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Syntheses and Structures of *N,N'*-Bis(6-(2-hydroxymethyl)pyridylmethyl)piperazine, Its Two Zinc(II) Complexes and the Cadmium(II) Complex of *N*-(6-(2-Hydroxymethyl)pyridylmethyl)-*N'*-(2-pyridylmethyl)piperazine

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The syntheses and crystal structures of *N,N'*-bis(6-(2-hydroxymethyl)-pyridylmethyl)piperazine ($C_{18}H_{24}N_4O_2$, **3**), its polymeric zinc(II) nitrate complex ($C_{18}H_{29}N_7O_{14}Zn_2$, **3a**) and dinuclear zinc(II) chloride complex ($C_{20}H_{27}N_5O_2Zn_2Cl_4$, **3b**) and mononuclear cadmium(II) nitrate complex of *N*-(6-(2-hydroxymethyl)pyridylmethyl)-*N'*-(2-pyridylmethyl)piperazine ($C_{17}H_{22}N_6O_7Cd$, **4a**) are described. Compound **3** was characterised by ^1H and ^{13}C NMR, mass spectrometry and elementary analysis. The structures of all compounds were determined by single crystal X-ray diffraction methods. Crystal data: **3**: monoclinic, space group $P2_1/n$ (no. 14), $a=7.816(1)$, $b=6.699(1)$, $c=16.567(3)$ Å, $\beta=91.94(1)°$, $V=866.9(2)$ Å^3, $Z=2$; **3a**: monoclinic, space group $P2/n$ (no. 13), $a=10.274(1)$, $b=11.018(1)$, $c=11.615(1)$ Å, $\beta=93.13(1)°$, $V=1312.8(2)$ Å^3, $Z=2$; **3b**: triclinic, space group $P\bar{1}$ (no. 2), $a=9.624(1)$, $b=11.381(1)$, $c=14.016(1)$ Å, $\alpha=106.21(1)$, $\beta=102.73(1)$, $\gamma=107.10(1)°$, $V=1323.9(2)$ Å^3, $Z=2$; **4a**: monoclinic, space group $P2_1/c$ (no. 14), $a=13.589(8)$, $b=9.006(5)$, $c=17.472(8)$ Å, $\beta=101.96(4)°$, $V=2092(2)$ Å^3, $Z=4$. In the metal complexes, zinc has a distorted square-pyramidal coordination and cadmium has a pentagonal bipyramidal coordination. In **3a** and **3b**, three coordination sites are occupied by one oxygen and two nitrogens of hexadentate **3** and the remaining two by the bridging hydroxyl group and a terminal water molecule in **3a** and by two terminal chlorine atoms in **3b**. In **4a**, five coordination sites of cadmium are occupied by four nitrogens and one oxygen of the pentadentate ligand, and the remaining two by monodentate nitrate groups.

Piperazine offers an aliphatic nitrogen-containing building block in which the ring is preorganized.[1] Piperazine itself is a good hydrogen-bond acceptor, which together with its metal complexing capabilities makes it an interesting building block for coordination and supramolecular chemistry.[2,3] *N,N'*-Alkyl disubstituted piperazines adopt the chair conformation with the *N*-substituents in equatorial positions,[2] but in some small- or medium-sized cyclic[4–7] and open-chain[8,9] metal complexes, piperazine has been found to exist in the boat conformation. Covalently bonded helical supermolecular systems have attracted a wide chemical interest in the last decade[10–16] but ligands forming *meso*-helicate structures have been rare in chemistry.[17–19] Piperazine-containing compounds have been reported to form weak complexes with some metal ions.[20] Some of those have been characterized by X-ray diffraction.[4,6]

Our aim was to synthesize piperazine-containing ligands in which we could utilise the versatile coordination function of the piperazine moiety. Earlier, we investigated the complexing capability of other piperazine-containing ligands,[21,22] for instance *N,N'*-bis(2-pyridylmethyl)piperazine (**1**)[23] and *N,N'*-bis(2-hydroxybenzyl)-piperazine (**2**).[24] The ligand **1** formed crystalline metal complexes with various transition metals and showed several coordination geometries, depending on the size and the electronic properties of the coordinated metal. In the metal complexes, both a chair and boat conformation were observed for the piperazine ring. The complexes with the boat conformation were mononuclear, whereas the complexes with the chair conformation were dinuclear or polynuclear. Owing to the strong intramolecular

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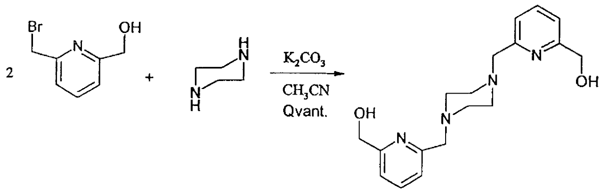
hydrogen bond between the hydroxyl hydrogen and the piperazine nitrogen, the complexation properties of **2** were very different. The hydrogen bond 'locks' the overall geometry of the ligand and makes the piperazine nitrogen less active due to the interaction between the free electron pair and the H atom. Ligand **2** did not form complexes easily, and the complexes formed were polynuclear where piperazine had a chair conformation. Because the complexing properties of **1** and **2** were so different, we became interested in studying a ligand which resembles both **1** and **2**, namely *N,N'*-bis(6-(2-hydroxymethyl)pyridylmethyl)piperazine (**3**). In addition, we studied the effect of having only one hydroxyl group in a similar ligand, namely *N*-(6-(2-hydroxymethyl)pyridylmethyl)-*N'*-(2-pyridylmethyl)piperazine (**4**). In this paper we present the syntheses and structures of *N,N'*-bis(6-(2-hydroxymethyl)pyridylmethyl)piperazine, its zinc(II) nitrate and zinc(II) chloride complex and cadmium(II) nitrate complex of *N*-(6-(2-hydroxymethyl)pyridylmethyl)-*N'*-(2-pyridylmethyl)piperazine.

Experimental

General. All chemicals and solvents were reagent grade and used as received. 2-Bromomethyl-6-hydroxymethylpyridine was prepared according to a published procedure.[25] ^{1}H and ^{13}C NMR spectra were recorded on a Jeol JNM GSX 270 FT NMR spectrometer for compound **3** and on a Bruker AM250 ASPECT 3000 spectrometer for **4**. All chemical shifts are relative to the internal tetramethylsilane. Mass spectrum was run on a VG AutoSpec HRMS spectrometer for **3** and Jeol JMS-300 spectrometer for **4**. For elementary analysis a Carlo Erba 1106 CHN+O/S instrument was applied.

Syntheses.

N,N'-*bis(6-(2-hydroxymethyl)pyridylmethyl)piperazine* (**3**). Piperazine can be *N*-alkylated easily with different aromatic halomethyl compounds in the presence of a suitable base.[26] Normally, these reactions proceed nicely and the yields are high. When a mixture of piperazine with 2 equiv. of 2-bromomethyl-6-hydroxymethylpyridine is refluxed for 4 h in a acetonitrile solution and potassium carbonate is used as a base, the formation of **3** is quantitative. A solution of 2-bromomethyl-6-hydroxymethylpyridine (5.3 mmol) in CH_3CN (30 ml) was slowly added into a stirred mixture of piperazine (2.67 mmol) and K_2CO_3 (2 g) in CH_3CN (30 ml) at room temperature. The mixture was refluxed for 4 h and the inorganic residue was filtered off. Evaporation of the solvent gave 0.88 g (99.5%) of a white solid, m.p. 156–158 °C. ^{1}H NMR ($CDCl_3$): δ 2.59 [bs,8 H, N(CH_2CH_2)N], 3.70 (s, 4 H, NCH_2Ar), 4.71 (s, 4 H, CH_2OH), 7.09 (d, 2 H, H_{Ar}), 7.32 (d, 2 H, H_{Ar}), 7.63 (t, 2 H, H_{Ar}) ppm. ^{13}C NMR ($CDCl_3$): δ 53.8, 64.6, 64.8, 119.4, 122.4, 137.8, 158.0, 158.9 ppm. HRMS *m/z* (M^+, $C_{18}H_{24}N_4O_2$) calcd. 328.1877, obsd. 328.1883. Anal. Calcd. for $C_{18}H_{24}N_4O_2$: C, 65.83; H, 7.37; N, 17.06. Found: C, 65.20; H, 7.40; N, 17.06. Single crystals for X-ray crystallography were obtained when the refluxed mixture was allowed to cool to room temperature. The synthesis of compound **3** is presented in Scheme 1.



