

Synthesis, Characterization and Thermal Studies of Bis(2-aminoethyl)methylamine(medien) Complexes of Cadmium(II). Single Crystal Structure of Cd(medien)I₂

Arunendu Mondal,^a Siddhartha Chaudhuri,^b Ashutosh Ghosh,^c Inamur Rahaman Laskar^a and Nirmalendu Ray Chaudhuri^{a,*}

^aDepartment of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032, India, ^bR.S.I.C., Bose Institute, Calcutta 700 009, India and ^cDepartment of Chemistry, University College of Science and Technology, 92, A.P.C. Road, Calcutta 700 099, India

Mondal, A., Chaudhuri, S., Ghosh, A., Laskar, I. R. and Chaudhuri, N. R., 1998. Synthesis, Characterization and Thermal Studies of Bis(2-aminoethyl)methylamine(medien) Complexes of Cadmium(II). Single Crystal Structure of Cd(medien)I₂. Acta Chem. Scand. 52: 1202–1208. © Acta Chemica Scandinavica 1998.

[Cd(medien)_m]X₂·nH₂O [where medien is bis(2-aminoethyl)methylamine. *m* = 2 and *n* = 0 when X is Cl⁻ (1), Br⁻ (2), I⁻ (3), NCS⁻ (4) and NO₃⁻ (5); *m* = 1 and *n* = 0 when X is Cl⁻ (1a), Br⁻ (2a) and I⁻ (3a); *m* = 2 and *n* = 3 when X is 0.5SO₄²⁻ (6) and 0.5SeO₄²⁻ (7); *m* = 1 and *n* = 1 when X is 0.5SO₄²⁻ (6a) and 0.5SeO₄²⁻ (7a)] have been synthesized from solution and investigated thermally in the solid state. Cd(medien)X₂ [X = Cl⁻ (1b), Br⁻ (2b), I⁻ (3a), 0.5SO₄²⁻ (6c) and 0.5SeO₄²⁻ (7c)] have been synthesized in the solid state pyrolytically from their corresponding parent bis complexes. Upon heating, Cd(medien)Cl₂ (1a) and Cd(medien)Br₂ (2a) undergo an endothermic irreversible phase transition [185–200 °C, Δ*H* = 6.5 kJ mol⁻¹ for Cd(medien)Cl₂; 190–210 °C, Δ*H* = 6.7 kJ mol⁻¹ for Cd(medien)Br₂]. [Cd(medien)₂](NCS)₂ shows two reversible phase transitions in the temperature ranges 94–102 and 155–162 °C, having Δ*H* values of 6.3 and 6.8 kJ mol⁻¹, respectively. [Cd(medien)₂](NO₃)₂ also shows a reversible endothermic phase transition on heating (166–177 °C, Δ*H* = 31.4 kJ mol⁻¹; 137–127 °C, Δ*H* = -29.0 kJ mol⁻¹). The transitions are assumed to be due to the conformational changes in the triamine chelate rings. A comparison of the thermal stabilities of bis(2-aminoethyl)amine(dien) and bis(2-aminoethyl)methylamine(medien) complexes of cadmium(II) shows that *T_i* (the initial temperature of decomposition) decreases on methyl substitution on the secondary amine nitrogen atom of bis(2-aminoethyl)amine. All the bis triamine complexes are proposed to exist in *s-fac* octahedral geometry. The single-crystal structure of Cd(medien)I₂ reveals that the coordination of cadmium is five-fold. Two nitrogen atoms of the ligand, together with one of the two iodine atoms, constitute the basal plane of a distorted trigonal bipyramid. Another nitrogen atom of the ligand and the second iodine atom at apical positions are located at a distance of -2.086(6) and 3.190(1) Å, respectively, from the basal plane.

The synthesis and characterization of bis complexes of bis(2-aminoethyl)amine (dien) with transition and non-transition metals are of interest as these complexes can potentially exist in three isomeric forms, i.e. *s-fac*, *u-fac* and *mer*.^{1–6} The most common geometry of these complexes is *mer*, which is also thermodynamically the most stable form. Mono complexes of dien and *N*-alkyl-substituted dien, such as bis(2-dimethylaminoethyl)methylamine(*me₃*dien), are of interest to coordination chemists,^{7–9} as the ligand after coordination to metal ion leaves a maximum of one to three positions in the

coordination sphere of the metal, which are generally filled by counter-anions having unidentate/bidentate/polydentate ligands in order to achieve various geometries and coordination numbers. Cannas *et al.*^{7,8} reported the syntheses and single-crystal structures of Cd(dien)Cl₂ and Cd(*me₃*dien)(NCS)₂. The former possesses octahedral polymeric structure bridged through Cl atoms, and the latter is a discrete penta-coordinated species. Recently this laboratory reported^{10–13} the synthesis and characterization of dien complexes of nickel(II), zinc(II) and cadmium(II). Some of these complexes show interesting thermal behavior in the solid phase, e.g. (i) *s-fac* ⇌ *mer* isomerism, (ii) conformational isomerism, (iii) dequa-

* To whom correspondence should be addressed.

tion followed by anion coordination, (iv) deaquation without anion coordination, and (v) formation of novel intermediates which may not be prepared from solution. However, work with the methyl-substituted derivative on secondary amine nitrogen of bis(2-aminoethyl)-amine(dien) is scanty in the literature. It is expected that the substituted methyl group may develop an extra steric strain in the triamine chelate ring, and thereby the complexes synthesized by this substituted triamine should differ in molecular structure as well as thermal behavior with respect to its dien complex analogue. To our knowledge only the synthesis and characterization of bis(2-aminoethyl)methylamine(medien) complex of cobalt(III) is described in the literature.^{14,15} Here we report the synthesis, characterization and thermal studies of bis(2-aminoethyl)methylamine complexes of CdX₂ (X = Cl⁻, Br⁻, I⁻, NCS⁻, NO₃⁻, SO₄²⁻ and SeO₄²⁻) as well as the single-crystal structure of Cd(medien)I₂. This is the first structural characterization of the medien complex of cadmium.

