

STRUCTURE AND SPECTROSCOPIC STUDIES OF Cd(II) COMPLEXES OF TRIS(2-PYRIDYL)AMINE: 1D AND 2D SUPRAMOLECULAR ASSEMBLIES

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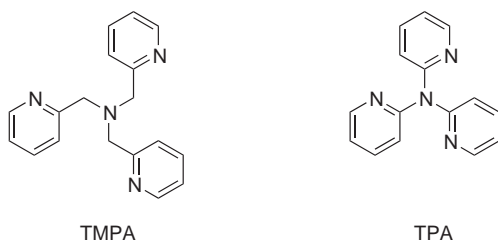
Cd(II) halide complexes $[Cd_2X_4(tpa)_2]$ (**1**: X = Cl, **2**: X = Br, **3**: X = I; tpa = tris(2-pyridyl)amine) have been synthesized. X-Ray diffraction analyses of **2** and **3** reveal their asymmetrical dinuclear structures: one Cd(II) atom is octahedrally coordinated to four N atoms of two tpa ligands and two bridging halides; the other Cd(II) is tetrahedrally coordinated to two terminal ($X_{(t)}$) and two bridging ($X_{(b)}$) halides. By multiple intra- and intermolecular π - π interactions between the tpa pyridine rings, the ligands of **2** and **3** are linked to form a 2D network and 1D linear structures, respectively. In the Raman and far-infrared spectra, the absorption bands due to Cd- $X_{(b)}$ stretching modes lie at lower wavenumbers compared to the Cd- $X_{(t)}$ stretches. It can be inferred from the spectroscopic data that **1** has a dinuclear structure similar to those of **2** and **3**.

Keywords: Cadmium complexes; Crystal structures; Pyridine ligands; Dinuclear complexes; Raman spectroscopy; 2D networks; π - π interactions; X-Ray diffraction; Crystal engineering.

One-, two- and three-dimensional infinite supramolecular coordination assemblies of Cd(II) have been the subject of great interest in recent years owing to their potential application in catalysis, optical properties, clathration, etc.¹⁻⁴

The d^{10} configuration of Cd(II) permits a wide variety of coordination numbers and geometries⁵. In studying the coordination assemblies, organic ligands as well as inorganic anions have been observed to control the structural diversity and stereochemistry of the metal centres⁶. The coordination chemistry of the tetradentate tripodal ligand tris(2-pyridylmethyl)amine (tmpa, Scheme 1) and its derivatives with Zn(II), Cd(II), Hg(II) and other metal ions has been extensively investigated⁷⁻¹⁴. By contrast, metal complexes of the tripod-like tris(2-pyridyl)amine (tpa) have been much less ex-

plored, especially its complexes with d^{10} metal(II). To our knowledge, only the Zn(II) complex $[\text{ZnCl}_2(\text{tpa})]$ has been reported¹⁵ while its Cd(II) complexes remain unknown. In contrast to the tetradentate coordination mode of tpa, tpa may act as a bidentate or as a tridentate ligand^{16,17}. Besides, tpa has a more rigid structure, which may be favorable for π - π interactions between the pyridine rings. The importance of π - π interactions in supramolecular coordination assemblies of various dimensions, containing rigid pyridine ligands, has been extensively demonstrated¹⁸⁻²⁰. Thus, tpa may be promising for the syntheses of novel supramolecular coordination assemblies with the participation of π - π interactions. This consideration stimulated us to synthesize the Cd(II) halide complexes of tpa and to undertake a systematic investigation of their structural and spectroscopic properties. We report the results in this work.