Scheme 1. Synthesis of compound **3**.

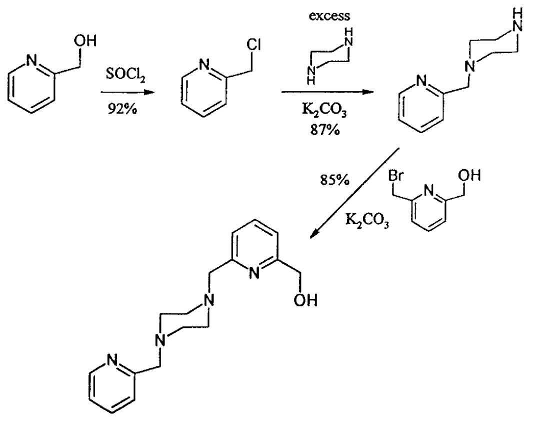
N,N'- *bis(6-(2-hydroxymethyl)pyridylmethyl)piperazine zinc(II) nitrate complex* (**3a**). A solution of *N,N'*-bis(6-(2-hydroxymethyl)pyridylmethyl)piperazine (20 mg) in CH_3CN (3 ml) was mixed with $Zn(NO_3)_2 \cdot 6H_2O$ (36.2 mg) in CH_3CN (5 ml) to achieve a solution with an approximate molar ratio of 1:2. By a slow evaporation of the solvent, single crystals were obtained.

Dichloro -N,N' *-bis(6-(2-hydroxymethyl)pyridylmethyl)-piperazine zinc(II)* (**3b**). The synthesis of **3b** was similar to **3a**. *N,N'*-Bis(6-(2-hydroxymethyl)pyridylmethyl)-piperazine (20 mg) was dissolved in CH_3CN (3 ml), and a solution of $ZnCl_2$ (16.6 mg) in CH_3CN (5 ml) was then added. Single crystals were obtained by a slow evaporation of this solution.

2-(Chloromethyl)pyridine. Thionyl chloride (40 ml) was stirred and cooled in an ice bath, and 2-(hydroxymethyl)pyridine (45.8 mmol) was added in portions over 1 h. The resulting solution was heated at reflux for 4 h, thionyl chloride was distilled, and the residue was washed with light petroleum ether (b.p. 40–60 °C). The crude 2-(chloromethyl)pyridine hydrochloride was dissolved in 50 ml of water and neutralised with an aqueous $NaHCO_3$ solution. The extraction of the aqueous phase with CH_2Cl_2 (4×40 ml), followed by drying with Na_2SO_4 and evaporation, resulted in a reddish oil. Yield 5.4 g (92%). ^{1}H NMR ($CDCl_3$): δ 4.64 (s, 2 H, CH_2Cl), 7.21 (m, 1 H, H_{Ar}), 7.44 (d, 1 H, H_{Ar}), 7.66 (m, 1 H, H_{Ar}), 8.55 (d, 1 H, H_{Ar}) ppm. ^{13}C NMR ($CDCl_3$): δ 46.7, 122.8, 123.0, 137.1, 149.4, 156.6 ppm. MS (EI): 127 (M^+).

N-*(2-Pyridylmethyl)piperazine.* A solution of 2-(Chloromethyl)pyridine (16.2 mmol) in CH_3CN (30 ml) was added into a stirred mixture of piperazine (81.3 mmol) and K_2CO_3 (2 g) in CH_3CN (100 ml). The resulting mixture was refluxed for 4 h and the inorganic residue was filtered off. Evaporation of the solvent, followed by sublimation of the free piperazine in vacuum, resulted in *N*-(2-pyridylmethyl)piperazine as a thick reddish oil. Yield 2.5 g (87%). ^{1}H NMR ($CDCl_3$): δ 1.71 (s, 1 H, NH), 2.41 (bs, 4 H, NCH_2CH_2NH), 2.85 (t, 4 H, NCH_2CH_2NH), 3.58 (s, 2 H, NCH_2Ar), 7.10 (m, 1 H, H_{Ar}), 7.35 (d, 1 H, H_{Ar}), 7.58 (m, 1 H, H_{Ar}), 8.49 (d, 1 H, H_{Ar}) ppm. ^{13}C NMR ($CDCl_3$): δ 46.6, 55.2, 65.9, 122.7, 123.9, 137.0, 149.9, 159.1 ppm. MS (EI): 177 (M^+).

N-*(6-(2-hydroxymethyl)pyridylmethyl)*-N′-*(2-pyridylmethyl)piperazine* (**4**). A solution of 2-bromomethyl-6-hydroxymethylpyridine (4.2 mmol) in CH_3CN (25 ml) was slowly added into a stirred mixture of *N*-(2-pyridylmethyl)piperazine (4.2 mmol) and K_2CO_3 (2 g) in CH_3CN (25 ml) at room temperature. The mixture was refluxed for 4 h and the inorganic residue was filtered off. The solvent was evaporated and the residue was dissolved in a hot petroleum ether (b.p. 60–95 °C) and filtered. Evaporation of the ether resulted in 1.0 g (85%) of **4** as a thick reddish oil. ^1H NMR ($CDCl_3$): δ 2.53 (s, 8 H, N[CH_2CH_2]$_2$N], 3.62 (s 2 H, NCH_2Ar), 3.64 (s, 2 H, NCH_2Ar), 4.69 (s, 2 H, CH_2OH), 7.12 (m, 2 H, H_{Ar}), 7.28 (d, 1 H, H_{Ar}), 7.35 (d, 1 H, H_{Ar}), 7.60 (m, 2 H, H_{Ar}), 8.49 (d, 1 H, H_{Ar}) ppm. ^{13}C NMR ($CDCl_3$): δ 53.8, 53.9, 64.6, 64.9, 65.2, 119.3, 122.3, 122.7, 123.9, 137.0, 137.7, 149.9, 158.1, 159.0, 159.1 ppm. MS (EI): 298 (M^+). The synthesis of **4** is presented in Scheme 2.



Scheme 2. Synthesis of compound **4**.

N-*(6-(2-hydroxymethyl)pyridylmethyl)*-N′-*(2-pyridylmethyl)piperazine cadmium(II) nitrate* (**4a**). *N*-(6-(2-hydroxymethyl)pyridylmethyl)-*N′*-(2-pyridylmethyl)-piperazine (12.2 mg) was dissolved in CH_3CN (5 ml). A solution of $Cd(NO_3)_2 \cdot 4H_2O$ (12.4 mg) in CH_3CN (5 ml) was slowly added into this solution. The mixture was placed in a sealed test-tube, and then left to stand at room temperature. Single crystals for X-ray analysis were obtained in one night.

