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Syntheses and Crystal Structures of *N,N'*-Bis(2-hydroxybenzyl)piperazine, its Nitrate Salt and Copper(II) Acetate Complex

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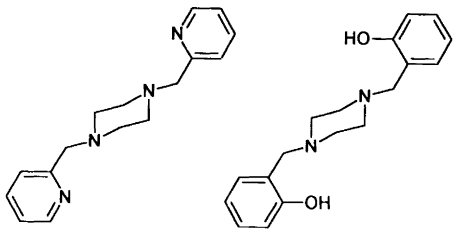
The syntheses and structures of *N,N'*-bis(2-hydroxybenzyl)piperazine ($C_{18}H_{22}N_2O_2$, **2**), its nitrate salt ($C_{18}H_{24}N_4O_8$, **2a**) and copper(II) acetate complex ($C_{22}H_{26}N_2O_6Cu_2$, **2b**) are described. Compound **2** was characterized by ^1H and ^{13}C NMR and mass spectrometry. The structures of all compounds were determined by X-ray structure analysis. Crystal data: **2**: monoclinic, space group $P2_1/c$ (No. 14), $a=6.745(6)$, $b=8.796(2)$, $c=13.407(2)$ Å, $\beta=98.99(3)°$, $V=785.7(7)$, $Z=2$; **2a**: orthorhombic, space group *Pbca* (No. 61), $a=9.773(4)$, $b=23.332(4)$, $c=8.963(1)$ Å, $V=2035.4(9)$, $Z=4$; **2b**: monoclinic, space group $P2_1/n$ (No. 14), $a=12.197(4)$, $b=7.061(3)$, $c=13.300(2)$ Å, $\beta=98.83(3)°$, $V=1131.9(7)$, $Z=2$. Compound **2b** has a polymeric structure via five-coordinated copper atoms.

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] The favoured conformation of *N,N'*-alkyl disubstituted piperazine is 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. Piperazine-containing compounds have been reported to form weak complexes with some metal ions.[10] Some of those have been characterized by X-ray diffraction.[4,6] Recently we have reported a macrocyclic piperazine ligand and its Cu^I complex showing protonated piperazine moieties in chair-conformation.[11]

Our aim was to synthesize piperazine containing ligands in which we could utilise the versatile coordination function of the piperazine moiety. Earlier a similar ligand, namely *N,N'*-bis(2-pyridylmethyl)piperazine (**1**) has been prepared by us,[12] and since it turned out to make crystalline metal complexes with various transition metals, we became interested to study the effect of substitution of the pyridine ring by a hydroxybenzyl ring (**2**).

Ligand **1** showed several coordination modes based on the size and electronic properties of the metal. Both chair- and boat-conformations were observed. The boat-conformation complexes were mononuclear, whereas the chair-conformation complexes were dinuclear or polynuclear. To our surprise the complexation properties of the 2-hydroxyl analog were very different. The similar procedure for obtaining crystalline complexes as used for **1** did not produce anything but the uncomplexed ligand itself (**2**) or its protonated forms (here the nitrate complex is presented). The dissimilarity of the two ligands must arise from the strong intramolecular hydrogen bond between the hydroxyl hydrogen and the piperazine nitrogen, which 'locks' the overall geometry of the ligand and also makes the piperazine nitrogen less active due to the interaction between the free electron pair and the H atom. Especially the transition-metal complexes of the boat form of ligand **2** would have been interesting to compare with the corresponding complexes of **1**.



1 **2**

In this paper the syntheses and structures of the *N,N'*-

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bis(2-hydroxybenzyl)piperazine, its nitrate salt and copper(II) acetate complex are described.

Experimental

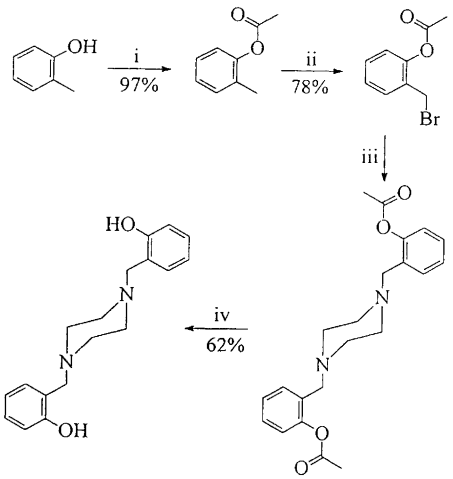
General. All chemicals and solvents were reagent grade and used as received. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AM250 ASPECT 3000 and a JEOL 270 GSX spectrometer. All chemical shifts reported are relative to the internal tetramethylsilane. Mass spectra were run on a JEOL JMS-300 spectrometer. The melting point (uncorrected) was measured with an Electrothermal IA9200 device.

