C5	0.21660 (16)	0.44953 (16)	0.18609 (18)	0.0353 (9)
O5	0.29759 (11)	0.54532 (10)	0.18667 (12)	0.0379 (7)
C6	0.13424 (16)	0.41969 (17)	0.0945 (2)	0.0391 (10)
C7	0.05436 (18)	0.31702 (19)	0.0887 (2)	0.0477 (12)
C8	0.05106 (18)	0.24283 (18)	0.1742 (2)	0.0498 (12)
C9	0.1300 (2)	0.27397 (18)	0.2676 (2)	0.0473 (12)
C10	0.21287 (16)	0.37532 (16)	0.2781 (2)	0.0379 (10)
C11	0.29367 (17)	0.40588 (17)	0.3905 (2)	0.0418 (10)
C12	0.2707 (3)	0.3151 (3)	0.4841 (4)	0.078 (2)
C13	0.4016 (2)	0.4457 (3)	0.3311 (3)	0.0703 (17)
C14	0.2939 (3)	0.4903 (3)	0.4773 (3)	0.0631 (16)
C15	−0.0375 (3)	0.1317 (2)	0.1690 (5)	0.075 (2)

Table 2. *Selected geometric parameters (Å, °)*

Cr—N1	2.109 (2)	C6—C7	1.396 (3)
Cr—O5	1.919 (3)	C7—C8	1.376 (4)
N1—C2	1.490 (4)	C8—C9	1.384 (4)
N1—C3	1.499 (4)	C8—C15	1.521 (3)
N1—C4	1.492 (2)	C9—C10	1.400 (3)
C2—C3^{i}	1.512 (4)	C10—C11	1.535 (3)
C4—C6	1.504 (4)	C11—C12	1.534 (5)
C5—O5	1.334 (2)	C11—C13	1.530 (4)
C5—C6	1.410 (3)	C11—C14	1.524 (5)
C5—C10	1.415 (3)		
N1—Cr—O5	91.14 (6)	N1—Cr—O5^{i}	92.67 (8)
N1—Cr—N1^{ii}	82.28 (8)	O5—Cr—O5^{ii}	93.41 (9)
N1—Cr—O5^{ii}	172.17 (6)		

Symmetry codes: (i) $-x+y, 1-x, z$; (ii) $1-y, 1+x-y, z$.

The structure was solved by the heavy-atom method. H atoms were located in difference maps, except for some on methyl groups which were calculated geometrically. The crystal structure contains a small solvent-accessible void at $(0,0,\frac{1}{2})$ with a volume of 55 Å^3 (*PLATON*; Spek, 1997). No residual density was found in that area.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *Xtal*3.4 *DIFDAT ADDREF ABSORB SORTRF* (Hall *et al.*, 1995). Program(s) used to solve structure: *Xtal*3.4. Program(s) used to refine structure: *Xtal*3.4 *CRYLSQ*. Molecular graphics: *Xtal*3.4. Software used to prepare material for publication: *Xtal*3.4 *BONDLA CIFIO*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1214). Services for accessing these data are described at the back of the journal.

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Cobalt(II) complexes of piperazine and derivatives: 1-methylpiperazin-4-ium trichloro(1-methylpiperazine-N^4)cobaltate(II)

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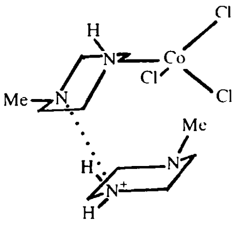
Abstract

The title compound, $(C_5H_{13}N_2)[CoCl_3(C_5H_{12}N_2)]$, contains a Co^{II} ion coordinated to three Cl atoms and to the unmethylated N atom of *N*-methylpiperazine in a distorted tetrahedral geometry. The six-membered ring of both the coordinated and free *N*-methylpiperazine molecules possesses the more stable chair conformation. In addition, other tautomeric forms may be present in small amounts in the crystals.

Comment

Piperazine (H_2ppz) is a cyclic 1,4-diamine that can coordinate metal ions as a monodentate, bidentate or bidentate–chelate ligand. The last form is very rare because the piperazine ring must assume the boat conformation, which is 17.2 kJ mol^{-1} less stable than the chair conformation (Niemeyer, 1979). Recently, we have studied several *N*-methylpiperazine (HMeppz) and *N,N'*-dimethylpiperazine (Me$_2$ppz) Pt^{II} complexes (Marzotto *et al.*, 1997, 1998*a*; Ciccarese *et al.*, 1998). A few of them show some antitumour activity, such as the boat chelate *cis*-[PtCl$_2$(Me$_2$ppz)], which resembles cisplatin. In order to gain further insight into the ability of coordination complexes to interact selectively with the N atoms of DNA nucleobases, we have synthesized some tetrahedral Co^{II} complexes containing *N*-methylated piperazine for possible biological applications. We report here the structure of the present compound, (I), mainly constituted by [H$_2$Meppz]$^+$ cations and $[CoCl_3(HMeppz)]^-$ anions. In addition, other tautomeric forms may be present in small amounts, such as the zwitterionic $[HMeppz][CoCl_3(H_2Meppz)]$ and the bi-divalent $[H_3Meppz]^{2+}[CoCl_3(Meppz)]^{2-}$ forms, which are obtained by a small shift of H atoms from the free *N*-methylpiperazine to the coordinated molecule and *vice versa*.