RESULTS

Structures of the $[\text{Cd}_2\text{X}_4(\text{tpa})]$ Complexes

Selected bond lengths and angles are listed in Table I. X-Ray structural analyses reveal that complexes **2** and **3** have dinuclear structures. The crystal structure of **2** consists of discrete non-centrosymmetric $[\text{Cd}_2\text{Br}_4(\text{tpa})_2]$ dimeric entities (Fig. 1). The coordination geometries around Cd(1) and Cd(2) are pseudooctahedral and pseudotetrahedral, respectively. Two tpa ligands coordinate to Cd(1) in bidentate modes, with one pyridine ring of each tpa ligand left uncoordinate. Br1 and Br2 act as bridges between Cd(1) and Cd(2). The N(6)-Cd(1)-Br(2) and N(4)-Cd(1)-Br(1) angles of $164.4(3)$ and $163.6(3)^\circ$ indicate a significant distortion of the octahedral coordination geometry of Cd(1). The Cd(1)-N distances are in the range of 2.361(12)-2.429(11) Å. The Cd(1)-Br_(b) distances (for the bridging Br⁻) are long, viz. 3.0046(17) and 2.9586(19) Å, while the Cd(2)-Br_(t) distances (for the terminal Br⁻) are much shorter, viz. 2.721(2) and 2.734(2) Å; the Cd(2)-Br_(b) distances are intermediate in this regard, viz. 2.881(2) and

2.8770(18) Å. These values indicate that the bonds between the bridging bromides and Cd are weaker than those of the terminal bromides. It is worth mentioning that intramolecular face-to-face π - π interactions occur between the tpa ligands coordinated to the same Cd(II) atom (Table II). The dinuclear complexes are further connected into a 2D network structure *via* weak intermolecular face-to-face π - π stacking interactions (Fig. 2 and Table II). The plane-plane and centroid-centroid distances between the pyridine rings lie in the range of 3.59–3.84 Å, with the plane-plane angles ranging between 0–9.3°. In summary, all three pyridine rings of the tpa ligand are involved in inter- and/or intramolecular π - π interactions.

TABLE I
Selected bond lengths (in Å) and angles (in °) for [Cd₂Br₄(tpa)₂] (2) and [Cd₂I₄(tpa)₂] (3)

Atoms	2	3	Atoms	2	3
Cd1–N2	2.397(6)	2.429(11)	Cd1–X2	2.752(1)	2.9586(19)
Cd1–N4	2.350(6)	2.361(12)	Cd2–X3	2.527(1)	2.721(2)
Cd1–N6	2.345(6)	2.373(12)	Cd2–X4	2.527(1)	2.734(2)
Cd1–N8	2.423(6)	2.404(10)	Cd2–X1	2.699(1)	2.881(2)
Cd1–X1	2.819(1)	3.0046(17)	Cd2–X2	2.678(1)	2.8770(18)
N4–Cd1–N2	78.8(2)	77.8(4)	N8–Cd1–X2	85.1(2)	87.4(3)
N4–Cd1–N6	92.0(2)	90.6(4)	N2–Cd1–X2	92.8(2)	93.6(3)
N4–Cd1–N8	99.6(2)	99.4(4)	X1–Cd1–X2	87.24(4)	90.06(5)
N6–Cd1–N8	77.8(2)	77.0(4)	X3–Cd2–X4	119.22(5)	116.12(8)
N6–Cd1–N2	104.4(2)	102.0(4)	X3–Cd2–X1	114.35(4)	117.43(7)
N8–Cd1–N2	177.3(2)	177.1(4)	X4–Cd2–X1	105.77(5)	102.99(7)
N4–Cd1–X1	163.4(2)	163.6(3)	X3–Cd2–X2	107.71(5)	107.32(7)
N6–Cd1–X1	92.6(2)	91.4(3)	X4–Cd2–X2	115.21(4)	117.06(6)
N8–Cd1–X1	96.9(2)	96.9(3)	X1–Cd2–X2	91.26(4)	94.24(5)
N2–Cd1–X1	84.6(1)	85.9(3)	Cd1–X1–Cd2	89.79(3)	87.14(5)
N4–Cd1–X2	93.0(2)	92.4(3)	Cd2–X2–Cd1	91.68(4)	88.08(5)
N6–Cd1–X2	162.7(1)	164.4(3)			