Syntheses. Piperazine can be *N*-alkylated easily with aromatic halomethyl compounds in the presence of suitable base.[13] Normally these reactions proceed nicely and the yields are high. The *N*-alkylation reagent 2-bromomethylphenoxyacetate was prepared starting from *o*-cresol. The hydroxyl group of *o*-cresol was protected by acetic acid anhydride, and the aromatic methyl group was brominated by *N*-bromosuccinimide, NBS.

2-Methylphenoxyacetate. Into a mixture of *o*-cresol (90 mmol) and acetic acid anhydride (30 ml) was added 5 drops of 97% H_2SO_4 and the solution was refluxed for 1 h. The solvent was evaporated and the residue was dissolved in $CHCl_3$ (50 ml). Extraction with $NaHCO_3$ solution, followed by drying with Na_2SO_4 and evaporation, resulted in 12.8 g (92%) of yellow liquid with the following spectral properties. ^1H NMR ($CDCl_3$): δ= 2.17 (s, 3 H, $\mathbf{CH_3}$Ar), 2.31 (s, 3 H, $\mathbf{CH_3}$CO), 6.99 (d, 1 H, $\mathbf{H_{Ar}}$), 7.12–7.24 (m, 3 H, $\mathbf{H_{Ar}}$) ppm.

2-Bromomethylphenoxyacetate. 2-Methylphenoxyacetate (85.2 mmol) and NBS (85.4 mmol) was mixed with CCl_4 (120 ml). Azobisisobutyronitrile, AIBN, was added into the refluxing mixture and the reaction was additionally catalysed with light. After 2 h the reaction vessel was allowed to cool to room temperature. The precipitate was filtered off and the organic layer was extracted with $NaHCO_3$ solution and dried with Na_2SO_4. Evaporation of the solvent gave 15.3 g (78%) of yellowish oil. This 2-bromomethylphenoxyacetate was observed to be quite unstable, and due to this reason it was used without further purifications in the *N*-alkylation reaction. Assigned ^1H NMR signals ($CDCl_3$) for the product were the following: δ=2.36 (s, 3 H, $\mathbf{CH_3}$CO), 4.41 (s, 2 H, $\mathbf{CH_2}$Br), 7.11 (d, 1 H, $\mathbf{H_{Ar}}$), 7.21 (d, 1 H, $\mathbf{H_{Ar}}$), 7.32 (d, 1 H, $\mathbf{H_{Ar}}$), 7.40 (d, 1 H, $\mathbf{H_{Ar}}$) ppm.

N,N'-*Bis(2-hydroxybenzyl)piperazine* (**2**). Into a stirred mixture of piperazine (30.6 mmol) and K_2CO_3 (16 g) in CH_3CN (50 ml) was added a solution of 2-bromomethylphenoxyacetate (66.8 mmol) in CH_3CN (75 ml). The resulting mixture was refluxed for 4 h, the inorganic residue was filtered off and the solvent was evaporated. The resulting thick reddish oil was dissolved in methanol (50 ml) and refluxed for 5 h. When the acetate groups were removed by methanol via transesterification, compound **2** precipitated spontaneously out from methanol while impurities stayed in the solution. Yield 6.2 g (62%), m.p. 209–211 °C. ^1H NMR ($CDCl_3$): δ=2.10–3.20 [bd, 8 H, N ($\mathbf{CH_2CH_2}$)$_2$N], 3.71 (s, 4 H, N$\mathbf{CH_2}$Ar), 6.77 (t, 2 H, $\mathbf{H_{Ar}}$), 6.80 (d, 2 H, $\mathbf{H_{Ar}}$), 6.96 (d, 2 H, $\mathbf{H_{Ar}}$), 7.16 (t, 2 H, $\mathbf{H_{Ar}}$), 10.59 (bs, 2 H, $\mathbf{OH}$) ppm. ^{13}C NMR ($CDCl_3$): δ=53.0, 61.9, 116.8, 120.0, 121.5, 129.4, 129.7, 158.2 ppm. MS (EI): 298 (M^+). The formation of two intramolecular hydrogen bonds (confirmed by X-ray structure analysis) between phenolic hydrogens and nitrogen atoms of the piperazine moiety changed drastically the solubility of **2**. Single crystals for X-ray crystallography were obtained by recrystallation from CH_3CN. The synthesis of compound **2** is presented in Scheme 1.



