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Synthesis and spectral investigation of manganese(II), cadmium(II) and oxovanadium(IV) complexes with 2,6-diacetylpyridine bis(2-aminobenzoylhydrazone): Crystal structure of manganese(II) and cadmium(II) complexes

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Abstract

The chelating behavior of 2,6-diacetylpyridine bis(2-aminobenzoylhydrazone) (H₂dapa) towards manganese(II), cadmium(II) and oxovanadium(IV) ions has been studied by elemental analyses, conductance measurements, magnetic properties and spectral (IR, ¹H NMR, UV–Vis and EPR) studies. The IR spectral studies suggest the pentadentate nature of the ligand with pyridine nitrogen, two azomethine nitrogens and two carbonyl oxygen atoms as the ligating sites. Six coordinate structure for [VO(H₂dapa)]SO₄ · H₂O and seven coordinate structures for [Mn(H₂dapa)(Cl)(H₂O)]Cl · 2H₂O and [Cd(H₂dapa)(Cl₂] · H₂O complexes have been proposed. Pentagonal bipyramidal geometry for [Mn(H₂dapa)(Cl)(H₂O)]Cl · 2H₂O and [Cd(H₂dapa)(Cl₂)] · H₂O complexes was confirmed by single crystal analysis. The X-band EPR spectra of the oxovanadium(IV) and manganese(II) complexes in the polycrystalline state at room (300 K) and also at liquid nitrogen temperature (77 K) were recorded and their salient features are reported.

Keywords: 2,6-Diacetylpyridine bis(2-aminobenzoylhydrazone); Transition metal compounds; Spectra; X-ray structures

1. Introduction

Hydrazones are of interest, because of their versatility in coordinating to metals, flexibility in assuming different conformations, pharmacological activity and their use in analytical methods. They can coordinate either in the neutral or in the anionic form. Furthermore the possibility of tautomerism makes their study extremely interesting [1].

The chelating properties of 2,6-diacetylpyridine bis(hydrazones) have been investigated towards several metal ions. Various 2,6-diacetylpyridine bis(hydrazones) have adopted pentagonal bipyramidal geometry on coordination with transition metal ions [2,3]. However, the nature of coordination depends also on the metal ion, pH of the medium, reaction conditions and also nature of the hydrazone [4,5]. The ligating diversity of this class of ligands is multiplied by their presence in protonated, deprotonated or even partially protonated forms, e.g. 2,6-diacetylpyridine bis(semicarbazone) has coordinated to tin(IV) in protonated form [3], while 2,6-diacetylpyridine bis(2thenoylhydrazone) and 2,6-diacetylpyridine bis(2furanoylhydrazone) have bound to tin(IV) in deprotonated and partially protonated forms, respectively [6,7].

With the aim of obtaining information about the chemical and structural properties of the metal complexes, especially with regard to the stereochemistry and the effects of

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the coordination on the conformation of the hydrazone, we have undertaken the study of manganese(II), cadmium(II) and oxovanadium(IV) complexes of 2,6-diacetylpyridine bis(2-amonobenzoylhydrazone). The earlier study on this ligand reports pentadentate or quinquidentate behavior [8].

2. Experimental

2.1. Reagents

All the solvents used were of analytical grade and were used without further purification. Methyl anthranilate and hydrazine hydrate were obtained from S.D. Fine Chem. Ltd. 2,6-Diacetylpyridine was procured from Corey organic limited, Hyderabad and was used without further purification. 2-Aminobenzoylhydrazide was prepared by known method [9].

2.2. Instrumentation and measurements

The metal content of the complexes was determined by EDTA titration after decomposition with a mixture of HCl and HClO₄. The chloride and sulfate content of the complexes were determined as silver chloride and barium sulfate gravimetrically. The carbon, hydrogen and nitrogen contents in each sample were determined using Heraus C H N rapid analyzer. IR spectra in the 4000–400 cm^{-1} range were measured with Thermo Nicolet 320 FT-IR spectrometer using KBr discs. ¹H NMR spectra were recorded in dmso- d_6 as the solvent at 400 MHz with a BRUKER AMX 400 spectrometer using tetramethylsilane (TMS) as an internal reference. Electronic spectra of the complexes were recorded with a Varian CARY 50 Bio UV-Vis spectrometer. The magnetic susceptibility measurements were carried out with a Faraday balance using Hg[Co(NCS)₄] as the calibrant and diamagnetic corrections were made by direct weighing of the ligand for diamagnetic pull. Conductance measurements were recorded in DMSO (10^{-3} M) using Elico conductivity bridge type CM-82, provided with a dip type conductivity cell fitted with platinum electrodes. EPR spectra were recorded on Varian E-4 Xband spectrometer using tetracyanoethylene (TCNE) as

'g' (g = 2.0027) marker at room temperature and also at liquid nitrogen temperature.

