# Synthesis and spectral studies of 2-salicylidine-4-aminophenyl benzimidazole and its reaction with divalent Zn, Cd and Hg: crystal structure of the cadmium bromide complex

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2-salicylidine-4-aminophenyl benzimidazole (SAPbzlH, LH) has been synthesised and its complexes, formulated as $ZnX_2Ly.nH_2O$ (X = Cl, $y$ = 1.5, $n$ = 1; X = Br, $y$ = 2, $n$ = 2; X = $CH_3COO$, $y$ = 1.5, $n$ = 2), $CdX_2L.CH_3OH.0.5H_2O$ (X = Cl, Br) and $HgX_2L.nH_2O$ (X = Cl, $n$ = 2; X = Br, $n$ = 0), have been characterised. A single crystal X–ray diffraction study of $[Cd_2Br_4L_2].2CH_3OH.H_2O$ has revealed its binuclear structure with dibromide and SAPbzlH bridges, the environment around each metal ion being distorted trigonal bipyramidal. A similar structure is envisaged for the chloride analogue of cadmium as well as the mercury complexes.

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**Keywords:** 2-salicylidine–4-aminophenyl benzimidazole, Zn(II), Cd(II), Hg(II) complexes, crystal structure

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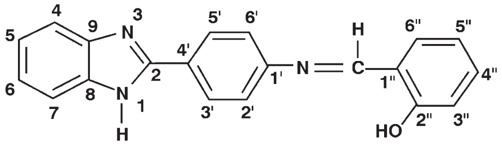
Benzimidazole and its derivatives have been extensively studied for their complexing ability with a number of transition metal ions.[1,2] This is because such complexes could exhibit antitumour, antineoplastic, fungicidal, insecticidal, antiviral, antimalarial and other pharmacological activities.[3–5] The study of metal complexes containing Schiff bases is also of interest as some of them have shown the ability to bind dioxygen reversibly[6] and act as catalysts in hydrogenation of olefins,[7] amino-group transfer from the donor to the acceptor[8] and photochromic properties.[9] Increased attention has also been paid to the study of such complexes as molecular models to understand biological systems containing the benzimidazole moiety.[10] N- heterocyles have the ability to bind as mono, bi or polydentate ligands to transition metal ions to produce mononuclear and/or polynuclear complexes. With this in mind, there have been investigations on the reactions of transition metal ions with a wide range of N-heterocycles.[11,12] We have synthesised the Schiff base, 2-salicylidine-4-aminophenyl benzimidazole (SAPbzlH; LH) and we report here its reactions with salts of Zn, Cd and Hg.

## Experimental

The chemicals used were of E-Merck grade. The solvents were distilled prior to their use.

Conductivity measurements were made on a digital conductivity meter (Elico model–180), at room temperature. Elemental analyses were carried out using Elementer Vario EI III and Carlo Erba-1108 instruments. The IR spectra of the complexes in KBr were recorded on a Nicolet impact 400D spectrometer in the range 4000–400 cm$^{1}$. The far-IR spectra of the complexes in polyethylene powder were recorded in the range 700–50 cm$^{-1}$ using a Bruker optical spectrometer IFF 66 V/S. The mass spectrum of the Schiff base was recorded on a ESI, Esquine 300 plus, Bruker Daltonics. The FAB mass determinations for the complexes of zinc were done using a Jeol SX 102/Da-600 mass spectrometer. $^1H$ NMR spectra of LH were recorded on a Bruker Avance DRX 500 NMR spectrometer with DMSO-$d_6$ as solvent at 300 K. The $^1H$ NMR spectra of the complexes in DMSO–$d_6$ (using TMS as internal reference) were recorded on a Bruker 400 MHz spectrometer. The $^{111}Cd$ solid state NMR spectrum of the cadmium bromide complex was recorded on a Bruker solid state 500 MHz NMR spectrometer with magic angle spinning (MAS) and using cadmium nitrate (–100 ppm) as the external reference.[13] Single crystal X-ray diffraction data of the cadmium bromide complex were collected at room temperature with a Bruker smart-CCD system with MoK/α radiation (λ = 0.71073 Å), operating in a π and ω scanning mode. A total of 3647 reflections were collected. Accurate unit cell parameters were determined from full matrix, least-square refinements. The diffraction refinements conform to a range θ = 0–25.0°. All hydrogen atom positions were fixed and refined isotropically.



**Scheme 1** LH (N–N–OH).

*SAPbzlH:* The 4-aminophenyl benzimidazole (4-APbzlH) was prepared according to the literature method.[14] The Schiff base, SAPbzlH was obtained as a solid by refluxing a mixture of 4-APbzlH (5.0 g; 24 mmol) and salicylaldehyde (3.05 mL; 29 mmol) in ethanol (35 mL) for about 6 h, followed by evaporation of the solvent to a small volume. The solid was washed with ether and recrystallised from ethanol and dried in a vacuum. The CHN analyses of the compound (Table 1) corresponded to the molecular formula $C_{20}H_{15}N_3O$.