Scheme 1. Synthesis of compound **2**. Reagents and conditions: (i) acetic acid anhydride, H_2SO_4, reflux; (ii) NBS, AIBN, CCl_4, reflux; (iii) piperazine, K_2CO_3, CH_3CN, reflux; (iv), CH_3OH, reflux.

N,N'-*Bis(2-hydroxybenzyl)piperazine nitrate* (**2a**). *N,N'*-Bis(2-hydroxybenzyl)piperazine (0.02 g) was dissolved in CH_3CN (3 ml), and the solution was heated. $Zn(NO_3)_2 \cdot 6H_2O$ (0.02 g) dissolved in CH_3CN (3 ml) was added to the piperazine solution to achieve approximate molar ratio 1:1. The mixture was cooled to room temperature and by slow evaporation of the solvent some single crystals were obtained.

N,N'-*Bis(2-hydroxybenzyl)piperazine copper(II) acetate* (**2b**). *N,N'*-Bis(2-hydroxybenzyl)-piperazine (0.400 g) was dissolved in CH_2Cl_2 (20 ml) and a solution of $Cu(CH_3COO)_2 \cdot 2H_2O$ (0.268 g) in methanol (50 ml) was added to give molar ratio 1:1. The resulting dark green mixture was refluxed for 1 h and cooled to ambient temperature. By slow evaporation of the solvent three different kinds of crystals (compound **2**, compound **2b** and copper acetate) were obtained.

Crystal structure determinations and refinements. Single-crystal data were collected with an Enraf Nonius CAD4 single crystal diffractometer. Crystals were mounted on top of a glass fibre and the data were collected at room

temperature, using graphite monochromatised Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) and $\omega/2\theta$ scan mode. 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 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 done for compound **2b** ($T_{max} = 99.96\%$, $T_{min} = 76.60\%$). Scattering factors were taken from Ref. 14. The structures were solved by direct methods using the SHELXS-86 program[15] and refined by full-matrix least-squares methods on F_o^2 using SHELXL-93.[16] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the hydroxyl groups and hydrogen attached to nitrogen in compound **2a** were located in a difference Fourier map. Other hydrogen atoms were calculated to 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 $U = 1.2U(C)$, $U = 1.2U(N)$ or $U = 1.5U(O)$. For compound **2a** a geometrical restraint was used to prevent an anomalous bond distance between nitrogen N1 and hydrogen H2. The refinements converged to $R = 0.0486$ (compound **2**), $R = 0.0491$ (compound **2a**) and $R = 0.0410$ (compound **2b**). The fractional coordinates and the U_{eq}-values are listed in Table 2, bond lengths in Table 3 and bond angles in Table 4. Tables of anisotropic thermal parameters, coordinates of calculated hydrogen atoms and listings of observed and calculated structure factors are available from the authors on request. Molecules are shown in Figs. 1–3 and the packing in Figs. 4–6. The coordination around copper in compound **2b** is presented in Fig. 7. Plots were generated with the program DIAMOND.[17]

Results and discussions

Structure of N,N'-*bis(2-hydroxybenzyl)piperazine.* The molecular structure of **2** is displayed in Fig. 1. Compound **2** is a linear molecule with a center of symmetry in the middle of the piperazine moiety. The observed bond lengths and angles are consistent with those reported in the literature.[18,19] The piperazine ring is in the energetically favoured chair conformation. In addition, there is a strong intramolecular hydrogen bond between the nitrogen and the hydroxyl group [N···H = 1.84(4) Å]. The deviation of O1 from the plane of the benzene ring is

Table 1. Crystallographic data for **2**, **2a** and **2b**.

