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PAPER

Metallacycles of cadmium, mercury dicarboxylates†

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A series of linear coordination polymers, metallacycles of cadmium(II) and mercury(II) of flexible carboxylic acid ligands, RCH{3-CH₃-,5-CH₃-,6-($-OCH_2CO_2H$)C₆H₂}, (when R = C₆H₅, (H₂L¹); 2-NO₂C₆H₄- (H₂L²) and 3-NO₂C₆H₄- (H₂L³)) are synthesized and characterized. [CdL¹ (py)₃]_n·3nH₂O (py = pyridine) is a linear coordination polymer, whereas [CdL²(py)(CH₃OH)]₂·CH₃OH is a dinuclear complex of cadmium with a Cd₂O₂ type of core. The latter is obtained from reaction of cadmium(II) acetate with H₂L² in methanol followed by reaction with pyridine. A similar reaction of cadmium(II) acetate with H₂L² in dimethylformamide results in the formation of a cadmium metallacycle, namely [CdL² (py)₂(H₂O)]₂·H₂O. The H₂L³ reacted with cadmium(II) acetate in the presence of pyridine to form a metallacycle [CdL³(py)₂(H₂O)]₂·3H₂O. The ligand H₂L² form mercury(II) metallacycle [HgL²(4mepy)₂]₂ in the presence of 4-methylpyridine (4-mepy) and the ligand H₂L³ forms metallacycle [HgL³(3-mepy)₂]₂·DMF in the presence of 3-methylpyridine (3-mepy). The potassium salts of H₂L¹ and H₂L² were found to be coordination polymers and these potassium coordination polymers were structurally characterized.

Introduction

Multidentate ligands have often been observed to coordinate with more than one metal centre to form infinitely extended structures, such as coordination polymers, polynuclear complexes or metallacycles.¹ Enormous efforts are being made for the construction of metal-organic frameworks and coordination polymers, as they show interesting material properties.² A variety of organic ligands with different backbones and functional groups have been used to form coordination motifs with various dimensions.³ The structural features of the outcome polymers are controlled by various factors, such as coordination modes, shape and size of ligands and the solvent used. Based on these, rigid bridging ligands with nitrogen or oxygen as donor atoms, such as 4,4'-bipyridine,⁴ terephthalic acid⁵ etc., are commonly used to generate polymeric networks with beautiful topologies. There is a growing trend in using flexible ligands for the construction of coordination polymers with intriguing network structures.⁶ Vshaped molecules with carboxylic acid functionality at the two ends are most appealing for the construction of various metalorganic frameworks because of two different metal binding sites

with a large spacer.⁷ The use of a flexible or less-rigid spacer for the construction of a coordination complex has an added advantage as they have many degrees of freedom and a few conformational restraints, which can give various topologies. These types of conformational flexible ligands give unique opportunities to construct novel structures with desirable characteristics. Complicacy in predicting the architecture of the coordination complexes derived from these types of flexible ligands arises due to different coordination modes of carboxylate ligands, which are further complicated by factors such as the variation of crystallization conditions. However, one may simplify this by restricting to one, or two binding modes of carboxylates⁸ leading to a coordination polymer, metallacycle and dinuclear complex, as shown in Scheme 1. Flexibility associated with CH2COOH parts and the shape and rigidity associated with the bis-phenol part makes this class of ligands unique, as cyclic structures may be anticipated when these ligands are attached to appropriate connections. Further to this interest in d¹⁰ metal ions-containing dicarboxylate coordination polymers, those with cadmium⁹ or mercury¹⁰ ions are especially of great importance. The cadmium dicarboxylate polymers show interesting optical properties⁹ and mercury dicarboxylates have medical applications,¹¹ such as their role in the treatment of renal failure. In addition to these, dicarboxylic acids in ionic liquids bind mercury ions and have the property to absorb gases.¹² The mercury can have relatively stable variable valences¹³ and can be easily functionalised to organometallics. Wide variations in the structure of cadmium carboxylate coordination polymers are possible by changing the reaction conditions.9 Further to this, they have the possibility for variations of coordination numbers⁹ and they are diamagnetic in nature; so these metal ions can be studied in solution by

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[†]Electronic supplementary information (ESI) available: The powder X-ray diffraction patterns of the cadmium complexes (4–7), IR spectra of the ligands and complexes, ESI mass of the ligands H_2L^2 and H_2L^3 , ¹HNMR spectra of complex 7 and 8, ¹H HOMOCOSY spectra of complexes 5 and 6, thermogravimetry of complexes 4–8 and 12, 13 are available. CCDC 840829, 806671, 837719, 844623, 837720, 837718, 851819, 851820, 859335–859337. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt30554b

common spectroscopic tools, like NMR spectroscopy. Thus, we identified cadmium and mercury as the metal ions for the



Scheme 1 The formation of metallacycle (A) (red arrows show the possible path for a metallacycle converted to a dinuclear complex); dinuclear complex (B); linear coordination polymer (C) from flexible V-shaped ligand.

synthesis of coordination polymers with dicarboxylic acid ligands with a flexible part anchored to a rigid V-shape geometry.

In the literature it is found that the presence of nitro substituent at *o*-, *m*- and *p*-positions of benzoates have a striking effect on the structure and dimensionality of the resulting coordination complexes.¹⁴ In our earlier studies, we have also found that nitro substituent on aromatic carboxylic acids decides the formation of mononuclear or dinuclear complexes.¹⁵ In addition, we have also used bis-phenol-based flexible V-shaped dicarboxylic acids (H_2L^1) to bind zinc to form penta-coordinated mononuclear complexes.¹⁶ In this study, we tried to explore whether an apparently innocent nitro substitution on this V-shaped ligand (H_2L^1) can bring about any change in the molecular architecture of cadmium and mercury complexes. Furthermore, we also attempted to explore the structural changes in these complexes by varying the position of the nitro group in these ligands (Scheme 2a).

Herein, we report the synthesis and characterisation of some cadmium and mercury complexes, which were synthesised under identical ambient conditions in methanol or dimethyl formamide. An interesting structural variation from the one dimensional coordination polymer (4) to metallacycle (7) is observed





Scheme 2 (a) Ligands H_2L^1 , H_2L^2 and H_2L^3 . (b) The formation of one dimensional coordination polymer (4), dinuclear complex (5) and metallacycles of cadmium (6 and 7).



Scheme 3 The synthesis of ligands 1-3.

on the introduction of the nitro substituent on the ligand. Again, it is also observed that on changing the solvent from methanol to dimethyl formamide, the dinuclear complex (5) is converted to a metallacycle (6) (Scheme 2b).

Experimental

The ligands RCH{3-CH₃-,5-CH₃-,6-($-OCH_2CO_2H)C_6H_2$ }₂, (when R = C₆H₅, (H₂L¹); 2-NO₂C₆H₄- (H₂L²) and 3-NO₂C₆H₄- (H₂L³)) used in this study were synthesized by functionalization of their respective parent bis-phenol. The ligand H₂L¹ (1) was prepared by reported procedure.¹⁶ The procedure was extended to ligand H₂L² (2) and H₂L³ (3).

Synthesis of the ligand H_2L^2 (2)

The bis-phenol (as in Scheme 3) (2a) (1.89 g, 5 mmol) was dissolved in dry acetone (30 ml). To this solution anhydrous potassium carbonate (1.38 g, 10 mmol) was added and stirred for 20 min. Then, methyl bromoacetate (0.95 ml, 10 mmol) was added and the reaction mixture was refluxed at 70 °C for 22 h. Progress of the reaction was monitored at regular intervals using TLC. After completion of the reaction, the reaction mixture was filtered. The solvent from the filtrate was removed under reduced pressure to obtain the crude product, which was further purified by thin layer chromatography (silica gel; hexane-ethyl acetate). Isolated yield: 78%. The ester (1.04 g, 2 mmol) was taken with sodium hydroxide (0.16 g, 4 mmol) in a mixed solvent of methanol-water (4:1, 20 ml) and refluxed for 1 h at 70 °C. After completion of the reaction, the solvent was removed under reduced pressure, then 10 ml of water was added to it and the solution was acidified with dilute hydrochloric acid (20 ml, 10%) solution to precipitate out the dicarboxylic acid. The solid was filtered and washed with water until it was free from acid. The product was isolated as a white solid and was further purified by recrystallising it from methanol. Isolated yield: 59%. IR (KBr, cm⁻¹): 3468 (bs), 2067 (w), 1748 (s), 1638 (s), 1526 (s), 1474 (m), 1441 (m), 1354 (m), 1300 (w), 1254 (w), 1235 (w), 1209 (m), 1143 (s), 1067 (m), 968 (w), 869 (w), 714 (m). ¹HNMR (DMSO-d₆, 400 MHz): 2.11 (s, 6H), 2.17 (s, 6H), 4.08 (s, 1H), 4.18 (s, 4H), 6.28 (s, 2H), 6.53 (s, 1H), 6.94 (s, 2H), 6.98 (d, J = 8 Hz, 1H), 7.51 (t, J = 8 Hz, 1H), 7.63 (t, J = 8 Hz, 1H), 7.99 (d, J = 8 Hz, 1H). Mass (ESI) $[M + Na^{+}]$: 516.681.

Synthesis of the ligand H_2L^3 (3)

Ligand 3 was synthesized by a similar procedure adopted for ligand H_2L^2 (2) and it was prepared starting from bis-phenol 3a.

To prepare **3a**, 3-nitrobenzaldehyde was used instead of 2-nitrobenzaldehyde. Overall yield: 70%. IR (KBr, cm⁻¹): 3433 (bs), 2079 (w), 1636 (s), 1523 (s), 1476 (m), 1352 (m), 1297 (w), 1234 (w), 1214 (m), 1142 (m), 1067 (m), 867 (w), 827 (w), 703 (m). ¹HNMR (DMSO-*d*₆, 400 MHz): 2.13 (s, 6H), 2.16 (s, 6H), 3.78 (s, 2H), 3.81 (s, 2H), 6.48 (s, 2H), 6.89 (s, 2H), 7.01 (s, 1H), 7. 51 (d, J = 7.6, 1H), 7.57 (t, J = 7.6 Hz, 1H), 7.79 (s, 1H), 8.05 (d, J = 7.6 Hz, 1H). LCMS [M + Na⁺]: 516.1430.

Synthesis of cadmium and mercury complexes

Complex [CdL¹(py)₃]_{*n*}·3*n*H₂O (4). To a well-stirred solution of H₂L¹ (0.224 g, 0.5 mmol) and sodium hydroxide (0.02 g) dissolved in methanol (10 ml), cadmium(II) acetate monohydrate (0.133 g, 0.5 mmol) was added. The white precipitate obtained was dissolved by the addition of the minimum amount of pyridine. The reaction mixture was filtered and the transparent liquid was kept for crystallization. After one week colorless needle-like crystals were obtained. Isolated yield: 50%. IR (KBr, cm⁻¹): 3426 (bs), 2924 (s), 2855 (w), 1600 (s), 1447 (s), 1415 (m), 1327 (w), 1245 (w), 1208 (m), 1141 (m), 1036 (s), 760 (w), 702 (s). ¹HNMR (DMSO-*d*₆): 2.11 (s, 6H), 2.14 (s, 6H), 4.01 (s, 4H), 6.37 (s, 1H), 6.43 (s, 2H), 6.85 (s, 2H), 6.98 (d, 6.2 Hz, 2H), 7.18 (t, 7.0 Hz, 1H), 7.21 (5.3 Hz, t, 3H), 7.79 (7.6 Hz, t, 6H), 8.58 (s, 6H).