$ZnX_2Ly.nH_2O$ (L = SAPbzl, X = Cl, $y$ = 1.5, $n$ = 1; X = Br, $y$ = 2, $n$ = 2; X = $CH_3COO$, $y$ = 1.5, $n$ = 2): to an ethanolic (7.5 mL) solution of zinc salt (0.60 mmol) [as chloride (0.08 g)/bromide (0.14 g)/acetate (0.14 g)] was added LH (0.38 g; 1.20 mmol) in ethanol (7.5 mL) and the mixture was refluxed for about 6 h on a steam-bath, during which time a coloured solid separated. The solid was washed with ethanol and dried in a vacuum.

$CdX_2L.CH_3OH.0.5H_2O$ (X = Cl, Br): To a methanolic (7.5 mL) solution of cadmium salt [(0.60 mmol) as chloride (0.12 g)/bromide (0.21 g)] was added LH (0.38 g; 1.20 mmol) in methanol (7.5 mL), the resultant solution was refluxed for about 6 h on a steam-bath and on cooling the mixture a coloured solid separated. The solid was washed with methanol and dried in a vacuum.

*Crystals of* $Cd_2Br_4L_2.2CH_3OH.H_2O$: To a methanolic solution (20 mL) of cadmium bromide (0.21 g, 0.6 mmol) was added LH (0.38 g, 1.2 mmol) in methanol (20 mL). The mixture was refluxed for 6 h on a steam bath and the solution was filtered. The filtrate was kept aside at room temperature for two days when coloured crystals separated. The crystals were washed with methanol and dried under vacuum.

$HgX_2L.nH_2O$ (X = Cl, $n$ = 2; X = Br, $n$ = 0): To a methanolic (7.5 mL) solution of mercuric salt [(0.60 mmol) as chloride (0.16 g)/bromide (0.22 g)] was added LH (0.38 g; 1.20 mmol) in methanol (7.5 mL) and the mixture was refluxed for about 6 h on a steam-bath and left overnight. A coloured solid separated and this was washed with methanol and dried in vacuum.

## Results and discussion

4-Aminophenyl benzimidazole reacts with salicylaldehyde in ethanol to produce the Schiff base 2-salicylidine-4-aminophenyl benzimidazole (SAPbzlH, LH). Physical properties and analytical data of LH are listed in Table 1. The mass spectrum of LH showed a molecular ion peak corresponding to M+1 at $m/z$ 314.

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**Table 1** Physical properties and analytical data of SAPbzlH and metal complexes

| Compound | Yield /% | Colour | Analytical data/%[a] | | | Λ[b] |
|---|---|---|---|---|---|---|
| | | | C | H | N | |
| SAPbzlH [L] | 89 | Yellow | 76.58<br>(76.67) | 4.72<br>(4.79) | 12.41<br>(13.41) | – |
| $ZnCl_2L_{1.5}.H_2O$ | 33 | Yellow | 57.67<br>(57.71) | 3.08<br>(3.92) | 10.31<br>(10.09) | 22 |
| $ZnBr_2L_2.2H_2O$ | 31 | Yellow | 54.08<br>(54.10) | 3.54<br>(3.83) | 9.22<br>(9.46) | 11 |
| $Zn(CH_3COO)_2L_{1.5}.2H_2O$ | 30 | Yellow | 58.61<br>(59.22) | 4.14<br>(4.71) | 9.36<br>(9.14) | 4 |
| $CdCl_2L.CH_3OH.0.5H_2O$ | 55 | Orange | 46.64<br>(46.90) | 3.14<br>(3.72) | 8.10<br>(7.81) | 10 |
| $CdBr_2L.CH_3OH.0.5H_2O$ | 47 | Orange | 41.52<br>(40.24) | 3.55<br>(3.19) | 7.12<br>(6.70) | 10 |
| $HgCl_2L.2H_20$ | 55 | Pale yellow | 37.31<br>(38.67) | 2.50<br>(3.06) | 6.52<br>(6.76) | 6 |
| $HgBr_2L$ | 50 | Orange | 36.0<br>(35.64) | 2.30<br>(2.22) | 6.62<br>(6.23) | 13 |

[a] Calculated values are in parentheses.
[b] Molar conductance (ohm$^{-1}$ cm$^2$ mol$^{-1}$) of 10$^{-3}$ M solutions in DMF around 25°C.

The IR spectrum of LH showed a band in the range 3450–3300 cm$^{-1}$ assigned to νOH and νNH.[15,16] The spectrum also displayed multiple peaks in the range 3050–2660 cm$^{-1}$ assigned to νCH of the phenyl and methine groups. Two bands at 1600 and 1618 cm$^{-1}$ are ascribed to the νN=CH of methine group and νC=C of the $C_6H_4$ rings respectively. A peak at 1572 cm$^{-1}$ is assigned to the νN=C of the imidazole ring. A band at 1276 cm$^{-1}$ is attributed to νC–O of the phenolic group (Table 2).