2.3. X-ray crystallography

Crystals suitable for X-ray studies were grown by slow evaporation technique from EtOH solution of the complexes. Crystal data were collected on a Bruker SMART APEX CCD diffractometer, experimental details and refinement results are listed in Table 4. All the hydrogen atoms were geometrically fixed and allowed to ride with the respective light atoms to which they are attached. The data were corrected for absorption using the program SAD-ABS available in the BRUKER system of programs [10] and the structures were refined by full-matrix least-squares on all measured F_{0}^{2} with SHELXL-97 [11].

2.4. Synthesis

2.4.1. Synthesis of 2,6-diacetylpyridine bis(2aminobenzoylhydrazone) (H₂dapa)

The ligand H_2 dapa was prepared by the known method [8] with a slight modification as given below.

A solution of 2,6-diacetylpyridine (6.52 g, 40 mmol) in 100 ml of EtOH was added to a solution of 2-aminobenzoylhydrazide (12.09 g, 80 mmol) in 100 ml of the same solvent, upon which the solution was refluxed for 2 h. A pale yellow microcrystalline product (yield 95%) was isolated on cooling and standing overnight. The product was recrystallized from MeOH and attempts to obtain X-ray quality crystals of this compound were unsuccessful. The purity of the ligand was checked by TLC. The synthetic route of H₂dapa is given in Scheme 1 with atom numbering.

2.4.2. Synthesis of metal complexes

Manganese(II), cadmium(II) and oxovanadium(IV) complexes were prepared by mixing a hot chloroform solution (5 ml) of H₂dapa (0.859 g; 2 mmol) and ethanolic solution (5 ml) of the corresponding metal salt (2 mmol). The solution was refluxed for 1 h and then allowed to stand. The slow evaporation of this resulted in to a microcrystalline



Scheme 1. Synthetic route of the ligand (H₂dapa).

product with yield varying in the 85–90% range. X-ray quality crystals of manganese(II) and cadmium(II) complexes were grown by slow evaporation technique.

3. Results and discussion

Some physical data for H_2 dapa and its metal complexes are given in Table 1. Elemental analyses establish 1:1 (metal:ligand) stoichiometry for the present complexes. Molar conductance values indicate 1:1 electrolytic nature for manganese(II) and oxovanadium(IV) complexes and non-electrolytic nature for cadmium(II) complex. All the complexes are insoluble in common organic solvents, but soluble in EtOH, DMF and DMSO solvents.

3.1. Magnetic and electronic spectral studies

Magnetic and electronic spectral data are summarized in Table 1. The observed effective magnetic moment (μ_{eff}) of oxovanadium(IV) complex is 1.86 BM, which is in good agreement with a d¹ system and is consistent with a mononuclear distorted octahedral structure [12]. The observed μ_{eff} value (5.93 BM) for the present manganese(II) complex confirms the high spin complex with five unpaired electrons. Cadmium(II) complex is diamagnetic as expected for d¹⁰ configuration [13].

Electronic spectrum of ligand showed a band at 390 nm due to the $n \rightarrow \pi^*$ transition of azomethine group. On com-

plexation this band has shifted to lower wavelength, suggesting the coordination of azomethine nitrogen [14].

Absorptions at 809 and 601 nm observed in the electronic spectrum of the oxovanadium(IV) complex, can be assigned to $b_2 \rightarrow e$ and $b_2 \rightarrow b_1$ transitions, respectively. The high energy $b_2 \rightarrow a_1$ transition was not observed. It might have been obscured in the broad charge transfer band, which sets in at about 357–333 nm, in distorted octahedral geometry around VO(IV) ion [15].

In case of manganese(II) and cadmium(II) complexes the d^5 and d^{10} configurations account for the absence of d–d bands.

3.2. Infrared spectra

Comparison of the main vibrational bands of H_2 dapa in its uncoordinated state and in the coordinated form is used to establish its ligating behavior and the data is compiled in Table 2.