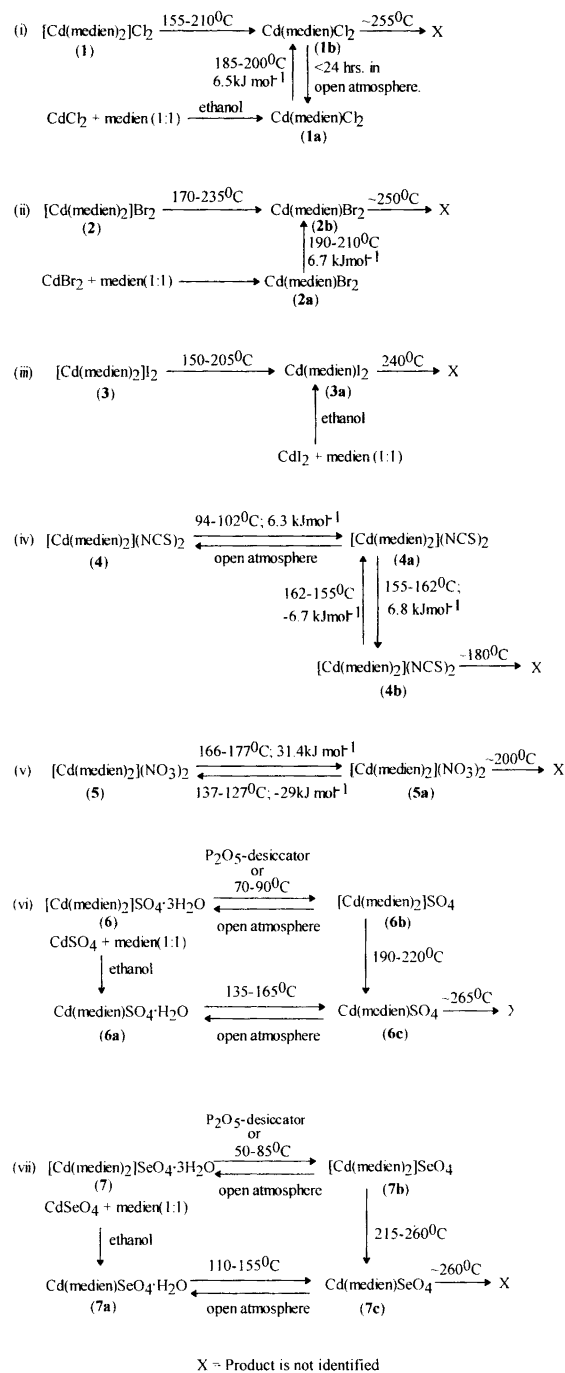
Experimental

Reagents. High-purity (98%) bis(2-aminoethyl)-methylamine(medien) was purchased from Aldrich Chemical Co. Inc. and used as received. All other chemicals used were of AR grade.

Preparation of the complexes. [Cd(medien)₂]X₂ [where X = Cl⁻ (1), Br⁻ (2), I⁻ (3), NCS⁻ (4) and NO₃⁻ (5)] were prepared by adding medien (2 mmol) dropwise with constant stirring to the corresponding metal salt (1 mmol) dissolved in ethanol (10 ml). The resulting solution was filtered, and the filtrate was kept in a desiccator for a few days. Fine crystals separated out were collected, washed with methanol and stored in a desiccator. The mono-triamine complexes Cd(medien)X₂ [where X = Cl⁻ (1a), Br⁻ (2a), I⁻ (3a)] were obtained by the same method but by varying the metal salt : ligand ratio to 1 : 1. The complexes Cd(medien)X₂ [where X = Cl⁻ (1b), Br⁻ (2b), I⁻ (3a)] have been synthesized pyrolytically in the solid state from their corresponding parent bis complexes (Scheme 1).

[Cd(medien)₂]AO₄ · 3H₂O [A = S (6) or Se (7)] were prepared by adding medien (2 mmol) dropwise with constant stirring to the corresponding metal salt (1 mmol) dissolved in a minimum quantity of water (5 ml). The resulting solution on treatment with propan-2-ol (5 ml) yielded the desired complex. They were separated, washed with propan-2-ol and stored in a desiccator. The mono-triamine analogues (6a and 7a) were obtained by adding triamine to the metal salt in a 1 : 1 ratio. The Cd(medien)AO₄ complexes [A = S (6c) and Se (7c)] have also been synthesized pyrolytically from their corresponding parent bis complexes (Scheme 1).