In the $^1$H NMR spectrum of SAPbzlH, (Scheme 1, and Fig.1 deposited in the ESI), two signals observed around 12.09 ppm are assigned to the protons of NH of the imidazole unit and phenolic OH. A signal around 9.00 ppm is assigned to H of N=CH.[17–19] Two doublets, one at δ 7.60 ($J_{HH}$ = 8.3Hz) and another at δ 8.25 ($J_{HH}$ = 8.3 Hz) are ascribed to two sets of protons 2′, 6′ and 3′,5′ (each set being equivalent) respectively.The resonance due to proton 4 is observed as a doublet at δ 7.53 ($J_{HH}$ = 7.4 Hz).[20] The signals due to protons 7 and 3″ overlap and appear like a triplet at δ 7.68 ($J_{HH}$ = 8.4 Hz). The assignments of the other protons resonances are listed in Table 3.

The divalent salts of Zn, Cd and Hg react with LH in the mole ratio 1:2 in ethanol/methanol at refluxing temperature to produce

**Table 2** IR and far-IR spectral data (cm$^{-1}$) of SAPbzlH and metal complexes

| Compound | νOH, νNH[a] | νN=CH, νC=C, νN=C | νC–O phenolic | νM–X$_t$[c] | νM–X$_b$[c] | νM–N | νM–O |
|---|---|---|---|---|---|---|---|
| SAPbzlH [L] | 3450–3300 | 1600,1618<br>1572 | 1276 | – | – | – | – |
| $ZnCl_2L_{1.5}.H_2O$ | 3550–3300 | 1600,1642<br>1539 | 1280 | 284(br)[c] | – | 338<br>315 | 210 |
| $ZnBr_2L_2.2H_2O$ | 3743–3328 | 1600, 1618<br>1537 | 1284 | 230(br)[c] | – | 435<br>375 | – |
| $Zn(CH_3COO)_2L_{1.5}.2H_2O$ | 3560–3370 | 1589;1604 $\nu_{asy}$ (coo)[b]<br>1400 $\nu_{sy}$ (coo)[b] | 1280 | – | – | – | – |
| $CdCl_2L.CH_3OH.0.5H_2O$ | 3550–3300 | 1600,1627<br>1531 | 1284 | 253 | 181 | 110(br)[c] | 110(br)[c] |
| $CdBr_2L.CH_3OH.0.5H_2O$ | 3490–3300 | 1600,1631<br>1529 | 1280 | 176 | 139 | 140(br)[c] | 140(br)[c] |
| $HgCl_2L.2H_20$ | 3570–3300 | 1600,1620<br>1531 | 1281 | – | – | – | – |
| $HgBr_2L$ | 3450–3220 | 1596,1618<br>1541 | 1278 | – | – | – | – |

[a] The bands due to $\nu_{OH}$ and $\nu_{NH}$ overlap giving a broad band.
[b] Asymmetric and symmetric stretching frequencies of acetate group.
[c] t, terminal; b, bridging; br, broad.

**Table 3** $^1$H NMR spectral data of SAPBzlH and metal complexes[a]

| Compound | Benzimidazole ring | | | | Amino phenyl ring | | | Salicylidine ring. | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | NH | $H_4$ | $H_7$ | $H_{5,6}$ | $H_{2'6'}$ | $H_{3'5'}$ | N=CH | OH | $H_{3''}$ | $H_{4''}$ | $H_{5''}$ | $H_{6''}$ |
| SAPbzlH [L] | 12.95 s | 7.53 d<br>(7.4) | 7.68 t<br>(8.4) | 7.20 q<br>(6.7,8.6) | 7.60 d<br>(8.3) | 8.25 d<br>(8.3) | 9.06 s | 12.97 s | 7.68 t<br>(8.4) | 7.00 t<br>(8.1,8.8) | 7.44 t<br>(7.3) | 7.00 t<br>(8.1,8.8) |
| $CdCl_2L.CH_3OH.0.5H_2O$ | 12.94 s | 7.53 d<br>(7.3) | 7.66 t<br>(8.7) | 7.21 m | 7.60 d<br>(8.4) | 8.25 d<br>(8.4) | 9.06 s | 12.97 s | 7.70 t<br>(8.7) | 7.21 t<br>(7.0) | 7.42 t<br>(7.1) | 6.99 t<br>(7.5) |
| $CdBr_2L.CH_3OH.0.5H_2O$ | 12.94 s | 7.52 d<br>(7.1) | 7.69 t<br>(9.0) | 7.20 m | 7.60 d<br>(8.4) | 8.26 d<br>(8.5) | 9.06 s | 12.97 s | 7.69 t<br>(9.0) | 6.90 t<br>(6.1) | 7.44 t<br>(7.2) | 6.90 t<br>(6.1) |
| $HgCl_2L.2H_20$ | 12.99 s | 7.62 d<br>(8.4) | 7.41 d<br>(7.5) | 7.23 m | 7.62 d<br>(8.4) | 8.27 d<br>(8.4) | 9.09 s | 12.99 s | 7.62 d<br>(8.4) | 7.10 t<br>(7.8) | 7.46 t<br>(7.1) | 7.10 t<br>(7.8) |
| $HgBr_2L$ | 12.96 s | 7.60 d<br>(8.3) | 7.68 d<br>(7.5) | 7.21 m | 7.60 d<br>(8.3) | 8.25 d<br>(8.5) | 9.06 s | 12.96 s | 7.60 d<br>(8.3) | 6.90 t<br>(7.9) | 7.43 t<br>(6.9) | 6.90 t<br>(7.9) |