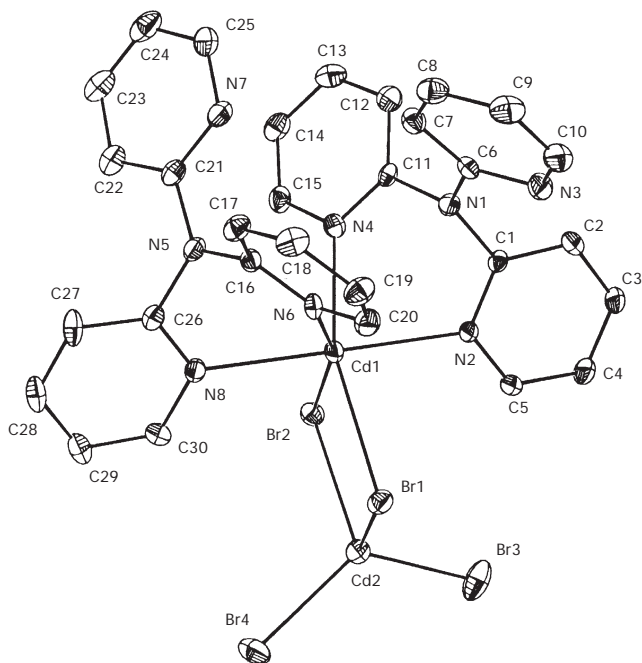


FIG. 1
ORTEP view of complex **2** showing the numbering scheme at the 30% probability level, with H atoms omitted for clarity

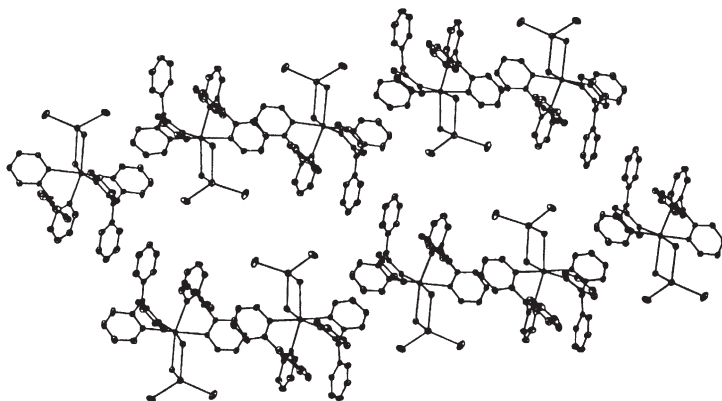


FIG. 2
2D network structure of complex **2**, showing intermolecular π - π interactions between the pyridine rings

Crystal **3** consists of discrete $[\text{Cd}_2\text{I}_4(\text{tpa})_2]$ entities. Multiple π - π interactions between the pyridine rings are also observed, resulting in a 1D structure (Fig. 3), with the plane-plane and the centroid-centroid distances between the pyridine rings in the range of 3.62–3.86 Å, and the plane-plane angles of 0–11.3°.

TABLE II
Parameters characterizing π - π stacking interactions between the pyridine rings in **2** and **3**^a

Ring 1	Ring 2	Complex 2		Complex 3	
		angle, °	distance, Å	angle, °	distance, Å
1	2	9.3	3.84 ^b	5.9	3.66
3	4	6.4	3.63 ^b	11.3	3.86
3	3 ^{#1}	0	3.59		
5	6 ^{#2}	5.8	3.82 ^b		
1	1 ^{#3}			0	3.71
6	6 ^{#4}			0	3.62

^a Atoms defining the pyridine rings, 1: C6 ~ C10, N3; 2: C16 ~ C20, N6; 3: C21 ~ C25, N7; 4: C11 ~ C15, N4; 5: C1 ~ C5, N2; 6: C26 ~ C30, N8. ^b Centroid-to-centroid distances for nonparallel rings. Symmetry operations #1: $-x + 1, -y, -z + 1$; #2: $x - 0.5, -y + 0.5, z + 0.5$; #3: $-x + 1, -y + 1, -z + 1$; #4: $-x, -y, -z + 1$.

