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Notes

Synthesis and structure characterization of two cadmium coordination polymers based on μ_2-bridging bidentate hydrazine ligand

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Synthesis, single crystal structures, spectral and thermal characteristics of two cadmium coordination polymers, viz., $[Cd(NO_3)_2(N_2H_4)_2]$ (**1**) $[Cd(C_3H_2O_4)(N_2H_4)]$ (where $C_3H_2O_4$ is malonate) (**2**) are reported. The μ_2-bridging bidentate binding mode of the crystallographically unique hydrazine ligands in (**1**) leads to a one-dimensional polymeric structure extending along *c* axis. The central Cd(II) in (**2**) exhibits hepta-coordination and is bonded to a unique malonate anion which exhibits a μ_3-bridging pentadentate coordination, extending the structure along the *a* axis. The bridging bidentate binding of the crystallographically independent hydrazine ligand extends along *b* axis resulting in a 2-D structure.

Keywords: Coordination polymers, Cadmium coordination polymers, Crystal structures, Hydrazines, Malonates, μ_2-Bridging bidentate, μ_3-Bridging pentadentate

The synthesis, structure and physical and chemical properties of various hydrazinium salts have been reported in literature[1]. Basically, hydrazine in an aqueous solution exists in different forms like N_2H_4, $N_2H_5^+$ and $N_2H_6^{2+}$. Several process methods have been developed for the synthesis of these salts, but typically, the method of preparation varies with the type of salt made[2]. Plenty of bis-hydrazine metal complexes have been prepared in basic medium (pH > 8) and well characterized by their spectral and thermal studies[3-7]. During the last two decades, a large number of metal carboxylates containing neutral hydrazine have been reported[8-12].

In contrast, though bridged hydrazine metal complexes including carboxylates can be easily precipitated from aqueous solution at higher pH, they are mostly obtained only as polycrystalline material. Due to the difficulty in obtaining the single crystals, only a few crystal structures of bis-hydrazine complexes have been reported in the literature[13-17]. Furthermore, mono-hydrazine complexes are rare and only a few articles have been published so far[18, 19].

Herein, we report the synthesis, spectral and thermal characterization and X-ray structure determination of two cadmium coordination polymers based on μ_2-bridging bidentate hydrazine ligand.

Experimental

All reagents and chemicals used for synthesis and analyses were obtained commercially and used without further purification. Doubly distilled water was used in all the experiments. All glassware used were washed with acetone, followed by rinsing with distilled water and dried in an oven before use.

The compositions of the complexes were determined by hydrazine and metal analyses. The metal content of the complexes were determined by EDTA complexometric titrations after decomposing a known amount of the complex with concentrated nitric acid. The hydrazine content in the complexes was determined volumetrically by titrating against 0.025 M potassium iodate solution under Andrew's condition[20]. Chemical analyses for carbon, hydrogen and nitrogen were performed using a Perkin-Elmer (model 1240 CHN) analyzer. Infrared spectra of the complexes were recorded on a Shimadzu spectrophotometer using KBr pellets in the range 4000–400 cm^{-1}. The simultaneous TG-DTA of the complexes in air was carried out using SWI TG/DTA 6200 thermal analyser. The thermal experiments were performed in air at a heating rate of 10 $^{o}C\ min^{-1}$ using platinum cups as sample holders.

X-ray data collection was performed with Bruker AXS Kappa Apex II CCD diffractometer equipped with graphite monochromated Mo-K_α (λ = 0.71073 Å) radiation at IIT Madras, Chennai, India. The automatic cell determination routine, with 36 frames at three different orientations of the detector, was employed to collect reflections for unit cell determination. Further, intensity data for structure determination were collected through an optimized strategy which gave an average 4-fold redundancy. The program APEX2-SAINT[21] was used for integrating the frames. Four-fold redundancy per reflection was utilized for achieving good multi-scan absorption correction using the program

SADABS[21]. Besides absorption, Lorentz, polarization and decay corrections were applied to intensity during data reduction. The structures were solved by direct methods using SIR92[22] and refined by full-matrix least squares techniques using SHELXL-97[23], computer program. Molecular graphics were drawn using ORTEP3[24]. Hydrogens on all carbon atoms were fixed at calculated positions and refined as riding model with C—H = 0.97 Å, $U_{iso}(H) = 1.2\ U_{eq}(C)$, whereas hydrogens on nitrogen were fixed from the difference electron density peaks and allowed to refine freely.