The bands at 3448 and 3357 cm⁻¹ in the infrared spectrum of the ligand may be assigned to the $v_{as}(HNH)$ and $v_{s}(HNH)$ vibrations of NH₂ groups and the band at 3273 cm⁻¹ to v(NH) group of the ligand. The persistence of these bands in the spectra of all the complexes indicate the non-involvement of these groups in coordination [16].

The bands at 1671, 1550, and 1262 cm⁻¹ assigned to amide-I [v(C=O)], amide-II [v(CN) + v(NH)] and amide-III [v(NH) + v(CN)] vibrations, respectively, have suffered

Table 1 Physical, analytical, magnetic moments, electronic spectral data and molar conductance data of the compounds

Compound	M.p. (°C)	Elemental ana	alysis: found (ca	lculated) (%)			$\Lambda_{\rm m}$	$\mu_{\rm eff}$	$ \begin{array}{l} \mu_{\rm eff} & \lambda_{\rm max} \\ ({\rm BM}) & ({\rm nm}) \end{array} $
		М	С	Н	Ν	Cl ⁻ /SO ₄ ²⁻	$(\Omega^{-1} \operatorname{cm}^2 \operatorname{mol}^{-1})$	(BM)	
H ₂ dapa	187		64.45 (64.34)	5.42 (5.35)	22.92 (22.83)				390
$[Mn(H_2dapa)(Cl)(H_2O)]Cl \cdot 2H_2O$	>250	10.83 (10.52)	46.85 (46.73)	4.61 (4.56)	16.42 (16.58)	11.73 (11.80)	46.20	5.89	366
$[Cd(H_2dapa)(Cl_2)] \cdot H_2O$	>250	17.87 (17.89)	43.72 (43.80)	3.83 (3.96)	15.67 (15.54)	11.00 (11.09)	1.78	Dia	368
$[VO(H_2 dapa)]SO_4 \cdot H_2O$	>250	10.86 (10.97)	45.31 (45.26)	4.03 (4.09)	16.08 (16.06)	15.82 (15.74)	43.72	1.86	809, 601, 357–333

Dia = diamagnetic.

Table 2

Infrared	spectral	bands	(cm^{-1})	and	their	assignments	in	H ₂ dapa	and i	ts metal	complexes
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H ₂ dapa	$[Mn(H_2dapa)(Cl)(H_2O)]Cl\cdot 2H_2O$	$[Cd(H_2dapa)(Cl_2)] \cdot H_2O$	$[VO(H_2 dapa)]SO_4 \cdot H_2O$	Assignment
	3550 b	3545 b	3500 b	$v(H_2O)$ band vibration
3448 w	3447 m	3465 m	3430 w	$v_{a}(NH_{2})$ band vibration
3357 s	3310 m	3340 s	3333 w	$v_{\rm s}(\rm NH_2)$ band vibration
3273 w	3169 sh	3218 sh	3185 sh	v(NH) band vibration
1671 s	1626 s	1630 s	1616 m	amide(I) band vibration
1616 w	1585 s	1582 s	1562 w	v(C=N) vibration
1550 s	1514 s	1518 s	1511 s	amide(II) band vibration
1262 s	1250 s	1244 s	1254 s	amide(III) band vibration
1588 s	1550 s	1549 s	1562 s	pyridine ring stretching vibrations
1486 m	1476 m	1477	1470 m	
1453 m	1449 m	1451 m	1453 m	
990 m	1012 m	1010 m	1022 sh	pyridine ring breathing band

Abbreviations: s, strong; m, medium; b, broad; sh, shoulder; w, weak; $v(V=O) = 980 \text{ cm}^{-1}$.

a negative shift in the spectra of all the complexes by about $35-20 \text{ cm}^{-1}$, indicating the participation of uncharged amide oxygen in coordination [17].

The absorption due to v(C=N) in the free ligand is observed at 1616 cm⁻¹ and has shifted to lower wave number (~1585–1548 cm⁻¹) in all the complexes, indicating coordination of the ligand through azomethine nitrogen [18].

The bands in the ligand spectrum at 1588, 1486, 1453 cm^{-1} were assigned to pyridine ring stretching vibrations. The shift of these bands in the spectra of complexes supports the coordination of pyridine nitrogen to the metal ion. The ring-breathing mode observed at 990 cm⁻¹ in the free ligand disappear in the complexes and is replaced by a band at 1010–1022 cm⁻¹. This shift is also indicative of coordination of pyridine nitrogen with metal ion [19].