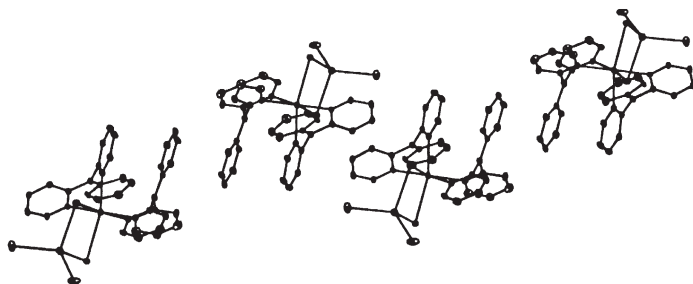


FIG. 3
1D linear packing of complex **3**, showing intermolecular π - π interactions between the pyridine rings

Syntheses

All the complexes have the formulae of $[\text{CdX}_2(\text{tpa})_2]$, with the same ligand–metal ratios of 1:1. The change in the ligand-to-metal ratio from 2:1 through 1:1 to 1:2 does not affect the identity of the products. The change in the reaction solvent does not affect the products, either. These observations indicate that the products are controlled by their relative stability, irrespective of the solvent and the molar ratios of the reagents.

IR and Raman Data

Spectral range 4000–500 cm^{-1} . The characteristic vibration bands of the 2-pyridine rings (1473, C=C, 743, $\delta_{\text{C-H}}$; 657, δ_{py} ; 617, γ_{py}) are doubled, one band of each doublet being nearly coincident with the corresponding one of free tpa and the other occurring at a higher or a lower frequency. This result can be interpreted in terms of the presence of both coordinated and noncoordinated 2-pyridine rings in the same ligand molecule.

Spectral range 500–100 cm^{-1} . The assignments (Table III) of far-IR and Raman (Fig. 4) metal–ligand stretching vibrations in the low-frequency region have been carefully made by studying the frequencies of the internal vibrations of the ligand (the wavenumbers principally depended on X) and the literature reports^{21–24}. Bands due to both Cd–X_(t) and Cd–X_(b) stretching modes are observed for the dinuclear complexes. The $\nu(\text{Cd-X}_{(t)})$ bands lie at much higher wavenumbers than $\nu(\text{Cd-X}_{(b)})$, in accordance with the relative strength of the coordination bonds. The wavenumbers of the $\nu(\text{Cd-X}_{(t)})$ bands decrease in the order Cd–Cl > Cd–Br > Cd–I. The presence of both

TABLE III
IR and Raman (R) Cd–halide and Cd–N stretching frequencies (cm^{-1}) for the complexes **1**, **2** and **3**

Complex	Technique	$\nu(\text{Cd-X}_{(t)})$	$\nu(\text{Cd-X}_{(b)})$	$\nu(\text{Cd-N})$
1	R	275	213, 211	322, 362, 417
	IR	274	227, 217	321, 367, 428
2	R	189	139	362, 404, 417
	IR	190	148	361, 408, 418
3	R/IR	169	125	321, 364, 406, 417

$\nu(\text{Cd-X}_{(b)})$ and $\nu(\text{Cd-X}_{(t)})$ bands in the Raman and far-IR spectra of **1** indicates that this complex has a dinuclear structure similar to those of **2** and **3**.

DISCUSSION

In this work, three Cd(II) complexes $[\text{Cd}_2\text{X}_4(\text{tpa})_2]$ ($\text{X} = \text{Cl}$ (**1**), Br (**2**), I (**3**)) have been synthesized. X-Ray diffraction analyses reveal that **2** and **3** are dinuclear, with unique asymmetrical structures instead of centrosymmetric arrangement, wherein two tpa ligands coordinate to the same metal atom. This observation can be related to the contribution of the weak intra-molecular π - π interactions between the tpa ligands coordinated to the same Cd(II) atom. Thus, Cd(II) halides can coordinate the bidentate tpa ligand, forming a four-coordinate unit, where the coordination sphere of the metal atom may be unsaturated, still having capacity to coordinate additional tpa in the presence of multiple π - π interactions between the pyridine rings. The halides may further bridge another metal atom; herewith, the asymmetrical dinuclear complexes are produced. By the action of the weak inter-molecular π - π interactions, the ligands are further linked to give 1D and 2D network structures. By contrast, in the reported Zn(II), Cd(II) and Hg(II) complexes of tmpa, the metal atom coordinates to the tetradentate tmpa ligand, in addition to one or two halides, affording relatively more saturated five-coordinate or six-coordinate mononuclear complexes, where no effect of π - π interactions is involved⁷.