Crystal structure determinations and refinements. Single-crystal X-ray data sets were collected with an Enraf Nonius CAD4 (**3**, **3a** and **3b**) and Syntex $P2_1$ (**4a**) single-crystal diffractometers. Crystals were mounted on top of glass fibres, and the data were collected at room temperature, using graphite monochromatised Cu K_α radiation (λ = 1.541 78 Å) and ω/2θ and ω scan modes. Crystal parameters and refinement results are presented in Table 1. Unit-cell dimensions and the orientation matrix were obtained from least-squares fitting of 25 (**3**, **3a** and **3b**) and 34 (**4a**) centered reflections. During data collection, an intensity check was made every 60 min with two reflections. No significant decomposition of the crystal occurred during the data collections. The data obtained were corrected for Lorentz and polarization effects. An empirical absorption correction (Ψ-scan) was applied to the data of **3**, **3a** and **3b** (T_{max}/T_{min} for compounds **3**, **3a** and **3b** are 99.88/94.25%, 99.89/90.31% and 99.87/74.73%, respectively). The absorption correction was not applied to the data of **4a** even though it would have been necessary. Scattering factors were taken from Ref. 27. The structures were solved by direct methods using the SHELXS-86 program[28] and refined by full-matrix least-squares methods on F_o^2 using SHELXL-93.[29] All non-disordered non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the hydroxyl groups in **3a** and **3b** and hydrogens of the water molecule in **3a** were located from the electron density map. Other hydrogen atoms were calculated in their idealized positions (C–H distance 0.93 Å for aromatic CH and 0.97 Å for CH_2). All hydrogen atoms were refined as riding atoms with $U = 1.2U(C)$ and $U = 1.5U(O)$. Geometrical restraints were necessary for the nitrate groups in compound **3a** and **4a**. In compound **3a**, there were also restraints to fix hydrogen–oxygen bond lengths in hydroxyl groups and the water molecule. For compound **3b**, geometrical restraints were used to prevent anomalous bond distances between oxygen and hydrogen in hydroxyl groups. The refinements converged to $R = 0.0471$ (compound **3**), $R = 0.0497$ (compound **3a**), $R = 0.0465$ (compound **3b**) and $R = 0.0788$ (compound **4a**). The fractional coordinates and the U_{eq}-values are listed in Table 2, bond lengths and angles in Table 3. Tables of anisotropic thermal parameters, coordinates of hydrogen atoms and a listing of observed and calculated structure factors are available from the authors upon request. All plots were generated with the program DIAMOND.[30]

Results and discussion

Structure of N,N′*-bis(6-(2-hydroxymethyl)pyridylmethyl)piperazine.* The molecular structure of **3** is displayed in Fig. 1. Compound **3** is a linear molecule which lies on a crystallographic symmetry element (centrosymmetry) in the middle of the piperazine moiety. The piperazine ring is in the energetically favoured chair conformation. The observed bond lengths and angles are consistent with published reports.[31,32] The pyridyl ring and atoms C3 and C9 are almost in the same plane. The deviations of C3 and C9 from the plane of the pyridyl ring are −0.005(3) and −0.031(3) Å, respectively. The torsion angles of N2–C8–C9–O1 and C8–C9–O1–H1 are 163.0(2) and −146.3(2.3)°. The distance for O1 from the plane of the pyridyl ring is 0.359(3) Å. The packing of **3** is presented in Fig. 2. The interactions between molecules are weak van der Waals forces.

Structure of the N,N′*-bis(6-(2-hydroxymethyl)pyridylmethyl)piperazine zinc(II) nitrate complex.* The basic unit

Table 1. Crystallographic data for **3**, **3a**, **3b** and **4a**.

Compound	**3**	**3a**	**3b**	**4a**
Chemical formula	$C_{18}H_{24}N_4O_2$	$C_{18}H_{29}N_7O_{14}Zn_2$	$C_{20}H_{27}N_5O_2Zn_2Cl_4$	$C_{17}H_{22}N_6O_7Cd$
Formula weight	328.41	698.22	642.01	534.81
Colour	Colourless	Colourless	Colourless	Colourless
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$ (No. 14)	$P2/n$ (No. 13)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a/Å	7.816(1)	10.274(1)	9.624(1)	13.589(8)
b/Å	6.699(1)	11.018(1)	11.381(1)	9.006(5)
c/Å	16.567(3)	11.615(1)	14.016(1)	17.472(8)
α/°	90	90	106.21(1)	90
β/°	91.94(1)	93.13(1)	102.73(1)	101.96(4)
γ/°	90	90	107.10(1)	90
V/Å^3	866.9(2)	1312.8(2)	1323.9(2)	2092(2)
Z	2	2	2	4
D_{calc}/Mg m^{-3}	1.258	1.766	1.611	1.698
$F(000)$	352	716	652	1080
λ(Cu K_α)/Å	1.54178	1.54178	1.54178	1.54178
μ(Cu K_α)/mm^{-1}	0.677	2.999	6.168	8.836
Crystal size/mm	0.1, 0.15, 0.15	0.1, 0.1, 0.20	0.1, 0.15, 0.2	0.15, 0.2, 0.2
Theta range for data collection/°	3–60	3–60	3–60	3–60
h_{min}, h_{max}	−8, +8	0, +11	0, +10	−14, +8
k_{min}, k_{max}	0, +7	0, +12	−12, +11	−1, +9
l_{min}, l_{max}	0, +18	−13, +13	−15, +15	−1, +19
No. of collected data	1340	1942	3909	3277
No. of unique data	1291 (R_{int}=0.0786)	1942	3909	2668 (R_{int}=0.0322)
No. of used data	1289	1941	3907	2668
No. of data with $I>2\sigma(I)$	1224	1769	2968	1679
R, wR^2 [$I>2\sigma(I)$]	0.0471, 0.1280	0.0497, 0.1268	0.0465, 0.1285	0.0788, 0.1793
R, wR^2 (all data)	0.0490, 0.1333	0.0540, 0.1326	0.0700, 0.1465	0.1279, 0.2090
S	1.099	1.053	1.025	1.079
No. of refined parameters	111	183	305	247
No. of restraints	—	35	2	25
Largest Cd1F^2 peak/e Å^{-3}	0.245	1.188	0.691	0.973
Convergence	<0.001	<0.001	<0.001	<0.001
Weighting (a/b)^a	0.0766/0.2379	0.0651/4.4830	0.0990/1.0749	0.0832/14.4744

^{a}Weighting scheme: $w=1/[\sigma^2(F_o^2)+(aP)^2+bP]$; $P=[\mathrm{Max}(F_o^2, 0)+2F_c^2]/3$.