Complex $[CdL^{2}(py)(CH_{3}OH)]_{2}$ ·CH₃OH (5). To a well-stirred solution of $H_{2}L^{2}$ (0.246 g, 0.5 mmol) and sodium hydroxide (0.02 g) dissolved in methanol (10 ml), cadmium(II) acetate monohydrate (0.133 g, 0.5 mmol) was added. A white precipitate was obtained, which was dissolved by the addition of the minimum amount of pyridine. The reaction mixture was filtered and the transparent liquid was kept for crystallization. After one week colorless needle-like crystals were obtained. Isolated yield: 60%. IR (KBr, cm⁻¹): 3427 (bs), 1630 (s), 1526 (m), 1475 (w), 1443 (w), 1419 (w), 1351 (w), 1324 (w), 1238 (w), 1212 (m), 1143 (m), 1051 (w), 1035 (w), 697 (m). ¹HNMR (DMSO-*d*₆): 2.10 (s, 1H), 2.15 (s, 6H), 4.10 (s, 4H), 6.25 (s, 2H), 6.65 (s, 1H), 6.88 (d, 8 Hz, 1H), 6.90 (s, 2H), 7.39 (t, 5.6 Hz, 2H), 7.49 (t, 7.6 Hz, 1H), 7.60 (t, 7.6 Hz, 1H), 7.79 (t, 6.4, 1H), 7.93 (d, 8 Hz, 1H), 8.58 (d, 6.2 Hz, 2H).

Complex $[CdL^{2}(py)_{2}(H_{2}O)]_{2}\cdot H_{2}O$ (6). This was prepared by exactly the same procedure as for 5, but instead of methanol dimethylformamide was used as the solvent. After one week light yellow crystals were obtained. Isolated yield: 80%. IR (KBr, cm⁻¹): 3435 (bs), 1602 (s), 1536 (m), 1473 (w), 1447 (w), 1415 (w), 1362 (w), 1321 (w), 1239 (w), 1214 (m), 1142 (m), 1031 (s), 933 (w), 860 (m), 691 (w). ¹HNMR (DMSO-*d*₆): 2.10 (s, 6H), 2.16 (s, 6H), 4.09 (s, 4H), 6.23 (s, 2H), 6.66 (s, 1H), 6.87 (d, 8.0 Hz, 1H), 6.90 (d, 6.4 Hz, 2H), 7.39 (t, 1.6 Hz, 4H), 7.51 (t, 7.6 Hz, 1H), 7.59 (t, 6 Hz, 1H), 7.79 (t, 1.6 Hz, 2H), 7.93 (t, 5.6 Hz, 1H), 8.58 (d, 4.0 Hz, 4H).

Alternatively, complex **6** can be prepared by dissolving complex **5** in a DMF–pyridine solvent and slow evaporation of the solvent at room temperature for several days.

Complex $[CdL^{3}(py)_{2}(H_{2}O)]_{2}\cdot 3H_{2}O$ (7). To a well-stirred solution of $H_{2}L^{3}$ (0.25 g, 0.5 mmol) and sodium hydroxide (0.02 g) dissolved in methanol (10 ml), cadmium(II) acetate

monohydrate (0.13 g, 0.5 mmol) was added. A white precipitate was obtained, which was dissolved by the addition of the minimum amount of pyridine. The reaction mixture was filtered and the transparent liquid was kept for crystallization. After one week colorless needle-like crystals were obtained. Isolated yield: 55%. IR (KBr, cm⁻¹): 3433 (bs), 2923 (m), 1633 (s), 1525 (w), 1446 (w), 1348 (w), 1213 (m), 1143 (m), 1055 (w), 864 (w), 698 (m). ¹HNMR (DMSO-*d*₆): 2.12 (s, 6H), 2.16 (s, 6H), 4.02 (d, 14.4 Hz, 4H), 4.08 (d, 14.4 Hz, 4H), 6.39 (s, 2H), 6.74 (s, 1H), 6.91 (s, 2H), 7.37 (t, 5.6 Hz, 2H), 7.50 (t, 6.8 Hz, 1H), 7.74 (s, 1H), 7.77 (t, 7.6 Hz, 2H), 8.02 (d, 6.8 Hz, 1H), 8.58 (s, 2H).

Complex [HgL²(py)₂]₂·**DMF** (8). To a well-stirred solution of H_2L^2 (0.25 g, 0.5 mmol) and sodium hydroxide (0.02 g) dissolved in dimethylformamide (10 ml), mercury(II) acetate (0.16 g, 0.5 mmol) was added. A white precipitate was obtained, which was dissolved in the minimum amount of pyridine. Any residue at this stage was filtered and the transparent liquid was kept for crystallization. After one week crystals were obtained. Isolated yield: 55%. IR (KBr, cm⁻¹): 3432 (bs), 1609 (s), 1537 (m), 1474 (w), 1415 (m), 1363 (w), 1321 (w), 1299 (w), 1239 (w), 1214 (w), 1142 (m), 1031 (m), 860 (w), 713 (m). ¹HNMR (DMSO-*d*₆): 2.11 (s, 6H), 2.17 (s, 6H), 4.24 (d, 15.2 Hz, 2H), 4.45 (d, 14 Hz, 2H), 6.26 (s, 2H), 6.75 (s, 1H), 6.87 (d, 7.6 Hz, 1H), 6.92 (s, 2H), 7.52 (t, 7.6 Hz, 4H), 7.60 (t, 7.2 Hz, 1H), 7.89 (t, 1.6 Hz, 1H), 7.94 (s, 2H), 7.97 (s, 1H), 8.69 (d, 4.4 Hz, 4H).

Alternatively, in the syntheses of complexes **4–11**, the use of potassium hydroxide instead of sodium hydroxide does not effect the formation of these products. Complex [{CdL¹(4-mepy)₂}·H₂O]_n (**9**) was prepared in a similar procedure to that for complex **4**, but 4-mepy was used instead of pyridine. Mercury complexes [HgL²(4-mepy)₂]₂ (**10**) and [HgL³(3-mepy)₂]₂·DMF (**11**) were prepared in a similar procedure as for **8**, but the two different isomeric methyl-pyridines were used instead of pyridine.

Synthesis of potassium complexes

Complex $[K_4(L^1)_2(\mu-H_2O)_2(H_2O)_2](H_2O)_n$ (12). To a wellstirred solution of ligand H_2L^1 (0.9 g, 2 mmol) in dimethylformamide, potassium acetate (4 mmol) was added. The reaction mixture was stirred for another half an hour to dissolve it and then filtered to remove any solid impurity. The transparent liquid was kept for crystallization. After one week colorless block crystals of **12** were obtained. Isolated yield 65%. IR (KBr, cm⁻¹): 3400 (s), 2921 (m), 1591 (s), 1467 (m), 1448 (m), 1416 (s), 1327 (m), 1297 (w), 1239 (w), 1212 (m), 1140 (m), 1033 (s), 933 (w), 861 (w), 779 (w), 946 (w), 706 (m).

Complex $[K_2L^2(H_2O)]_n$ (13). The potassium salt of H_2L^2 (13) was also synthesized in a similar way to 12, but it was synthesised from ligand H_2L^2 . Isolated yield: 60%. IR (KBr, cm⁻¹): 3389 (s), 2923 (m), 1599 (s), 1537 (s), 1473 (m), 1413 (s), 1364 (w), 1320 (m), 1298 (m), 1239 (m), 1214 (m), 1141 (m), 1030 (s), 932 (w), 860 (m), 822 (w), 786 (w), 713 (m), 582 (w).

X-ray crystallography

Diffraction data for compounds were collected using a Bruker Nonius SMART Apex CCD diffractometer equipped with graphite monochromator and Apex CCD camera. The SMART software was used for data collection and also for indexing the reflections and determining the unit cell parameters. Data reduction and cell refinement were performed using SAINT software and the space groups of these crystals were determined from systematic absences by XPREP and further justified by the refinement results. The structures were solved by direct methods and refined by full-matrix least-square calculations using SHELXTL software. All of the non-H atoms were refined in the anisotropic approximation against F^2 of all reflections. The Hatoms attached to heteroatoms in these crystals were located in the difference Fourier synthesis maps and refined with isotropic displacement coefficients. The locations of acidic protons were justified by a difference Fourier synthesis map and in the refinement these were allowed for as riding atoms. The crystallographic parameters are listed in Table 1. Some of the labile hydrogen atoms in the complexes 4-7 could not be located.

Results and discussion

Ligands synthesis and characterisation

The dicarboxylic acid ligands H_2L^1 (1), H_2L^2 (2) and H_2L^3 (3) were synthesized by multi-step synthetic procedures starting from bis-phenols (1a–3a). The bis-phenols (1a–3a) were reacted with methyl bromoacetate to obtain the corresponding ester (1b–3b). The esters (1b–3b) were further hydrolyzed to the dicarboxylic acids. The reaction steps are illustrated in Scheme 2. These esters and acids are characterized from their spectroscopic properties, such as ¹HNMR, IR, mass spectra, and also by determining some of their structures.

We have already reported the X-ray crystal structure of $H_2L^{1.16}$ The structure determined by single crystal X-ray of the ligand H_2L^2 shows a propeller-like geometry (Fig. 1). The ligand has two carboxylic group containing arms that are attached to a central carbon to provide a V-shape geometry in two dimensions. The propeller-like geometry originates from the projection of the two aromatic rings bearing a central methine carbon (C11). The arms bearing flexible carboxylic acid groups are attached to the two aromatic rings through oxygen atoms. Thus, the flexible arms are suitably oriented to adopt a favorable conformation for coordination to metal ions. We could not obtain suitable crystals of ligand H_2L^3 for its X-ray structure determination, however, we have established its structure by other spectroscopic techniques.