(I)

The Co^{II} ion is always tetrahedrally coordinated to three Cl atoms, and to the piperazine N atom bearing an H atom (Fig. 1). The tetrahedral coordination is rather distorted (Table 1): for instance, the Cl2—Co—Cl3 angle of 119.06 (4)° deviates by almost 10° from the ideal tetrahedral value of 109.47°. The Co—Cl mean distance [2.256 (9) Å] is within the range of Co^{II}—Cl distances found in mononuclear Co^{II} tetrahedral complexes having a 3Cl + 1N coordination donor set (Cooley *et al.*, 1995; Lemoine *et al.*, 1996), but it is significantly shorter than those observed in the tetrachlorocobaltate(II) anion, for instance, in $[H_4ppz]^{2+}[CoCl_4]^{2-}\cdot H_2O$ [2.280 (1) Å; Tran Qui & Palacios, 1990] or in $[Co(Me_2SO)_6]^{2+}[CoCl_4]^{2-}$ [2.284 (6) Å; Ciccarese *et al.*, 1993]. The increase of the Co—Cl distance on increasing the number of Cl atoms may be explained in terms of electronegativity (Pauling, 1948), or by considering the higher *s* character in the title complex compared with that in the $[CoCl_4]^{2}$ complex (Bent, 1961). The Co—Cl3 distance is markedly longer than Co—Cl1 and Co—Cl2 as a consequence of the intermolecular hydrogen bond between Cl3 and N3 (Table 2).

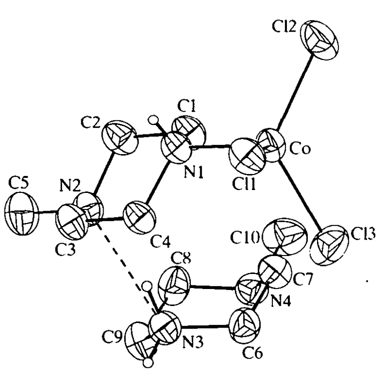


Fig. 1. Displacement ellipsoid plot (50% probability) of the molecular structure of (I). H atoms bound to N are drawn as small circles of arbitrary radii; other H atoms have been omitted for clarity.

Both coordinated and free *N*-methylpiperazine exhibit the six-membered ring in a chair conformation, with the N—CH_3 group in an equatorial position. The coordinated piperazine possesses an equatorial $CoCl_3$ group, and consequently an axial N1—H1 bond. The bond lengths and angles of *N*-methylpiperazine in (I) are in agreement with the accepted values (Vanier & Brisse, 1982) and, as usual, do not show any relation to the protonation state of the *N*-methylpiperazine. An $[H_2Meppz]^+$ cation forms two hydrogen bonds with the *N*-methylpiperazine coordinated to Co^{2+}, the stronger one between N3 and N2 and the other, weaker, one between N1 and $N4^i$ [symmetry code: (i) *x*, *y*, $z-1$] (Table 2). A third asymmetric bifurcated hydrogen bond is formed between N3—H3N*A* and the Cl1 and Cl3 atoms of the negative inorganic $CoCl_3$ moiety of the neighbouring molecule at ($2-x$, $1-y$, $1-z$). The Fourier synthesis shows one maximum near N1 (0.78 e $Å^{-3}$) due to H1 and two maxima near N2 (0.66 and 0.58 e $Å^{-3}$) due to HN3*A* and HN3*B*. In addition, two low but visible maxima close to N2 (0.26 e $Å^{-3}$) and N4 (0.20 e $Å^{-3}$) possess bond distances and angles appropriate for H atoms bonded to N2 and N4. Furthermore, the *R* factors obtained by including all four disordered H atoms are slightly smaller $\{R[F^2 > 2\sigma(F^2)] = 3.29, R(F^2) = 5.53, \omega R(F^2) = 9.70\%, S = 1.073\}$ than those obtained including only two ordered H atoms $\{R[F^2 > 2\sigma(F^2)] = 3.31, R(F^2) = 5.54, \omega R(F^2) = 9.80\%, S = 1.076\}$. Therefore, it is probably the case that a few molecules are protonated at N2 instead of N3 and/or at N4 instead of N1 as a consequence of a small hydrogen shift, from HN3*B* to H2 [Δ = 1.08 (3) Å] and/or from H1 to H4 (Δ = 1.34 Å), respectively (Table 2). Obviously, similar hydrogen jumps have already been reported for other compounds (Bandoli *et al.*, 1980; Colligiani *et al.*, 1980; Jeffrey & Saenger, 1994).