of the polymeric $Zn_2(C_{18}H_{24}N_4O_2)(H_2O)_2(OH)(NO_3)_3$ complex molecule is presented in Fig. 3. The basic molecular structure is a dinuclear $Zn_2L(H_2O)_2(OH)$ unit with a centre of inversion, and the piperazine ring is in a chair conformation. The units are linked via a hydroxyl group which is placed on a two-fold axis, forming a zigzag chain along the a-axis. Similar hydroxyl bridges between zinc atoms have been widely identified.[33–35] The electrical charge is balanced by three nitrate groups per basic molecule. One of the nitrate groups lies on a two-fold axis; N4 and O41 are in special positions and O42* (unlabelled in Fig. 3) is symmetrically generated by O42. Both nitrate groups of an asymmetric unit are disordered. In figures, only the molecules with larger occupation factors (0.61 for N3, O31, O32 and O33 and 0.75 for N4, O41, O42 and O42*) are drawn. In tables, atoms with smaller occupation factors are marked with a prime. The crystalline water (O11, H111 and H112), together with nitrate groups, assists in joining polymerized chains together in the c-direction. Hydrogen bonds between molecules in the ac-plane are presented in Fig. 4. A full list of hydrogen bond lengths (from the program DIAMOND) is in Table 4. Along the b-axis the intermolecular contacts are weak van der Waals forces between pyridyl rings. Metal–ligand distances range from 1.925(2) Å (Zn1···O12) to 2.238(4) Å (Zn1···N1). The bond lengths coincide with published reports.[36,37] The zinc atom has a distorted square-pyramidal five coordination with N1, N2, O1 and O11 in the basal plane, and O12 occupies the apical position. The zinc atom is displaced 0.548(2) Å from the basal plane of the pyramid. The Zn–Zn distance is 3.5 Å and indicates absence of any appreciable metal–metal bonding. Despite the complex structure, the pyridyl ring, C3 and C9 lie almost in the same plane. C3 and C9 lie −0.107(8) and −0.002(8) Å of the plane of the pyridyl ring, respectively. The torsion angle is −10.1(1)° to N2–C8–C9–O1 and 172.6(5.7)° to C8–C9–O1–H11.

*Structure of dichloro-*N,N′*-bis(6-(2-hydroxymethyl)-pyridylmethyl)piperazine zinc(II).* The molecular structure of $Zn_2(C_{18}H_{24}N_4O_2)Cl_4\cdot CH_3CN$ (**3b**) is presented in Fig. 5. Like **3**, **3b** is also linear, and the piperazine ring is in the chair conformation. The asymmetric unit consists of two independent halves of molecules, A and B, in a slightly different orientation, and an acetonitrile

Table 2. Fractional coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($Å^2 \times 10^3$) with e.s.d.s in parentheses.

Atom[a]	x	y	z	U_{eq}[b]
Compound **3**				
O1	7631(2)	6801(2)	4020(1)	68(1)
N1	653(2)	1699(2)	4564(1)	40(1)
N2	3381(2)	4754(2)	3910(1)	42(1)
C1	−1134(2)	1581(3)	4803(1)	44(1)
C2	1300(2)	−344(3)	4444(1)	45(1)
C3	734(2)	2877(3)	3815(1)	47(1)
C4	2533(2)	3233(2)	3549(1)	42(1)
C5	3252(2)	2076(3)	2961(1)	52(1)
C6	4898(3)	2466(3)	2734(1)	56(1)
C7	5782(2)	4015(3)	3104(1)	50(1)
C8	4985(2)	5120(3)	3687(1)	42(1)
C9	5845(2)	6865(3)	4105(1)	54(1)
Compound **3a**				
Zn1	890(1)	1495(1)	2897(1)	34(1)
N1	873(3)	1014(3)	4769(3)	29(1)
N2	1153(4)	3153(3)	3627(3)	32(1)
O1	570(4)	2862(4)	1490(3)	58(1)
C1	1363(4)	−221(4)	5077(4)	33(1)
C2	401(4)	−1179(4)	4699(4)	34(1)
C3	1818(5)	1918(4)	5258(4)	37(1)
C4	1586(4)	3150(4)	4748(4)	34(1)
C5	1848(5)	4221(5)	5317(5)	44(1)
C6	1694(5)	5301(5)	4736(5)	49(1)
C7	1256(5)	5297(4)	3592(5)	46(1)
C8	984(4)	4197(4)	3061(4)	36(1)
C9	512(5)	4094(5)	1823(5)	42(1)
O11	−546(4)	527(3)	2117(3)	43(1)
O12	2500	749(4)	2500	40(1)
N3	741(8)	−2009(6)	1113(6)	41(2)
O31	383(7)	−1150(7)	548(7)	57(2)
O32	321(8)	−3109(7)	779(7)	68(2)
O33	1446(9)	−1832(8)	1995(8)	90(2)
N3′	143(13)	−2221(10)	1169(9)	41(2)
O31′	−10(13)	−1213(10)	663(11)	57(2)
O32′	848(13)	−3019(11)	648(11)	68(2)
O33′	−157(14)	−2303(12)	2141(11)	90(2)
N4	−2500	2869(5)	2500	41(1)
O41	−2500	3976(6)	2500	64(2)
O42	−2465(6)	2286(5)	1577(4)	54(1)
O42′	−3255(18)	2419(15)	1719(13)	54(1)
Compound **3b**				
Zn1A	2769(1)	8017(1)	5137(1)	49(1)
Zn1B	576(1)	7867(1)	13(1)	39(1)
Cl1A	4609(2)	7293(2)	5681(1)	73(1)
Cl2A	2343(2)	7820(1)	3434(1)	58(1)
Cl1B	−1554(2)	7487(2)	454(1)	64(1)
Cl2B	63(1)	7810(1)	−1681(1)	49(1)
N1A	681(5)	6352(4)	5003(3)	47(1)
N2A	1527(5)	9031(5)	5763(3)	51(1)
N1B	1119(4)	6043(4)	−184(3)	35(1)
N2B	2968(4)	8678(4)	599(3)	37(1)
O1A	4376(6)	10141(5)	5994(4)	90(2)
O1B	1366(5)	10042(4)	1025(4)	77(1)
C1A	324(7)	5153(5)	4083(4)	54(1)
C2A	969(6)	6061(5)	5977(4)	51(1)
C3A	−543(6)	6882(6)	4874(5)	58(2)
C4A	52(7)	8298(6)	5607(5)	55(1)
C5A	−831(8)	8882(7)	6068(5)	68(2)
C6A	−180(10)	10216(8)	6681(5)	78(2)
C7A	1311(9)	10946(7)	6801(5)	71(2)
C8A	2147(7)	10329(6)	6330(4)	55(1)
C9A	3772(8)	11073(6)	6419(5)	73(2)
C1B	1478(6)	5745(5)	789(4)	40(1)
C2B	−46(6)	4813(5)	−1062(4)	39(1)
C3B	2556(6)	6444(5)	−456(4)	44(1)
C4B	3633(5)	7818(5)	271(4)	41(1)
C5B	5227(6)	8265(7)	568(5)	57(2)
C6B	6120(6)	9588(7)	1177(5)	62(2)
C7B	5425(6)	10429(6)	1488(5)	58(2)
C8B	3812(6)	9946(5)	1184(4)	45(1)
C9B	2948(6)	10812(5)	1472(5)	56(1)
C11	6076(9)	15200(9)	7061(8)	104(3)
C10	4735(11)	14980(10)	7358(7)	103(3)
N3	3638(12)	14783(14)	7551(8)	187(6)
Compound **4a**				
Cd1	2471(1)	1287(1)	1400(1)	76(1)
N1	2438(7)	−1261(11)	1900(6)	52(2)
N2	3114(7)	1335(12)	2725(5)	52(2)
C1	1490(9)	−1923(16)	1474(8)	62(4)
C2	3285(10)	−1907(17)	1608(8)	66(4)
C3	2588(10)	−1266(16)	2747(7)	67(4)
C4	3128(9)	63(16)	3142(7)	55(3)
C5	3581(11)	31(18)	3926(8)	71(4)
C6	3995(12)	1312(20)	4284(8)	81(4)
C7	4017(10)	2590(17)	3861(8)	66(4)
C8	3557(11)	2556(16)	3074(8)	65(4)
C9	3397(14)	3962(20)	2608(9)	100(5)
O1	3092(13)	3755(13)	1770(7)	139(5)
N1A	2258(7)	−775(12)	457(6)	59(3)
N2A	1825(8)	2237(15)	176(6)	65(3)
C1A	1315(10)	−1450(15)	613(8)	63(4)
C2A	3073(10)	−1827(17)	718(8)	68(4)
C3A	2165(11)	−189(19)	−341(7)	74(4)
C4A	1728(10)	1350(18)	−443(7)	63(4)
C5A	1251(11)	1840(21)	−1188(8)	75(5)
C6A	949(12)	3292(21)	−1278(9)	81(5)
C7A	1060(12)	4187(21)	−652(9)	89(5)
C8A	1522(12)	3631(20)	67(8)	83(5)
N3	4877(9)	1686(13)	1153(7)	80(4)
O31	4016(12)	1454(26)	839(11)	96(5)
O32	5037(16)	2475(31)	1755(13)	143(8)
O31′	4259(17)	695(25)	1147(16)	96(5)
O32′	4632(23)	2979(23)	1241(24)	143(8)
O33	5599(8)	1448(11)	864(6)	92(3)
N4	377(12)	2442(17)	1695(8)	93(4)
O41	656(10)	1196(16)	1558(7)	120(4)
O42	939(11)	3460(18)	1807(9)	138(5)
O43	−521(11)	2552(15)	1739(8)	129(4)

