.4335 (12) Å          |
| b                                  | 14.7512 (18) Å         |
| c                                  | 14.7815 (18) Å         |
| β                                  | 100.131 (2)°           |
| Volume                             | 2024.9 (4) Å³          |
| Z, calculated density              | 4, 2.463 Mg/m³         |
| Absorption coefficient             | 9.993 mm⁻¹             |
| F(000)                             | 1408                   |
| Crystal size                       | 0.35 × 0.23 × 0.19 mm  |
| Theta range for data collection    | 1.97–28.28°            |
| Limiting indices                   | −12 ≤ h ≤ 12, 0 ≤ k ≤ 19, 0 ≤ l ≤ 19 |
| Reflections collected/unique       | 4969/4960 [R(int) = 0.0000] |
| Refinement method                  | Full-matrix least-squares on F² |
| Data/restraints/parameters         | 4969/0/181             |
| Goodness-of-fit on F²              | 1.057                  |
| Final R indices (l > 2σ(l))        | R₁ = 0.0237, wR₂ = 0.0468 |
| R indices (all data)               | R₁ = 0.0328, wR₂ = 0.0494 |
| Largest diff peak and hole         | 0.595 and −0.885 e. Å⁻³ |

Table 3 Selected bond distances (Å) and bond angles (°) of complex 1

| Atoms     | Length | Atoms     | Length |
|-----------|--------|-----------|--------|
| Cd1-N14   | 2.346 (2) | C12-N13  | 1.472 (4) |
| Cd1-N20   | 2.357 (2) | N14-C15  | 1.475 (4) |
| Cd1-N7    | 2.365 (3) | C15-C16  | 1.516 (4) |
| Cd1-N13   | 2.365 (3) | C16-N17  | 1.469 (4) |
| Cd1-N17   | 2.410 (2) | N17-C18  | 1.471 (4) |
| Cd1-N10   | 2.422 (3) | C18-C19  | 1.512 (4) |
| N7-C8     | 1.474 (4) | C19-N20  | 1.476 (4) |
| C8-C9     | 1.517 (5) | Cd2-Br5  | 2.5721 (5) |
| C9-N10    | 1.463 (4) | Cd2-Br4  | 2.5809 (5) |
| N10-C11   | 1.468 (4) | Cd2-Br6  | 2.5835 (4) |
| C11-C12   | 1.514 (5) | Cd2-Br3  | 2.6313 (5) |

Supplementary material

Crystallographic data for complex 1 has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 1404033. Copies of this information may be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

Authors’ contributions

IW developed the synthesis, IW and IMA, undertook synthesis. FA help in analysis and interpretation of data collected and involved in drafting of manuscript. AB carried out some physical measurements. SA revision of draft for important intellectual content. NS and NK carried out the X-ray diffraction
measurement and help in writing the manuscript. All authors read and approved the final manuscript.

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References
1. Mitzi DB (2001) Templating and structural engineering in organic–inorganic perovskites. J Chem Soc Dalton Trans 1–12
2. Martinez‑Manez R, Sancenon F, Biylak M, Hecht M, Rurack K (2011) Mimicking tricks from nature with sensory organic–inorganic hybrid materials. J Mater Chem 21:2358–12604
3. Rakibuddin M, Gazi S, Ananthakrishnan R (2015) Iron (II) phenanthroline‑nitrilotriacetic acid(II), and DimethylammoniumTetrabromocadmate(II). Z Naturforsch 55a:1027–1036
4. Rakibuddin M, Gazi S, Ananthakrishnan R (2014) Bromine NQR and crystal structures of TetraaniliniumDecaborromicotramadicate and 4‑methylpyridinium tribromocadmate. Z Naturforsch 49a:213–222
5. Ishihara H, Krishnan VG, Guo SQ, Weiss A (1994) Isolated versus condensed anion structure V: x‑ray structure analysis and 11Br NQR of t‑butylammoniumtribromocadmate(II)‑1/2 water, i‑propylammoniumtribromocadmate(II), and tris‑trimethylammonium hydroxidiniumTetramacromicotramadicate(II)‑tetra hydrate, [H3NNH3+]CdBr5‑4H2O. Z Naturforsch 55a:390–396
6. Ishihara H, Horuchi K, Krishnan VG, Guo SQ, Weiss A (1996) Isolated versus condensed anion structure II; the influence of the cations (1,3‑propanediammonium, 1,4‑phenylendiammonium, and n‑propylammonium) on structures and phase transitions of CdBr4[2−] salts A salts. Z Naturforsch 51a:1216–1228
7. Hines CC, Reichert WM, Griffin ST, Bond AH, Snowwhite PE, Rodgers RD (2006) Exploring control of cadmium halide coordination polymers via control of cadmium (II) coordination sites utilizing short multidentate ligands. J Mol Struct 796(1):76–85
8. Ishihara H, Dou SQ, Horuchi K, Krishnan VG, Guo SQ, Weiss A (1996) Isolated versus condensed anion structure II; the influence of the cations (1,3‑propanediammonium, 1,4‑phenylendiammonium, and n‑propylammonium) on structures and phase transitions of CdBr4[2−] salts A salts. Z Naturforsch 55a:390–396