Cadmium and mercury complexes of the ligands

The cadmium complex of the ligand H_2L^1 , $[CdL^1(py)_3]_n \cdot 3nH_2O$ (4) is a coordination polymer $(H_2L^1 = (C_6H_5)CH\{3-CH_3-,5-CH_3-, 6-(-OCH_2CO_2H)C_6H_2\}_2$ and py = pyridine). The ligand H_2L^2 (2) either formed dinuclear complex $[CdL^2(py) (CH_3OH)]_2 \cdot CH_3OH$ (5) or metallacycle $[CdL^2(py)_2(H_2O)]_2 \cdot H_2O$ (6) (where $H_2L^2 = (2-NO_2-C_6H_4)CH\{3-CH_3-,5-CH_3-,6-(-OCH_2CO_2H)C_6H_2\}_2$) depending on the solvent used; whereas the

Table 1	Crystallographic	parameters	of ligand	and con	iplexes
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Compound no.	2	4	5	6
Formulae	C ₂₇ H ₂₇ NO ₈	C ₄₂ H ₄₁ CdN ₃ O ₉	C ₆₈ H ₇₄ Cd ₂ N ₄ O ₂₂	C ₇₄ H ₇₄ Cd ₂ N ₆ O ₂₀
CCDC no.	840829	806671	837719	844623
Mol. wt.	493.50	844.18	1524.11	1592.19
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group Temperature (K)	$P2_1/n$ 296(2)	$P2_1/c$ 296(2)	$P2_1/c$ 296(2)	$P2_1/c$ 296(2)
Wavelength (Å)	0 71073	0 71073	0 71073	0 71073
a (Å)	16.297(3)	16.3357(5)	17.4571(11)	12.5560(10)
b(A)	9.222(2)	14.1196(5)	21.0538(12)	25.231(2)
c (Å)	16.374(4)	18.3475(6)	9.2040(5)	12.2248(10)
α (°)	90.00	90.00	90.00	90.00
β (°)	94.019(15)	104.841(2)	93.921(4)	101.953(4)
$\gamma(3)$ $V(\lambda^3)$	90.00	90.00	90.00	90.00
7 (A)	2434.8(9)	4090.7(2)	2	2
Density (Mg m^{-3})	1.335	1.371	1.500	1.396
Abs. coeff./mm ⁻¹	0.099	0.591	0.710	0.635
Abs. correction	none	none	none	empirical
<i>F</i> (000)	1040	1736	1564	1632
Total reflection	4427	7341	5843	9492
Reflections, $I \ge 2\sigma(I)$ Mov. θ^{0}	2439	4341	38/6	68/U 28/8
Ranges $(h \mid k \mid)$	-16 < h < 19	-19 < h < 19	$-19 \le h \le 20$	-16 < h < 16
Runges (n, n, r)	$-11 \le k \le 11$	$-16 \le k \le 16$	-24 < k < 25	$-32 \le k \le 33$
	$-19 \le l \le 19$	$-22 \leq l \leq 22$	$-10 \le l \le 10$	$-15 \le l \le 16$
Complete to 2θ (%)	97.00	99.1	93.0	99.0
Data/restrain/parameter	4427/0/331	7341/0/500	5843/0/440	9492/0/460
$\frac{\text{Goof}(F^2)}{P \log F^2} = 2 - (P)$	1.062	0.820	1.259	1.294
R indices $[I > 2\sigma(I)]$ R indices (all data)	0.0658	0.0366	0.0789	0.0867
Residual electron density	0.1210	0.0715	1.81	0.1088
	0.20	0.11	1.01	0.97
Compound no	7	0	12	12
Compound no.	7	8	12	13
Compound no.	7 C ₇₄ H ₇₀ Cd ₂ N ₆ O ₂₆	8 C ₈₆ H ₉₆ Hg ₂ N ₁₀ O ₂₀	12 C ₂₇ H ₃₀ K ₂ O ₁₁	13 C ₂₇ H ₂₇ K ₂ NO ₁₁
Compound no. Formulae CCDC no. Mol. wt	7 C ₇₄ H ₇₀ Cd ₂ N ₆ O ₂₆ 837720 1684 16	8 C ₈₆ H ₉₆ Hg ₂ N ₁₀ O ₂₀ 837718 1990 91	12 C ₂₇ H ₃₀ K ₂ O ₁₁ 851819 608 71	13 C ₂₇ H ₂₇ K ₂ NO ₁₁ 851820 619 70
Compound no. Formulae CCDC no. Mol. wt. Crystal system	7 C ₇₄ H ₇₀ Cd ₂ N ₆ O ₂₆ 837720 1684.16 triclinic	8 C ₈₆ H ₉₆ Hg ₂ N ₁₀ O ₂₀ 837718 1990.91 triclinic	12 C ₂₇ H ₃₀ K ₂ O ₁₁ 851819 608.71 monoclinic	13 C ₂₇ H ₂₇ K ₂ NO ₁₁ 851820 619.70 orthorhombic
Compound no. Formulae CCDC no. Mol. wt. Crystal system Space group	7 C ₇₄ H ₇₀ Cd ₂ N ₆ O ₂₆ 837720 1684.16 triclinic PI	$\frac{8}{\substack{C_{86}H_{96}Hg_2N_{10}O_{20}\\837718\\1990.91\\triclinic\\P\bar{l}}}$	12 C ₂₇ H ₃₀ K ₂ O ₁₁ 851819 608.71 monoclinic P2 ₁ /c	13 C ₂₇ H ₂₇ K ₂ NO ₁₁ 851820 619.70 orthorhombic <i>Pbca</i>
Compound no. Formulae CCDC no. Mol. wt. Crystal system Space group Temperature (K)	7 C ₇₄ H ₇₀ Cd ₂ N ₆ O ₂₆ 837720 1684.16 triclinic PI 296(2)	$\frac{8}{\begin{array}{c} C_{86}H_{96}Hg_2N_{10}O_{20}\\ 837718\\ 1990.91\\ triclinic\\ P\bar{I}\\ 296(2) \end{array}}$	12 C ₂₇ H ₃₀ K ₂ O ₁₁ 851819 608.71 monoclinic <i>P</i> 2 ₁ / <i>c</i> 296(2)	13 C ₂₇ H ₂₇ K ₂ NO ₁₁ 851820 619.70 orthorhombic <i>Pbca</i> 296(2)
Compound no. Formulae CCDC no. Mol. wt. Crystal system Space group Temperature (K) Wavelength (Å)	$\begin{array}{c} 7 \\ C_{74}H_{70}Cd_2N_6O_{26} \\ 837720 \\ 1684.16 \\ triclinic \\ PI \\ 296(2) \\ 0.71073 \end{array}$	$\begin{array}{c} 8 \\ \hline C_{86}H_{96}Hg_2N_{10}O_{20} \\ 837718 \\ 1990.91 \\ triclinic \\ \mathcal{P}\bar{1} \\ 296(2) \\ 0.71073 \\ \end{array}$	12 C ₂₇ H ₃₀ K ₂ O ₁₁ 851819 608.71 monoclinic <i>P</i> 2 ₁ / <i>c</i> 296(2) 0.71073	13 C ₂₇ H ₂₇ K ₂ NO ₁₁ 851820 619.70 orthorhombic <i>Pbca</i> 296(2) 0.71073
Compound no. Formulae CCDC no. Mol. wt. Crystal system Space group Temperature (K) Wavelength (Å) a (Å)	7 C ₇₄ H ₇₀ Cd ₂ N ₆ O ₂₆ 837720 1684.16 triclinic <i>P</i> I 296(2) 0.71073 11.7715(8) 11.7715(8)	$\begin{array}{c} 8\\ \hline C_{86}H_{96}Hg_2N_{10}O_{20}\\ 837718\\ 1990.91\\ triclinic\\ P\bar{I}\\ 296(2)\\ 0.71073\\ 9.7843(3)\\ 9.7843(3)\\ \end{array}$	12 $C_{27}H_{30}K_{2}O_{11}$ 851819 608.71 monoclinic $P_{2_{1}/c}$ 296(2) 0.71073 17.4531(15) 17.4531(15)	13 C ₂₇ H ₂₇ K ₂ NO ₁₁ 851820 619.70 orthorhombic <i>Pbca</i> 296(2) 0.71073 13,8855(4)
Compound no. Formulae CCDC no. Mol. wt. Crystal system Space group Temperature (K) Wavelength (Å) a (Å) b (Å) -(Å)	$\begin{array}{c} 7\\ C_{74}H_{70}Cd_2N_6O_{26}\\ 837720\\ 1684.16\\ triclinic\\ PI\\ 296(2)\\ 0.71073\\ 11.7715(8)\\ 12.4713(9)\\ 15.2045(11)\\ \end{array}$	$\begin{array}{c} 8\\ \\ C_{86}H_{96}Hg_2N_{10}O_{20}\\ 837718\\ 1990.91\\ triclinic\\ P\bar{I}\\ 296(2)\\ 0.71073\\ 9.7843(3)\\ 12.7257(4)\\ 19.1614(6)\\ \end{array}$	12 $C_{27}H_{30}K_{2}O_{11}$ 851819 608.71 monoclinic $P_{2_{1}/c}$ 296(2) 0.71073 17.4531(15) 14.4853(15) 14.8653(15)	13 C ₂₇ H ₂₇ K ₂ NO ₁₁ 851820 619.70 orthorhombic <i>Pbca</i> 296(2) 0.71073 13.8855(4) 12.4867(3) 12.4867(3)
Compound no. Formulae CCDC no. Mol. wt. Crystal system Space group Temperature (K) Wavelength (Å) a (Å) b (Å) c (Å) a (a)	7 $C_{74}H_{70}Cd_2N_6O_{26}$ 837720 1684.16 triclinic PI 296(2) 0.71073 11.7715(8) 12.4713(9) 15.3045(11) 80.416(3)	$\begin{array}{c} \textbf{8} \\ \hline \\ C_{86}H_{96}Hg_2N_{10}O_{20} \\ 837718 \\ 1990.91 \\ triclinic \\ P\bar{1} \\ 296(2) \\ 0.71073 \\ 9.7843(3) \\ 12.7257(4) \\ 19.1614(6) \\ 90.829(2) \\ \end{array}$	12 $C_{27}H_{30}K_2O_{11}$ 851819 608.71 monoclinic $P_{2_1/c}$ 296(2) 0.71073 17.4531(15) 14.4853(15) 11.8689(10) 90.00	13 C ₂₇ H ₂₇ K ₂ NO ₁₁ 851820 619.70 orthorhombic <i>Pbca</i> 296(2) 0.71073 13.8855(4) 12.4867(3) 33.5892(10) 90.00
Compound no. Formulae CCDC no. Mol. wt. Crystal system Space group Temperature (K) Wavelength (Å) a (Å) b (Å) c (Å) α (°) β (°)	$\begin{array}{c} 7\\ \hline C_{74}H_{70}Cd_2N_6O_{26}\\ 837720\\ 1684.16\\ triclinic\\ PI\\ 296(2)\\ 0.71073\\ 11.7715(8)\\ 12.4713(9)\\ 15.3045(11)\\ 80.416(3)\\ 80.098(3)\\ \end{array}$	$\begin{array}{c} \textbf{8} \\ \hline \\ C_{86}H_{96}Hg_2N_{10}O_{20} \\ 837718 \\ 1990.91 \\ triclinic \\ P\overline{I} \\ 296(2) \\ 0.71073 \\ 9.7843(3) \\ 12.7257(4) \\ 19.1614(6) \\ 90.829(2) \\ 97.845(2) \\ \end{array}$	12 $C_{27}H_{30}K_2O_{11}$ 851819 608.71 monoclinic $P_{2_1/c}$ 296(2) 0.71073 17.4531(15) 14.4853(15) 11.8689(10) 90.00 78 186(4)	13 C ₂₇ H ₂₇ K ₂ NO ₁₁ 851820 619.70 orthorhombic <i>Pbca</i> 296(2) 0.71073 13.8855(4) 12.4867(3) 33.5892(10) 90.00 90.00