[a] Spectra have been recorded in DMSO-d$_6$; δ in ppm and coupling constants in Hz are given in parentheses; s, singlet; d, doublet; t, triplet; q, quintet; m, multiplet.

complexes of the compositions, $ZnX_2Ly.nH_2O$ (X = Cl, $y$ = 1.5, $n$ = 1; X = Br, $y$ = 2, $n$ = 2; X = $CH_3COO$, $y$ = 1.5, $n$ = 2), $CdX_2L.CH_3OH.0.5H_2O$ (X = Cl, Br) and $HgX_2L.nH_2O$ (X = Cl, $n$ = 2; X = Br, $n$ = 0). Physical properties and analytical data of metal complexes are given in Table 1. The complexes are insoluble in common organic solvents except in DMF and DMSO. The low molar conductance values of $10^{-3}$ M DMF solutions of the complexes indicate their non-electrolytic nature.[21]

A comparison of the IR spectra of the complexes with that of LH reveals minor shifts in the positions of the bands. The νC–O of the phenolic group shows a marginal shift towards higher wavenumbers, suggesting weak coordination of oxygen to the metal ion.[22] A peak observed at 1572 $cm^{-1}$ due to νN=C of the Schiff base has shifted to lower wavenumber by 30–40 $cm^{-1}$ in the spectrum of the complexes, indicating the coordination of the imidazole nitrogen to the metal ion.[23] In the far-IR spectrum of zinc chloride complex, a broad band observed at 284 $cm^{-1}$ is assigned to $\nu Zn–Cl_t$ (t = terminal) and other bands at 338 and 315 $cm^{-1}$ and 210 $cm^{-1}$ are assigned to νZn–N and νZn–O respectively.[24] In the case of the zinc bromide complex, the bands observed at 435, 375 and 230 $cm^{-1}$ (broad) are assigned to νZn–N and $\nu Zn–Br_t$ respectively.[25] In the case of a cadmium chloride complex, the bands observed at 281 and 253 $cm^{-1}$ are assigned to $\nu Cd–Cl_t$ and $\nu Cd–Cl_b$ (b = bridging) respectively and the corresponding ones for the bromide analogue are observed at 176 and 139 $cm^{-1}$. The ratios $\nu Cd–Br_t/\nu Cd–Cl_t$, $\nu Cd–Cl_b/\nu Cd–Cl_t$ and $\nu Cd–Br_b/\nu Cd–Br_t$ are around 0.7 and in the expected range.[24] Additional bands observed at 110 (chloride complex) and 140 $cm^{-1}$ (bromide complex) are broad and are assigned to νCd–N and νCd–O.[24]

The FAB-mass spectra of $Zn_2Cl_4(SAPbzlH)_3.2H_2O$ and $Zn_2(CH_3COO)_4(SAPbzlH)_3.4H_2O$ exhibit a large number of peaks, some of them being higher than those of the molecular ion peaks. The latter may be due to the association of fragmented species. For the chloride complex, two prominent peaks observed at $m/z$, 1068 and 664 are attributed to fragmented species, $Zn_2(SAPbzlH)_3$-2H and $Zn_2(SAPbzlH)_2$-$C_6H_4OH$ respectively. Similarly for the acetate complex, two prominent peaks observed at $m/z$, 1128 and 753 are assigned to the fragmented species $Zn_2(SAPbzlH)_3(CH_3COO)$–H and $Zn_2(SAPbzlH)_2$–4H respectively.