Measurements. Thermal analyses (TG-DTA) were carried out using a Shimadzu DT-30 thermal analyzer under



Scheme 1.

a flow of nitrogen (flow rate 30 ml min⁻¹). The sample (particle size 50-200 mesh) was heated in a platinum crucible at a rate of 10 °C min⁻¹ with inert alumina as a reference. The enthalpy changes of the phase transitions were calculated by a Perkin-Elmer DSC-7 differential scanning calorimeter using indium metal as calibrant (heating/cooling rate 10 °C min⁻¹). Elemental analyses (C, H, N) were performed using a Perkin-Elmer 2400 series(II) CHN analyser and cadmium was estimated following the method described in the literature.¹⁶ IR

spectra (4000–400 cm^{-1}) at room temperature were obtained using a Perkin-Elmer IR 783 spectrophotometer, and the IR spectrum above room temperature and far-IR spectrum were recorded by a home-made high-temperature sample holder with a Jasco IRA3 IR and Nicolet FTIR spectrophotometer, respectively. The X-ray powder diffraction experiment was performed at room temperature using Seifert XRD-3000P, where the source of X-rays was Cu radiation (30 kV; 30 mA); the primary slits were 3 mm/soller/2 mm and the secondary slits were soller/0.2 mm. Conductivity measurements were made using Systronics 304 conductivity bridge.

The complexes were recrystallized several times and the purity assured from their reproducible elemental analyses (Table 1), IR spectra, thermal (TG-DTA) and X-ray powder diffraction data. The complexes synthesized from solution are stable in an open atmosphere and can be stored indefinitely in a desiccator over CaCl_2 .

X-Ray crystallography. The diffraction data were collected on a Nonius MACH3 diffractometer with graphite monochromated radiation using the ω - 2θ scan technique over the range $2 \leq \theta \leq 25^\circ$ ($-9 \leq h \leq 9$, $0 \leq k \leq 11$, $0 \leq l \leq 19$). The data were corrected for Lorentz and polarisation factors, and empirical absorption corrections were carried out using ψ -scan data from three reflections with $\chi \approx 90^\circ$ using the NRCVAX suite of programs.¹⁷ Out of a total of 2187 independent reflections measured, 1927 were considered to be 'observed' with $I > 2\sigma(I)$. Crystal data are summarized in Table 2.

The structure was solved by the Patterson heavy-atom method and refined by full-matrix least-squares on I using the program SHELXL93.¹⁸ The non-hydrogen atoms were refined using anisotropic thermal parameters while the hydrogen atoms, generated geometrically, were refined using the 'riding' option in SHELXL93. The refinement converged to the R -indices $R_1 = 0.0376$, $wR_2 = 0.1087$ for the 'observed' data, and $R_1 = 0.0448$ and

Table 2. Crystallographic data for the complex $\text{Cd}(\text{medien})_2$ (**3a**).

Formula	$\text{C}_5\text{H}_{15}\text{N}_3\text{I}_2\text{Cd}$
Color	Colorless
Formula weight (f_w)	483.4
Crystal system	Monoclinic
Space group	$P2_1/n$
$a/\text{\AA}$	7.8814(6)
$b/\text{\AA}$	10.0188(5)
$c/\text{\AA}$	16.1304(12)
$\beta/^\circ$	101.448(6)
$V/\text{\AA}^3$	1248.3(2)
Z	4
Radiation $\lambda/\text{\AA}$	$\text{Mo K}\alpha$ (0.71073)
$F(000)$	880
μ/mm^{-1}	6.654
$\rho_{\text{calcd}}/\text{Mg m}^{-3}$	2.572
Crystal size/mm	$0.40 \times 0.25 \times 0.15$
θ range/ $^\circ$	$2 \leq \theta \leq 25$
Unique reflections	2187
Observed reflections [$I > 2\sigma(I)$]	1927
$R_1,^a wR_2^b$	0.0376, 0.1087
Weighting parameters (A, B) ^c	0.0628, 6.36
Goodness-of-fit (S) ^d	1.095
Maximum Δ/esd	0.001
Final $\Delta\rho$, max/min/ $e \text{\AA}^{-3}$	0.831/−0.878

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $wR_2 = [\sum (w(F_o^2 - F_c^2)^2) / \sum (w(F_o^2)^2)]^{1/2}$. ^c $w = 1 / [\sigma^2(F_o^2) + (AP)^2 + BP]$, where $P = (F_o^2 + 2F_c^2) / 3$. ^d $S = [\sum (w(F_o^2 - F_c^2)^2) / (N - P)]^{1/2}$, where N is the number of data and P is the total number of parameters refined.

$wR_2 = 0.1114$ for all data, with an 'extinction coefficient' which refined to 0.0127(7). The 'goodness-of-fit', S , was 1.095. The maximum and minimum peaks in a final difference electron density synthesis were 0.831 and $-0.878 e \text{\AA}^{-3}$.

Results and discussion

Bis complexes of bis(2-aminoethyl)amine(dien) potentially exist in three geometrical isomeric forms, i.e. *s-fac*,

Table 1. Elemental analyses data of bis(2-aminoethyl)methylamine (medien) complexes of cadmium(II).

