1,4-Bis(2-salicylideneaminoethyl)piperazine, a Sexidentate Binucleating Ligand

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Abstract. $C_{22}H_{28}N_4O_2$, $M_r = 380$, monoclinic, $P2_1/a$, $a = 13.328$ (3), $b = 11.654$ (2), $c = 6.384$ (2) Å, $\beta = 94.02$ (1)°, $V = 989.2$ Å^3, $D_x = 1.141$ Mg m^{-3}, $Z = 2$. The structure was solved by direct methods and refined to $R = 0.048$ for 956 observed reflections. The molecules lie on crystallographic inversion centers; the piperazine ring has the chair conformation. Intermolecular H bonds (2.589 Å) between O and N are present.

Introduction. There is continuing interest in the nature of the spin–spin interactions in magnetically condensed systems (Hodgson, 1975). The main reason for this is the fundamental importance of exchange interactions in theories of chemical bonding and in research in magnetic materials. Bridged dimers formed by Schiff bases and other ligands with paramagnetic metals are of particular interest in this regard because as a group they present a wide variety of structural types and magnetic interactions. Schiff base (I) is known to act as a sexidentate ligand in a variety of metal complexes (Sinn, Sim, Dose, Tweedle & Wilson, 1978) which, apparently because of the considerable flexibility of (I), are all mononuclear.

(I)
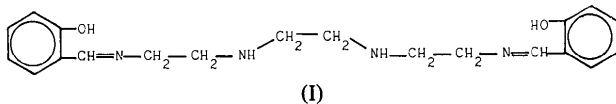
The steric constraint imposed by the presence of the piperazine ring should coax ligand (II) more than (I) into coordinating to two metal centers. This might afford an opportunity of systematically studying the effect of small variations in molecular structure on exchange coupling by preparing series of related dimeric compounds that differ in a controlled manner. Accordingly, we have synthesized ligand (II). In order to understand the detailed stereochemical and electronic structural changes of the ligand accompanying complex formation, an X-ray structural determination of (II) was deemed useful.

(II)
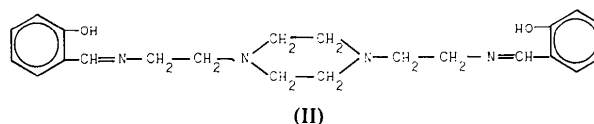
The title compound was prepared by reacting the novel Schiff base 2-bromo-1-salicylideneaminoethane (obtained from 1-amino-2-bromoethane and salicylaldehyde) with piperazine in benzene. Details of the synthesis will appear elsewhere (Chiari, Piovesana, Tarantelli & Zanazzi, 1981). Recrystallization from methanol afforded yellow crystals with m.p. 422–425

Table 1. *Positional and thermal parameters with e.s.d.'s in parentheses*

For non-hydrogen atoms $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{13} \cos \beta)$.

	x	y	z	U_{iso} or U_{eq} (Å^2)
O	0.6236 (2)	0.2642 (2)	0.1386 (4)	0.059 (1)
N(1)	0.6805 (2)	0.3307 (2)	−0.2214 (5)	0.048 (2)
N(2)	0.9255 (2)	0.4295 (2)	−0.4084 (5)	0.038 (2)
C(1)	0.5318 (2)	0.3055 (3)	0.0753 (7)	0.042 (2)
C(2)	0.4548 (2)	0.2956 (3)	0.2110 (7)	0.047 (2)
C(3)	0.3607 (3)	0.3384 (3)	0.1520 (7)	0.050 (2)
C(4)	0.3412 (3)	0.3903 (3)	−0.0422 (3)	0.056 (2)
C(5)	0.4167 (2)	0.3989 (3)	−0.1753 (7)	0.051 (2)
C(6)	0.5128 (2)	0.3566 (2)	−0.1222 (6)	0.039 (2)
C(7)	0.5923 (2)	0.3673 (3)	−0.2668 (7)	0.044 (2)
C(8)	0.7559 (3)	0.3474 (4)	−0.3733 (3)	0.051 (2)
C(9)	0.8437 (2)	0.4131 (3)	−0.2696 (7)	0.045 (2)
C(10)	0.8990 (2)	0.5134 (3)	−0.5726 (7)	0.048 (2)
C(11)	1.0160 (2)	0.4693 (3)	−0.2879 (7)	0.045 (2)
HO	0.668 (4)	0.274 (5)	0.016 (9)	0.12 (2)
H(2)	0.469 (3)	0.257 (4)	0.351 (8)	0.07 (1)
H(3)	0.308 (3)	0.335 (3)	0.235 (7)	0.05 (1)
H(4)	0.277 (3)	0.419 (3)	−0.072 (6)	0.07 (1)
H(5)	0.402 (3)	0.433 (3)	−0.317 (7)	0.06 (1)
H(7)	0.574 (2)	0.405 (3)	−0.399 (6)	0.04 (1)
H(81)	0.784 (3)	0.273 (4)	−0.416 (7)	0.08 (1)
H(82)	0.726 (3)	0.392 (4)	−0.491 (7)	0.06 (1)
H(91)	0.873 (3)	0.364 (4)	−0.158 (7)	0.06 (1)
H(92)	0.820 (2)	0.491 (3)	−0.215 (6)	0.06 (1)
H(101)	0.878 (3)	0.484 (3)	−0.653 (5)	0.06 (1)
H(102)	0.878 (3)	0.590 (3)	−0.510 (6)	0.05 (1)
H(111)	1.002 (3)	0.539 (4)	−0.216 (7)	0.06 (1)
H(112)	1.035 (2)	0.413 (3)	−0.179 (6)	0.04 (1)