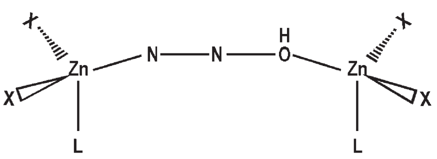
The proton NMR spectra of metal complexes exhibit resonances due to the co-ordinated Schiff base. In the case of zinc(II) complexes, it appears that the compounds decompose in dmso-$d_6$ and the spectra show complex features. The presence of methanol and water in cadmium complexes is indicated in the $^1H$ NMR spectrum (Fig. 2 deposited in the ESI) by a quartet and a doublet around 4.1 ppm ($J_{HH}$ = 5.2Hz) and 3.2 ppm ($J_{HH}$ = 5.2Hz) respectively for hydroxyl and methyl protons. The signal due to water molecule has perhaps merged with that of DMSO-$H_2O$ peak at δ 3.4 ppm. The spectral data of the complexes are listed in Table 3.

The $^1H$ NMR spectra of both Cd and Hg complexes (Figs 2 and 3 deposited in the ESI) do not reveal any observable shifts in the resonances as compared to those of the uncoordinated Schiff base. As Cd and Hg possess filled d-orbitals there may not be much electron density drift from the Schiff base to metal to influence the positions of the proton resonances. The solid state $^{111}Cd$ NMR spectrum of the cadmium bromide complex shows a single resonance at 124.5 ppm, indicating that the cadmium ions are in identical environments.[26]

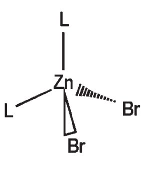
Based on analytical, spectral, molar conductance and FAB mass data, a ligand- bridged dinuclear structure (**1**; X = Cl, $CH_3COO$) for the zinc chloride and acetate complexes and mononuclear structure (**2**) for the zinc bromide complex are proposed, the metal ion being in a tetrahedral environment in each case.

*Crystallography*

Crystals of $Cd_2Br_4L_2.2CH_3OH.H_2O$ were obtained from a methanol reaction mixture. These are associated with methanol and water molecules.[27] The latter molecules are not coordinated to the metal ion and behave as solvated species. The arrangement of molecules in the crystal lattice suggests repetition of the unit cell to produce a polymer.



**1**



**2**

The X-ray crystal data and structural refinements for the complex $Cd_2Br_4L_2.2CH_3OH.H_2O$ are listed in Table 4. The fractional coordinates of the atoms and isotropic displacement parameters are given in Table 5 (deposited in the ESI). Selected bond distances and bond angles are listed in Table 6.

The complex is five-coordinate with respect to each of the Cd(II) ions. The geometry around each metal ion is distorted trigonal bipyramidal (Fig. 4); the trigonal plane consists of cadmium ($Cd_1$) surrounded by a nitrogen atom $N_1$ of bridged SAPbzlH and two bromide ions (one terminal $Br_1$ and the other bridging $Br_2$). Axial positions are occupied by oxygen ($O_1$) of bridged SAPbzlH and bridged bromide ion ($Br'_2$).

The bond angles in the trigonal plane are 137.5, 110.2 and 110.3° respectively, the average being 119.34°. There has been a deviation

**Table 4** Crystal data and structural refinements of $Cd_2Br_4L_2.2CH_3OH.H_2O$

| | |
|---|---|
| Chemical formula | $C_{42}H_{36}Br_4Cd_2N_6O_5$ |
| Formula weight | 1249.20 |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ |
| Unit cell dimensions | |
| $a$ = 8.9091 (16) Å | α = 79.182 (3)° |
| $b$ = 8.9371(16) Å | β = 86.401 (3)° |
| $c$ = 13.919(3) Å | γ = 72.915 (3)° |
| Unit cell volume | 1040.5 (3) $Å^3$ |
| Formula number, Z | 1 |
| Density (calculated) | 1.981 g $cm^{-3}$ |
| Crystal size max (mm) | 0.35 |
| Crystal size mid (mm) | 0.30 |
| Crystal size min (mm) | 0.25 |
| Absorption coefficient/mm | 4.914 |
| F(000) | 602 |
| Data collection in a θ range | 1.49°–25.00° |
| Diffraction reflection range | $-10 < h > =10$<br>$-10 < k > =10$<br>$-16 < l > =16$ |
| Diffraction reflection unique : | |
| Number of reflections | 3647 |
| Goodness of fit on $F^2$ | 1.298 |
| Reflection threshold | I > 2/ σ (I) |
| $R^1$ = 0.0691, $wR^2$ = 0.1893 | |
| (R indices defined as $R^1$) | |