Complex	Elemental analyses (%) ^a			
	Cd	C	H	N
$[\text{Cd}(\text{medien})_2]\text{Cl}_2$ (1)	26.8(26.9)	28.9(28.7)	7.2(7.1)	20.0(20.1)
$\text{Cd}(\text{medien})\text{Cl}_2$ (1a)	37.2(37.4)	19.9(20.0)	4.9(5.0)	13.9(14.0)
$\text{Cd}(\text{medien})\text{Cl}_2$ (1b)	37.0(37.4)	20.3(20.0)	4.7(5.0)	13.8(14.0)
$[\text{Cd}(\text{medien})_2]\text{Br}_2$ (2)	22.2(22.2)	23.7(23.7)	5.8(5.9)	16.6(16.6)
$\text{Cd}(\text{medien})\text{Br}_2$ (2a)	28.9(28.8)	15.6(15.4)	3.8(3.8)	10.6(10.8)
$\text{Cd}(\text{medien})\text{Br}_2$ (2b)	28.5(28.8)	15.7(15.4)	3.6(3.8)	10.5(10.8)
$[\text{Cd}(\text{medien})_2]\text{I}_2$ (3)	18.6(18.7)	20.0(20.0)	4.8(5.0)	13.7(14.0)
$\text{Cd}(\text{medien})\text{I}_2$ (3a)	23.0(23.2)	12.3(12.4)	2.9(3.1)	8.5(8.7)
$[\text{Cd}(\text{medien})_2](\text{NCS})_2$ (4)	24.3(24.3)	31.0(31.1)	6.2(6.5)	24.0(24.2)
$[\text{Cd}(\text{medien})_2](\text{NO}_3)_2$ (5)	23.7(23.9)	25.5(25.5)	6.2(6.4)	23.6(23.8)
$[\text{Cd}(\text{medien})_2]\text{SO}_4 \cdot 3\text{H}_2\text{O}$ (6)	22.6(22.6)	24.0(24.1)	7.3(7.2)	16.8(16.9)
$\text{Cd}(\text{medien})\text{SO}_4 \cdot \text{H}_2\text{O}$ (6a) ^b	32.7(32.7)	17.5(17.4)	4.8(4.9)	12.2(12.2)
$[\text{Cd}(\text{medien})_2]\text{SeO}_4 \cdot 3\text{H}_2\text{O}$ (7)	20.7(20.7)	22.0(22.1)	6.5(6.6)	15.5(15.4)
$\text{Cd}(\text{medien})\text{SeO}_4 \cdot \text{H}_2\text{O}$ (7a) ^b	28.8(28.8)	15.2(15.4)	4.4(4.3)	10.6(10.7)

^aPercentages in parentheses are theoretically calculated values. ^bElemental analyses of **6c** and **7c** could not be done as they instantaneously transform to **6a** and **7a** in an open atmosphere.

u-fac and *mer*.¹⁻⁶ The *mer* isomer is thermodynamically the most stable, and this is the most common geometry of the bis-triamine complexes reported so far. For the dien complexes IR spectroscopy has been found to be a valuable method for the characterization of the different isomeric forms.² However, Fujita *et al.*¹⁴ and Searle *et al.*¹⁵ isolated only the *s-fac* isomer of [Co(medien)₂]³⁺ and showed that the equilibrium geometric isomer distribution of [Cd(medien)₂]³⁺ is *s-fac*:*u-fac*:*mer* = 100:0:0. Furthermore, the single-crystal structure analysis of [Ni(medien)₂](NO₃)₂ reveals that it possesses *s-fac* octahedral geometry. Its IR spectrum has been compared to those of the present bis complexes of cadmium(II). It has been found that the IR spectra are quite similar, particularly in the ligand band position, indicating that all the bis complexes of cadmium(II) possess the *s-fac* geometrical isomeric form

The single-crystal structure of Cd(medien)I₂ reveals that it possesses distorted trigonal bipyramidal geometry. Figure 1 shows an ORTEP¹⁹ drawing of the molecule with the atom numbering scheme used; the thermal ellipsoids are drawn at 30% probability. The packing diagram, showing the contents of one unit cell of the compound Cd(medien)I₂, is given in Fig. 2. The final atomic coordinates and equivalent isotropic displacement parameters are given in Table 3. Complete bond distances and angles are listed in Table 4. The coordination of the Cd ion is five-fold. The nitrogen atoms N(1) and N(8) of the ligand, together with one of the iodine ions I(2), constitute the basal plane of a distorted trigonal bipyramid with the N(8) and I(1) displaced by -2.086(6) and 3.190(1) Å, respectively, from this plane. The cadmium ion is at a distance of 0.305(1) Å from the plane in the direction of I(1). In coordinating to the Cd ion, the ligand forms two five-membered chelate rings, namely Cd-N(1)-C(2)-C(3)-N(4) and Cd-N(8)-C(7)-C(6)-N(4); the first ring has a twist

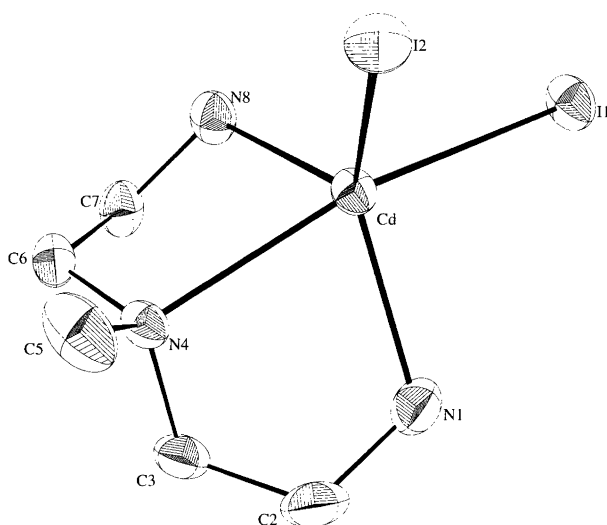


Fig. 1. ORTEP plot of Cd(medien)I₂ (3a) with atom numbering scheme.