[a] Disordered atoms are marked with a prime. [b] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

solvent molecule. The torsion angle, N2–C8–C9–O1, is −9.3(8)° for molecule A and −174.7(6.2)° for molecule B. As in compounds **3** and **3a**, C3 and C9 lie close to the plane of the pyridyl ring in both molecules. A zinc atom has a distorted square-pyramidal five-coordination with Cl2 in the apical position and N1, N2, O1 and Cl1 in the basal plane. Similar coordination of zinc has been published and bond lengths coincide with those publications.[38] The packing of **3b** is presented in Fig. 6.

Table 3. Selected bond distances and angles (in Å, °) with e.s.d.s. in parentheses.[a]

Compound **3**

C9–O1	1.408(2)	C1–C2[1]	1.507(2)
C9–C8	1.505(2)	C3–C4	1.506(2)
N1–C1	1.467(2)	C4–C5	1.379(3)
N1–C3	1,474(2)	C5–C6	1.378(3)
N1–C2	1.475(2)	C6–C7	1.379(3)
N2–C8	1.342(2)	C7–C8	1.382(3)
N2–C4	1.344(2)		
O1–C9–C8	111.1(2)	N2–C4–C5	122.2(2)
C1–N1–C3	108.95(12)	N2–C4–C3	116.2(2)
C1–N1–C2	108.69(12)	C5–C4–C3	121.6(2)
C3–N1–C2	111.00(13)	C6–C5–C4	119.5(2)
C8–N2–C4	117.91(14)	C5–C6–C7	118.7(2)
N1–C1–C2[1]	111.28(13)	C6–C7–C8	118.9(2)
N1–C2–C1[1]	111.05(13)	N2–C8–C7	122.8(2)
N1–C3–C4	113.47(13)	N2–C8–C9	115.0(2)
		C7–C8–C9	122.2(2)

Symmetry transformations used to generate equivalent atoms: [1] $-x, -y, -z+1$

Compound **3a**

Zn1–O12	1.925(2)	N2–C8	1.332(6)
Zn1–O11	1.997(3)	N2–C4	1.352(6)
Zn1–N2	2.026(4)	C1–C2	1.496(7)
Zn1–O1	2.234(4)	C3–C4	1.496(7)
Zn1–N1	2.238(4)	C4–C5	1.372(7)
O1–C9	1.413(7)	C5–C6	1.372(8)
N1–C3	1.482(6)	C6–C7	1.380(8)
N1–C1	1.488(6)	C7–C8	1.381(7)
N1–C2[1]	1.489(6)	C8–C9	1.497(7)
N3–O31	1.197(9)	N4–O41	1.219(9)
N3–O33	1.238(10)	N4–O42	1.253(6)
N3–O32	1.337(10)	N4–O42[3]	1.253(6)
N3′–O33′	1.191(13)	N4–O42′	1.26(2)
N3′–O31′	1.262(13)	N4–O42′[3]	1.26(2)
N3′–O32′	1.308(13)		
O12–Zn1–O11	106.67(14)	O1–Zn1–N1	149.5(2)
O12–Zn1–N2	112.9(2)	C3–N1–Zn1	100.0(3)
O11–Zn1–N2	138.5(2)	C1–N1–Zn1	115.4(3)
O12–Zn1–O1	101.9(2)	C2[1]–N1–Zn1	115.3(3)
O11–Zn1–O1	87.3(2)	C8–N2–Zn1	124.2(3)
N2–Zn1–O1	73.1(2)	C4–N2–Zn1	115.5(3)
O12–Zn1–N1	100.62(11)	C9–O1–Zn1	117.0(3)
O11–Zn1–N1	105.65(14)	Zn1[2]–O12–Zn1	129.5(3)
N2–Zn1–N1	79.34(14)		
C3–N1–C1	108.4(3)	C5–C4–C3	124.6(4)
C3–N1–C2[1]	109.3(4)	C4–C5–C6	119.6(5)
C1–N1–C2[1]	107.8(3)	C5–C6–C7	119.6(5)
C8–N2–C4	120.3(4)	C6–C7–C8	118.7(5)
N1–C1–C2	111.4(4)	N2–C8–C7	121.3(5)
N1[1]–C2–C1	112.0(4)	N2–C8–C9	115.8(4)
N1–C3–C4	111.8(4)	C7–C8–C9	122.9(5)
N2–C4–C5	120.5(5)	O1–C9–C8	108.6(4)
N2–C4–C3	114.9(4)		
O31–N3–O33	118.5(8)	O41–N4–O42	120.9(3)
O31–N3–O32	118.3(8)	O41–N4–O42[3]	120.9(3)
O33–N3–O32	123.2(8)	O42–N4–O42[3]	118.3(7)
O33′–N3–O31′	118.4(12)	O41–N4–O42′	113.1(8)
O33′–N3′–O32′	124.5(12)	O41–N4–O42′[3]	113.1(8)
O31′–N3′–O32′	115.7(11)	O42′–N4–O42′[3]	134(2)

Symmetry transformations used to generate equivalent atoms: [1] $-x, -y, -z+1$; [2] $-x+1/2, y, -z+1/2$; [3] $-x-1/2, y, -z+1/2$

Table 3. (*Continued.*)