**Table 6** Selected bond distances and bond angles

| Bond distances (Å) | |
|---|---|
| Cd(1)–Br(1) | 2.5880(16) |
| Cd′(1)–Br(2) | 2.7183(17) |
| Cd(1)–Br(2) | 2.7318(17) |
| Cd(1)–O(1) | 2.377(9) |
| Cd(1)–N(1) | 2.299(11) |
| C (7)–N(1) | 1.338(17) |
| C (1) –N(1) | 1.393(17) |
| C (7)–N(2) | 1.365(16) |
| C (6)–N(2) | 1.351(18) |
| C (11)–N(3) | 1.424(18) |
| N(3)–C(20) | 1.332(18) |
| **Bond angles (°)** | |
| N(1)–Cd(1)–O(1) | 83.6(4) |
| N(1)–Cd(1)–Br(1) | 110.2(3) |
| O(1)–Cd(1)–Br(2) | 77.8 (2) |
| N(1)–Cd(1)–Br(2) | 137.5(3) |
| Br(1)–Cd(1)–Br(2) | 110.32(5) |
| Br(2)–Cd(1)–Br(2) | 84.87(5) |
| C(14)–O(1)–Cd(1) | 122.5(8) |
| C(1)–N(1)–Cd(1) | 120.8(8) |
| O(1)–Cd(1)–Br′(2) | 157.0(2) |

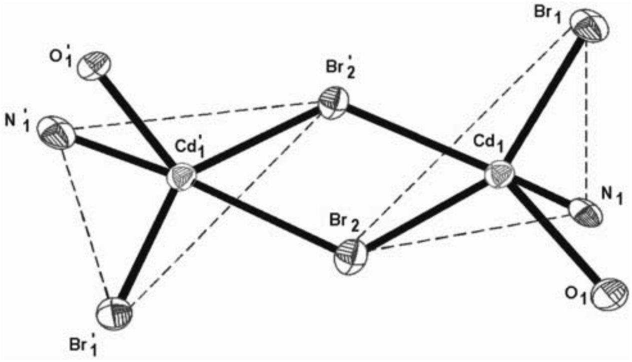


**Fig 4** Skeletal structure of $Cd_2Br_4L_2$.

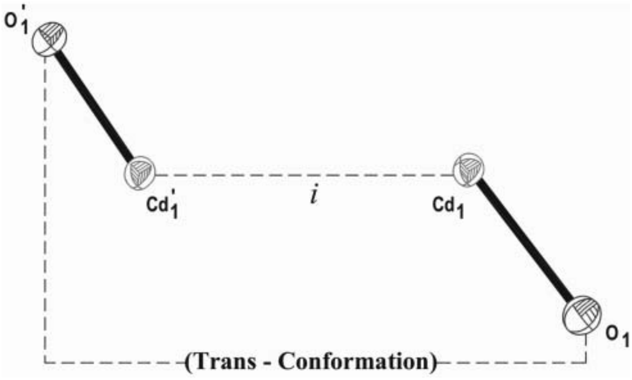


**Fig 5**

of each of these from the regular trigonal plane bond angle of 120°. The axial bond angle is 157° ($O_1$–$Cd_1$–$Br'_{2)}$ as against 180°.[28,29] The deviations of planar as well as axial bond angles from regular trigonal bipyramidal geometry indicate a distortion in the trigonal bipyramidal geometry around each Cd(II) ion.

The $Cd'_1$–$Br_2$ (bridging) and $Cd'_1$–$Br_2$ (bridging) distances are 2.732 and 2.718 Å respectively. Both the bridging distances are longer than the $Cd_1$–$Br_1$ (terminal) bond length of 2.588 Å. The $Cd_1$–$N_1$ and $Cd_1$–$O_1$ bond distances are 2.298 and 2.374 Å respectively and are comparable with those reported for related complexes.[30,31] In the dimer, half the molecule is related to the other half by the centre of inversion (Fig. 5).

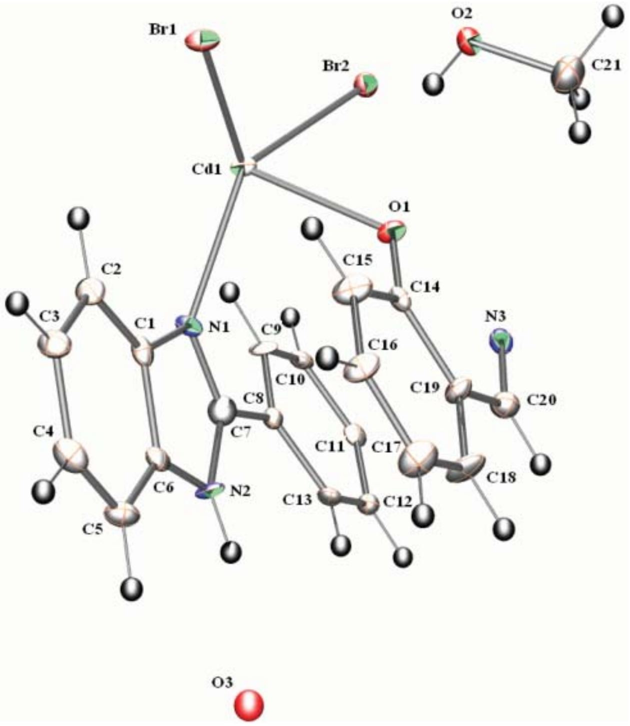


**Fig. 6** Partial ORTEP diagram of $Cd_2Br_4L_2.2CH_3OH.H_2O$.

The total number of asymmetric molecules in the unit cell with space group, $P\overline{1}$ is one. The complex molecule as a whole exhibits a *trans*-conformation about the centre of inversion above and below which the coordinated Br (bridging) atoms are located (Fig. 4). The $Cd_1$ ….. $Cd'_1$ distance is 4.022(1) Å. This is comparable with that reported (4.047 Å) for a polynuclear Cd(II) complex with dibromo bridges.[32] A perspective view of the molecular structure of the title compound with the atom numbering scheme is given in the ORTEP diagram (Fig.6)