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K. A prismatic crystal with dimensions $0 \cdot 5 \times 0 \cdot 2 \times 0 \cdot 2$ mm was mounted on a PW 1100 four-circle diffractometer equipped with graphite-monochromated Mo radiation. The crystal was monoclinic, space group $P2_1/a$ (from systematic extinctions). Lattice constants were determined by a least-squares method from the setting angles of 25 reflections. Intensity data were measured with the $\theta/2\theta$ scan technique in the range $3 < \theta < 25°$, with a scan speed of $0 \cdot 05°$ s^{-1} and a scan width of $1 \cdot 6°$. Lp corrections were applied but no correction for absorption $[\mu(\text{Mo } K\alpha) = 0 \cdot 048 \text{ mm}^{-1}]$ was made; 956 unique reflections with $I \geq 3\sigma(I)$ were used in the refinement. The structure was solved by direct methods (*SHELX* 76, Sheldrick, 1976) and refined by full-matrix least squares. H atoms were found in a difference Fourier synthesis and refined with individual isotropic thermal parameters. All nonhydrogen atoms were refined anisotropically.

The refinement converged to $R = 0 \cdot 048$, $R_w = 0 \cdot 055$ $\{R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}\}$ for 183 parameters: reflections were weighted as $w = 1/[\sigma^2(F_o) + 0 \cdot 0064 F_o^2]$. Atomic scattering factors of the *SHELX* system of programs were used. Final atomic coordinates are given in Table 1.* Bond distances and angles are listed in Tables 2 and 3 respectively.

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36198 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. A perspective view of a molecule of the title compound is shown in Fig. 1. The molecule lies on the inversion center. All distances and angles are close to the expected values. The mean C—C distance between sp^3-hybridized C atoms is $1 \cdot 507$ Å; the C—N double bond is $1 \cdot 265$ Å; the C—N single-bond length averages $1 \cdot 460$ Å; the C—O distance is $1 \cdot 350$ Å; the mean C—H bond length is $0 \cdot 98$ Å. The phenyl ring is planar in the limits of experimental error. The equation of the best ring plane, together with the atomic deviations from it, are reported in Table 4. The average distance between C atoms in the ring is $1 \cdot 386$ Å. The piperazine ring has the chair conformation; the atoms are alternately displaced from the least-squares plane by $0 \cdot 237$ Å. Some torsion angles in the molecule are listed in Table 5.

The molecules are packed in the crystal nearly perpendicularly to the z axis, and are well separated: no intermolecular contacts shorter than the respective van der Waals diameters were found.
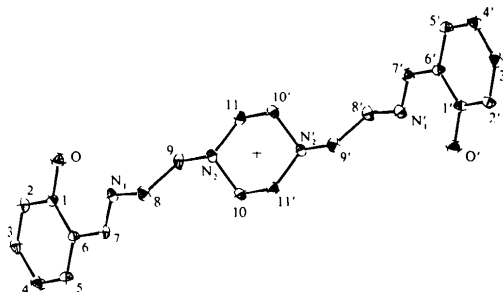

Fig. 1. *ORTEP* (Johnson, 1965) view of the title compound with the numbering of the atoms.