Compound	**2**	**2a**	**2b**
Chemical formula	$C_{18}H_{22}N_2O_2$	$C_{18}H_{24}N_4O_8$	$C_{22}H_{26}N_2O_6Cu_2$
Formula weight	298.38	424.41	541.53
Colour	Colourless	Colourless	Green
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$ (No. 14)	*Pbca* (No. 61)	$P2_1/n$ (No. 14)
a/Å	6.745(6)	9.733(4)	12.197(4)
b/Å	8.796(2)	23.332(4)	7.061(3)
c/Å	13.407(2)	8.963(1)	13.300(4)
β/°	98.99(3)	—	98.83(2)
V/Å^3	785.7(7)	2035.4(9)	1131.9(7)
Z	2	4	2
D_{calc}/Mg m^{-3}	1.261	1.385	1.589
$F(000)$	320	896	556
λ(Mo K_α)/Å	0.71073	0.71073	0.71073
μ(Mo K_α)/mm^{-1}	0.083	0.110	1.920
Crystal size/mm	0.1,0.1,0.2	0.05,0.15,0.20	0.1,0.2,0.4
θ range for data collection/°	2–25	2–25	2–25
h_{min}, h_{max}	0, +8	0, +11	0, +14
k_{min}, k_{max}	0, +10	0, +27	0, +8
l_{min}, l_{max}	−15, +15	0, +10	−15, +15
No. of collected data	1375	1786	2086
No. of unique data	1375	1786	1988 ($R_{int} = 0.0275$)
No. of used data	1374	1782	1988
No. of data with $I > 2\sigma(I)$	573	645	1408
R, wR^2 [$I > 2\sigma(I)$]	0.0486, 0.0856	0.0491, 0.0963	0.0410, 0.1020
R, wR^2 (all data)	0.1965, 0.1208	0.2245, 0.1393	0.0798, 0.1202
S	0.979	0.985	1.077
No. of refined parameters	103	142	146
No. of restraints	—	1	—
Largest ΔF^2 peak /e Å^{-3}	0.151	0.301	0.436
Convergence	<0.001	<0.001	<0.001
Weighting (a/b)[a]	0.0377/0.00	0.0523/0.00	0.0697/0.1384

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

Table 2. Fractional coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($Å^2 \times 10^3$) with e.s.d.s in parentheses. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	U_{eq}
Compound **2**				
O1	2031(3)	7660(3)	1309(2)	60(1)
N1	4900(4)	5700(3)	959(2)	45(1)
C1	6680(5)	5837(4)	461(2)	53(1)
C2	3909(5)	4255(4)	671(2)	51(1)
C3	5460(5)	5834(4)	2066(2)	51(1)
C4	3675(5)	5996(4)	2597(2)	44(1)
C5	2119(5)	6968(4)	2224(2)	46(1)
C6	621(5)	7289(4)	2785(2)	55(1)
C7	635(6)	6604(4)	3710(3)	63(1)
C8	2124(6)	5612(4)	4085(2)	59(1)
C9	3632(5)	5315(4)	3530(2)	53(1)
H1	2907(55)	7130(42)	930(28)	89
Compound **2a**				
O1	8471(3)	3864(1)	5530(3)	54(1)
N1	5098(3)	4400(1)	5405(3)	32(1)
C1	6126(4)	4676(2)	4395(4)	37(1)
C2	4515(4)	4833(2)	6444(4)	37(1)
C3	5685(4)	3895(2)	6256(5)	42(1)
C4	6269(4)	3452(2)	5238(5)	37(1)
C5	7665(4)	3449(2)	4882(5)	39(1)
C6	8195(4)	3050(2)	3909(5)	50(1)
C7	7355(5)	2636(2)	3318(5)	62(2)
C8	5984(5)	2621(2)	3683(5)	60(1)
C9	5445(4)	3027(2)	4634(5)	51(1)
O21	2872(3)	4220(1)	3479(3)	57(1)
O22	2151(3)	3909(2)	5566(4)	93(1)
O23	723(3)	4058(2)	3802(4)	84(1)
N2	1908(4)	4062(2)	4297(5)	53(1)
H1	9146(48)	3855(22)	5021(56)	81
H2	4348(29)	4247(14)	4776(32)	38
Compound **2b**				
Cu1	9000(1)	1328(1)	5060(1)	37(1)
O1	9516(3)	−128(4)	4025(2)	35(1)
N1	9235(3)	3789(5)	4333(3)	31(1)
C1	10391(4)	4134(6)	4160(3)	33(1)
C2	8861(3)	5465(6)	4856(3)	34(1)
C3	8480(4)	3524(7)	3348(4)	41(1)
C4	8866(4)	2042(7)	2669(3)	36(1)
C5	9342(4)	308(6)	3027(3)	34(1)
C6	9651(4)	−977(7)	2334(4)	45(1)
C7	9479(4)	−602(9)	1297(4)	54(2)
C8	9012(4)	1084(9)	946(4)	55(2)
C9	8713(4)	2387(8)	1622(4)	48(1)
O2	8116(3)	2321(5)	6052(3)	53(1)
O3	7836(3)	−579(5)	5578(3)	57(1)
C10	7609(4)	772(7)	6110(4)	45(1)
C11	6771(6)	616(10)	6825(6)	85(2)