Usually, the zwitterionic form strengthens the metal–N bond (Marzotto *et al.*, 1998*b*) because of the closeness of the electrostatic charges counterbalanced within the same molecule. On the contrary, in the present case, the ionic form $[H_2Meppz]^+[CoCl_3(HMeppz)]^-$ is the most abundant. This may be due to the positive charge on N3, which is assumed given the protonation of H3N*B*, reinforcing the bifurcated hydrogen bond involving the partially negative Cl1 and Cl3.

Zwitterionic complexes of Co^{2+} are already known, and for related literature the interested reader is referred to the following: Kolodny *et al.* (1973), Vallarino *et al.* (1973), Steffen & Palenik (1978), Gerloch & Manning (1981) and Bruni *et al.* (1991).

Experimental

The title compound was synthesized by dropwise addition of a solution of $CoCl_2\cdot 6H_2O$ (0.714 g, 3.0 mmol) in EtOH (15 ml), to a solution of *N*-methylpiperazine (HMeppz, 98%; 0.340 ml, 3.0 mmol) in EtOH (5 ml), followed by stirring for 2 h at 323 K. The resulting blue solution, containing an intense blue powder precipitate, was left to evaporate slowly. Light-blue parallelepiped crystals appeared after 2 weeks on the walls of flask just above the solution level. These crystals were gathered, washed with Et_2O–EtOH (2:1 *v*/*v*) and dried under vacuum; they proved to be of good quality with well formed crystal faces [yield: 0.024 g (2.2%)]. Found: C 32.69, H 6.95, N 15.22, Cl 28.95%; calculated for $C_{10}H_{25}Cl_3CoN_4$: C 32.76, H 6.87, N 15.29, Cl 29.01%.

Crystal data

$(C_5H_{13}N_2)[CoCl_3(C_5H_{12}N_2)]$
$M_r = 366.62$
Triclinic
$P\bar{1}$
$a = 8.956\,(2)$ Å
$b = 11.760\,(3)$ Å
$c = 8.781\,(2)$ Å
$\alpha = 103.20\,(3)^\circ$
$\beta = 108.60\,(4)^\circ$
$\gamma = 91.40\,(3)^\circ$
$V = 848.6\,(3)$ Å^3
$Z = 2$
$D_x = 1.435$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71070$ Å
Cell parameters from 25 reflections
$\theta = 14–20^\circ$
$\mu = 1.474$ mm^{-1}
$T = 293\,(2)$ K
Parallelepiped
$0.5 \times 0.3 \times 0.1$ mm
Light blue

Data collection

Philips PW1100/20 diffractometer
$\omega/2\theta$ scans
Absorption correction: semi-empirical *via* ψ scan (North *et al.*, 1968)
$T_{\min} = 0.69$, $T_{\max} = 0.86$
4102 measured reflections
4102 independent reflections

3096 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 28.01^\circ$
$h = -11 \rightarrow 11$
$k = -15 \rightarrow 15$
$l = 0 \rightarrow 11$
3 standard reflections every 60 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.097$
$S = 1.073$
4102 reflections
163 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0554P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = -0.001$
$\Delta\rho_{\max} = 0.679$ e Å^{-3}
$\Delta\rho_{\min} = -0.432$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Co—N1	2.055 (2)	Co—Cl1	2.2509 (11)
Co—Cl2	2.2438 (9)	Co—Cl3	2.2730 (9)
N1—Co—Cl2	105.53 (6)	N1—Co—Cl3	105.66 (6)
N1—Co—Cl1	108.83 (7)	Cl2—Co—Cl3	119.06 (4)
Cl2—Co—Cl1	111.30 (4)	Cl1—Co—Cl3	106.02 (4)
N1—C1—C2—N2	−56.7 (2)	N3—C6—C7—N4	−56.2 (3)
N2—C3—C4—N1	56.3 (2)	N4—C8—C9—N3	58.3 (3)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···N3	0.910 (3)	1.971 (3)	2.862 (3)	166.2 (2)
N3—H3N*B*···N2	0.900 (3)	1.977 (3)	2.862 (3)	167.4 (2)
N1—H1···N4^{i}	0.910 (3)	2.215 (3)	3.116 (3)	170.3 (2)
N3—H3N*A*···Cl3^{ii}	0.900 (3)	2.505 (2)	3.349 (2)	156.4 (2)
N3—H3N*A*···Cl1^{ii}	0.900 (3)	2.968 (3)	3.473 (3)	117.2 (2)
N4—H4···N1^{iii}	0.909 (3)	2.249 (3)	3.116 (3)	159.1 (2)

Symmetry codes: (i) $x, y, z - 1$; (ii) $2 - x, 1 - y, 1 - z$; (iii) $x, y, 1 + z$.