Compound (**1**) was prepared as follows: An aqueous solution (50 mL) containing a mixture of propionic acid (1.48 mL, 0.02 mol) and 99% hydrazine hydrate (2 mL, 0.04 mol) was added slowly to the aqueous solution (50 mL) of cadmium nitrate hexahydrate (3.0847 g, 0.01 mol). The precipitate which formed immediately was filtered and then the resulting solution was concentrated to half of its volume and allowed to crystallize. The needle-like crystals formed after 2-3 days were filtered, washed with water and then dried. These crystals were soluble in water and insoluble in alcohol and other organic solvents. Yield: 74%. Anal. (%): Calc.: H, 2.68; N, 27.97; N_2H_4, 21.30; Cd, 37.41. Found: H, 2.50; N, 27.80; N_2H_4, 21.20; Cd, 38.00.

Compound (**2**) was prepared with malonic acid. An aqueous solution (50 mL) containing a mixture of malonic acid (1.04 g, 0.01 mol) and 99% hydrazine hydrate (2 mL, 0.04 mol) was added slowly with constant stirring to an aqueous solution (100 mL) containing cadmium nitrate hexahydrate (3.0847 g, 0.01 mol). The precipitate, formed immediately after adding the ligand solution to the metal solution, was separated by filtration and the clear solution was concentrated to half of its volume. The resultant clear solution was filtered and kept aside at room temperature. The crystals were collected the next day, washed with water and then dried in air. Yield: 61% Anal. (%): Calc.: C, 14.62; H, 2.45; N, 11.37; N_2H_4, 12.98; Cd, 45.60. Found: C, 14.10; H, 2.50; N, 11.80; N_2H_4, 13.10; Cd, 46.20.

Results and discussion

Compounds (**1**) and (**2**) were prepared by the aqueous reaction of cadmium nitrate hexahydrate with an aqueous solution containing hydrazine hydrate in the presence of propionic acid or malonic acid. It is observed that in the case of propionic acid, the carboxylic acid is not incorporated in the product, while use of the dicarboxylic malonic acid affords a nitrate free product containing malonate ion as the charge balancing anion.

The infrared spectra of both the complexes show two sharp bands in the region 3200–3400 cm^{-1}, which is assigned to the N-H stretching of hydrazine molecule (Supplementary data, Figs S1 and S2). Generally, the coordinate (terminal) M-N-N stretching for hydrazinium cation is observed in the range 1000–1010 cm^{-1}, but in the present complexes, a strong band at 965–975 cm^{-1} was observed in both the compounds, which supports the N-N stretching of bridged mode of hydrazine.

Thermal degradation studies of (**1**) and (**2**) were carried out. Complex (**1**) exhibited a single step decomposition in the temperature range 250–280 °C and the corresponding DTA showed an exotherm at 256 °C (Supplementary data, Fig. S3). The final product obtained was CdO as expected. The malonatohydrazine cadmium(II) (**2**) shows a sharp exotherm at 227 °C indicating the loss of one hydrazine molecule in the temperature range 220–250 °C in the first stage. The intermediate further undergoes ligand pyrolysis in the temperature range 380–420 °C to give CdO as a final residue. The DTA corresponding to this stage shows an exotherm at 405 °C (Supplementary data, Fig. S4).

The crystal data for the complexes are summarized in Table 1 and selected bond lengths are given in Table 2. The bond angles and hydrogen bonds for the complexes are given in Table S1 and S2 (Supplementry data) respectively.

Compound **1** crystallizes in the triclinic space group P-1. Its structure consists of an unique Cd(II) ion, two crystallographically independent nitrate anions and two unique hydrazine ligands, all of which are situated in the general positions (Fig. 1). The central Cd(II) is bonded to four N atoms from four different hydrazine ligands and to two O atoms (O1, O6) of the nitrate anions which function as terminal ligand, and has a distorted octahedral geometry. The nitro groups are disposed *trans* to each other in the octahedron. One of the nitrate anions is disordered over two positions (N2, O6, O7, O8 and N2', O6', O7', O8') with the occupancy ratio of 0.78:0.22. The disorder was resolved by successive Fourier electron density maps and least squares refinements. Sum of the occupancies of the disordered components were restrained as 1 during refinement. The corresponding bond distances of disordered groups were restrained to equal within an allowed standard deviation of 0.01 Å. Anisotropic displacement