Compound **3b**

Zn1A–N2A	2.066(5)	Zn1B–N2B	2.069(4)
Zn1A–O1A	2.228(4)	Zn1B–Cl1B	2.226(14)
Zn1A–N1A	2.232(4)	Zn1B–N1B	2.250(4)
Zn1A–C11A	2.245(2)	Zn1B–O1B	2.267(4)
Zn1A–C12A	2.264(2)	Zn1B–Cl2B	2.2941(14)
O1A–C9A	1.412(8)	O1B–C9B	1.393(7)
N1A–C1A	1.477(6)	N1B–C2B	1.485(6)
N1A–C3A	1.477(7)	N1B–C3B	1.487(6)
N1A–C2A	1.482(7)	N1B–C1B	1.489(6)
N2A–C8A	1.330(7)	N2B–C8B	1.322(6)
N2A–C4A	1.341(7)	N2B–C4B	1.356(6)
C1A–C2A′	1.519(7)	C1B–C2B[2]	1.512(6)
C3A–C4A	1.495(8)	C3B–C4B	1.489(7)
C4A–C5A	1.388(8)	C4B–C5B	1.382(7)
C5A–C6A	1.376(10)	C5B–C6B	1.381(9)
C6A–C7A	1.367(10)	C6B–C7B	1.356(9)
C7A–C8A	1.377(8)	C7B–C9B	1.397(7)
C8A–C9A	1.493(9)		
N2A–Zn1A–O1A	72.7(2)	N2B–Zn1B–Cl1B	144.35(12)
N2A–Zn1A–N1A	78.4(2)	N2B–Zn1B–N1B	78.11(14)
O1A–Zn1A–N1A	147.4(2)	Cl1B–Zn1B–N1B	106.77(10)
N2A–Zn1A–Cl1A	139.06(14)	N2B–Zn1B–O1B	71.8(2)
O1A–Zn1A–Cl1A	92.5(2)	Cl1B–Zn1B–O1B	88.06(12)
N1A–Zn1A–Cl1A	99.81(13)	N1B–Zn1B–O1B	144.5(2)
N2A–Zn1A–Cl2A	109.07(13)	N2B–Zn1B–Cl2B	102.68(11)
O1A–Zn1A–Cl2A	101.8(2)	Cl1B–Zn1B–Cl2B	110.83(6)
N1A–Zn1A–Cl2A	101.69(11)	N1B–Zn1B–Cl2B	100.1(10)
C1A–Zn1A–Cl2A	111.28(6)	O1B–Zn1B–Cl2B	104.4(2)
C1A–N1A–C3A	111.9(4)	C2B–N1B–C3B	108.1(4)
C1A–N1A–C2A	109.7(4)	C2B–N1B–C1B	108.8(3)
C3A–N1A–C2A	112.1(4)	C3B–N1B–C1B	108.4(4)
C1A–N1A–Zn1A	110.4(3)	C2B–N1B–Zn1B	115.3(3)
C3A–N1A–Zn1A	103.3(3)	C3B–N1B–Zn1B	100.8(3)
C2A–N1A–Zn1A	109.3(3)	C1B–N1B–Zn1B	114.8(3)
C8A–N2A–C4A	120.7(5)	C8B–N2B–C4B	121.3(4)
C8A–N2A–Zn1A	122.9(4)	C8B–N2B–Zn1B	124.1(3)
C4A–N2A–Zn1A	116.3(4)	C4B–N2B–Zn1B	114.4(3)
C9A–O1A–Zn1A	118.5(4)	C9B–O1B–Zn1B	118.5(3)
N1A–C1A–C2A[1]	112.9(4)	N1B–C1B–C2B[2]	112.1(4)
N1A–C2A–C1A[1]	113.2(4)	N1B–C2B–C1B[2]	111.2(4)
N1A–C3A–C4A	110.7(5)	N1B–C3B–C4B	110.4(4)
N2A–C4A–C5A	120.1(6)	N2B–C4B–C5B	119.6(5)
N2A–C4A–C3A	115.2(5)	N2B–C4B–C3B	116.2(4)
C5A–C4A–C3A	124.6(6)	C5B–C4B–C3B	124.1(5)
C6A–C5A–C4A	119.3(6)	C6B–C5B–C4B	119.5(5)
C7A–C6A–C5A	119.6(6)	C7B–C6B–C5B	119.6(5)
C6A–C7A–C8A	119.6(6)	C6B–C7B–C8B	119.5(5)
N2A–C8A–C7A	120.9(6)	N2B–C8B–C7B	120.4(5)
N2A–C8A–C9A	116.9(5)	N2B–C8B–C9B	116.4(4)
C7A–C8A–C9A	122.2(6)	C7B–C8B–C9B	123.0(5)
O1A–C9A–C8A	108.2(5)	O1B–C9B–C8B	108.9(4)
C10–N3	1.119(12)		
C11–C10	1.415(12)		
N3–C10–C11	177.2(11)		

Symmetry transformations used to generate equivalent atoms: [1] $-x, -y+1, -z+1$; [2] $-x, -y+1, -z$

Table 3. (*Continued*.)

Compound **4a**			
Cd1-N2	2.300(9)	N1A-C2A	1.46(2)
Cd1-N2A	2.302(11)	N1A-C3A	1.47(2)
Cd1-O1	2.417(13)	N1A-C1A	1.49(2)
Cd1-N1	2.459(10)	N2A-C8A	1.32(2)
Cd1-N1A	2.460(11)	N2A-C4A	1.33(2)
Cd1-O31	2.50(2)	C3A-C4A	1.50(2)
Cd1-O41	2.539(13)	C4A-C5A	1.40(2)
Cd1-O31′	2.61(2)	C5A-C6A	1.37(2)
C9-O1	1.45(2)	C6A-C7A	1.34(2)
N1-C3	1.45(2)	C7A-C8A	1.38(2)
N1-C2	1.47(2)		
N1-C1	1.47(2)	N3-O31	1.20(2)
N2-C8	1.34(2)	N3-O32	1.25(2)
N2-C4	1.36(2)	N3-O33	1.212(12)
C1-C1A	1.53(2)	N3-O31′	1.22(2)
C2-C2A	1.52(2)	N3-O32′	1.23(2)
C3-C4	1.50(2)	N4-O41	1.22(2)
C4-C5	1.38(2)	N4-O42	1.18(2)
C5-C6	1.38(2)	N4-O43	1.24(2)
C6-C7	1.37(2)		
C7-C8	1.39(2)		
C8-C9	1.50(2)		
N1-Cd1-N1A	61.6(3)	N3-O31-Cd1	130.4(13)
N2-Cd1-O31	102.6(5)	N3-O31′-Cd1	121(2)
N2A-Cd1-O31	78.6(6)	N4-O41-Cd1	109.8(11)
O1-Cd1-O31	77.0(6)	C3-N1-C2	113.5(10)
N1-Cd1-O31	105.9(6)	C3-N1-C1	115.8(10)
N1A-Cd1-O31	77.0(5)	C2-N1-C1	109.3(10)
N2-Cd1-O41	93.8(4)	C3-N1-Cd1	110.9(8)
N2A-Cd1-O41	85.5(4)	C2-N1-Cd1	100.0(7)
O1-Cd1-O41	107.1(5)	C1-N1-Cd1	106.1(7)
N1-Cd1-O41	80.9(4)	C8-N2-C4	119.7(10)
N1A-Cd1-O41	93.8(4)	C8-N2-Cd1	121.0(8)
O31-Cd1-O41	163.5(5)	C4-N2-Cd1	119.0(8)
N2-Cd1-O31′	90.1(7)	N1-C1-C1A	108.9(10)
N2A-Cd1-O31′	96.2(7)	N1-C2-C2A	109.8(11)
O1-Cd1-O31′	87.0(6)	N1-C3-C4	114.8(11)
N1-Cd1-O31′	87.4(6)	N2-C4-C5	120.3(13)
N1A-Cd1-O31′	73.6(5)	N2-C4-C3	118.5(11)
O31-Cd1-O31′	19.9(6)	C5-C4-C3	121.1(13)
O41-Cd1-O31′	165.9(6)	C6-C5-C4	119.4(14)
O1-Cd1-N1A	149.2(4)	C7-C6-C5	120.7(12)
N2-Cd1-N2A	157.0(4)	C6-C7-C8	117.4(13)
N2-Cd1-O1	71.0(4)	N2-C8-C7	122.5(12)
N2A-Cd1-O1	87.2(4)	N2-C8-C9	116.5(12)
N2-Cd1-N1	72.0(4)	C7-C8-C9	120.3(13)
N2A-Cd1-N1	130.2(4)	O1-C9-C8	114.9(14)
O1-Cd1-N1	142.5(4)	C9-O1-Cd1	113.5(9)
N2-Cd1-N1A	131.0(4)	C2A-N1A-C3A	116.1(10)
N2A-Cd1-N1A	71.9(4)	C2A-N1A-C1A	107.7(11)
C8A-N2A-Cd1	122.2(9)	C3A-N1A-C1A	114.2(10)
C4A-N2A-Cd1	119.2(10)	C2A-N1A-Cd1	107.8(8)
		C3A-N1A-Cd1	109.8(9)
C1A-N1A-Cd1	99.9(7)	O31-N3-O33	125.0(13)
C8A-N2A-C4A	118.6(13)	O31-N3-O32	118(2)
N1A-C1A-C1	109.1(10)	O33-N3-O32	115.9(14)
N1A-C2A-C2	108.7(10)	O33-N3-O31′	118.7(14)
N1A-C3A-C4A	113.4(11)	O31′-N3-O32′	119(2)
N2A-C4A-C5A	121(2)	O33-N3-O32′	119(2)
N2A-C4A-C3A	119.2(12)		
C5A-C4A-C3A	119.7(14)	O42-N4-O41	122(2)
C6A-C5A-C4A	119(2)	O42-N4-O43	123(2)
C7A-C6A-C5A	120(2)	O41-N4-O43	116(2)
C6A-C7A-C8A	119(2)		
N2A-C8A-C7A	123(2)		