Table 2. *Bond lengths* (Å)

O—C(1)	1·350 (4)	O—HO	1·02 (6)
C(1)—C(2)	1·393 (5)	C(2)—H(2)	1·01 (5)
C(2)—C(3)	1·377 (5)	C(3)—H(3)	0·90 (4)
C(3)—C(4)	1·388 (6)	C(4)—H(4)	0·93 (4)
C(4)—C(5)	1·366 (5)	C(5)—H(5)	1·00 (4)
C(6)—C(1)	1·401 (5)	C(7)—H(7)	0·96 (4)
C(6)—C(7)	1·459 (5)	C(8)—H(81)	1·00 (4)
C(7)—N(1)	1·265 (4)	C(8)—H(82)	0·97 (4)
N(1)—C(8)	1·458 (4)	C(9)—H(91)	0·97 (4)
C(8)—C(9)	1·511 (5)	C(9)—H(92)	1·03 (4)
C(9)—N(2)	1·465 (4)	C(10)—H(101)	0·96 (3)
N(2)—C(10)	1·459 (4)	C(10)—H(102)	1·02 (4)
N(2)—C(11)	1·459 (4)	C(11)—H(111)	0·96 (4)
C(10)—C(11)'	1·503 (4)	C(11)—H(112)	0·98 (4)
O···N(1)	2·589 (4)		

Symmetry code: (') $2 - x, 1 - y, -1 - z$.

Table 3. *Bond angles* (°)

O—C(1)—C(2)	118·4 (4)	C(6)—C(7)—N(1)	122·0 (4)
O—C(1)—C(6)	121·5 (3)	C(7)—N(1)—C(8)	118·4 (3)
C(2)—C(1)—C(6)	120·0 (3)	N(1)—C(8)—C(9)	109·0 (3)
C(1)—C(2)—C(3)	119·8 (4)	C(8)—C(9)—N(2)	112·8 (3)
C(2)—C(3)—C(4)	120·8 (4)	C(9)—N(2)—C(10)	111·6 (2)
C(3)—C(4)—C(5)	119·3 (3)	C(9)—N(2)—C(11)	110·2 (3)
C(4)—C(5)—C(6)	121·8 (4)	C(10)—N(2)—C(11)	108·4 (2)
C(5)—C(6)—C(1)	118·3 (3)	N(2)—C(10)—C(11)'	111·1 (3)
C(5)—C(6)—C(7)	120·8 (4)	N(2)—C(11)—C(10)'	111·1 (3)
C(1)—C(6)—C(7)	120·9 (3)		

Table 4. *Least-squares planes of the benzene and piperazine rings, and deviations* (Å) *of atoms from them*

The equations of the least-squares planes are given in the form
$Ax + By + Cz = D$ in direct space.

(*a*) Benzene: $A = 3 \cdot 123, B = 10 \cdot 329, C = 2 \cdot 439, D = 4 \cdot 993$

C(1)	0·007	C(4)	0·001	*O	0·023
C(2)	−0·004	C(5)	0·002	*C(7)	0·001
C(3)	0·000	C(6)	−0·006	*N(1)	0·009

(*b*) Piperazine: $A = -3 \cdot 012, B = 10 \cdot 206, C = 2 \cdot 818, D = 0 \cdot 682$

N(2)	−0·237
C(10)	0·237
C(11)	0·237

* Atoms not included in the calculation of the plane.

Table 5. *Torsion angles* (°)

Signs are given according to the convention of Klyne & Prelog (1960). E.s.d.'s are $0 \cdot 9°$.

C(7)–N(1)–C(8)–C(9)	123·0	N(2)–C(11)–C(10)'· N(2)'	59·3
N(1) C(8)–C(9)–N(2)	177·4	C(11)- C(10)'- N(2)'–C(11)'	-57·7
C(8)–C(9) N(2)–C(10)	72·4	C(10)' N(2)' C(11)'· C(10)	57·7
C(8) -C(9) N(2)–C(11)	−167·1		

Tests of the mode of coordination of (II) to bi- or trivalent metal ions (Cu^{II}, Fe^{III}) indicate sexidentate binucleating behavior, with a change from a chair to a boat conformation for the piperazine ring. Structural work on these compounds is in progress.