Compound no. Formulae CCDC no. Mol. wt. Crystal system Space group Temperature (K) Wavelength (Å) a (Å) b (Å) c (Å) a (°) β (°) γ (°)	$\begin{array}{c} 7\\ \hline C_{74}H_{70}Cd_2N_6O_{26}\\ 837720\\ 1684.16\\ triclinic\\ PI\\ 296(2)\\ 0.71073\\ 11.7715(8)\\ 12.4713(9)\\ 15.3045(11)\\ 80.416(3)\\ 80.098(3)\\ 67.749(3)\\ \end{array}$	$\begin{array}{c} \textbf{8} \\ \hline \\ C_{86}H_{96}Hg_2N_{10}O_{20} \\ 837718 \\ 1990.91 \\ triclinic \\ P\overline{I} \\ 296(2) \\ 0.71073 \\ 9.7843(3) \\ 12.7257(4) \\ 19.1614(6) \\ 90.829(2) \\ 97.845(2) \\ 111.982(2) \end{array}$	$\begin{array}{c} \textbf{12} \\ \hline C_{27}H_{30}K_2O_{11} \\ 851819 \\ 608.71 \\ monoclinic \\ P2_1/c \\ 296(2) \\ 0.71073 \\ 17.4531(15) \\ 14.4853(15) \\ 11.8689(10) \\ 90.00 \\ 78.186(4) \\ 90.00 \end{array}$	13 C ₂₇ H ₂₇ K ₂ NO ₁₁ 851820 619.70 orthorhombic <i>Pbca</i> 296(2) 0.71073 13.8855(4) 12.4867(3) 33.5892(10) 90.00 90.00 90.00
Compound no. Formulae CCDC no. Mol. wt. Crystal system Space group Temperature (K) Wavelength (Å) a (Å) b (Å) c (Å) a (°) β (°) γ (°) V (Å ³)	$\begin{array}{c} 7\\ \hline C_{74}H_{70}Cd_2N_6O_{26}\\ 837720\\ 1684.16\\ triclinic\\ PI\\ 296(2)\\ 0.71073\\ 11.7715(8)\\ 12.4713(9)\\ 15.3045(11)\\ 80.416(3)\\ 80.098(3)\\ 67.749(3)\\ 2035.8(2) \end{array}$	$\begin{array}{c} \textbf{8} \\ \hline \\ C_{86}H_{96}Hg_2N_{10}O_{20} \\ 837718 \\ 1990.91 \\ triclinic \\ P\overline{I} \\ 296(2) \\ 0.71073 \\ 9.7843(3) \\ 12.7257(4) \\ 19.1614(6) \\ 90.829(2) \\ 97.845(2) \\ 111.982(2) \\ 2186.08(12) \end{array}$	$\begin{array}{c} \textbf{12} \\ \hline C_{27}H_{30}K_2O_{11} \\ 851819 \\ 608.71 \\ monoclinic \\ P2_1/c \\ 296(2) \\ 0.71073 \\ 17.4531(15) \\ 14.4853(15) \\ 11.8689(10) \\ 90.00 \\ 78.186(4) \\ 90.00 \\ 2937.1(4) \end{array}$	13 C ₂₇ H ₂₇ K ₂ NO ₁₁ 851820 619.70 orthorhombic <i>Pbca</i> 296(2) 0.71073 13.8855(4) 12.4867(3) 33.5892(10) 90.00 90.00 90.00 5823.8(3)
Compound no. Formulae CCDC no. Mol. wt. Crystal system Space group Temperature (K) Wavelength (Å) a (Å) b (Å) c (Å) a (°) β (°) γ (°) V (Å ³) Z	$\begin{array}{c} 7\\ \hline C_{74}H_{70}Cd_2N_6O_{26}\\ 837720\\ 1684.16\\ triclinic\\ PI\\ 296(2)\\ 0.71073\\ 11.7715(8)\\ 12.4713(9)\\ 15.3045(11)\\ 80.416(3)\\ 80.098(3)\\ 67.749(3)\\ 2035.8(2)\\ 1\\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 $	$\begin{array}{c} \textbf{8} \\ \hline \\ C_{86}H_{96}Hg_2N_{10}O_{20} \\ 837718 \\ 1990.91 \\ triclinic \\ P\overline{l} \\ 296(2) \\ 0.71073 \\ 9.7843(3) \\ 12.7257(4) \\ 19.1614(6) \\ 90.829(2) \\ 97.845(2) \\ 111.982(2) \\ 2186.08(12) \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ $	12 $C_{27}H_{30}K_2O_{11}$ 851819 608.71 monoclinic $P_{2_1/c}$ 296(2) 0.71073 17.4531(15) 14.4853(15) 11.8689(10) 90.00 78.186(4) 90.00 2937.1(4) 4	13 C ₂₇ H ₂₇ K ₂ NO ₁₁ 851820 619.70 orthorhombic <i>Pbca</i> 296(2) 0.71073 13.8855(4) 12.4867(3) 33.5892(10) 90.00 90.00 90.00 5823.8(3) 8
Compound no. Formulae CCDC no. Mol. wt. Crystal system Space group Temperature (K) Wavelength (Å) a (Å) b (Å) c (Å) a (°) β (°) γ (°) V (Å ³) Z Density (Mg m ⁻³) $\Delta = 0$	$\begin{array}{c} 7\\ \hline C_{74}H_{70}Cd_2N_6O_{26}\\ 837720\\ 1684.16\\ triclinic\\ PI\\ 296(2)\\ 0.71073\\ 11.7715(8)\\ 12.4713(9)\\ 15.3045(11)\\ 80.416(3)\\ 80.098(3)\\ 67.749(3)\\ 2035.8(2)\\ 1\\ 1.374\\ 0.600\end{array}$	$\begin{array}{c} \textbf{8} \\ \hline \\ C_{86}H_{96}Hg_2N_{10}O_{20} \\ 837718 \\ 1990.91 \\ triclinic \\ P\overline{I} \\ 296(2) \\ 0.71073 \\ 9.7843(3) \\ 12.7257(4) \\ 19.1614(6) \\ 90.829(2) \\ 97.845(2) \\ 111.982(2) \\ 2186.08(12) \\ 1 \\ 1.512 \\ 2.602 \end{array}$	12 $C_{27}H_{30}K_2O_{11}$ 851819 608.71 monoclinic $P_{2_1/c}$ 296(2) 0.71073 17.4531(15) 14.4853(15) 11.8689(10) 90.00 78.186(4) 90.00 2937.1(4) 4 1.377 0.290	13 C ₂₇ H ₂₇ K ₂ NO ₁₁ 851820 619.70 orthorhombic <i>Pbca</i> 296(2) 0.71073 13.8855(4) 12.4867(3) 33.5892(10) 90.00 90.00 90.00 5823.8(3) 8 1.414 0.295
Compound no. Formulae CCDC no. Mol. wt. Crystal system Space group Temperature (K) Wavelength (Å) a (Å) b (Å) c (Å) a (°) β (°) γ (°) V (Å ³) Z Density (Mg m ⁻³) Abs. coeff. (mm ⁻¹)	$\begin{array}{c} 7\\ \hline C_{74}H_{70}Cd_2N_6O_{26}\\ 837720\\ 1684.16\\ triclinic\\ PI\\ 296(2)\\ 0.71073\\ 11.7715(8)\\ 12.4713(9)\\ 15.3045(11)\\ 80.416(3)\\ 80.098(3)\\ 67.749(3)\\ 2035.8(2)\\ 1\\ 1.374\\ 0.600\\ popp\\ \end{array}$	$\begin{array}{c} \textbf{8} \\ \hline \\ C_{86}H_{96}Hg_2N_{10}O_{20} \\ 837718 \\ 1990.91 \\ triclinic \\ P\overline{I} \\ 296(2) \\ 0.71073 \\ 9.7843(3) \\ 12.7257(4) \\ 19.1614(6) \\ 90.829(2) \\ 97.845(2) \\ 111.982(2) \\ 2186.08(12) \\ 1 \\ 1.512 \\ 3.582 \\ omnimal \end{array}$	12 $C_{27}H_{30}K_2O_{11}$ 851819 608.71 monoclinic $P_{2_1/c}$ 296(2) 0.71073 17.4531(15) 14.4853(15) 11.8689(10) 90.00 78.186(4) 90.00 2937.1(4) 4 1.377 0.380 pono	13 C ₂₇ H ₂₇ K ₂ NO ₁₁ 851820 619.70 orthorhombic <i>Pbca</i> 296(2) 0.71073 13.8855(4) 12.4867(3) 33.5892(10) 90.00 90.00 90.00 5823.8(3) 8 1.414 0.385 popo
Compound no. Formulae CCDC no. Mol. wt. Crystal system Space group Temperature (K) Wavelength (Å) a (Å) b (Å) c (Å) a (°) β (°) γ (°) γ (°) γ (°) γ (°) γ (Å) Z Density (Mg m ⁻³) Abs. correction F(000)	$\begin{array}{c} 7\\ \hline C_{74}H_{70}Cd_2N_6O_{26}\\ 837720\\ 1684.16\\ triclinic\\ PI\\ 296(2)\\ 0.71073\\ 11.7715(8)\\ 12.4713(9)\\ 15.3045(11)\\ 80.416(3)\\ 80.098(3)\\ 67.749(3)\\ 2035.8(2)\\ 1\\ 1.374\\ 0.600\\ none\\ 860\\ \end{array}$	$\begin{array}{c} \textbf{8} \\ \hline \\ C_{86}H_{96}Hg_2N_{10}O_{20} \\ 837718 \\ 1990.91 \\ triclinic \\ P\overline{I} \\ 296(2) \\ 0.71073 \\ 9.7843(3) \\ 12.7257(4) \\ 19.1614(6) \\ 90.829(2) \\ 97.845(2) \\ 111.982(2) \\ 2186.08(12) \\ 1 \\ 1.512 \\ 3.582 \\ empirical \\ 1002 \\ \end{array}$	12 $C_{27}H_{30}K_2O_{11}$ 851819 608.71 monoclinic $P_{2_1/c}$ 296(2) 0.71073 17.4531(15) 14.4853(15) 11.8689(10) 90.00 78.186(4) 90.00 2937.1(4) 4 1.377 0.380 none 1272	13 C ₂₇ H ₂₇ K ₂ NO ₁₁ 851820 619.70 orthorhombic <i>Pbca</i> 296(2) 0.71073 13.8855(4) 12.4867(3) 33.5892(10) 90.00 90.00 90.00 90.00 5823.8(3) 8 1.414 0.385 none 2576
Compound no. Formulae CCDC no. Mol. wt. Crystal system Space group Temperature (K) Wavelength (Å) a (Å) b (Å) c (Å) a (°) β (°) γ (°) V (Å ³) Z Density (Mg m ⁻³) Abs. correction F(000) Total reflection	$\begin{array}{c} 7\\ \hline C_{74}H_{70}Cd_2N_6O_{26}\\ 837720\\ 1684.16\\ triclinic\\ PI\\ 296(2)\\ 0.71073\\ 11.7715(8)\\ 12.4713(9)\\ 15.3045(11)\\ 80.416(3)\\ 80.098(3)\\ 67.749(3)\\ 2035.8(2)\\ 1\\ 1.374\\ 0.600\\ none\\ 860\\ 7252 \end{array}$	$\begin{array}{c} \textbf{8} \\ \hline \\ C_{86}H_{96}Hg_2N_{10}O_{20} \\ 837718 \\ 1990.91 \\ triclinic \\ P\bar{1} \\ 296(2) \\ 0.71073 \\ 9.7843(3) \\ 12.7257(4) \\ 19.1614(6) \\ 90.829(2) \\ 97.845(2) \\ 111.982(2) \\ 2186.08(12) \\ 1 \\ 1.512 \\ 3.582 \\ empirical \\ 1002 \\ 7501 \\ \end{array}$	12 $C_{27}H_{30}K_2O_{11}$ 851819 608.71 monoclinic $P_{2_1/c}$ 296(2) 0.71073 17.4531(15) 14.4853(15) 11.8689(10) 90.00 78.186(4) 90.00 2937.1(4) 4 1.377 0.380 none 1272 7250	13 C ₂₇ H ₂₇ K ₂ NO ₁₁ 851820 619.70 orthorhombic <i>Pbca</i> 296(2) 0.71073 13.8855(4) 12.4867(3) 33.5892(10) 90.00 90.00 90.00 5823.8(3) 8 1.414 0.385 none 2576 7251