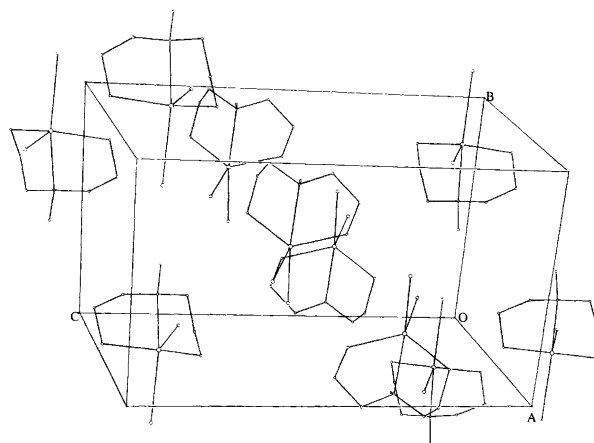


Fig. 2. Packing diagram showing the contents of one unit cell of the compound Cd(medien)I₂ (3a).

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$).

Atom	x	y	z	U_{eq}^a
Cd	3189(1)	-1095(1)	1133(1)	38(1)
N(1)	2743(11)	-1512(8)	-287(5)	56(2)
C(2)	3072(15)	-2923(11)	-456(6)	66(3)
C(3)	2271(12)	-3812(9)	100(5)	51(2)
N(4)	2990(8)	-3569(6)	1004(4)	39(1)
C(5)	4675(13)	-4240(10)	1282(8)	76(3)
C(6)	1768(13)	-4006(8)	1540(6)	55(2)
C(7)	356(11)	-3018(9)	1555(6)	51(2)
N(8)	1090(10)	-1726(7)	1853(5)	50(2)
I(1)	2140(1)	1675(1)	885(1)	55(1)
I(2)	6500(1)	-851(1)	2045(1)	48(1)

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4. Bond lengths (in Å) and angles (in °) of Cd(medien)I₂ (3a).

Cd-N(1)	2.287(7)	C(2)-C(3)	1.491(13)
Cd-N(8)	2.291(7)	C(3)-N(4)	1.475(10)
Cd-N(4)	2.491(6)	N(4)-C(5)	1.477(10)
Cd-I(2)	2.7399(8)	N(4)-C(6)	1.483(11)
Cd-I(1)	2.9002(8)	C(6)-C(7)	1.492(12)
N(1)-C(2)	1.472(13)	C(7)-N(8)	1.461(11)
N(1)-Cd-N(8)	118.3(3)	N(1)-C(2)-C(3)	110.6(7)
N(1)-Cd-N(4)	74.9(2)	N(4)-C(3)-C(2)	111.7(7)
N(8)-Cd-N(4)	74.2(2)	C(3)-N(4)-C(5)	111.8(7)
N(1)-Cd-I(2)	119.7(2)	C(3)-N(4)-C(6)	111.2(7)
N(8)-Cd-I(2)	117.3(2)	C(5)-N(4)-C(6)	109.7(8)
N(4)-Cd-I(2)	99.87(14)	C(3)-N(4)-Cd	104.6(5)
N(1)-Cd-I(1)	93.1(2)	C(5)-N(4)-Cd	112.9(5)
N(8)-Cd-I(1)	96.9(2)	C(6)-N(4)-Cd	106.4(4)
N(4)-Cd-I(1)	158.31(14)	N(4)-C(6)-C(7)	112.7(7)
I(2)-Cd-I(1)	101.77(2)	N(8)-C(7)-C(6)	110.2(7)
C(2)-N(1)-Cd	111.3(6)	C(7)-N(8)-Cd	110.9(5)

conformation with puckering parameters $q_2 = 0.460(10)$ Å, $\phi_2 = 90.0(10)^\circ$, while the second ring has an envelope conformation with parameters $q_2 = 0.456(9)$ Å, $\phi_2 = 73.9(9)^\circ$.²⁰ The geometries of the two halves of the ligand, constituting the two chelate rings,

are similar within the limits of accuracy. The slight angle strain observed on the sp^3 hybridized carbon and nitrogen atoms of the ligand may be attributed to the requirements of the formation of the five-membered rings.

The far-IR spectra of $Cd(\text{medien})X_2$ [$X = Cl^-$ (**1a**), Br^- (**2a**), I^- (**3a**)] have been recorded. The band positions for $Cd-X$ are observed to shift toward lower wavelength as chloride is replaced by bromide, and bromide is replaced by iodide. In each case there is a pair of bands, e.g. 225, 221 ($\nu M-Cl$); 168, 152 ($\nu M-Br$); 144, 130 ($\nu M-I$), although the IR spectral profiles do not differ from each other. An attempt to synthesize single crystals of $Cd(\text{medien})X_2$ yielded only $Cd(\text{medien})I_2$ (**3a**). Based on the single-crystal structure of $Cd(\text{medien})I_2$ (**3a**), as well as conductance data ($\Lambda_m = 40-60 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ in dry methanol) and IR spectra of $Cd(\text{medien})X_2$, it is proposed that the analogous chloro and bromo complexes exist as pentacoordinated species in which the halide ions are coordinated terminally. IR spectral bands of SO_4/SeO_4 are overlapped by the triamine bands. As a result the nature of the coordination in $Cd(\text{medien})AO_4 \cdot H_2O$ [$A = S$ (**6a**) or Se (**7a**)] remains unexplored. On the other hand the water species is supposed to be coordinated on the basis of IR spectra [$\rho_r(H_2O)$ at 720cm^{-1} and $\rho_w(H_2O)$ at 690cm^{-1}] and the temperature range of dehydration ($135-165^\circ\text{C}$ for **6a**; $110-140^\circ\text{C}$ for **7a**) derived from their TG curves (*vide infra*). Assuming noncoordination of AO_4 , both molecules should possess tetrahedral geometry, whereas they can also exist as octahedral/pentacoordinate species, depending on the bidentate chelate/monodentate behavior of AO_4 ($A = S$ or Se).