In [VO(H₂dapa)]SO₄ · H₂O, the strong non-ligand band observed in the region ~980 cm⁻¹ is assigned to v(V=O)[20]. The bands in the region 1115 and 610 cm⁻¹ confirm presence of ionic sulfate. Free sulfate ion belongs to the T_d point group and is expected to show only two fundamental IR active vibrations $v_3(F_2)$; i.e. $v_d(S=O)$, and $v_4(F_2)$, i.e. $\delta_d(O=S=O)$ [21].

A broad band in the region $3500-3200 \text{ cm}^{-1}$ indicates the presence of lattice held water molecule/s in all the complexes [17].

3.3. ¹H NMR spectral studies

¹H NMR spectra of H₂dapa and its cadmium(II) complex were recorded in DMSO- d_6 solvent and the data along with the assignments are included in Table 3. Scheme 1 shows numbering system of H₂dapa. Only one set of signals were observed for the ligand and its cadmium(II) complex indicating that the two arms of the ligand in its uncoordinated state as well as in coordinated form are magnetically equivalent in solution on the corresponding NMR time scale.

The spectrum of H_2 dapa exhibits three singlets at 10.64, 6.24 and 2.54 ppm, which are due to the N3H, N4H2 and C6H3 protons, respectively. A triplet at 7.91 [C4H] and doublet at 8.10 ppm [C3H] corresponds to one and two

Table 3 $^1\mathrm{H}$ NMR spectral data of H2dapa and its cadmium(II) complex

Chemical shifts in δ (ppm)							
Protons	H ₂ dapa	Cadmium(II) complex ^a					
N3H	10.64 (s, 2H)	10.64					
N4H2	6.24 (s, 4H)	6.24					
C6H3	2.54 (s, 6H)	2.54					
C4H	7.21 (t, 1H, $J = 7.60$ Hz)	8.22					
СЗН	8.10 (d, 2H, $J = 7.72$ Hz)	8.22					
C13H	7.61 (d, 2H, $J = 7.68$ Hz)	7.61					
C12H	6.62 (t, 2H, $J = 7.20$ Hz)	6.62					
C11H	7.23 (m, 2H)	7.23					
C10H	6.80 (d, 2H, $J = 8.2$ Hz)	6.80					

^a Due to the poor solubility, splitting pattern was not clearly observed.

protons of pyridine moiety, respectively. Two doublets, one triplet and a multiplet appearing at 7.61 [C13H], 6.80 [C10H], 6.62 [C12H] and 7.23 ppm [C11H] are attributed to eight aromatic protons of 2-aminobenzoylhydrazide moiety.

In cadmium(II) complex, the signals due to N3H and N4H2 appeared at the same position as in the ligand (10.64 and 6.24 ppm, respectively), indicating the non-involvement of NH₂ group in coordination. The triplet [C4H] and doublet [C3H] have merged into a broad signal and shifted to 8.22 ppm. This change along with the shift of the band due to C6H3 groups [2.63 ppm] suggest the involvement of pyridine nitrogen and azomethine nitrogens in coordination [22]. The broad bands of eight aromatic protons of 2-aminobenzoylhydrazide moiety appear at the same position as in the ligand.

3.4. EPR studies

The EPR spectra of VO^{2+} polycrystalline sample at room temperature and at liquid nitrogen temperature exhibit an eight-line pattern corresponding to the usual parallel and perpendicular components of g and hyperfine (hf) Atensor. The EPR spectrum of VO^{2+} polycrystalline sample at room temperature is shown in Fig. 1.

In an octahedral ligand field for d¹-VO(IV) complex, the ground state is ${}^{2}T_{2g}$. Owing to the spin-orbit coupling, the degenerate ${}^{2}T_{2g}$ state may further split by distortion, e.g. by Jahn–Teller effects or by a tetragonal ligand field, in to ${}^{2}E_{g}$ and ${}^{2}B_{2g}$ levels. Kivelson and Lee have theoretically predicted a value of 170 cm⁻¹ for λ (spin-orbit coupling constant) for C_{4v} -symmetry [23]. The λ value in the present oxovanadium(IV) complex (63.72 cm⁻¹) is within the reasonable limits of predicted value. The reduction in λ value for the VO²⁺ ion in this complex can be accounted in terms of the structural nature of the compound. The spectral parameter values for the VO^{IV} complex [$g_{\parallel} = 1.992$, $g_{\perp} = 2.02$, $g_{\circ} = 2.01$, $A_{\parallel} = -107.14$, $A_{\perp} = -35$, $A_{\circ}(G) = -55.713$] are consistent with the reported values for structurally analogous oxovanadium(IV) Schiff bases which have a slightly distorted octahedral environment with the unpaired electron occupying predominantly the b₂ level in the ground state [24].