Compound no. Formulae CCDC no. Mol. wt. Crystal system Space group Temperature (K) Wavelength (Å) a (Å) b (Å) c (Å) a (°) β (°) γ (°) V (Å ³) Z Density (Mg m ⁻³) Abs. correction F(000) Total reflection Reflections, $I > 2\sigma(I)$	$\begin{array}{c} 7\\ \hline C_{74}H_{70}Cd_2N_6O_{26}\\ 837720\\ 1684.16\\ triclinic\\ PI\\ 296(2)\\ 0.71073\\ 11.7715(8)\\ 12.4713(9)\\ 15.3045(11)\\ 80.416(3)\\ 80.098(3)\\ 67.749(3)\\ 2035.8(2)\\ 1\\ 1.374\\ 0.600\\ none\\ 860\\ 7252\\ 6287\\ \end{array}$	$\begin{array}{c} \textbf{8} \\ \hline \\ C_{86}H_{96}Hg_2N_{10}O_{20} \\ 837718 \\ 1990.91 \\ triclinic \\ P\overline{I} \\ 296(2) \\ 0.71073 \\ 9.7843(3) \\ 12.7257(4) \\ 19.1614(6) \\ 90.829(2) \\ 97.845(2) \\ 111.982(2) \\ 2186.08(12) \\ 1 \\ 1.512 \\ 3.582 \\ empirical \\ 1002 \\ 7501 \\ 5716 \end{array}$	12 $C_{27}H_{30}K_2O_{11}$ 851819 608.71 monoclinic $P_{2_1/c}$ 296(2) 0.71073 17.4531(15) 14.4853(15) 11.8689(10) 90.00 78.186(4) 90.00 2937.1(4) 4 1.377 0.380 none 1272 7250 5475	13 C ₂₇ H ₂₇ K ₂ NO ₁₁ 851820 619.70 orthorhombic <i>Pbca</i> 296(2) 0.71073 13.8855(4) 12.4867(3) 33.5892(10) 90.00 90.00 90.00 90.00 5823.8(3) 8 1.414 0.385 none 2576 7251 5245
Compound no. Formulae CCDC no. Mol. wt. Crystal system Space group Temperature (K) Wavelength (Å) a (Å) b (Å) c (Å) a (°) β (°) γ (°) V (Å ³) Z Density (Mg m ⁻³) Abs. correction F(000) Total reflection Reflections, $I > 2\sigma(I)$ Max. θ /°	$\begin{array}{c} 7\\ \hline C_{74}H_{70}Cd_2N_6O_{26}\\ 837720\\ 1684.16\\ triclinic\\ PI\\ 296(2)\\ 0.71073\\ 11.7715(8)\\ 12.4713(9)\\ 15.3045(11)\\ 80.416(3)\\ 80.098(3)\\ 67.749(3)\\ 2035.8(2)\\ 1\\ 1.374\\ 0.600\\ none\\ 860\\ 7252\\ 6287\\ 25.50\\ \end{array}$	$\begin{array}{c} \textbf{8} \\ \hline \\ C_{86}H_{96}Hg_2N_{10}O_{20} \\ 837718 \\ 1990.91 \\ triclinic \\ PI \\ 296(2) \\ 0.71073 \\ 9.7843(3) \\ 12.7257(4) \\ 19.1614(6) \\ 90.829(2) \\ 97.845(2) \\ 111.982(2) \\ 2186.08(12) \\ 1 \\ 1.512 \\ 3.582 \\ empirical \\ 1002 \\ 7501 \\ 5716 \\ 25.50 \end{array}$	$\begin{array}{c} \textbf{12} \\ \hline C_{27}H_{30}K_2O_{11} \\ 851819 \\ 608.71 \\ monoclinic \\ P2_1/c \\ 296(2) \\ 0.71073 \\ 17.4531(15) \\ 14.4853(15) \\ 11.8689(10) \\ 90.00 \\ 78.186(4) \\ 90.00 \\ 2937.1(4) \\ 4 \\ 1.377 \\ 0.380 \\ none \\ 1272 \\ 7250 \\ 5475 \\ 28.29 \end{array}$	13 C ₂₇ H ₂₇ K ₂ NO ₁₁ 851820 619.70 orthorhombic <i>Pbca</i> 296(2) 0.71073 13.8855(4) 12.4867(3) 33.5892(10) 90.00 90.00 90.00 90.00 5823.8(3) 8 1.414 0.385 none 2576 7251 5245 28.34
Compound no. Formulae CCDC no. Mol. wt. Crystal system Space group Temperature (K) Wavelength (Å) a (Å) b (Å) c (Å) a (°) β (°) γ (°) V (Å ³) Z Density (Mg m ⁻³) Abs. correction F(000) Total reflection Reflections, $I > 2\sigma(I)$ Max. θ /° Ranges (h , k , I)	$\begin{array}{c} 7\\ \hline \\ C_{74}H_{70}Cd_2N_6O_{26}\\ 837720\\ 1684.16\\ triclinic\\ PI\\ 296(2)\\ 0.71073\\ 11.7715(8)\\ 12.4713(9)\\ 15.3045(11)\\ 80.416(3)\\ 80.098(3)\\ 67.749(3)\\ 2035.8(2)\\ 1\\ 1.374\\ 0.600\\ none\\ 860\\ 7252\\ 6287\\ 25.50\\ -14 \leq h \leq 14 \end{array}$	$\begin{array}{c} \textbf{8} \\ \hline \\ C_{86}H_{96}Hg_2N_{10}O_{20} \\ 837718 \\ 1990.91 \\ triclinic \\ P\bar{1} \\ 296(2) \\ 0.71073 \\ 9.7843(3) \\ 12.7257(4) \\ 19.1614(6) \\ 90.829(2) \\ 97.845(2) \\ 111.982(2) \\ 2186.08(12) \\ 1 \\ 1.512 \\ 3.582 \\ empirical \\ 1002 \\ 7501 \\ 5716 \\ 25.50 \\ -11 \leq h \leq 11 \\ \end{array}$	12 $C_{27}H_{30}K_2O_{11}$ 851819 608.71 monoclinic $P_{2_1/c}$ 296(2) 0.71073 17.4531(15) 14.4853(15) 11.8689(10) 90.00 78.186(4) 90.00 2937.1(4) 4 1.377 0.380 none 1272 7250 5475 28.29 $-23 \le h \le 23$	13 $C_{27}H_{27}K_2NO_{11}$ 851820 619.70 orthorhombic <i>Pbca</i> 296(2) 0.71073 13.8855(4) 12.4867(3) 33.5892(10) 90.00 90.00 90.00 90.00 5823.8(3) 8 1.414 0.385 none 2576 7251 5245 28.34 $-18 \le h \le 16$
Compound no. Formulae CCDC no. Mol. wt. Crystal system Space group Temperature (K) Wavelength (Å) a (Å) b (Å) c (Å) a (°) β (°) γ (°) γ (°) γ (°) γ (°) γ (Å) Z Density (Mg m ⁻³) Abs. correction F(000) Total reflection Reflections, $I > 2\sigma(I)$ Max. θ /° Ranges (h, k, I)	7 $C_{74}H_{70}Cd_2N_6O_{26}$ 837720 1684.16 triclinic PI 296(2) 0.71073 11.7715(8) 12.4713(9) 15.3045(11) 80.416(3) 80.098(3) 67.749(3) 2035.8(2) 1 1.374 0.600 none 860 7252 6287 25.50 -14 $\leq h \leq 14$ -15 $\leq k \leq 15$ 18.614 -15 $\leq k \leq 15$ 18.614 -15 $\leq k \leq 15$	$\begin{array}{c} \textbf{8} \\ \hline \\ C_{86}H_{96}Hg_2N_{10}O_{20} \\ 837718 \\ 1990.91 \\ triclinic \\ P\overline{I} \\ 296(2) \\ 0.71073 \\ 9.7843(3) \\ 12.7257(4) \\ 19.1614(6) \\ 90.829(2) \\ 97.845(2) \\ 111.982(2) \\ 2186.08(12) \\ 1 \\ 1.512 \\ 3.582 \\ empirical \\ 1002 \\ 7501 \\ 5716 \\ 25.50 \\ -11 \leq h \leq 11 \\ -15 \leq k \leq 15 \\ 22 \leq 1 \leq 22 \end{array}$	12 $C_{27}H_{30}K_{2}O_{11}$ 851819 608.71 monoclinic $P_{2_1/c}$ 296(2) 0.71073 17.4531(15) 14.4853(15) 11.8689(10) 90.00 78.186(4) 90.00 2937.1(4) 4 1.377 0.380 none 1272 7250 5475 28.29 $-23 \le h \le 23$ $-16 \le k \le 19$ 15.5 16.5 16.5 16.5 16.5 16.5 16.5 16.5 16.5 16.5 16.5 17.5 1	13 $C_{27}H_{27}K_2NO_{11}$ 851820 619.70 orthorhombic <i>Pbca</i> 296(2) 0.71073 13.8855(4) 12.4867(3) 33.5892(10) 90.00 90.00 90.00 5823.8(3) 8 1.414 0.385 none 2576 7251 5245 28.34 $-18 \le h \le 16$ $-16 \le k \le 16$
Compound no. Formulae CCDC no. Mol. wt. Crystal system Space group Temperature (K) Wavelength (Å) a (Å) b (Å) c (Å) a (°) β (°) γ (°) γ (°) γ (°) γ (°) γ (Å) Z Density (Mg m ⁻³) Abs. correction F(000) Total reflection Reflections, $I > 2\sigma(I)$ Max. θ /° Ranges (h, k, I)	$\begin{array}{c} 7\\ \hline \\ C_{74}H_{70}Cd_2N_6O_{26}\\ 837720\\ 1684.16\\ triclinic\\ PI\\ 296(2)\\ 0.71073\\ 11.7715(8)\\ 12.4713(9)\\ 15.3045(11)\\ 80.416(3)\\ 80.098(3)\\ 67.749(3)\\ 2035.8(2)\\ 1\\ 1.374\\ 0.600\\ none\\ 860\\ 7252\\ 6287\\ 25.50\\ -14 \leq h \leq 14\\ -15 \leq k \leq 15\\ -18 \leq 1 \leq 18\\ 95.6 \end{array}$	$\begin{array}{c} \textbf{8} \\ \hline \\ C_{86}H_{96}Hg_2N_{10}O_{20} \\ 837718 \\ 1990.91 \\ triclinic \\ P\bar{1} \\ 296(2) \\ 0.71073 \\ 9.7843(3) \\ 12.7257(4) \\ 19.1614(6) \\ 90.829(2) \\ 97.845(2) \\ 111.982(2) \\ 2186.08(12) \\ 1 \\ 1.512 \\ 3.582 \\ empirical \\ 1002 \\ 7501 \\ 5716 \\ 25.50 \\ -11 \leq h \leq 11 \\ -15 \leq k \leq 15 \\ -23 \leq 1 \leq 23 \\ 92.1 \\ \end{array}$	12 $C_{27}H_{30}K_2O_{11}$ 851819 608.71 monoclinic $P_{2_1/c}$ 296(2) 0.71073 17.4531(15) 14.4853(15) 11.8689(10) 90.00 78.186(4) 90.00 2937.1(4) 4 1.377 0.380 none 1272 7250 5475 28.29 $-23 \le h \le 23$ $-16 \le k \le 19$ $-15 \le 1 \le 15$ 90.5	13 $C_{27}H_{27}K_2NO_{11}$ 851820 619.70 orthorhombic <i>Pbca</i> 296(2) 0.71073 13.8855(4) 12.4867(3) 33.5892(10) 90.00 90.00 90.00 90.00 5823.8(3) 8 1.414 0.385 none 2576 7251 5245 28.34 -18 ≤ h ≤ 16 -16 ≤ k ≤ 16 -43 ≤ l ≤ 44 09.6