The H atoms were fixed riding at geometrical positions, with N—H 0.91 (N3—H 0.90), methylene C—H 0.97 and methyl C—H 0.96 Å, and with U fixed at $1.2U_{eq}$ of the N or C atom to which they were bonded, or at $1.5U_{eq}$ for the C5 and C10 methyl H atoms.

Data collection: Philips PW1100/20 software. Cell refinement: Pavia University Philips PW1100/20 software. Data reduction: *RIFLUP*80 (Biagini Cingi *et al.*, 1980). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1379). Services for accessing these data are described at the back of the journal.

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[*N*-Salicyl-*N*,*N*-bis(salicylidenenitriloethyl)amino]iron(III) acetonitrile solvate†

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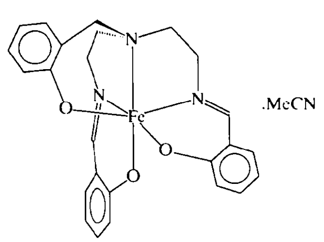
Abstract

The title complex, $[Fe(C_{25}H_{24}N_3O_3)]\cdot CH_3CN$, contains a tripodal ligand incorporating one phenolic group and two Schiff base moieties derived from salicylaldehyde and diethylenetriamine. The Fe^{III} centre is six-coordinate within an octahedral configuration. The bridgehead N atom lies 2.273 (2) Å from the metal; this is significantly longer than the other two Fe—N bond lengths of 2.122 (3) and 2.193 (2) Å.

Comment

Tripodal metal complexes have been widely investigated due to their special relevance to fields such as modelling metalloproteins (Sanyal *et al.*, 1995) and catalyzing the hydrolysis of activated phosphate esters (Young *et al.*, 1995), as well as their unique structural nature (Kichner *et al.*, 1987). We have previously reported several such compounds and studied their structural features (Gou *et al.*, 1991, 1992, 1993; Gong *et al.*, 1998). We have now directed our attention towards the preparation of novel tripodal ligands using diethylenetriamines as the amine precursors in order to synthesize new pendant-arm macrocyclic complexes *via* a sodium-template method (Gou & Fenton, 1994) and we report here an iron(III) complex, (I), of a new asymmetric tripodal ligand.



(I)

In the title complex, the Fe^{III} centre is coordinated by six donor atoms, namely three phenolic O atoms, two N atoms from C=N moieties and the bridgehead N atom. The differing lengths of the three pendant arms of the ligand result in a geometry about the metal which is significantly distorted from octahedral. Thus, the O2—Fe1—N1 angle is bent from linearity to 158.88 (9)°. The bond lengths Fe1—N2 and Fe1—N3 [2.122 (3) and 2.193 (2) Å, respectively] are clearly shorter than that between Fe1 and the bridgehead N1 atom [2.273 (2) Å]. The three Fe—O bond lengths [Fe1—O1 1.963 (2), Fe1—O2 1.924 (2) and Fe3—O3 1.900 (2) Å] are non-equivalent, presumably also as a consequence of the different pendant-arm lengths, but within the normal range.

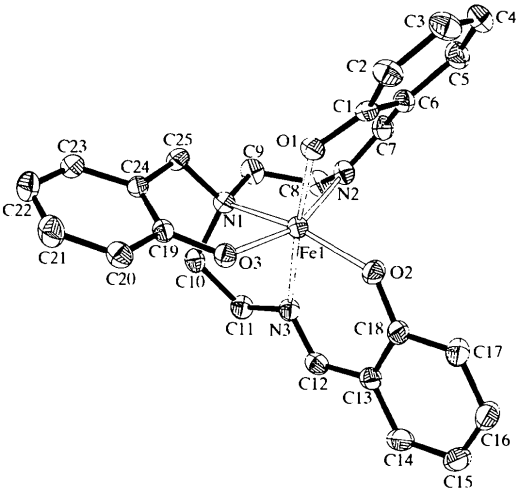


Fig. 1. The structure of the cation complex with the atom-numbering scheme. Displacement ellipsoids are shown at the 30% probability level, and H atoms and the acetonitrile solvate molecule have been omitted for clarity.

The structure of the title complex differs from that of a symmetric tripodal ligand derived from the condensation product of 2,2′,2″-triaminoethylamine and salicylaldehyde (Cook *et al.*, 1976), where the Fe centre has

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† Alternative name: {2,2′-[(salicylnitrilo)bis(ethylenenitrilomethylidene)]diphenolato-*N*,*N*′,*N*″,*O*,*O*′,*O*″}iron(III) acetonitrile solvate.

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