The EPR spectra of manganese(II) complex in polycrystalline state at room temperature and liquid nitrogen temperature exhibit a broad isotropic signal centered at 2.0, which is equal to the free electron g-value (g = 2.0027). The broadening of the spectrum is due to spin relaxation [25].

3.5. X-ray crystal structure determinations

3.5.1. Crystal structural description of

$[Mn(H_2dapa)(Cl)(H_2O)]Cl \cdot 2H_2O$

Crystal data collection and refinement of $[Mn(H_2da-pa)(Cl)(H_2O)]Cl \cdot 2H_2O$ is summarized in Table 4. The crystal structure consists of cation $[Mn(H_2dapa)(Cl)(H_2O)]^+$,



Fig. 1. EPR spectrum of complex [VO(H2dapa)]SO4 · H2O at room temperature.

Table 4				
Crystal data and structural refinement for	[Mn(H2dapa)(Cl)(H2O)]Cl	2H2O and [[Cd(H ₂ dapa)(Cl ₂)] ·	H_2O

	$[Mn(H_2dapa)(Cl)(H_2O)]Cl\cdot 2H_2O$	$[Cd(H_2dapa)(Cl_2)] \cdot H_2O$
Compound	$C_{23}H_{27}Cl_2MnN_70_5$	C ₂₃ H ₂₇ Cl ₂ CdN ₇ 0 ₄
CCDC number	257382	257383
Molecular mass	609.37	648.817
Colour/shape	purple/rectangular	pale yellow/rectangular
$T\left(\mathrm{K} ight)$	293(2)	293(2)
Crystal system	triclinic	tetragonal
Space group	P_1	$P4_2/n$
a (Å)	9.780(7)	10.368(3)
b (Å)	11.983(9)	10.368(3)
c (Å)	12.256(9)	23.498(1)
β (°)	108.282(12)	90.00
$V(\text{\AA}^3)$	1297.2(17)	2526(2)
Ζ	2.00	4.00
$D_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.560	1.706
Index ranges	$-12 \leq h \leq 12, -14 \leq k \leq 13, -15 \leq l \leq 15$	$-13 \leq h \leq 13, -13 \leq k \leq 12, -29 \leq l \leq 29$
<i>F</i> (000)	630	1312
Absorption coefficient (mm^{-1})	0.764	1.22
Radiation	Μο Κα	Μο Κα
Wavelength (Å)	0.71073	0.71073
Reflection collected	8723	19803
Independent reflections (R_{int})	4874 (0.0307)	2740 (0.0260)
$T_{\rm max}$ and $T_{\rm min}$	0.9527 and 0.8272	0.9347 and 0.8176
Crystal size (mm)	$0.26 \times 0.14 \times 0.06$	$0.19 \times 0.11 \times 0.06$
Number of parameters	351	223
Goodness-of-fit	1.006	1.061
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0796, wR_2 = 0.2060$	$R_1 = 0.0270, wR_2 = 0.0618$
	$R_1 = 0.1164, wR_2 = 0.2284$	$R_1 = 0.0366, wR_2 = 0.0661$
Largest difference in peak and hole ($e \text{ Å}^{-3}$)	0.870 and -0.540	0.423 and -0.245

chloride anion and two lattice held water molecules. The ORTEP and molecular packing diagrams are displayed in Figs. 2 and 3. The selected bond lengths and angles are given in Table 5 and possible hydrogen bonds are listed in Table 6.

It can be seen that the $[Mn(H_2dapa)(Cl)(H_2O)]$ -Cl \cdot 2H₂O complex is seven coordinate and has pentagonal bipyramidal (PBP) structure. The dapa acts as a quinquedentate ligand coordinating through three nitrogen [N(1), N(2) and N(5)] and two oxygen [O(1) and O(2)] atoms, encircling the manganese ion and occupying the equatorial belt. The apices of the bipyramid are filled by a chloride ion and the oxygen atom from the water molecule. Previously, similar cationic heptacoordinated complexes with pentagonal bipyramidal geometry have been reported by Pelizzi et al. [8] and Palenik and Wester [26].