Although tpa can function not only as a bidentate chelating ligand but also as a tridentate ligand, only the former binding mode is observed in the

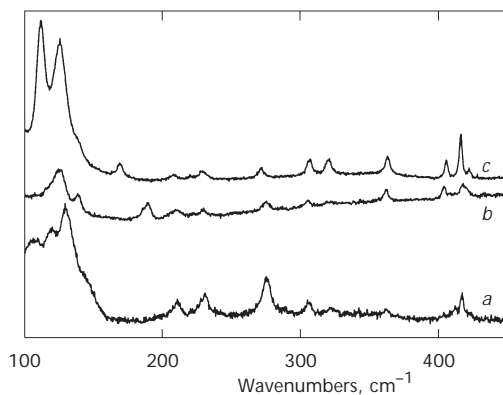


FIG. 4
Raman spectra (100–450 cm^{-1}) of the studied complexes: *a* **1**, *b* **2**, *c* **3**

studied complexes. This observation can be attributed to the steric hindrance between the two tpa ligands in the dinuclear complexes coordinated to the same metal atom.

In conclusion, by halide variation, novel asymmetrical dinuclear Cd(II) halide complexes of tpa with 1D and 2D supramolecular structures have been synthesized and structurally characterized. On the structure basis, Raman and IR spectra of these complexes have been reported.

EXPERIMENTAL

Materials and Measurements

The ligand tpa was synthesized by the reported method¹⁵. All the other reagents were used as received, without further purification. IR spectra (wavenumbers in cm^{-1}) were recorded on a Bruker Vector-22 spectrometer. Microanalyses of C, H and N were carried out with a GmbH VarioEL elemental analyzer. Raman spectra were recorded with solid samples, using a LARBRAM-HR confocal laser micro Raman spectrometer.

Syntheses

$[Cd_2Cl_4(tpa)_2]$ (1). KCl (0.030 g, 0.4 mmol) in a small amount of water was added to a solution of $Cd(NO_3)_2 \cdot 6H_2O$ (0.069 g, 0.20 mmol) and tpa (0.050 g, 0.20 mmol) in methanol (50 ml). The reaction mixture was refluxed for 3 h, then concentrated to *ca* 5 ml *in vacuo*, and filtered. The filtrate was left in the dark at room temperature for slow evaporation of the solvent. Colorless crystals were obtained after a few days. Yield 0.052 g (60%). For $C_{30}H_{24}Cd_2Cl_4N_8$ (863.2) calculated: 45.48% C, 3.05% H, 14.14% N; found: 45.69% C, 2.98% H, 14.22% N. IR (KBr pellet): 3061, 1599 s, 1567 m, 1471 s, 1462 s, 1429 s, 1322 s, 1283 s, 1155 m, 1103 w, 1052 w, 1017 w, 994 w, 954 w, 793 m, 770 s, 756 s, 741 m, 655 m, 642 w, 638 w, 617 w, 542 w, 513 w, 495 w, 420 w, 410 w.

$[Cd_2Br_4(tpa)_2]$ (2). Complex 2 was prepared by a similar method, reacting tpa (0.050 g, 0.20 mmol), $Cd(NO_3)_2 \cdot 6H_2O$ (0.069 g, 0.20 mmol) and KBr (0.048 g, 0.4 mmol). Yield: 0.075 g (72%). For $C_{30}H_{24}Br_4Cd_2N_8$ (1041.0) calculated: 34.61% C, 2.32% H, 10.76% N; found: 34.90% C, 2.43% H, 10.94% N. IR (KBr pellet): 3055 w, 1599 s, 1567 m, 1471 s, 1461 s, 1443 m, 1429 s, 1320 s, 1281 s, 1154 m, 1102 w, 1052 w, 1017 w, 994 w, 953 w, 932 w, 792 w, 768 m, 754 m, 741 w, 655 m, 640 w, 627 w, 617 w, 541 w, 420 w, 409 w.