Table 1 — Crystal data and structure refinement for **1** and **2**

	(**1**)	(**2**)
CCDC No.	976540	1055303
Empirical formula	$Cd\ H_8N_6O_6$	$C_3H_6\ Cd\ N_2O_4$
Formula weight	300.52	246.5
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	Triclinic, P-1	Monoclinic, $P2_1/c$
Unit cell dimensions	a = 6.91600(10) Å	a = 7.2908(3) Å
	α = 80.5700(10)°	α = 90°
	b = 7.01500(10) Å	b = 12.2477(5) Å
	β = 80.6400(10)°	β = 98.199(2)°
	c = 8.6420(2) Å	c = 6.8703(3) Å
	γ = 68.9500(10)°	γ = 90°
Volume	383.546(12) $Å^3$	607.22(4) $Å^3$
Z, Calculated density	2, 2.602 mg/m^3	2, 2.696 mg/m^3
Absorption coefficient	2.867 mm^{-1}	3.549 mm^{-1}
F(000)	292	472
Crystal size	0.25×0.20×0.15 mm	0.20×0.20×0.15 mm
Theta range for data collection	2.40–27.99°	2.82–24.99°
Limiting indices	$-9 \leq h \leq 9$, $-9 \leq k \leq 9$, $-11 \leq l \leq 11$	$-8 \leq h \leq 8$, $-14 \leq k \leq 14$, $-6 \leq l \leq 8$
Reflections collected / unique	8603/ 1850 [$R_{(int)}$ = 0.0234]	5088/ 1063 [$R_{(int)}$ = 0.0258]
Completeness to theta	27.99 (99.8%)	24.99 (99.8%)
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.6856 and 0.5236	0.6365 and 0.5236
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	1850/ 7/ 188	1063/ 6/ 108
Goodness-of-fit on F^2	1.162	1.231
Final R indices [I>2sigma(I)]	R1 = 0.0137, wR2 = 0.0337	R1 = 0.0148, wR2 = 0.0364
R indices (all data)	R1 = 0.0139, wR2 = 0.0338	R1 = 0.0154, wR2 = 0.0366
Extinction coefficient	0.120(2)	0.0326(9)
Largest diff. peak and hole	0.488 and –0.801 e $Å^{-3}$	0.301 and –0.241 e $Å^{-3}$

Table 2 — Selected bond lengths (Å) for $[Cd(NO_3)_2(N_2H_4)_2]$ (**1**) and $Cd(C_3H_2O_4)(N_2H_4)$ (**2**)

(**1**)		(**2**)	
Cd1-O6	2.413(6)	Cd1-O1	2.5200(19)
Cd1-N3	2.3509(13)	Cd1-O2	2.3164(18)
Cd1-O1	2.4550(12)	Cd1-O3	2.3271(19)
Cd1-N6	2.3480(13)	Cd1-O3#1	2.3628(19)
Cd1-N5	2.3445(13)	Cd1-O4	2.627(2)
Cd1-N4 #1	2.3251(13)	Cd1-N1	2.295(2)
		Cd1-N2#2	2.331(2)

Symmetry transformations used to generate equivalent atoms: #1 -*x*,-*y*,-*z*; #2 -*x*,-*y*,-*z*+1.

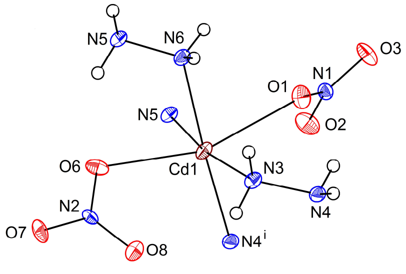

Fig. 1 — Crystal structure of $[Cd(NO_3)_2(N_2H_4)_2]$ (**1**), showing the atom labelling scheme and the coordination sphere of Cd(II) in (**1**). Displacement ellipsoids are drawn at 30% probability level excepting for H atoms, which are shown as spheres of arbitrary radius. The nitrate anion (N2) is disordered. For clarity the disordered atoms are not displayed. [Symmetry code: i) -*x*, -*y*, -*z*].

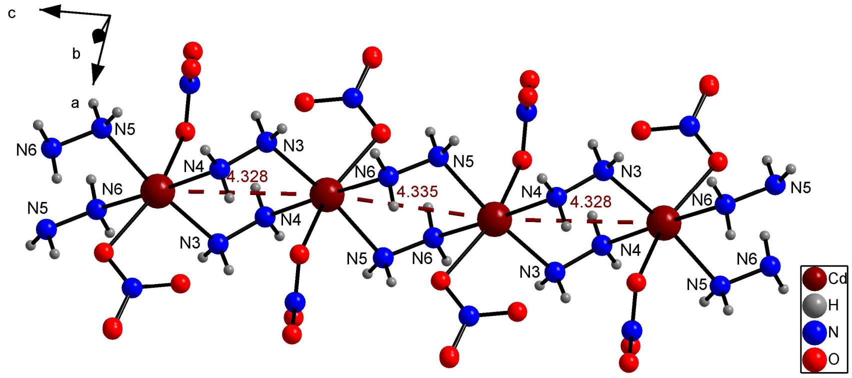

Fig. 2 — Alternating pairs of unique hydrazine ligands link the Cd(II) ions in (**1**) into a one-dimensional chain extending along *c* axis with alternating Cd···Cd separations of 4.328 and 4.335 Å respectively. For clarity only a portion of the infinite chain is shown.