Fig. 2. ORTEP representation of the complex $[Mn(H_2dapa)(Cl)(H_2O)]Cl\cdot 2H_2O$ with labeling of the atoms.



Fig. 3. The crystal packing of complex $[Mn(H_2dapa)(Cl)(H_2O)]Cl \cdot 2H_2O$ viewed along the most representative direction.

The C–C bond distances in aromatic rings are in the normal range of 1.33–1.46 Å, which is characteristic of delocalised aromatic rings. The bond distances Mn(1)-N(1) 2.252(5), Mn(1)-N(2) 2.254(5), Mn(1)-N(5) 2.284(5), Mn(1)-O(1) 2.192(4), Mn(1)-O(2) 2.178(4), Mn(1)-Cl(1) 2.493(3) and Mn(1)-O(10) 2.261(5) Å are in good agreement with the bond distances found in similar seven coordinated pentagonal bipyramidal Mn(II) com-

Table 5										
Selected	bond	lengths	(Å)	and	bond	angles	(°)	for	[Mn(H ₂ dapa)(C	Cl)-
(H ₂ O)]C	$1 \cdot 2H_2$	O and [C	Cd(H	2dapa	a)(Cl ₂)	$] \cdot H_2O$	com	plex	tes	

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[Mn(H2dapa)(Cl)(H2C	$O)]Cl \cdot 2H_2O$	$[Cd(H_2dapa)(Cl_2)] \cdot H_2C$)
Bond lengths		Bond lengths	
Mn(1) - O(2)	2.178(4)	Cd(1) - O(1)	2.369(17)
Mn(1)-O(1)	2.192(4)	Cd(1)–O(1)	2.369(17)
Mn(1)-N(1)	2.252(5)	Cd(1) - N(1)	2.362(3)
Mn(1)-N(2)	2.254(5)	Cd(1)-N(2)	2.399(18)
Mn(1)–O(10)	2.261(5)	Cd(1)-Cl(1)	2.598(10)
Mn(1) - N(5)	2.284(5)	$Cd(1)-N(2_2)$	2.399(18)
Mn(1)-Cl(1)	2.493(3)	$Cd(1)-Cl(1_2)$	2.598(10)
N(5)-C(17)	1.269(7)	N(2)–C(2)	1.278(3)
N(2)-C(2)	1.263(8)	$N(2_2)-C(2_2)$	1.278(3)
O(2)–C(16)	1.218(7)	O(1)–C(3)	1.234(3)
O(1)–C(3)	1.227(7)	O(1_2)-C(3_2)	1.234(3)
Bond angles		Bond angles	
O(2)-Mn(1)-O(1)	84.00(16)	O(1_2)-Cd-O(1)	94.59(8)
O(1)-Mn(1)-N(2)	69.16(16)	(O1)-Cd(1)-N(2)	66.35(6)
N(1)-Mn(1)-N(2)	68.69(18)	N(1)-Cd(1)-N(2)	66.58(4)
N(1) Mn(1) - N(5)	68.40(18)	N(1)-Cd(1)-N(2_2)	66.58(4)
O(2)-Mn(1)-N(5)	68.49(17)	$(O1_2)-Cd(1)-N(2_2)$	66.35(6)
O(10)-Mn(1)-Cl(1)	176.53(12)	$Cl(1)-Cd(1)-Cl(1_2)$	173.35(2)

plexes [8,26]. The bond distances N(5)-C(17) 1.269(7), N(2)-C(2) 1.263(8), O(1)-C(3) 1.227(7) and O(2)-C(16) 1.218(7) Å are indicative of double bonds. The C-C-C bond angles in aromatic rings are around 120° with the variation being less than 2°, which is characteristic of sp²hybridized carbons. The bond angles in the pentagonal base O(1)-Mn(1)-N(2) 69.16(16)°, N(1)-Mn(1)-N(2)68.69(18)°, N(1)-Mn(1)-N(5) 68.40(18)°, O(2)-Mn(1)-N(5) 68.49(17)° are quite close to the ideal 72° (ideal pentagonal bipyramidal geometry), while the angle involving the two oxygen atoms O(2)-Mn(1)-O(1) is considerably greater [84.00(16)°] and these angles are also in good agreement with the bond angles found in $[Mn(H_2dapab)]$ $(CH_3OH)Cl]Cl \cdot 2H_2O$ and $[Mn(DAPSC)(H_2O)Cl]Cl \cdot$ 2H₂O complexes, suggests similar ONNNO donor properties in both ligands [8,26].