Table 3. Bond distances (Å) with e.s.d.s in parentheses.

Compound	**2**	**2a**	**2b**
O1–C5	1.362(3)	1.376(5)	1.347(5)
N1–C1	1.467(4)	1.495(4)	1.483(5)
N1–C2	1.460(3)	1.487(4)	1.480(5)
N1–C3	1.477(4)	1.515(4)	1.493(6)
C1–C2*	1.510(4)[i]	1.506(5)[ii]	1.502(6)[iii]
C3–C4	1.498(4)	1.491(5)	1.504(6)
C4–C5	1.386(4)	1.396(5)	1.407(6)
C4–C9	1.390(4)	1.387(5)	1.398(6)
C5–C6	1.379(4)	1.375(5)	1.386(6)
C6–C7	1.377(4)	1.373(6)	1.389(7)
C7–C8	1.366(5)	1.374(6)	1.371(8)
C8–C9	1.376(4)	1.376(5)	1.374(7)
O21–N2		1.247(4)	
O22–N2		1.215(4)	
O23–N2		1.235(4)	
Cu1–N1			2.030(4)
Cu1–O1			1.901(3)
Cu1–O1*			2.191(3)[iv]
Cu1–O2			1.958(3)
Cu1–O3			2.146(4)
O2–C10			1.264(6)
O3–C10			1.244(6)
C10–C11			1.503(7)

Symmetry transformations used to generate equivalent atoms (marked with *): [i] $-x+1, -y+1, -z$; [ii] $-x+1, -y+1, -z+1$; [iii] $-x+2, -y+1, -z+1$; [iv] $-x+2, -y, -z+1$.

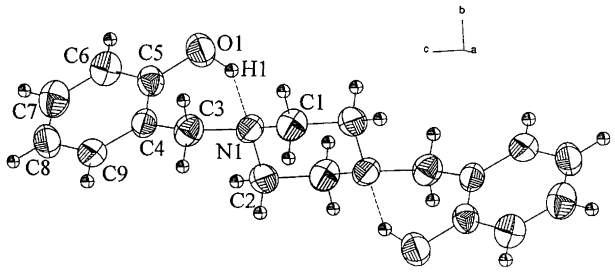


Fig. 1. The molecular structure of $C_{18}H_{22}N_2O_2$ (**2**) with the atomic numbering used. Intramolecular hydrogen bonds are indicated by dashed lines. Thermal ellipsoids are plotted at the 50% probability level.

−0.026(5) Å and the torsion angle of C4–C5–O1–H1 is 17.5(2.4)°.The packing of **2** is presented in Fig. 4. The interactions between molecules are weak van der Waals forces.