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4. Rakibuddin M, Gazi S, Ananthakrishnan R (2014) Bromine NQR and crystal structures of TetraaniliniumDecaborromicotramadicate and 4‑methylpyridinium tribromocadmate. Z Naturforsch 49a:213–222
5. Ishihara H, Krishnan VG, Guo SQ, Weiss A (1994) Isolated versus condensed anion structure V: x‑ray structure analysis and 11Br NQR of t‑butylammoniumtribromocadmate(II)‑1/2 water, i‑propylammoniumtribromocadmate(II), and tris‑trimethylammonium hydroxidiniumTetramacromicotramadicate(II)‑tetra hydrate, [H3NNH3+]CdBr5‑4H2O. Z Naturforsch 55a:390–396
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7. Hines CC, Reichert WM, Griffin ST, Bond AH, Snowwhite PE, Rodgers RD (2006) Exploring control of cadmium halide coordination polymers via control of cadmium (II) coordination sites utilizing short multidentate ligands. J Mol Struct 796(1):76–85
8. Ishihara H, Dou SQ, Horuchi K, Krishnan VG, Guo SQ, Weiss A (1996) Isolated versus condensed anion structure II; the influence of the cations (1,3‑propanediammonium, 1,4‑phenylendiammonium, and n‑propylammonium) on structures and phase transitions of CdBr4[2−] salts A salts. Z Naturforsch 55a:390–396

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3. Rakibuddin M, Gazi S, Ananthakrishnan R (2015) Iron (II) phenanthroline‑nitrilotriacetic acid(II), and DimethylammoniumTetrabromocadmate(II). Z Naturforsch 55a:1027–1036
4. Rakibuddin M, Gazi S, Ananthakrishnan R (2014) Bromine NQR and crystal structures of TetraaniliniumDecaborromicotramadicate and 4‑methylpyridinium tribromocadmate. Z Naturforsch 49a:213–222
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6. Ishihara H, Horuchi K, Krishnan VG, Guo SQ, Weiss A (1996) Isolated versus condensed anion structure II; the influence of the cations (1,3‑propanediammonium, 1,4‑phenylendiammonium, and n‑propylammonium) on structures and phase transitions of CdBr4[2−] salts A salts. Z Naturforsch 51a:1216–1228
30. Saghatforoush, L., Aminkhani, A., Ershad, S., Karimnezhad, G.H., Ghammamy, S.H., Kabiri, R. (2008) Preparation of zinc (II) and cadmium (II) complexes of the tetradeinate Schiff base ligand 2-((E)-(2-(2-(pyridine-2-yl)-ethylthio) ethylimino)methyl)-4-bromophenol (PyBrsalH). Molecules 13:804–811

31. Majumder, A., Rosair, G.M., Mallick, A., Chattopadhyay, N., Mitra, S. (2006) Synthesis, structures and fluorescence of nickel, zinc and cadmium complexes with the N, N, O-tridentate Schiff base N-2-pyridylmethylidene-2-hydroxy-phenylamine. Polyhedron 25:1753–1762

32. Warad, I., Abdoh, M., Shivalingegowda, N., Lokanath, N.K., Salghi, R., Al-Nuri, M., Jodeh, S., Radi, S., Hammouti, B. (2015) Synthesis, spectral, electrochemical, crystal structure studies of two novel di-μ-halo-bis[halo (2, 9-dimethyl-4, 7-diphenyl-1, 10-phenanthroline) cadmium(II)] dimer complexes and their thermolysis to nanometal oxides. J Mol Struct 1099:323–329

33. Ye, X.R., Daraio, C., Wang, C., Talbot, J.B. (2006) Room temperature solvent-free. Synthesis of monodisperse magnetite nanocrystals. J Nanosci Nanotechnol 6:852–856

34. Dong, W., Zhu, C.S. (2003) Optical properties of surface-modified CdO nanoparticles. Opt Mater 22(3):227–233

35. Klug, H.P. (1954) X-ray diffraction procedures for polycrystalline and amorphous materials. Wiley, New York

36. Patel, R.N., Singh, N., Shukla, K.K., Nicolás-Gutiérrez, J., Castineiras, A., Vaidyanathan, V.G., Nair, B.U. (2005) Characterization and biological activities of two copper(II) complexes with diethylenetriamine and 2,2-bipyridine or 1,10-phenanthroline as ligands. Spectrochim Acta Part A 62:261–268

37. Spackman, M.A., Laytaker, D. (2009) Design and understanding of solid-state and crystalline materials. Cryst Eng Commun 11:19–32

38. Spackman, M.A., McKinnon, J.J. (2002) Fingerprinting intermolecular interactions in molecular crystals. Cryst Eng Commun 4:378–392

39. Wolff, S.K., Grimwood, D.I., McKinnon, J.J., Laytaker, D., Spackman, M.A. (2007) Crystal explorer 2.1. University of Western Australia, Perth

40. Bruker (2009) APEX2, SAINT and SADABS. Bruker AXS Inc, Madison

41. Sheldrick, G.M. (2008) A short history of SHELX. Acta Cryst A64:112–122

42. Spek, A.L. (2009) Structure validation in chemical crystallography. Acta Cryst D65:148–155