The molecule is coplanar. Mn(1) atom lies $0.144(6)^{\circ}$ above the $N_3O_2[N(1), N(2), N(5), O(1) \text{ and } O(2)]$ basal set of atoms. Plane I [N(1), C(1), C(21), C(20), C(19), C(18)] forms a dihedral angle of 8.71(1)° with plane II [C(10), C(11), C(12), C(13), C(14), C(15), N(7)], 15.09(1)° with plane III [C(4), C(9), C(8), C(7), C(6), C(5), N(4)], $2.65(2)^{\circ}$ with plane IV [N(1), N(2), N(5), O(1), O(2), Mn(1)]. While plane II form dihedral angles of $7.05(2)^{\circ}$ and 6.61(1)° with planes III and IV, respectively. Plane III forms a dihedral angle of 12.57(1)° with plane IV. In the molecular packing, pairs of [Mn(dapa)(Cl)(H₂O)]-Cl · 2H₂O are observed. These pairs are built by intermolecular hydrogen bonding through the proton from coordinated water molecules [O(10)H(101)H(102)], the anions [Cl(3)], the lattice held water molecules [O(3)H(31A)H(31B) and O(4)H(41A)H(41B)] and the coordinated chloride molecules [Cl(1)]. Two NH₂ [N(7)H(7A)H(7B) and N(4)H(4A)H(H4B)] groups present

Table 6 Hydrogen bonds for $[Mn(H_2dapa)(Cl)(H_2O)]Cl \cdot 2H_2O$ and $[Cd(H_2dapa)(Cl_2)] \cdot H_2O$

D–H···A	D-H (Å)	$H \cdots A$ (Å)	$D \cdots A$ (Å)	$\angle D - H \cdot \cdot \cdot A$ (°)
Manganese(II) complex				
$O(10)-H(101)\cdots Cl(1)^i$	0.993(5)	2.136(2)	3.121(5)	170.77(3)
$O(3)-H(31B)\cdots Cl(1)^{i}$	1.185(8)	2.065(2)	3.221(7)	164.28(5)
$O(4)-H(41B)\cdots Cl(3)^{i}$	1.042(1)	2.265(2)	3.250(11)	157.10(6)
$N(4)-H(4B)\cdots O(1)^{i}$	0.860(5)	2.011(5)	2.639(8)	129.06(5)
$N(7)-H(7B)\cdots O(2)^{i}$	0.860(7)	1.985(5)	2.618(9)	129.46(5)
$C(9)-H(9)\cdots O(3)^{ii}$	0.930(8)	2.500(1)	3.281(4)	141.75(5)
$N(3)-H(3)\cdots O(3)^{ii}$	0.860(5)	2.437(1)	3.275(1)	164.82(4)
$O(4)-H(41A)\cdots O(3)^{ii}$	1.069(1)	1.964(1)	2.974(1)	156.42(6)
$C(22)-H(22C)\cdots O(3)^{ii}$	0.960(6)	2.322(8)	3.116(1)	139.55(5)
$O(3)-H(31A)\cdots O(4)^{ii}$	1.124(1)	2.007(1)	2.974(1)	142.01(7)
$N(4)-H(4A)\cdots O(10)^{iii}$	0.860(7)	2.166(5)	3.015(9)	169.12(5)
Cadmium(II) complex				
$N(4)-H(4)\cdots O(1)^{i}$	0.820(0.036)	2.037(0.033)	2.666(0.003)	133.05(3.08)
$C(9)-H(9)\cdots O(2)^i$	0.944(0.028)	2.255(0.027)	3.173(0.004)	163.83(2.34)
$C(22)-H(22A)\cdots O(2)^{i}$	0.779(0.034)	2.538(0.033)	3.288(0.004)	162.16(3.19)
$O(2)-H(2A)\cdots Cl(1)^{ii}$	0.813(0.033)	2.486(0.33)	3.295(0.0025)	172.85(3.07)
$O(2)-H(2B)\cdots Cl(1)^{iii}$	0.777(0.035)	2.440(0.035)	3.215(0.003)	175.89(3.44)

Symmetry transformations used to generate equivalent atoms: (i) x, y, z, (ii) -x + 1, -y + 1, -z + 1, (iii) -x + 1, -y, -z + 1; and (i) x, y, z, (ii) x + y - 1, z, (iii) -x + 1, -y + 2, -z.

in the complex are *syn* to CO [C(3)O(1) and C(16)O(2)] groups and each hydrogen atom of NH₂ group are engaged in intramolecular hydrogen bonding with each oxygen atom of CO groups.