Thermal analysis. $[Cd(\text{medien})_2]Cl_2$ (**1**) and $[Cd(\text{medien})_2]Br_2$ (**2**) upon heating transform to $Cd(\text{medien})Cl_2$ (**1b**) and $Cd(\text{medien})Br_2$ (**2b**) as an intermediate product in the temperature range $155-210$ and $170-235^\circ\text{C}$, respectively. Both species upon further heating start to decompose at ca. 250°C and transform straightaway into their corresponding metal salts without showing any plateau in their TG curves. On the other hand $Cd(\text{medien})Cl_2$ (**1a**) and $Cd(\text{medien})Br_2$ (**2a**) synthesized from solution isomerize to $Cd(\text{medien})Cl_2$ (**1b**) and $Cd(\text{medien})Br_2$ (**2b**) in the solid state in the temperature ranges $185-200^\circ\text{C}$ ($\Delta H = 6.5 \text{kJ mol}^{-1}$) and $190-210^\circ\text{C}$ ($\Delta H = 6.7 \text{kJ mol}^{-1}$), respectively (Scheme 1). The species **1b** reverts slowly in an open atmosphere, but it can be stored in a desiccator, whereas the species **2b** does not revert. An IR spectral study of isomeric pairs (**1a**, **1b**) and (**2a**, **2b**) has been carried out. The spectra of each of the pairs do not show any noticeable difference in the region $300-150 \text{cm}^{-1}$, where the $M-X$ vibrations appear to exclude the possibility of configurational isomerism. However, IR-active bands of the triamine ligand in each pair differ appreciably in the regions $1000-3000$ and $750-1150 \text{cm}^{-1}$. In our earlier study²¹ two conformational isomers of $[NiL_2](NCS)_2$ ($L = NN'$ -dimethylethane-1,2diamine), which were char-

acterized by X-ray single-crystal analysis, showed a similar difference in their spectra. X-Ray powder diagrams also show a difference between the pairs (**1a**, **1b**) and (**2a**, **2b**) (Table 5). In our earlier studies^{22,23} similar differences have been found in X-ray powder diffraction patterns of the isomers, which did not differ in their coordination geometries but merely in the conformation of the chelate rings. Therefore the X-ray powder diffraction patterns of the pair (**1a**, **1b**) and (**2a**, **2b**) are not inconsistent with the conclusion that they are conformational isomers to each other. $[Cd(\text{medien})_2]I_2$ (**3**) upon heating transforms to $Cd(\text{medien})I_2$ (**3a**) in the temperature range $150-205^\circ\text{C}$ (Scheme 1). The species **3a** can also be synthesized immediately from solution. Here the species **3a** does not isomerize like (**1a**, **2a**). It decomposes directly to CdI_2 without showing any intermediate complex species.

$[Cd(\text{medien})_2](NCS)_2$ (**4**) undergoes a phase transition yielding an isomer $[Cd(\text{medien})_2](NCS)_2$ (**4a**) ($94-102^\circ\text{C}$, $\Delta H = 6.3 \text{kJ mol}^{-1}$; Scheme 1). This, on cooling to ambient temperature, does not show any drift in the DSC curve. However, on immediate reheating after cooling to ambient temperature it shows a heating curve identical to its first heating curve. The species **4a** upon further heating again isomerizes to $[Cd(\text{medien})_2](NCS)_2$ (**4b**) ($155-162^\circ\text{C}$, $\Delta H = 6.8 \text{kJ mol}^{-1}$) which reverts to **4a** on cooling ($162-155^\circ\text{C}$, $\Delta H = -6.7 \text{kJ mol}^{-1}$). IR spectra of **4** (at ambient temperature), **4a** (at 115°C) and **4b** (at 180°C) have been obtained (Fig. 3). The $\nu(NCS)$ band of **4** shows three sharp peaks at $2000-2200 \text{cm}^{-1}$, but in the case of **4a** and **4b** only one peak has been observed, rather than three. This suggests that the thiocyanate moiety in **4** is involved in the interaction of hydrogen bonding with hydrogens attached to the amine nitrogen. The spectra of **4a** and **4b** also differ in the region $750-1200 \text{cm}^{-1}$, where the IR-active bands of the triamine ligands generally appear, suggesting that the species

Table 5. Prominent lines d (in Å) in the X-ray powder patterns of the complexes.^a

Complex	$d/\text{Å}$
$Cd(\text{medien})Cl_2$ (1a)	6.55(s), 4.42(m), 4.28(m), 4.03(w), 3.27(w), 3.07(s), 2.95(w), 2.45(s), 2.36(s), 2.18(w), 2.14(w), 2.03(w), 1.96(w)
$Cd(\text{medien})Cl_2$ (1b)	7.70(s), 5.99(s), 5.17(w), 4.73(w), 4.23(s), 4.12(w), 3.85(w), 3.70(w), 3.34(w), 3.26(w), 2.94(w), 2.68(w), 2.56(w)
$Cd(\text{medien})Br_2$ (2a)	6.62(s), 5.08(m), 4.48(s), 4.32(m), 4.07(s), 3.86(w), 3.29(s), 3.08(s), 2.94(w), 2.65(w), 2.54(w), 2.46(s), 2.38(m), 2.16(w), 1.90(w), 1.61(w)
$Cd(\text{medien})Br_2$ (2b)	7.88(s), 6.10(s), 4.84(w), 4.29(s), 3.63(w), 3.49(m), 3.05(w), 2.33(w)

^aKey: s, strong; m, medium; w, weak.