$[Cd_2I_4(tpa)_2]$ (3). Complex 3 was prepared by a similar method reacting tpa (0.050 g, 0.20 mmol), $Cd(NO_3)_2 \cdot 6H_2O$ (0.069 g, 0.20 mmol) and KI (0.066 g, 0.40 mmol). Yield: 0.083 g (68%). For $C_{30}H_{24}Cd_2I_4N_8$ (1229.0) calculated: 29.32% C, 1.97% H, 9.12% N; found: 29.46% C, 1.96% H, 8.76% N. IR (KBr pellet): 3069 w, 1599 s, 1566 m, 1473 s, 1471 m, 1462 s, 1439 m, 1427 s, 1320 s, 1279, 1153 m, 1052 m, 1014 m, 993 w, 952 w, 790 m, 767 s, 753 m, 739 m, 654 m, 640 w, 627 w, 616 w, 541 m, 493 w, 465 w, 420 w, 408 w.

Crystallographic Data Collection and Refinement of the Structures

A single crystal was mounted on a glass fiber. All measurements were carried out with a Rigaku RAXIS-IV image plate area detector with graphite-monochromated $MoK\alpha$ radiation.

TABLE IV
Crystal data and structure refinement for the complexes **2** and **3**

Parameter	2	3
Molecular formula	C ₃₀ H ₂₄ Br ₄ Cd ₂ N ₈	C ₃₀ H ₂₄ Cd ₂ I ₄ N ₈
Formula weight	1041.01	1228.97
Crystal color and habit	colorless, prism	colorless, prism
Crystal dimension, mm	0.28 × 0.25 × 0.20	0.20 × 0.20 × 0.20
System	monoclinic	triclinic
Space group	<i>P2(1)/n</i>	<i>P-1</i>
<i>T</i> , K	291(2)	291(2)
<i>a</i> , Å	11.090(2)	12.499(3)
<i>b</i> , Å	25.809(5)	14.134(3)
<i>c</i> , Å	12.075(2)	11.282(2)
α, °	90	107.80(3)
β, °	100.07(3)	101.23(3)
γ, °	90	87.33(3)
<i>V</i> , Å ³	3403(1)	1861(6)
<i>Z</i>	4	2
<i>D_c</i> , g cm ⁻³	2.032	2.193
<i>F</i> (000)	1984	1136
μ(MoKα), mm ⁻¹	5.980	4.492
θ range, °	1.58–27.53	1.51–27.52
<i>hkl</i> range	0/14, –33/33, –15/15	0/16, –18/18, –14/12
No. of unique diffractions	6287	6669
No. of observed diffractions ^a	3970	5316
No. of parameters	398	398
<i>R</i> , <i>wR</i> for observed diffractions ^b	5.72, 9.48	7.13, 19.18
<i>R</i> , <i>wR</i> for all diffractions ^b , %	11.16, 12.42	8.97, 20.11
<i>R</i> _{int}	0.0546	0.0000
GOF for all data ^c	1.020	1.102
Residual electron density, e Å ⁻³	0.721/–0.647	1.555/–1.352

^a Diffractions with $I > 2\sigma(I)$. ^b $R(F) = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$, $wR(F^2) = \frac{[\sum (w(F_o^2 - F_c^2)^2)]^{1/2}}{[\sum w(F_o^2)]^{1/2}}$.
^c $GOF = [\sum (w(F_o^2 - F_c^2)^2) / (N_{\text{diffrs}} - N_{\text{params}})]^{1/2}$.

The data were collected at 18 ± 1 °C and corrected for Lorentz and polarization effects. A correction for secondary extinction was also applied. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on observed reflections ($I > 2.00\sigma(I)$) and variable parameters. All calculations were performed using SHELX97 software package^{25,26}. Abbreviated crystal data are summarized in Table IV. CCDC 184925 (for structure 2) 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 336033; or deposit@ccdc.cam.ac.uk).

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