[a] Disordered atoms are marked with a prime.

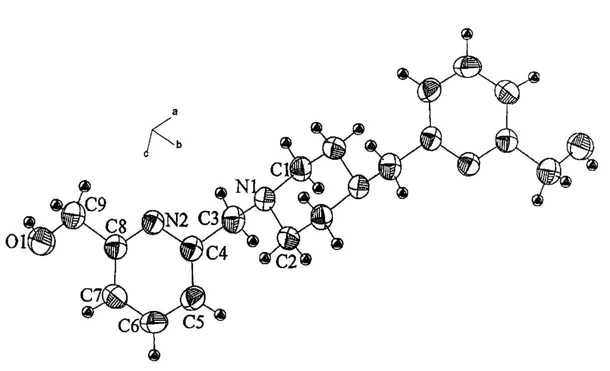


Fig. 1. The molecular structure of $C_{18}H_{24}N_4O_2$ (**3**) with the atomic numbering used. Thermal ellipsoids are plotted at the 50% probability level.

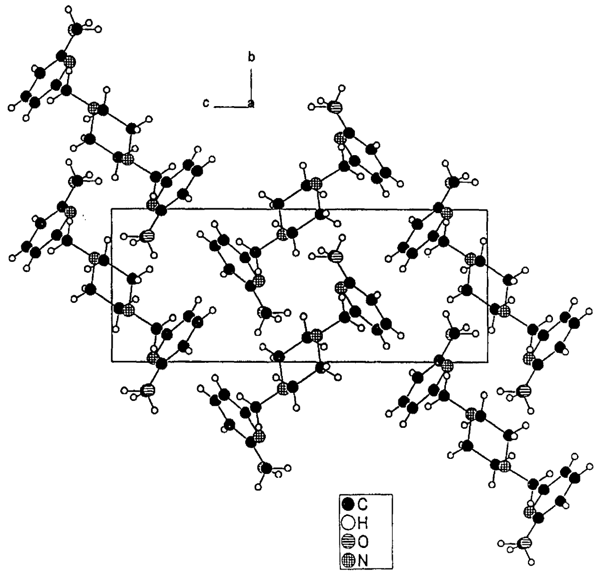


Fig. 2. The crystal packing of $C_{18}H_{24}N_4O_2$ (**3**).

Compound **3b** has an ABAB layer structure along the *c*-axis. Acetonitrile molecules stand between layers A and B. The interaction between molecules in the *bc*-plane are weak van der Waals forces between pyridyl rings. An *a*-direction hydrogen bond between Cl2 and H1 links adjacent molecules together. Hydrogen bond lengths are presented in Table 4.

Structure of N-*(6-(2-hydroxymethyl)pyridylmethyl)*-N′-*(2-pyridylmethyl)piperazine cadmium(II) nitrate* (**4a**). The unsymmetrical molecular structure of $Cd(C_{17}H_{22}N_4O)(NO_3)_2$ (**4a**) is presented in Fig. 7. The conformation of the piperazine ring is the slightly twisted boat conformation instead of the energically favorable chair conformation. The torsion angles N1–C1–C1A–N1A and N1–C2–C2A–N1A are 12.6(1.5) and 16.2(1.6)°, respectively. The cadmium atom has a distorted pentagonal bipyramidal seven-coordination. All five donor atoms of ligand **4** coordinate to Cd^{II} in an approximately planar array, while two monodentate nitrate ions occupy axial sites. The same kinds of coordinations of cadmium

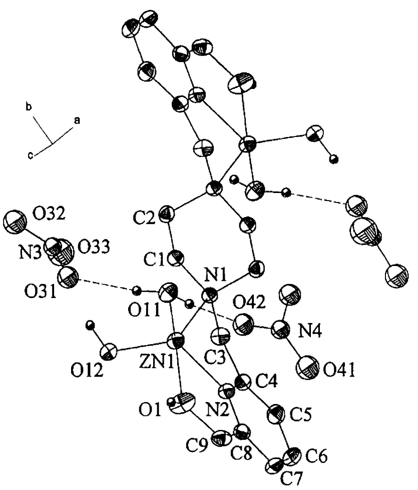


Fig. 3. The basic molecular structure and atomic numbering of the asymmetric unit of $C_{18}H_{29}N_7O_{14}Zn_2$ (**3a**) polymer. Hydrogen bonds are indicated by dashed lines. Thermal ellipsoids are plotted at the 30% probability level. Only the nitrate goup with larger occupation factor has been drawn. Hydrogen atoms bonded to carbon atoms are omitted for clarity. An oxygen atom generated with symmetry is unlabelled. The symmetry operation applied is $-x+1/2, y, -z+1/2$.

have been published but quite often the nitrate ion acts as a bidentate ligand[39–41] instead of a monodentate.[42] All bond lengths coincide with published reports.[43] Aromatic pyridine nitrogen is a better electron donor than tertiary piperazine nitrogen, and the metal–pyridine nitrogen bond distance is shorter than a metal–piperazine nitrogen bond. This also coincides with **3a** and **3b**. Cadmium–ligand distances range from 2.300(9) Å for Cd1–N2 to 2.61(9) Å for Cd1–O31′ of disordered nitrate. In figures, only the oxygens with an occupation factor of 0.57 (O31 and O32) are drawn. The coordination sphere of cadmium is presented in Fig. 8. The largest peak in the remaining electron density map exists 1.27 Å from O1. This is most probably the hydrogen atom of the hydroxyl group, but it cannot be refined sensibly. The distance from this peak to O42 is 2.11 Å, and so

Table 4. Hydrogen bonding geometry (in Å, °) for **3a** and **3b**.[a]

D–H···A	D–H	H···A	D···A	∠(D–H···A)
Compound **3a**				
O11—H111···O31	0.87	1.94	2.80	172
O11–H111···O31′	0.87	1.80	2.63	161
O11–H112···O42	0.88	1.94	2.81	172
O11–H112···O42′*	0.88	2.32	2.81	115
O12–H121···O33	0.86	2.32	3.09	149
O1–H11···O32	0.86	1.95	2.76	156
O1–H11···O32′	0.86	2.00	2.82	159
Compound **3b**				
O1–H1A···Cl2A*	0.88	2.25	3.06	153
O1B–H1B···Cl2B*	0.89	2.33	3.17	157

[a] Disordered atoms are marked with a prime and the symmetry generated atoms are marked with an asterisk. All bond lengths and angles are obtained from the program DIAMOND.