Compound no. Formulae CCDC no. Mol. wt. Crystal system Space group Temperature (K) Wavelength (Å) a (Å) b (Å) c (Å) a (°) β (°) γ (°) V (Å ³) Z Density (Mg m ⁻³) Abs. coreft (mm ⁻¹) Abs. correction F(000) Total reflection Reflections, $I > 2\sigma(I)$ Max. θ /° Ranges (h , k , I) Complete to 2θ (%) Data/restrain/narameter	7 $C_{74}H_{70}Cd_2N_6O_{26}$ 837720 1684.16 triclinic PI 296(2) 0.71073 11.7715(8) 12.4713(9) 15.3045(11) 80.416(3) 80.098(3) 67.749(3) 2035.8(2) 1 1.374 0.600 none 860 7252 6287 25.50 $-14 \le h \le 14$ $-15 \le k \le 15$ $-18 \le 1 \le 18$ 95.6 7252(0)(491)	$\begin{array}{c} \textbf{8} \\ \hline \\ C_{86}H_{96}Hg_2N_{10}O_{20} \\ 837718 \\ 1990.91 \\ triclinic \\ P\overline{I} \\ 296(2) \\ 0.71073 \\ 9.7843(3) \\ 12.7257(4) \\ 19.1614(6) \\ 90.829(2) \\ 97.845(2) \\ 111.982(2) \\ 2186.08(12) \\ 1 \\ 1.512 \\ 3.582 \\ empirical \\ 1002 \\ 7501 \\ 5716 \\ 25.50 \\ -11 \leq h \leq 11 \\ -15 \leq k \leq 15 \\ -23 \leq 1 \leq 23 \\ 92.1 \\ 7501/0/539 \\ \end{array}$	12 $C_{27}H_{30}K_{2}O_{11}$ 851819 608.71 monoclinic $P_{2_1/c}$ 296(2) 0.71073 17.4531(15) 14.4853(15) 11.8689(10) 90.00 78.186(4) 90.00 2937.1(4) 4 1.377 0.380 none 1272 7250 5475 28.29 $-23 \le h \le 23$ $-16 \le k \le 19$ $-15 \le 1 \le 15$ 99.5 7250/4/381	13 $C_{27}H_{27}K_2NO_{11}$ 851820 619.70 orthorhombic <i>Pbca</i> 296(2) 0.71073 13.8855(4) 12.4867(3) 33.5892(10) 90.00 90.00 90.00 5823.8(3) 8 1.414 0.385 none 2576 7251 5245 28.34 $-18 \le h \le 16$ $-16 \le k \le 16$ $-43 \le l \le 44$ 99.6 7251/2/382
Compound no. Formulae CCDC no. Mol. wt. Crystal system Space group Temperature (K) Wavelength (Å) a (Å) b (Å) c (Å) a (°) β (°) γ (°) V (Å ³) Z Density (Mg m ⁻³) Abs. coreft (mm ⁻¹) Abs. correction F(000) Total reflection Reflections, $I > 2\sigma(I)$ Max. θ /° Ranges (h , k , I) Complete to 2θ (%) Data/restrain/parameter Goof (F^2)	7 $C_{74}H_{70}Cd_2N_6O_{26}$ 837720 1684.16 triclinic PI 296(2) 0.71073 11.7715(8) 12.4713(9) 15.3045(11) 80.416(3) 80.098(3) 67.749(3) 2035.8(2) 1 1.374 0.600 none 860 7252 6287 25.50 -14 $\leq h \leq 14$ -15 $\leq k \leq 15$ -18 $\leq 1 \leq 18$ 95.6 7252/0/491 1.079	$\begin{array}{c} \textbf{8} \\ \hline \\ $	12 $C_{27}H_{30}K_{2}O_{11}$ 851819 608.71 monoclinic $P_{2_1/c}$ 296(2) 0.71073 17.4531(15) 14.4853(15) 11.8689(10) 90.00 78.186(4) 90.00 2937.1(4) 4 1.377 0.380 none 1272 7250 5475 28.29 $-23 \le h \le 23$ $-16 \le k \le 19$ $-15 \le 1 \le 15$ 99.5 7250//4/381 1.027	13 $C_{27}H_{27}K_2NO_{11}$ 851820 619.70 orthorhombic <i>Pbca</i> 296(2) 0.71073 13.8855(4) 12.4867(3) 33.5892(10) 90.00 90.00 90.00 90.00 5823.8(3) 8 1.414 0.385 none 2576 7251 5245 28.34 -18 ≤ h ≤ 16 -16 ≤ k ≤ 16 -43 ≤ l ≤ 44 99.6 7251/2/382 1.098
Compound no. Formulae CCDC no. Mol. wt. Crystal system Space group Temperature (K) Wavelength (Å) a (Å) b (Å) c (Å) a (°) β (°) γ	7 $C_{74}H_{70}Cd_2N_6O_{26}$ 837720 1684.16 triclinic PI 296(2) 0.71073 11.7715(8) 12.4713(9) 15.3045(11) 80.416(3) 80.098(3) 67.749(3) 2035.8(2) 1 1.374 0.600 none 860 7252 6287 25.50 $-14 \le h \le 14$ $-15 \le k \le 15$ $-18 \le 1 \le 18$ 95.6 7252/0/491 1.079 0.0384	$\begin{array}{c} \textbf{8} \\ \hline \\ $	12 $C_{27}H_{30}K_{2}O_{11}$ 851819 608.71 monoclinic P_{21}/c 296(2) 0.71073 17.4531(15) 14.4853(15) 11.8689(10) 90.00 78.186(4) 90.00 2937.1(4) 4 1.377 0.380 none 1272 7250 5475 28.29 $-23 \le h \le 23$ $-16 \le k \le 19$ $-15 \le 1 \le 15$ 99.5 7250//4/381 1.027 0.0957	13 $C_{27}H_{27}K_2NO_{11}$ 851820 619.70 orthorhombic <i>Pbca</i> 296(2) 0.71073 13.8855(4) 12.4867(3) 33.5892(10) 90.00 90.00 90.00 90.00 5823.8(3) 8 1.414 0.385 none 2576 7251 5245 28.34 -18 ≤ h ≤ 16 -16 ≤ k ≤ 16 -43 ≤ l ≤ 44 99.6 7251/2/382 1.098 0.0646
Compound no. Formulae CCDC no. Mol. wt. Crystal system Space group Temperature (K) Wavelength (Å) a (Å) b (Å) c (Å) a (°) β (°) γ (°) V (Å ³) Z Density (Mg m ⁻³) Abs. coreft (mm ⁻¹) Abs. correction F(000) Total reflection Reflections, $I > 2\sigma(I)$ Max. θ /° Ranges (h , k , l) Complete to 2θ (%) Data/restrain/parameter Goof (F^2) R indices [$I > 2\sigma(I)$] R indices (all data)	$\begin{array}{c} 7\\ \hline \\ C_{74}H_{70}Cd_2N_6O_{26}\\ 837720\\ 1684.16\\ triclinic\\ PI\\ 296(2)\\ 0.71073\\ 11.7715(8)\\ 12.4713(9)\\ 15.3045(11)\\ 80.416(3)\\ 80.098(3)\\ 67.749(3)\\ 2035.8(2)\\ 1\\ 1.374\\ 0.600\\ none\\ 860\\ 7252\\ 6287\\ 25.50\\ -14 \leq h \leq 14\\ -15 \leq k \leq 15\\ -18 \leq 1 \leq 18\\ 95.6\\ 7252/0/491\\ 1.079\\ 0.0384\\ 0.0449\\ \end{array}$	$\begin{array}{c} \textbf{8} \\ \hline \\ $	12 $C_{27}H_{30}K_2O_{11}$ 851819 608.71 monoclinic $P_{2_1/c}$ 296(2) 0.71073 17.4531(15) 14.4853(15) 11.8689(10) 90.00 2937.1(4) 4 1.377 0.380 none 1272 7250 5475 28.29 $-23 \le h \le 23$ $-16 \le k \le 19$ $-15 \le 1 \le 15$ 99.5 7250//4/381 1.027 0.0957 0.1154	13 $C_{27}H_{27}K_2NO_{11}$ 851820 619.70 orthorhombic <i>Pbca</i> 296(2) 0.71073 13.8855(4) 12.4867(3) 33.5892(10) 90.00 90.00 90.00 90.00 5823.8(3) 8 1.414 0.385 none 2576 7251 5245 28.34 -18 ≤ h ≤ 16 -16 ≤ k ≤ 16 -43 ≤ l ≤ 44 99.6 7251/2/382 1.098 0.0646 0.0882
Compound no. Formulae CCDC no. Mol. wt. Crystal system Space group Temperature (K) Wavelength (Å) a (Å) b (Å) c (Å) a (°) β (°) γ (°) V (Å ³) Z Density (Mg m ⁻³) Abs. coeff. (mm ⁻¹) Abs. coeff. (mm ⁻¹) Abs. coeff. (mm ⁻¹) Abs. coeff. (mm ⁻¹) Abs. corection F(000) Total reflection Reflections, $I > 2\sigma(I)$ Max. θ /° Ranges (h , k , I) Complete to 2θ (%) Data/restrain/parameter Goof (F^2) R indices [$I > 2\sigma(I)$] R indices (all data) Residual electron density	$\begin{array}{c} 7\\ \hline \\ C_{74}H_{70}Cd_2N_6O_{26}\\ 837720\\ 1684.16\\ triclinic\\ PI\\ 296(2)\\ 0.71073\\ 11.7715(8)\\ 12.4713(9)\\ 15.3045(11)\\ 80.416(3)\\ 80.098(3)\\ 67.749(3)\\ 2035.8(2)\\ 1\\ 1.374\\ 0.600\\ none\\ 860\\ 7252\\ 6287\\ 25.50\\ -14 \leq h \leq 14\\ -15 \leq k \leq 15\\ -18 \leq 1 \leq 18\\ 95.6\\ 7252/0/491\\ 1.079\\ 0.0384\\ 0.0449\\ 0.63\\ \end{array}$	$\begin{array}{c} \textbf{8} \\ \hline \\ C_{86}H_{96}Hg_2N_{10}O_{20} \\ 837718 \\ 1990.91 \\ triclinic \\ PI \\ 296(2) \\ 0.71073 \\ 9.7843(3) \\ 12.7257(4) \\ 19.1614(6) \\ 90.829(2) \\ 97.845(2) \\ 111.982(2) \\ 2186.08(12) \\ 1 \\ 1.512 \\ 3.582 \\ empirical \\ 1002 \\ 7501 \\ 5716 \\ 25.50 \\ -11 \leq h \leq 11 \\ -15 \leq k \leq 15 \\ -23 \leq 1 \leq 23 \\ 92.1 \\ 7501/0/539 \\ 0.995 \\ 0.0341 \\ 0.0503 \\ 0.54 \\ \end{array}$	12 $C_{27}H_{30}K_2O_{11}$ 851819 608.71 monoclinic $P_{2_1/c}$ 296(2) 0.71073 17.4531(15) 14.4853(15) 11.8689(10) 90.00 78.186(4) 90.00 2937.1(4) 4 1.377 0.380 none 1272 7250 5475 28.29 $-23 \le h \le 23$ $-16 \le k \le 19$ $-15 \le 1 \le 15$ 99.5 7250//4/381 1.027 0.0957 0.1154 0.66	13 $C_{27}H_{27}K_2NO_{11}$ 851820 619.70 orthorhombic <i>Pbca</i> 296(2) 0.71073 13.8855(4) 12.4867(3) 33.5892(10) 90.00 90.00 90.00 90.00 5823.8(3) 8 1.414 0.385 none 2576 7251 5245 28.34 $-18 \le h \le 16$ $-16 \le k \le 16$ $-43 \le l \le 44$ 99.6 7251/2/382 1.098 0.0646 0.0882 0.52