Structure of N,N'-*bis(2-hydroxybenzyl)piperazine nitrate.* The molecular structure of compound **2a**, presented in Fig. 2, is similar to **2**. Compound **2a** is also linear, there is a center of symmetry in the middle of the piperazine moiety and the piperazine ring is in the chair conformation. Owing to the protonation of the *N* atom there is no intramolecular hydrogen bond; the torsion angle of C4–C5–O1–H1 is −163.5(3.7)°. The deviation of O1 from the benzene ring plane is 0.043(6) Å. The nitrate group links adjacent molecules via hydrogen bonds. Hydrogen bonds exist between O21 and H2 [O21 ··· H2 = 1.85(3) Å] and O23 and H1′ of the other molecule [O23 ··· H1′ = 1.94(1) Å], as displayed in Fig. 2. The interactions between molecules are van der Waals forces between benzene rings in the direction of the *b*-axis and between CH_2 groups in the direction of the *c*-axis. Owing to the weak interactions in the *c*-direction **2a** has a layer structure in the *ab*-plane. The crystal structure of **2a** is displayed in Fig. 5.

Table 4. Bond angles (°) with e.s.d.s in parentheses.

Compound	2	2a	2b
C1–N1–C2	108.9(2)	110.0(3)	108.1(3)
C1–N1–C3	110.6(3)	112.8(3)	110.9(3)
C2–N1–C3	111.7(2)	110.9(3)	108.7(3)
N1–C1–C2*	110.3(3)[i]	110.7(3)[ii]	111.1(4)[iii]
N1–C2–C1*	110.5(2)[i]	111.3(3)[ii]	111.7(3)[iii]
N1–C3–C4	112.8(3)	112.0(3)	114.0(4)
C5–C4–C9	118.0(3)	118.0(4)	118.3(4)
C5–C4–C3	120.5(3)	121.0(4)	123.6(4)
C9–C4–C3	121.2(3)	121.0(4)	118.1(4)
O1–C5–C6	117.9(3)	122.0(4)	119.2(4)
O1–C5–C4	121.6(3)	117.0(4)	121.8(4)
C6–C5–C4	120.5(3)	121.0(4)	119.0(4)
C7–C6–C5	120.0(3)	119.8(4)	121.4(5)
C8–C7–C6	120.8(4)	120.3(5)	119.7(5)
C7–C8–C9	119.0(4)	120.0(5)	119.8(5)
C8–C9–C4	121.7(3)	120.9(4)	121.8(5)
O22–N2–O23		121.1(4)	
O22–N2–O21		119.4(4)	
O23–N2–O21		119.6(4)	
O1–Cu1–O2			163.71(14)
O1–Cu1–N1			91.80(13)
O2–Cu1–N1			98.45(14)
O1–Cu1–O3			101.69(14)
O2–Cu1–O3			63.15(14)
N1–Cu1–O3			147.0(2)
O1–Cu1–O1*			81.71(12)[iv]
O2–Cu1–O1*			104.90(14)[iv]
N1–Cu1–O1*			115.49(13)[iv]
O3–Cu1–O1*			96.31(14)[iv]
C5–O1–Cu1			124.8(3)
C5–O1–Cu1*			128.9(3)[iv]
Cu1–O1–Cu1*			98.29(12)[iv]
C2–N1–Cu1			112.6(3)
C1–N1–Cu1			114.9(3)
C3–N1–Cu1			101.4(3)

Symmetry transformations used to generate equivalent atoms (marked with *): [i] $-x+1, -y+1, -z$; [ii] $-x+1, -y+1, -z+1$; [iii] $-x+2, -y+1, -z+1$; [iv] $-x+2, -y, -z+1$.

Structure of N,N′-*bis(2-hydroxybenzyl)piperazine copper(II) acetate.* The polymeric complex molecule of the copper(II) acetate is presented in Fig. 3. The basic molecular structure is a dinuclear neutral complex with two copper atoms and two acetate groups coordinated to the ligand **2**, which is in a chair conformation. The asymmetric unit consists of half of the ligand molecule, one copper atom and one acetate group. Metal–ligand distances range from 1.901(3) (Cu1···O1) to 2.191(3) (Cu1···O1′). The bond lengths coincide with those reported in the literature.[20] The coordination of the copper atom is shown in Fig. 7. The copper atom has a distorted square-pyramidal five-coordination with N1, O1, O2 and O3 in the basal plane and O1′ from the other molecule occupies the apical position. The two distorted square-pyramidal polyhedra share the same pyramidal edge O1–O1′. The copper atom is displaced 0.338(2) Å from the basal plane of the pyramid. The Cu–Cu distance is 3.1 Å and indicates absence of any appreciable metal–metal bonding. The acetate ion acts as a bidentate ligand. The bonding of the two acetate