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The Absolute Configuration of the Tropane Alkaloid 6β,7β-Epoxy-1αH,5αH-tropan-3α-yl (−)-2,3-Dihydroxy-2-phenylpropionate from its n-Butylbromide

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Abstract. $C_{17}H_{21}NO_5.C_4H_9Br$, $M_r = 456·38$, orthorhombic, $P2_12_12_1$, $a = 7·215$ (1), $b = 12·974$ (2), $c = 22·466$ (2) Å, $Z = 4$, $D_c = 1·44$ Mg m^{-3}. Final $R = 0·027$ for 1978 observed reflexions. The tropane alkaloid is narrowly related to scopolamine with an additional OH group at the asymmetric atom of the tropic acid residue. The absolute configuration around this atom is S, which is the inverse of that around the corresponding atom in scopolamine.

Introduction. Moorhoff (1975) has separated a new alkaloid from extracts of leaves of *Datura sanguinea*, which he identified as 6β,7β-epoxy-1αH,5αH-tropan-3α-yl (−)-2,3-dihydroxy-2-phenylpropionate. It is narrowly related to scopolamine; instead of tropic acid (3-hydroxy-2-phenylpropionic acid) the new alkaloid contains 2,3-dihydroxy-2-phenylpropionic acid, which has an additional OH group at the asymmetric C atom. The main object of the present structure determination of the n-butylbromide of the new alkaloid was to establish the absolute configuration at the asymmetric centre of the 2,3-dihydroxy-2-phenylpropionic acid residue.

1978 reflexions with $2\theta \leq 130°$ and intensities above the 2σ level were measured on a Nonius CAD-4 single-crystal diffractometer employing graphite-monochromatized Cu $K\alpha$ radiation. No absorption correction was applied (crystal dimensions $0·3 \times 0·3 \times 0·4$

Table 1. *Fractional coordinates* ($\times 10^5$ *for* Br, $\times 10^4$ *for* C,N,O) *and equivalent isotropic thermal parameters* ($Å^2 \times 10^3$) *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* \, \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	U_{eq}
Br	5509 (6)	15143 (3)	19336 (2)	39·3 (1)
C(1)	5576 (4)	4611 (3)	3030 (2)	27 (1)
C(2)	5945 (5)	4778 (3)	2362 (2)	35 (1)
C(3)	5542 (5)	3824 (3)	1976 (2)	33 (1)
C(4)	5751 (5)	2763 (3)	2276 (2)	31 (1)
C(5)	5432 (5)	2796 (3)	2952 (2)	27 (1)
C(6)	3462 (5)	3183 (3)	3035 (2)	30 (1)
C(7)	3548 (5)	4300 (3)	3088 (2)	34 (1)
N(8)	6639 (4)	3645 (2)	3226 (2)	21 (1)
O(9)	3045 (4)	3680 (2)	3599 (2)	41 (1)
O(10)	3610 (4)	3860 (2)	1765 (2)	30 (1)
C(11)	3242 (5)	4543 (3)	1333 (2)	33 (1)
O(12)	4391 (5)	5107 (3)	1117 (2)	59 (1)
C(13)	1180 (5)	4556 (3)	1167 (2)	28 (1)
C(14)	545 (6)	5676 (3)	1203 (2)	41 (1)
O(15)	1173 (6)	6165 (3)	1731 (2)	57 (1)
O(16)	99 (4)	4009 (2)	1591 (2)	30 (1)
C(17)	922 (5)	4139 (3)	531 (2)	29 (1)
C(18)	2025 (7)	4494 (3)	71 (2)	46 (1)
C(19)	1769 (8)	4125 (4)	−511 (2)	57 (1)
C(20)	394 (9)	3407 (4)	−620 (2)	65 (2)
C(21)	−723 (11)	3084 (4)	−166 (2)	75 (2)
C(22)	−459 (7)	3434 (4)	413 (2)	50 (1)
C(23)	8615 (5)	3637 (3)	2998 (2)	30 (1)
C(24)	6796 (5)	3505 (3)	3910 (2)	33 (1)
C(25)	7982 (7)	4307 (4)	4219 (2)	49 (1)
C(26)	7887 (7)	4150 (4)	4899 (2)	53 (1)
C(27)	8786 (10)	3206 (5)	5135 (3)	81 (2)