ligand H_2L^3 (3) formed a metallacycle $[CdL^3(py)_2(H_2O)]_2 \cdot 3H_2O$ (7) (where $H_2L^3 = (3-NO_2-C_6H_4)CH\{3-CH_3-, 5-CH_3-, 6-(-OCH_2CO_2H)C_6H_2\}_2$). In all of the complexes, the metal ions are linked by carboxylate functional groups present at two ends of the ligands. A similar reaction of H_2L^2 with mercury(II) acetate in DMF gave metallacycle $[HgL^2(py)_2]_2$ ·DMF (8). The



Fig. 1 The crystal structure of ligand H_2L^2 (H-atoms are omitted).



Fig. 2 Zig-zag one dimensional coordination polymer 4 formed by ligand L^1 .

crystal structures of all of these complexes were determined. Despite the facts that all of the skeletal parameters, other than the substituent on the aromatic ring of the ligands, are similar and the syntheses of these complexes were carried out at ambient conditions, the number of pyridine molecules per cadmium ion in these complexes varies. This suggests that the substituent present at the remote site of the aromatic ring guides the incoming pyridine molecules to the coordination sphere of cadmium ions.

The coordination polymer **4** has seven coordinated cadmium ions, each having a pentagonal bipyramidal geometry. These geometries are constructed by three monodentate pyridine ligands and two chelating carboxylate groups from two independent ligands. The coordination polymer has a spiral structure (Fig. 2). Each pentagonal bipyramid has two pyridine ligands at its axial positions. The equatorial positions are occupied by four oxygen atoms of carboxylate ligands and a nitrogen atom of a pyridine ligand. The metal–ligand bond parameters are listed in Table 2. A similar reaction of H_2L^1 with cadmium(II) acetate in the presence of 4-methylpyridine (4-mepy) yielded linear coordination polymer [{CdL¹(4-mepy)₂}·H₂O]_n (9). It has a similar structure to that of **4**, but due to poor data quality the structure is not discussed, but is available as ESI.[†] The V-shaped carboxylic acid ligands along with less flexible ligands were used in the synthesis of cadmium metallo-organic frameworks of different dimensions,^{7,9,10} but the formation of metallacycles from those ligands were not observed.

The ¹HNMR spectra of coordination polymer **4** is shown in Fig. 3. There are three singlets at 2.11 ppm, 2.14 ppm and 4.01 ppm; the former two signals are for two different types of methyl groups on the aromatic rings and the latter is for $-CH_2O-$ group. Again, the singlet peaks at 6.37 ppm, 6.43 ppm and 6.85 ppm appear for the methine proton and aromatic protons of methyl group-containing ring, respectively. The peaks for the coordinated pyridine molecule appear at 7.39 (triplet), 7.79 (doublet) and 8.58 ppm (singlet), as illustrated in Fig. 3.

The reaction of cadmium(II) acetate with H_2L^2 in MeOH-pyridine forms a dinuclear complex [CdL²(py)(CH₃OH)]₂·CH₃OH (5), where both of the cadmium ions are in identical environments (Fig. 4a). Each cadmium ion has one pyridine and one methanol molecule in its coordination sphere and the methanol ligands are independently attached to two cadmium ions. They project away from each other at two ends of the dimeric structure. The presence of methanol molecules as ligands at the terminal ends inhibits the formation of a polymeric structure. It helps in providing an adequate geometry to the carboxylate ligands to form a bridged structure. The nitro group present at the orthoposition of the aromatic ring also plays a role by providing the adequate twist to the carboxylate group to form the Cd₂O₂ type core. Such effects were revealed in 2-nitrobenzoate complexes in our earlier studies with metal ions, such as zinc, manganese and cadmium.¹⁵ Alternatively, the 2-nitro benzoate provides the appropriate orientation to two carboxylate groups attached two metal ions to form the Cd₂O₂ core.^{15c} Complex 5 has one pyridine ligand per cadmium ion and these two metal ions in close proximity form the seven coordinate dinuclear complex and the metal-metal distance in this dinuclear complex is found to be 3.97 Å. Generally, to form Cd_2O_2 core with η^1 and η^3 -carboxylate binding mode the cadmium-cadmium separations has to be magnitude^{15a} of 3.8 to 4.15 Å. The selected bond angles and bond distances are listed in Table 3.

The ¹HNMR spectra of dinuclear complex **5** is shown in Fig. 5a. From the spectra, it is seen that here also there are three singlets at 2.10 ppm, 2.15 ppm and 4.10 ppm for two types of methyl protons and $-CH_2O-$, respectively. Again, the singlets at 6.23 ppm, 6.90 ppm and 6.65 ppm are due to the aromatic protons of the methyl group-containing aromatic ring and methine proton of the parent bis-phenol molecule, respectively. The signals for the protons of the coordinated pyridine molecules appear at 7.39 ppm (triplet), 7.79 ppm (triplet) and 8.58 ppm (doublet), these assignments are confirmed by recording HOMO-COSY spectra (ESI[†]).

Ligand **2** reacted with $Cd(O_2CCH_3)_2$ in dimethylformamide (DMF) and pyridine to form metallacycle $[CdL^2(py)_2(H_2O)]_2 \cdot H_2O$ (**6**). This metallacycle may be attributed to opening of a Cd_2O_2 core in a dinuclear complex that could have been an intermediate compound. Each cadmium ion has a coordination number of seven, comprised of two chelating carboxylates and a water molecule along with two pyridine ligands. Although the DMF was used as the solvent, we did not observe DMF molecules in its crystal lattice as the solvent of crystallization, nor it was observed as a ligand. However, DMF can easily interact with different functional groups (in this case either nitro or

 Table 2
 The bond lengths and angles in coordination polymer 4

M–L	$d_{\mathrm{M-L}}(\mathrm{\AA})$	∠L-M-L	Angle (°)	∠L-M-L	Angle (°)	∠L-M-L	Angle (°)
Cd1–N3	2.333(3)	N3-Cd1-N2	95.27(11)	N2Cd1O5	129.82(10)	O5-Cd1-O6	51.12(9)
Cd1–N2	2.344(3)	N3-Cd1-O1	84.24(10)	01-Cd1-05	93.83(9)	N3-Cd1-O2	82.01(10)
Cd101	2.360(2)	N2-Cd1-O1	136.16(10)	N1-Cd1-O5	100.54(11)	N2-Cd1-O2	82.98(9)
Cd1–N1	2.375(3)	N3-Cd1-N1	170.04(10)	N3-Cd1-O6	107.21(11)	O1-Cd1-O2	53.44(8)
Cd1–O5	2.474(3)	N2-Cd1-N1	88.85(11)	N2-Cd1-O6	82.30(10)	N1-Cd1-O2	89.52(10)
Cd106	2.478(3)	O1-Cd1-N1	86.51(10)	O1-Cd1-O6	139.73(10)	O5-Cd1-O2	145.35(9)
Cd1–O2	2.548(3)	N3-Cd1-O5	83.78(11)	N1-Cd1-O6	82.30(11)	O6-Cd1-O2	163.28(10)



Fig. 3 The ¹HNMR spectrum of the coordination polymer 4 in DMSO- d_6 .



Fig. 4 (a) The structure of dinuclear complex 5 and (b) the structure of metallacycle 6. In both cases the uncoordinated solvent molecules are omitted for clarity.

carboxylic acid) during the course of the reaction, to guide the carboxylate to form a metallacycle. The structure of the complex determined by X-ray single crystal diffraction is shown in Fig. 4b. The very weak bonds Cd1–O7 and Cd1–O2 are 2.501(6) and 2.555(5) Å, whereas the Cd1–O8 and Cd1–O1 are 2.327(5) and 2.308(5) Å, respectively, supporting that the carboxylates are ligated as bidentate chelate. The metal–ligand bond

distances and bond angles are listed in Table 3. The cadmium ions have pentagonal bipyramid structures, in which one pyridine and two carboxylate groups occupy the equatorial positions; a water molecule and a pyridine molecule occupy the axial positions.

From the ¹HNMR spectra of the metallacycle **6** (Fig. 5b) it is seen that there are three singlets at 2.09 ppm, 2.15 ppm and 4.12 ppm for two types of methyl protons of aromatic rings and

M–L	$d_{\mathrm{M-L}}$ (Å)	∠L-M-L	Angle (°)	∠L-M-L	Angle (°)	∠L-M-L	Angle (°)
				For 5			
Cd1–N3	2.333(3)	O9-Cd1-O7	87.85(18)	N2-Cd1-O7	89.14(18)	O1-Cd1-O2	113.83(18)
Cd1–N2	2.344(3)	O2Cd1O8	112.39(17)	O2Cd1O7	148.80(18)	O7-Cd1-O2	78.47(16)
Cd1-O5	2.474(3)	N2-Cd1-O8	142.6(2)	O8-Cd1-O7	55.56(16)	O8-Cd1-O2	81.05(16)
Cd1–O2	2.548(3)	O9 Cd1-O8	98.20(18)	O9-Cd1-O1	82.1(2)	O2-Cd1-O2	70.9(2)
Cd–O6	2.478(3)	N2-Cd1-O2	91.20(19)	N2-Cd1-O1	128.9(2)	N2-Cd1-O2	80.01(18)
Cd1-O1	2.360(2)	O9-Cd1-O2	123.32(19)	O2-Cd1-O1	53.94(18)	O9-Cd1-O2	163.95(18)
Cd1–N1	2.375(3)	O9Cd1N2	91.54(19)	O8Cd1O1	88.27(18)	O7-Cd1-O1	140.63(17
				For 6			
Cd1–O1	2.308(5)	O1-Cd1-N3	136.38(19)	N3-Cd1-N2	91.7(3)	O1-Cd1-O2	53.46(16)
Cd1–N3	2.312(6)	O1-Cd1-O9	82.17(19)	O9-Cd1-N2	178.0(2)	N3-Cd1-O2	84.6(2)
Cd109	2.322(5)	N3-Cd1-O9	87.7(2)	O8-Cd1-N2	89.6(3)	O9-Cd1-O2	90.7(2)
Cd108	2.327(5)	O1-Cd1-O8	89.98(17)	N3-Cd1-O8	132.9(2)	O8-Cd1-O2	142.51(18)
Cd1–N2	2.334(6)	O1-Cd1-N2	97.0(2)	O9-Cd1-O7	88.2(2)	N2-Cd1-O2	87.3(2)
Cd1–O7	2.501(6)	O1-Cd1-O7	141.39(17)	O8-Cd1-O7	52.96(19)	O7-Cd1-O2	164.53(18)
Cd1–O2	2.555(5)	N3-Cd1-O7	80.0(2)	N2-Cd1-O7	93.5(2)		

 Table 3
 The metal-ligand bond parameters of dinuclear complex 5 and metallacycle 6



Fig. 5 The ¹HNMR spectra of (a) dinuclear complex 5 and (b) metallacycle 6 in DMSO- d_6 .