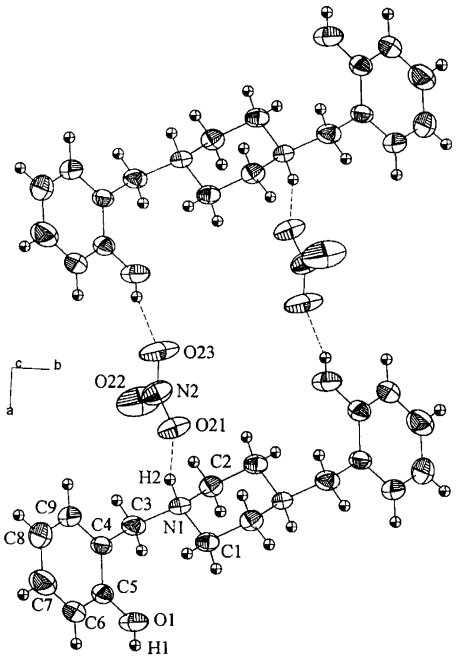


Fig. 2. The molecular structure of $C_{18}H_{24}N_4O_8$ (**2a**) and bonding between molecules. Hydrogen bonds are indicated by dashed lines. Thermal ellipsoids are plotted at the 50% probability level.

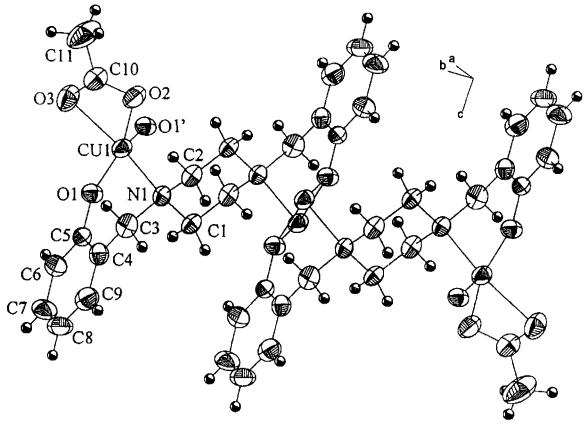


Fig. 3. Part of the polymer structure of $C_{22}H_{26}N_2O_6Cu_2$ (**2b**). Thermal ellipsoids are plotted at the 50% probability level. Two acetate groups attached to copper atoms in the middle are not drawn.

oxygen atoms to the copper is distinctly asymmetric; Cu–O distances are 1.958(3) Å and 2.146(4) Å. The packing of the compound **2b** is presented in Fig. 6. The uncharged molecules are polymerized in the *b*-direction via coppers, forming a zigzag chain. In the *ab*-plane the interaction between molecules are van der Waals forces between acetate groups and adjacent ligand molecules. Compound **2** does not form metal complexes as easily as **1**, so the substitution of nitrogen by hydroxyl group decreases the complexing capability of investigated ligand.

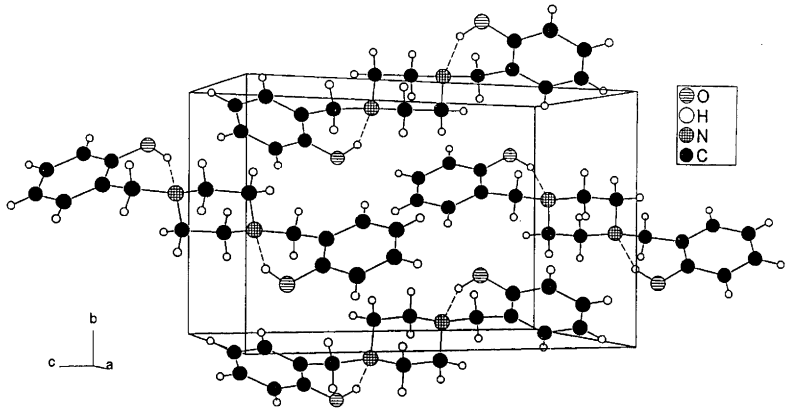


Fig. 4. The crystal packing of $C_{18}H_{22}N_2O_2$ (**2**).