3.5.2. Crystal structural description of $[Cd(H_2dapa)(Cl_2)] \cdot H_2O$

Crystal data collection and refinement of $[Cd(H_2dapa)-(Cl_2)] \cdot H_2O$ is summarized in Table 4. The molecular structure (ORTEP) of the neutral cadmium(II) complex, $[Cd(H_2dapa)(Cl_2)] \cdot H_2O$ is depicted in Fig. 4. Selected bond lengths and angles in the complex are listed in Table 5. Possible hydrogen bonds are given in Table 6.

As in the case of manganese(II) complex, a pentagonal bipyramidal geometry around the metal is observed in cadmium(II) complex also. The atoms N(1), N(2), O(1), O(1_2) and N(2_2) are occupying the equatorial belt forming four planar five membered chelate rings with Cl(1) and Cl(1_2) in the axial positions. The bond lengths and angles in Cd(II) complex reveal that, the whole molecule is symmetrical and hence only one set of bond distances and angles are observed.

The bond distances Cd(1)–N(1) 2.362(3), Cd(1)–N(2) 2.399(18), Cd(1)–N(2_2) 2.399(18), Cd(1)–O(1) 2.369(17), Cd(1)–O(1_2) 2.369(17), Cd(1)–Cl(1) 2.598(10) and Cd(1)–Cl(1_2) 2.598(10) Å are in good agreement with the bond distances found in a similar seven coordinated complex with pentagonal bipyramidal geometry reported by Pelizzi et al. [27]. The bond distances N(2)–C(2) 1.278(3), N(2_2)–C(2_2) 1.278(3), O(1)–C(3) 1.234(3) and O(1_2)–C(3_2) 1.234(3) Å are indicative of double bonds. The C–C–C bond angles are around 120° with the variation being less than 3°, which is characteristic of sp²-hybridized carbons in the pentagonal base. The bond angles N(1)–Cd(1)–N(2) 66.58(4)°,



Fig. 4. ORTEP representation of the complex $[Cd(H_2dapa)(Cl_2)]\cdot H_2O$ with labeling of the atoms.

N(1)–Cd(1)–N(2_2) 66.58(4)°, O(1)–Cd(1)–N(2) 66.35(6)°, O(1)–Cd(1)–N(2_2) 66.35(6)° are close to the ideal 72° (ideal pentagonal bipyramidal geometry) while the angle involving the two oxygen atoms O(1)–Cd(1)–O(1_2) is considerably greater [94.59(8)°] and these angles are also in good agreement with the bond angles found in [Cd(H₂daps)(Cl₂)]CH-Cl₃ · CH₃OH complex suggests similar ONNNO donor properties in the ligand [27].

The molecular packing diagram of the $[Cd(H_2dapa) (Cl_2)] \cdot H_2O$ complex in the unit cell is illustrated in Fig. 5. The molecule is planar. It shows the presence of four intramolecular and six intermolecular hydrogen bonds. Molecular packing is mainly dictated by a three-dimensional hydrogen-bonding network involving cations,



Fig. 5. The crystal packing of complex $[Cd(H_2dapa)(Cl_2)]\cdot H_2O$ viewed along the most representative direction.

anions and water molecules. The lattice held water molecule is engaged in hydrogen bonding with two chloride ions of the two complex molecules. Two NH₂ [N(4)H(4A)H(4B) and N(4_2)H(4_A)H(4_B)] groups present in the complex are *syn* to CO [C(3)O(1) and C(3_2)O(1_2)] groups and each hydrogen atom of NH₂ group are engaged in hydrogen bonding with each oxygen atom of CO groups by intraand inter-molecular hydrogen bonding.

The N_3O_2 [N(1), N(2), O(1), O(1_2) and N(2_2)] basal set of atoms including the metal center is completely planar from the mean least-square plane.

4. Supplementary material

Crystallographic data, bond lengths and bond angles of structures have been deposited with the Cambridge Crystallographic Data Center, with the deposition numbers: CCDC 257382 and 257383. Copies of this information are available free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http:// www.ccdc.cam.ac.uk).

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