 $-CH_2O-$, respectively. Again, the singlets at 6.24 ppm, 6.90 ppm and 6.65 ppm are due to the aromatic protons of methyl groups attached to aromatic rings and methine proton of

the parent bis-phenol molecule, respectively. The signals for the protons of the coordinated pyridine molecules appear at 7.39 ppm (triplet), 7.81 ppm (triplet) and 8.59 ppm (doublet).



Fig. 6 The FT-IR (KBr, cm^{-1}) of the dinuclear complex 5 (top) and the metallacycle 6 (bottom).

From the ¹HNMR spectra of **5** and **6**, it is seen that although the position of the peaks are almost similar, the splitting pattern and coupling constant values are different, suggesting that in solution they retain their identity. Furthermore, the coupling scheme interpreted from ¹HNMR is confirmed by recording HOMO-COSY spectra (ESI⁺).

The formation of different types of structures in different solvents shows that the solvent guides the coordination of pyridine into the coordination spheres of the metal ions in these complexes. Conversely, the numbers of pyridine molecules also decide the formation of a dinuclear metal complex or metallacycle. This result demonstrates a process that has close analogy to the off and on of a metallacycle through the coordination effect. This important observation has relevance and analogy with tunable on–off responses for select guest molecules^{17,18} by metal–organic frameworks, in which molecules may come close to self-assemble or get dis-assembled by solvent molecules or by an external ligands. Furthermore, there are examples of cyclic molecules adopting different polymorphic structures to controls pores in transport processes.¹⁹

The PXRD patterns of complex **5** and **6** are distinguishable (ESI[†]). The experimental PXRD pattern of complex **6** is in excellent agreement with the theoretical pattern, however, the PXRD pattern of complex **5** is in agreement with the simulated Miller indices, but with a slight shifting of the peaks in θ -values. We do not have a proper explanation for the shift. Thermogravimetry shows that the compound easily loses methanol on heating at 25–70 °C. The IR spectra of complexes **5** and **6** are distinguishable, as the carbonyl stretching of complex **5** appears at 1630 cm⁻¹, whereas the carbonyl stretching of complex **6**.

Metallacycle $[CdL^{3}(py)_{2}(H_{2}O)]_{2}\cdot 3H_{2}O$ (7) was obtained from the reaction of cadmium(II) acetate with $H_{2}L^{3}$ (3) in methanol and pyridine, where both of the cadmium ions are in identical environments (Fig. 7). The other coordination sites of the metal atoms are occupied by two pyridine molecules and a water molecule. It is evident from the Cd–O bond distances that the carboxylate groups in this complex are a combination of a



Fig. 7 The structure of metallacycle 7 (solvent molecules are omitted for clarity).



Fig. 8 The powder X-ray diffraction pattern of complex 7 (the upper one is experimental, whereas the lower one is simulated).

monodentate and another bidentate with distorted chelate structure, where Cd1-O2, Cd1-O7 and Cd1-O9 bond distances are 2.346 Å, 2.263 Å and 2.341 Å, respectively. These distances are within the limit of generally observed Cd-O bond distances in related compounds. Whereas the Cd1-O1 separation at 2.524 Å and Cd1-O8 separations at 2.677 Å are long for the formation of a bond, but the Cd1-O1 can be suggested as weakly interacting.^{2b,15c} This makes the two slightly different coordination modes of the two carboxylate attached to a cadmium ion. The Cd1-N2 and Cd1-N3 distances in the complex are 2.361 Å and 2.332 Å, respectively. Thus, the molecule adopts distorted pentagonal bipyramid geometry, in which one pyridine and two carboxylates connected to Cd1 make the five-member geometry and the axial bonds are Cd-N2 and Cd1-O9 bonds. The bond angles ∠N3-Cd1-O2, ∠N3-Cd-O7 and ∠O2-Cd1-O7 are 134.32°, 139.46° and 85.07°, respectively. If the two weak contacts are not taken into consideration, then each of the cadmium ions in the complex can be described as a distorted trigonal bipyramid. Nonetheless, the overall structure of the metallacycle is highly symmetric and contains a mirror plane that bisects it into two halves. Each equivalent half contains one cadmium ion with one carboxylate, two pyridine and one water molecules. The simulated and the experimental powder X-ray diffraction patterns of 7 are shown in Fig. 8. All of the principal peaks for different





Fig. 9 (a) The X-ray single crystal structure of metallacycle 8. The hydrogen atoms and solvents are omitted for clarity. (b) Weak interactions of DMF molecules in the crystal lattice of 8.

Table 4 The metal-ligand bond lengths and bond angles of complex 8

M–L	$d_{\mathrm{M-L}}(\mathrm{\AA})$	∠L-M-L	Angle (°)
Hg1–N3 Hg1–O1 Hg1–O8 Hg1–N2	2.227(3) 2.233(3) 2.291(3) 2.381(4)	N3-Hg1-O1 N3-Hg1-O8 O1-Hg1-O8 N3-Hg1-N2 O1-Hg1-N2 O8-Hg1-N2	119.95(13) 142.46(13) 87.03(13) 103.76(13) 101.88(13) 94.40(14)

Miller indices are observed, confirming the phase purity and homogeneity of the samples.

Since both metallacycles as well as a binuclear complex of cadmium with the H_2L^2 are observed, we have examined the effect of size of the metal ions in deciding their formation. Thus, mercury metallacycle $[HgL^2(py)_2]_2$ ·DMF (8) was prepared by reacting H_2L^2 with mercury(II) acetate in DMF, followed by treatment with pyridine (Fig. 9a). In this case, we were not successful in obtaining crystals from the reaction carried out in methanol. The size of mercury being bigger than cadmium, it accommodated two pyridine ligands and retained a cyclic structure, where each mercuric ion has a distorted tetrahedral geometry. The metal–ligand bond parameters are listed in Table 4. The Hg1–O2 and Hg1–O7 separations are 2.91 Å and 2.68 Å, respectively, suggesting that there is no Hg–O bond between

these atoms. This shows that the carboxylates are coordinated in a monodentate fashion to the mercury(π). From the ¹HNMR spectrum of the mercury-containing metallacycle, it is seen that signals from the hydrogen atoms of coordinated pyridine molecules appear at 7.52 ppm, 7.91 ppm and 8.69 ppm (ESI⁺).

The packing pattern of the mercury complex suggests that the solvent molecules are held between the interstitial spaces of the metallacycles. The coordinating carboxylate groups on the cyclic part have no interactions with the DMF molecules of the lattice. The carbonyl oxygen of DMF and a C–H bond of the aromatic ring of a ligand provide C15–H···O9 interactions (d_{D-H} , 0.929 Å; d_{D-A} , 3.295 Å; $\angle D$ –H···A, 140.6°) to hold the DMF in the interstices, as shown in Fig. 9b.

We have also obtained macrocyclic compounds of mercury with composition $[HgL^{2}(4\text{-mepy})_{2}]_{2}$ (10) and $[HgL^{3}(3\text{-mepy})_{2}]_{2}$ ·DMF (11) from ligands $H_{2}L^{2}$ and $H_{2}L^{3}$ in the presence of 4-methylpyridine (4-mepy) or 3-methylpyridine (3mepy) under similar reaction conditions to those used for the preparation of 8. Since their data quality are poor, they are not discussed to elucidate their geometry, but the crystallographic information files are provided as ESI.†

Potassium complexes of the ligands

Since the presence of a nitro group enabled us to isolate two different structures of cadmium complexes, we have examined the structure of the potassium salts as these may be used as precursors for the preparation of the cadmium complexes through cation exchange reactions. The reaction of H_2L^1 or H_2L^2 with potassium hydroxide in DMF resulted in $[K_4(L^1)_2(\mu-H_2O)_2(H_2O)_2](H_2O)_n$ (12) and $[K_2L^2(H_2O)]_n$ (13), respectively. Potassium complex 12 is a 2-D coordination polymer. The polymer is comprised of potassium ions that have a coordination geometry of seven with a pentagonal bipyramid structure, as well as with six coordination potassium ions with distorted octahedral geometry (Fig. 10a). It has two different types of water ligands; one set is bridging and the other is monodentate.

In coordination polymer 13, the interesting feature is the coordination of the nitro group present at the ortho-position of the aromatic ring (Fig. 10b). The coordination polymer has two different coordination environments for potassium; these are seven and eight coordination geometry. The nitro group also acts as a bridging ligand to hold two potassium ions. Between the two ethereal oxygen atoms of the ligand L^2 , one oxygen atom coordinates, while the other remains uncoordinated. In alkali metal carboxylate polymers ethereal oxygen plays an important role in providing the final geometry.²⁰ But due to the involvement of oxygen atoms of the nitro group in coordination, it hindered the coordination of one of the ethereal oxygens. From this observation, it is clear that the presence of a nitro group at the ortho-position plays a role by coordination to the alkali metal cation in the synthesis of complexes 5 and 6 when potassium hydroxide or sodium hydroxide is used to generate the dicarboxvlate anions.



Fig. 10 The repeat units of the coordination polymer of potassium salt (a) 12 (b) 13 (hydrogen atoms are omitted for clarity).

Thermogravimetry

For coordination polymer 4, in the temperature range 50-180 °C, 34.2% weight loss occurs (theoretical weight loss 34.5%) due to the loss of three coordinated pyridine and three uncoordinated water molecules. Again, when dinuclear complex 5 was heated, it is seen that 7.64% weight loss occurs in the temperature range 25-70 °C (theoretical weight loss 7.4%) due to the loss of three methanol (two coordinated and one uncoordinated) and one water molecules. When it was further heated, it loses two molecules of the ligand (H_2L^2) , where the weight loss was 68.5% (theoretical weight loss 69.0%). When metallacycle 6 was heated it lost three water molecules in the temperature range 65-85 °C, which on further heating loses four pyridine molecules in the temperature range 120-250 °C. The metallacycle 7 loses four coordinated pyridine and four water molecules of crystallization on heating up to 165 °C. When it was heated further, it lost two molecules of the ligand (H_2L^3) at above 165 °C. Metallacycle 8 loses four coordinated pyridine molecules and two uncoordinated DMF molecules when heated to 215 °C, which on further

heating loses two molecules of H_2L^2 . Potassium salts 12 and 13 lose five water and three water molecules in the temperature ranges 50–150 °C and 55–130 °C, respectively, on heating.

In conclusion, we have shown the formation of metallacycle and coordination polymers of cadmium and mercury from three flexible dicarboxylate ligands. As an exceptional case, we found the formation of a dinuclear complex, as well as the metallacycle of cadmium of ligand H_2L^2 by changing the solvent from methanol to dimethylformamide. It is suggested that the solvent used in these reactions guides the number of incoming ancillary ligands, such as pyridine, that are anchored to cadmium. Again, this series of complexes also clearly demonstrates the role of the nitro group on the ligand; it is shown that even when it doesn't coordinate to the cadmium or mercury ions, its presence has a striking effect on the structure of cadmium and mercury complexes. These types of substituent effect in controlling and tuning the molecular architecture of the coordination polymers would be a potentially effective approach. Strikingly, the ability of the nitro group on the ligand attached to potassium suggests the role of the alkali metal ion in guiding these types of coordination polymer frames. Although there have been substantial contributions to cadmium coordination chemistry, the approach to obtain metallacycles have not been pursued. We have demonstrated that a flexible tether (-CH₂CO₂) with rigid directing functionality (in this case the bis-phenol part) makes it possible to obtain metallacycles in ambient conditions.

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