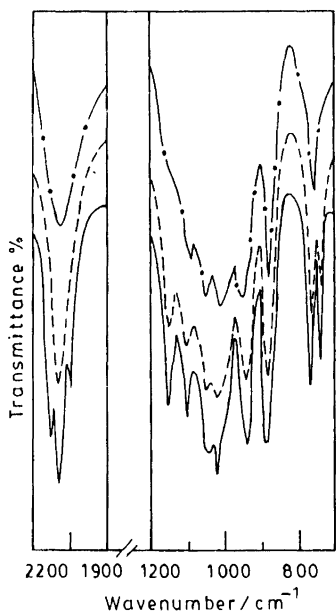


Fig. 3. IR spectra of $[\text{Cd}(\text{medien})_2](\text{NCS})_2$ (**4**) (—), $[\text{Cd}(\text{medien})_2](\text{NCS})_2$ (**4a**) (-----) and $[\text{Cd}(\text{medien})_2](\text{NCS})_2$ (**4b**) (-.-.-).

4, **4a** and **4b** are isomeric with each other and that the chromophoric view around cadmium is retained during isomerization. $[\text{Cd}(\text{medien})_2](\text{NO}_3)_2$ (**5**), on the other hand, undergoes a one-step reversible ($5 \rightleftharpoons 5a$) phase transition (heating 166–177 °C; $\Delta H = 31.4 \text{ kJ mol}^{-1}$; cooling 137–127 °C, $\Delta H = -29.0 \text{ kJ mol}^{-1}$, Scheme 1) upon heating. The species **5a** decomposes on further heating. IR spectra of **5** (at ambient temperature) and **5a** (at ca. 180 °C) have been taken. The spectra show differences in the regions 3000–3400 and 1300–1500 cm^{-1} (Fig. 4), where νNH_2 , δCH_2 and $\rho_w\text{CH}_2$ bands appear. This suggests that **5** and **5a** are also conformational isomers (*vide supra*).

$[\text{Cd}(\text{medien})_2]\text{SO}_4 \cdot 3\text{H}_2\text{O}$ (**6**) and $[\text{Cd}(\text{medien})_2]\text{SeO}_4 \cdot$

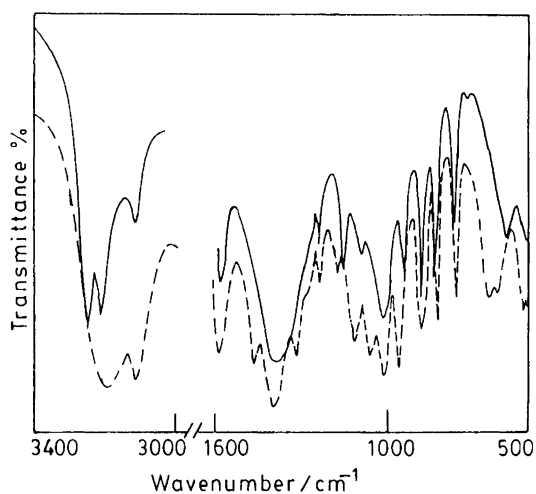


Fig. 4. IR spectra of $[\text{Cd}(\text{medien})_2](\text{NO}_3)_2$ (**5**) (-----) and $[\text{Cd}(\text{medien})_2](\text{NO}_3)_2$ (**5a**) (—).

$3\text{H}_2\text{O}$ (**7**) undergo dehydration in the temperature ranges 70–90 and 50–85 °C, respectively. Both the species also become dehydrated on storage in a desiccator containing P_2O_5 . The dehydrated species **6b** and **7b** become rehydrated on storage in a humid atmosphere. The species **6b** and **7b** upon further heating decompose to yield $\text{Cd}(\text{medien})\text{AO}_4$ [$\text{A} = \text{S}$ (**6c**) or Se (**7c**)] (Scheme 1). These two dehydrated mono-triamine species (**6c**, **7c**) exist as monohydrates at ambient temperature. $\text{Cd}(\text{medien})\text{AO}_4 \cdot \text{H}_2\text{O}$ (**6a**, **7a**) synthesized directly from solution undergo dehydration at 135–165 and 110–155 °C, respectively, to yield $\text{Cd}(\text{medien})\text{SO}_4$ (**6c**) and $\text{Cd}(\text{medien})\text{SeO}_4$ (**7c**), and they are rehydrated on exposure to a humid atmosphere (60% and above). Data for TG-DTA and DSC have been deposited.