The molecular packing of the complex is shown in Fig. 7. A weighted plane calculation shows that all the atoms in the benzimidazole moiety are in one plane.

Similarly, atoms belonging to the phenolic ring are also in one plane, but these two moieties are inclined with respect to each other by a dihedral angle of 16.1 (1)°. However, the $Cd_1$ atom is not in the plane defined by the planes comprising the above moieties. Furthermore,

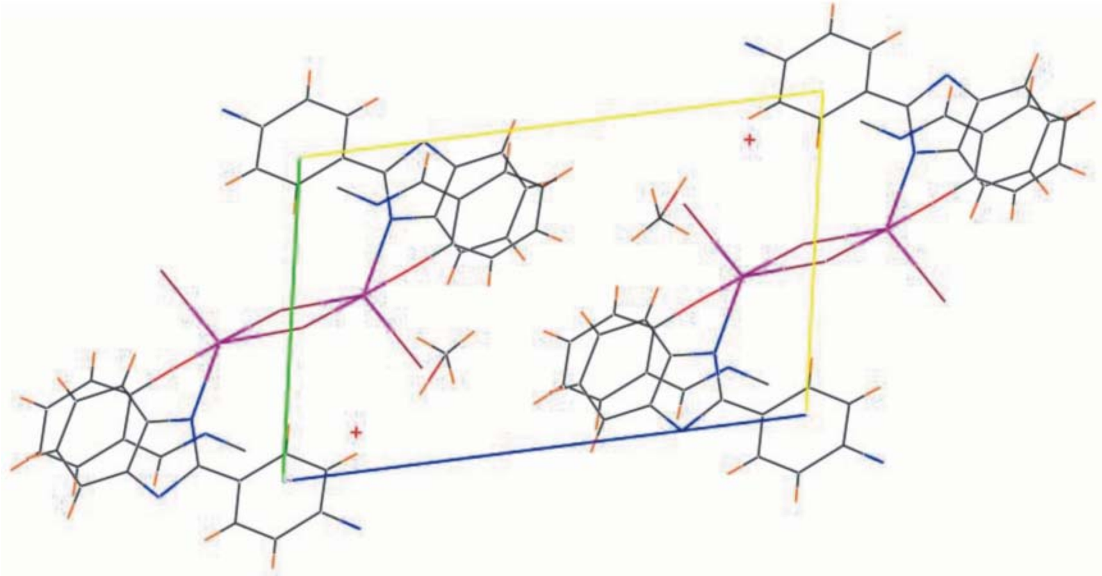
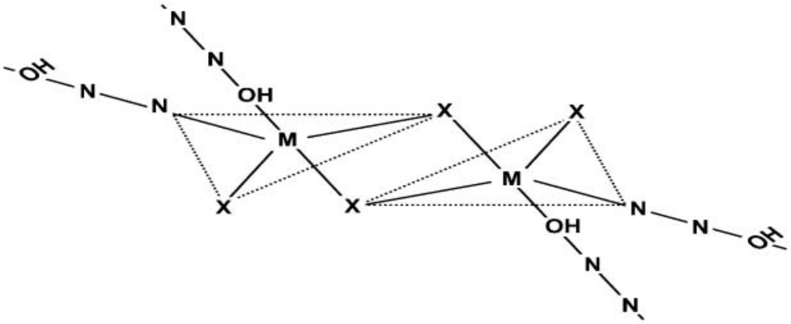


**Fig. 7** Molecular packing of cadmium bromide complex.



**3** (M = Cd, Hg ; X = Cl, Br)

$Br_1$ and $Br_2$ are in another plane with respect to the planes of the two benzimidazole and phenolic groups. The benzimidazole ring of one SAPbzlH and the phenolic ring of another SAPbzlH, both coordinated to the same metal ion, may have very weak intramolecular π–π interactions due to slipped stacking, [N(1)–C(16) = 4.231 A°; Fig. 6], and this perhaps is responsible for stabilising the packing.[33]

The results support a dihalo- and ligand-bridged polynuclear structure **3** for the cadmium complexes. A similar structure has been envisaged for the mercury analogues.

## Electronic Supplementary Information

Figures 1, 2 and 3, and Table 5 are deposited in the ESI available via http://stl.publisher.ingentaconnect.com/content/stl/jcr/

CCDC 740121 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via 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; E-mail : deposit@ccdc.cam.ac.uk).