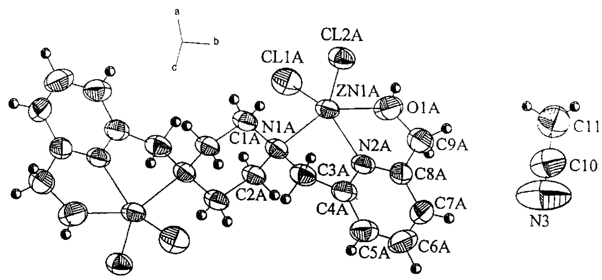


Fig. 5. The molecular structure of $C_{20}H_{27}N_5O_2Zn_2Cl_4$ (**3b**). Thermal ellipsoids are plotted at the 50% probability level. Only molecule A has been drawn.

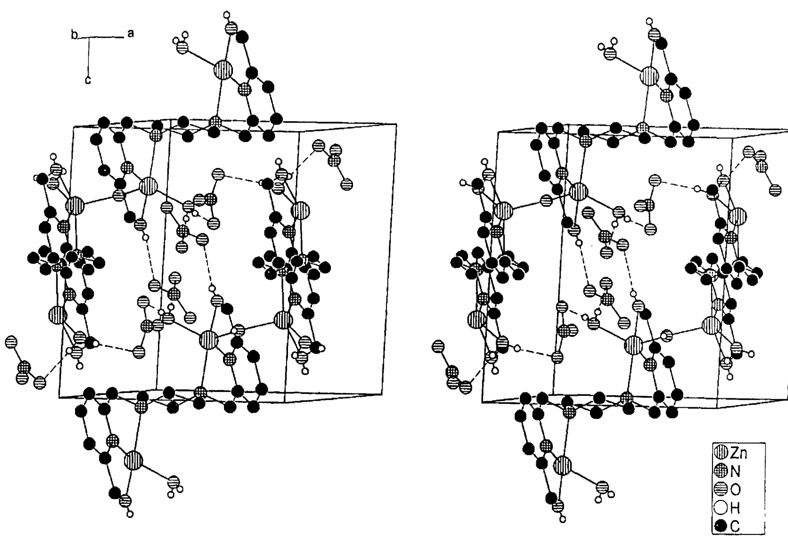


Fig. 4. Stereo plot of the layer structure of $C_{18}H_{29}N_7O_{14}Zn_2$ (**3a**) in the *ac*-plane. Hydrogen bonds are indicated by dashed lines. Only the nitrate goup with a larger occupation factor has been drawn.

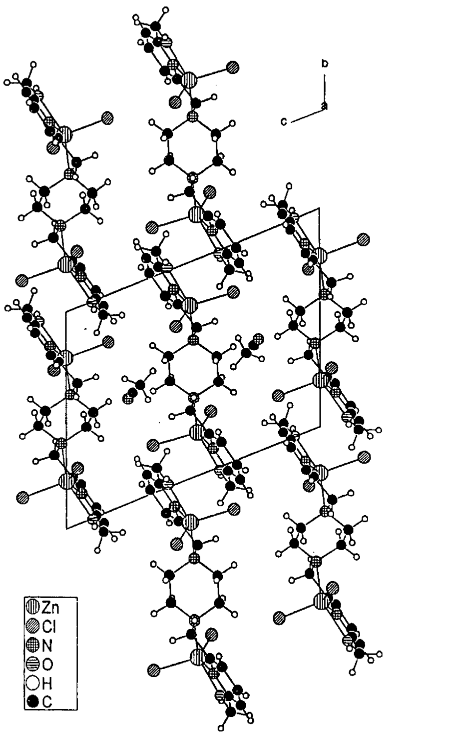


Fig. 6. The crystal packing of $C_{20}H_{27}N_5O_2Zn_2Cl_4$ (**3b**).

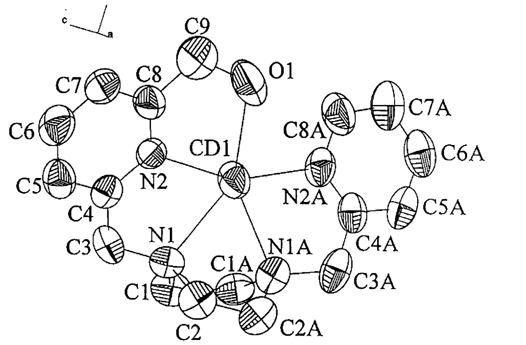


Fig. 7. The structure and atomic numbering of $C_{17}H_{22}N_6O_7Cd$ (**4a**). Thermal ellipsoids are plotted at the 50% probability level. The nitrate goups and hydrogen atoms have not been drawn for clarity.

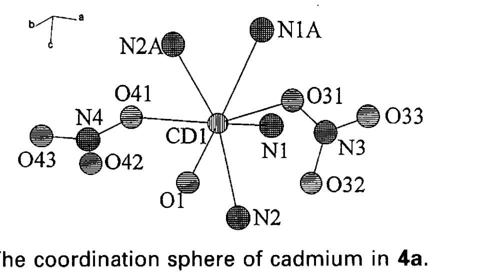


Fig. 8. The coordination sphere of cadmium in **4a**.

there is also a hydrogen bond interaction between the ligand and the nitrate group. Interactions between molecules are van der Waals forces. The packing of **4a** is presented in Fig. 9.

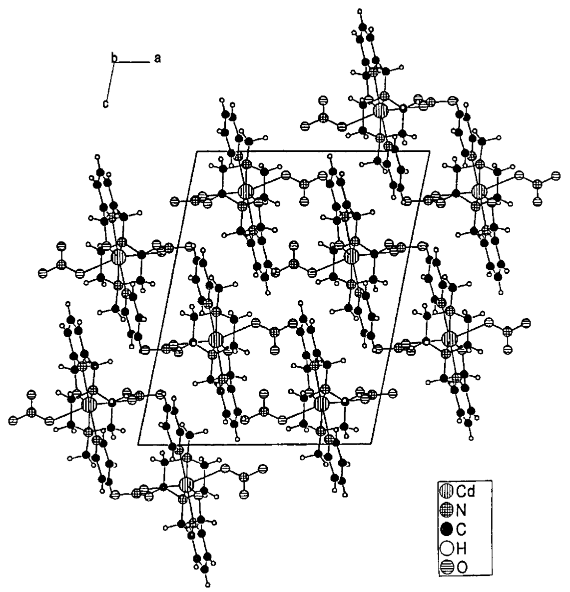


Fig. 9. The crystal packing of compound **4a**.

Conclusions

The complexing capability of *N,N′*-bis(6-(2-hydroxymethyl)pyridylmethyl)piperazine (**3**) is between that of *N,N′*-bis(2-pyridylmethyl)piperazine (**1**) and *N,N′*-bis(2-hydroxybenzyl)piperazine (**2**). In compound **3**, there is no intramolecular hydrogen bond that should be broken before complexing like in compound **2**, and for this reason the complex formation is easier. In **3**, the piperazine nitrogen is also more active, because there is no interaction between the free electron pair of the nitrogen and any other atom before complexing, as in **2**. On the other hand, in **3** there are more electron pairs to be bonded than in **1**, and the steric hindrance of hydroxymethyl groups prevents the formation of complexes where the piperazine ring is in the boat conformation. If there is only one hydroxymethyl group, as in *N*-(6-(2-hydroxymethyl)pyridylmethyl)-*N′*-(2-pyridylmethyl)-piperazine (**4**), the boat conformation is obtained.

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