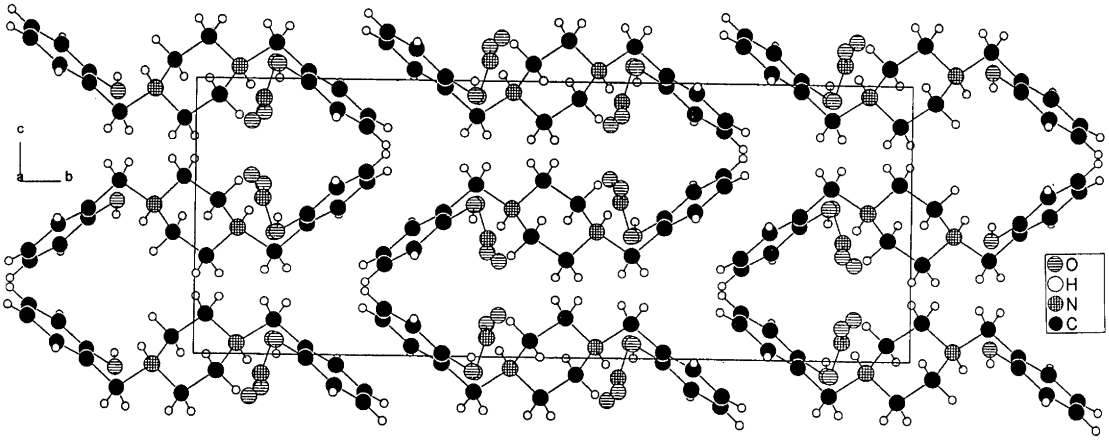


Fig. 5. The crystal packing of $C_{18}H_{24}N_4O_8$ (**2a**).

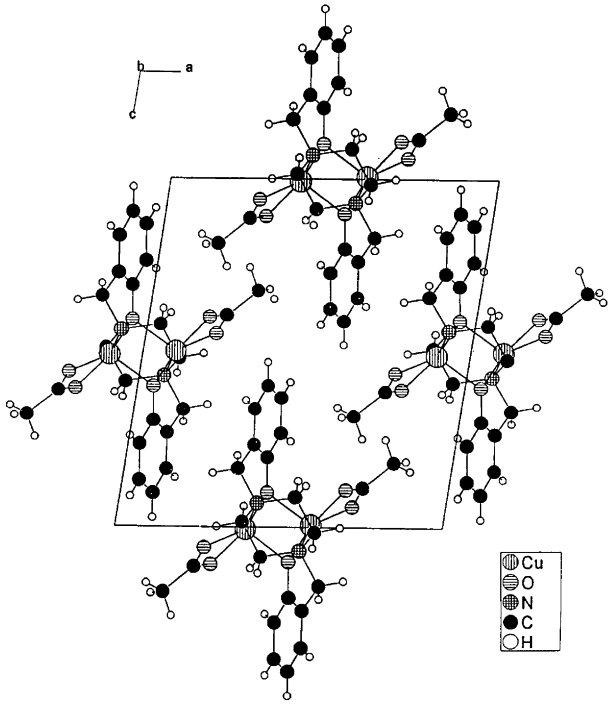


Fig. 6. The crystal packing of $C_{22}H_{26}N_2O_6Cu_2$ (**2b**).

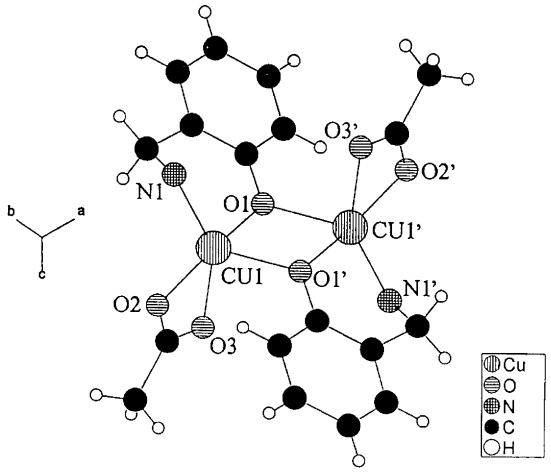


Fig. 7. Coordination of copper in **2b**. Symmetry operation applied is $-x+2, -y, -z+1$.

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