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## References

1 L. Song, Y. Xie, H. Wang and Y. Zhangguo, *Huaxue ZaZhi*., 2000, **10**, 92.
2 N. Bharti, M.R. Maurya, F. Naqvi and A. Azam, *Bioorg. Med. Chem. lett*., 2000, **10**, 2243.
3 M. Stavros, V. Athanasios, D. Konstantinos, P. Moschos, S.T. Asterios and S.V. Loannis, *J. Inorg. Bio. Chem*., 1988, **34**, 265.
4 G.V. Reddy, N.R. Rao and M.C. Ganorkar, *Indian J. Chem*., 1987, **26A**, 789.
5 P. Souza, J.A.G. Vazquez, J.R. Masaguer and A. Arguero, *Trans. Met. Chem*., 1986, **11**, 229.
6 R.D. Jones, D.A. Summer Ville and F. Basolo, *Chem. Rev*., 1979, **79**, 139.
7 G. Henrici-Olive and S. Olive, *The chemistry of the catalyzed hydrogenation of carbon monoxide*, Springer, Berlin, 1984, p.152.
8 H. Dugas and C. Penney, *Bio-organic chemistry*, Springer, New york, 1981, p. 435.
9 J.D. Margerum and L.J. Miller, *Photochromism*, Wiley, 1971, p.569.
10 C.J. Matthews, W. Clegg, S.L. Health, N.C. Martin, M.N. Stuart-Hill and J.C. Lockhart, *Inorg. Chem*., 1998, **37**, 199.
11 V. Gayathri, E.G. Leelamani, N.M.N. Gowda, G.K.N. Reddy, *Polyhedron*, 1997, **16** No. 7, 1169.
12 S. Sathyanarayana and K.R. Nagasundara, *J. Chem. Research.*, 2007, 387.
13 Z. Talebpour, N. Alizadeh, H.R. Bijanzadeh and M. Shamsipur, *J. Incl. Phenom*., 2004, **49**, 101.
14 J.W. Hein, R.J. Alhum and J.J. Liquitt, *J. Am. Chem. Soc.,* 1957, **79,** 427.
15 P. Tamayo, M.M. Antonia, J.R. Masaguer and M. Cristina, *Trans. Met. Chem*., 1989, **14,** 283.
16 G.G. Mohamed and Z.H. Abd EI–wahab, *J. Therm. Anal. Calorim*., 2003, **73**, 347.
17 H.D. Yin, Q.B. Wang and S.C. Xue, *J. Organomet. Chem*., 2005, **690**, 435.
18 V. Gayathri, E.G. Leelamani, N.M.N. Gowda, G.K.N. Reddy, *Polyhedron*, 1999, **18**, 235.
19 A.G.J. Ligtenbarg, R. Hage, A. meetsma and B.L. Feringa, *J. Chem. Soc., Perkin Trans*., 1999, **2**, 807.
20 H.G. Bheemanna, V. Gayathri and N.M.N. Gowda, *J. Chem. Res*., 2006, **8**, 530.
21 W.J. Geary, *Coord. Chem. Rev*., 1971, **7,** 81.
22 R.K. Dubey, *J. Indian. Chem. Soc*., 2006, **83**, 1087.
23 M.A. Mendiola, JR. Masaguer and C. Molleda, *Synth. React. Inorg Met-Org. Chem*., 1992, **22,** 955.
24 J.R. Ferraro, *Low-frequency vibrations of Inorganic and co-ordination compounds*, Plenum press, New York, 1971, pp. 96-211.
25 K. Nakamoto, *Infrared and Raman spectra of Inorganic and co-ordination compounds*, (Wiley interscience), New York, 1978, p. 60.
26 G. Mendoza–Diaz, G. Rigotti, O.E. Piro, E.E. Sileo, *Polyhedron*., 2005, **24**, 777.
27 Guo-Biao Cao, *Acta Crystallogr*., 2007, E**63,** m1149.
28 C.J. Matthews, C. William, L.H. Sarah, C.M. Nicola, M.N. Stuart Hill and C.L. Joyce, *Inorg. Chem.,* 1998, **37**, 199.
29 A.W. Addison, T. Nageswara Rao, J. Reedijk, J.V. Rijin and C.V. Gerrit, *J. Chem.Soc. Dalton Trans*., 1984, 1349.
30 D. Manfred, H. Gabriela and L. Wolfgang, *Acta Crystallogr*., 2006, E**62**, m429.
31 L. Bing-Xin and X. Duan-Jun, *Acta Crystallogr*., 2004, C**60,** m39.
32 Z. Bi-Song, *Acta Crystallogr*., 2007, E**63,** m1562.
33 J. Christoph, *J.Chem.Soc.Dalton Trans*., 2000, 3885.