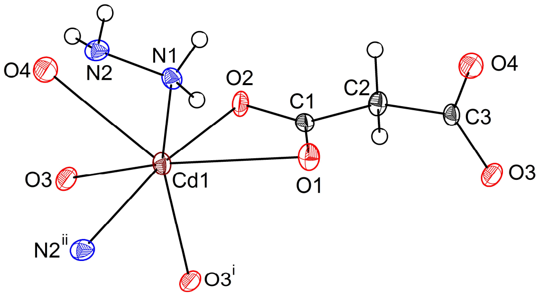

Fig. 3 — Crystal structure of [Cd($C_3H_2O_4$)(N_2H_4)] (**2**) showing the hepta-coordination around Cd(II) and the atom labelling scheme. Displacement ellipsoids are drawn at 30% probability level excepting for H atoms, which are shown as spheres of arbitrary radius. [Symmetry code: i) -*x*, -*y*, -*z*; ii) -*x*, -*y*, 1-*z*].

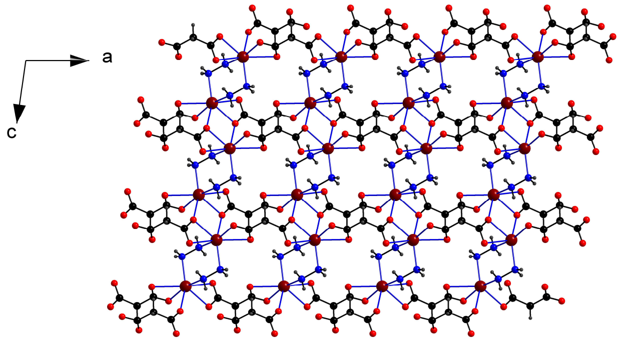

Fig. 4 — A view of the packing in the crystallographic *ac* plane showing the 2-D structure of (**2**).

parameters (U_{ij}) of atoms in the disordered groups were restrained to be equal within the limits of allowed standard deviation. The thermal parameters of the atoms of the disordered moieties were restrained to show approximate isotropic behaviour within an effective standard deviation of 0.02 Å^2.

Both the unique hydrazine ligands function as μ_2-bridging bidentate ligands (Supplementary data, Fig. S5(a & b)) resulting in slightly different Cd···Cd separations. The binding of a pair of unique hydrazine ligands leads to the formation of a six membered {Cd_2N_4} ring. Analysis of the crystal structure reveals that the Cd(II) ions are linked into a one-dimensional (1-D) chain, (Fig. 2) with alternating Cd···Cd separations of 4.328 and 4.335 Å respectively. In the 1-D chain, each Cd(II) is hexa-coordinated and is bonded to two O atoms of the terminal nitrate ligands.

Compound (**2**) crystallizes in monoclinic crystal system with P2$_1$/c space group. The asymmetric unit contains a unique malonate and one hydrazine in addition to Cd(II). The central metal Cd(II) is hepta-coordinated to two nitrogen atoms of two different hydrazine ligands and five oxygen atoms of three different malonate ligands forming a distorted trigonal prism geometry (Fig. 3 and Supplementary data, Fig. S6). The μ_2-bridging bidentate binding mode of the unique hydrazine ligand in (**2**) results in a Cd···Cd separation of 4.234 Å. (Supplementary data, Fig. S7) Note that a pair of unique (N1N2) ligands links a pair of Cd(II) ions forming a Cd_2N_4 six membered ring motif. The crystallographically unique malonate ligand exhibits a μ_3-bridging pentadentate binding mode forming five Cd-O bonds. Each malonate is linked to three Cd(II). Alternatively, each Cd(II) is linked to three different malonate ligands (Supplementary data, Fig. S8) The μ_3-bridging pentadentate binding mode, leads to three different Cd···Cd separations of 3.755, 6.939 and 7.291 Å (Supplementary data, Fig. S9). The bridging binding mode of the malonate ligand results in the formation of a 1-D chain extending along the *a* axis, whereas the bridging binding mode of the hydrazine ligands serves to link the Cd-malonate chains along *c* axis resulting in a 2-D layer structure (Fig. 4).

In both the complexes (**1**) and (**2**) the bidentate bridging mode of unique hydrazine ligand forms Cd_2N_4 six membered ring motifs. The Cd···Cd separation in Cd_2N_4 ring motif in (**1**) is found to be 4.328 Å and 4.335 Å, whereas in (**2**) it is 4.234 Å

Supplementary data

Crystallographic data for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre under depository numbers CCDC 976540 and 1055303 for (**1**) and (**2**) respectively. These data may be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Other supplementary data associated with this article are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_57A(07)905-909_SupplData.pdf.

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