Conclusions

The structures of mono(medien) complexes of CdX_2 ($\text{X} = \text{Cl}^-$, Br^- and I^-) reveal that Cd^{II} is pentacoordinated. The mono(dien) complexes on the other hand are invariably hexacoordinated. The methyl substitution on the secondary nitrogen of the triamine is thus responsible for changing the coordination number from six to five. The structures of the bis-medien complexes of cadmium(II) are also different from those of the dien complexes. The *s-fac* geometry is most common in the former, whereas the latter preferred geometry is *mer*. It is proposed that the following pairs of complexes [(**1a**, **1b**); (**2a**, **2b**); {(**4**, **4a**), **4a**, **4b**), (**4**, **4b**)} and (**5**, **5a**)] are conformational isomers to each other. A comparative study on the thermal behavior of bis and mono medien complexes of cadmium(II) shows that all the bis complexes undergo decomposition upon heating through the formation of their respective mono analogues as intermediates in the solid state, barring $[\text{Cd}(\text{medien})_2](\text{NCS})_2$ (**4**) and $[\text{Cd}(\text{medien})_2](\text{NO}_3)_2$ (**5**), which decompose straightaway to unidentified products. The inability of complexes **4** and **5** to yield mono species may be due to the lower decomposition temperatures of the NCS^- and NO_3^- anions. The decomposition temperatures of $[\text{Cd}(\text{medien})_2]\text{X}_2$ [$\text{X} = \text{Cl}^-$ (**1**), Br^- (**2**) and I^- (**3**)] are lower than $[\text{Cd}(\text{medien})_2]\text{AO}_4$ [$\text{A} = \text{S}$ (**6b**), Se (**7b**)] (Scheme 1). However, this difference is not so pronounced in the case of mono complexes. A comparison of the thermal stabilities of dien and medien complexes of cadmium(II) (Table 6) shows that T_i (initial temperature of decomposition) decreases on methyl substitution on the secondary amine nitrogen atom of bis(2-aminoethyl)amine.

Acknowledgements. We thank the Regional Sophisticated Instrumentation Centre, Bose Institute, Calcutta, for the single-crystal X-ray diffractometer facility. Financial support by the Council of Scientific and Industrial Research, New Delhi as a grant to N.R.C. is also acknowledged.

Table 6. Comparative chart of T_i (initial temperature of decomposition in °C) for some of the bis- and mono-triamine (dien and medien) complexes of cadmium(II).

Complex	L = dien	L = medien
[CdL ₂]Cl ₂	185	155
CdLCl ₂	255	255
[CdL ₂]Br ₂	190	170
CdLBr ₂	260	250
[CdL ₂]SO ₄	195	190
CdLSO ₄	290	265
[CdL ₂]SeO ₄	215	215
[CdL ₂](NCS) ₂	180	180
[CdL ₂](NO ₃) ₂	265	200

References

- Harada, K. *Bull. Chem. Soc. Jpn.* 66 (1993) 2889.
- Searle, G. H. and House, D. A. *Aust. J. Chem.* 40 (1987) 361 and references therein.
- Schmidtke, H. H. and Grathoff, D. *Inorg. Chim. Acta* 2 (1968) 357.
- Curtis, N. F. and Powell, H. K. J. *J. Chem. Soc. A* (1968) 3069.
- Keene, F. R. and Searle, G. H. *J. Chem. Soc., Chem. Commun.* (1968) 893.
- Dwyer, M. and Searle, G. H. *J. Chem. Soc., Chem. Commun.* (1972) 726.
- Cannas, M., Marongiu, G. and Saba, G. *J. Chem. Soc., Dalton Trans.* (1980) 2090.
- Cannas, M., Carta, G., Cristini, A. and Marongiu, G. *J. Chem. Soc., Dalton Trans.* (1976) 210.
- Barr, D., Edwards, A. J., Raithby, P. R., Rennie, M-A., Verhorevoort, K. L. and Wright, D. S. *J. Organomet. Chem.* 493 (1995) 175.
- Mukherjee, A. K., Koner, S., Ghosh, A., Chaudhuri, N. R., Mukherjee, M. and Welch, A. J. *J. Chem. Soc., Dalton Trans.* (1994) 2367.
- Koner, S., Ghosh, A. and Chaudhuri, N. R. *Transition Metal Chem.* 15 (1990) 394.
- Koner, S., Ghosh, A. and Chaudhuri, N. R. *Thermochim. Acta* 159 (1990) 55.
- Koner, S., Ghosh, A. and Chaudhuri, N. R. *Transition Metal Chem.* 13 (1988) 291.
- Kojima, M., Iwagaki, M., Yoshikawa, Y. and Fujita, J. *Bull. Chem. Soc. Jpn.* 50 (1977) 3216.
- Searle, G. H., Lincoln, S. F., Teague, S. G. and Rowe, D. G. *Aust. J. Chem.* 32 (1979) 519.
- Vogel's Textbook of Quantitative Inorganic Analysis*, 4th Edn., E.L.B.S. and Longman, p. 393.
- Gabe, E. J., LePage, Y., Charland, J.-P., Lee, F. L. and White, P. S. *J. Appl. Crystallogr.* 22 (1989) 384.
- Sheldrick, G. M. *SHELX93. Program for the Solution of Crystal Structure*, University of Gottingen, Germany 1993.
- Johnson, C. K. *ORTEP. Report ORNL-5138*. Oak National Laboratory, Oak Ridge, TN 1976.
- Cremer, D. and Pople, J. A. *J. Am. Chem. Soc.* (1975) 1354.
- Mukherjee, A. K., Mukherjee, M., Welch, A. J., Ghosh, A., De, G. and Chaudhuri, N. R. *J. Chem. Soc., Dalton Trans.* (1987) 997.
- De, G., Biswas, P. K. and Chaudhuri, N. R. *J. Chem. Soc., Dalton Trans.* (1984) 2591.
- Mukherjee, A. K., Mukherjee, M., Ray, S., Ghosh, A. and Chaudhuri, N. R. *J. Chem. Soc., Dalton Trans.* (1990) 2347.

Received March 24, 1998.