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Tris{2-[(4-chlorophenyl)iminomethyl]-pyrrolato-*N*,*N*′}cobalt(III)

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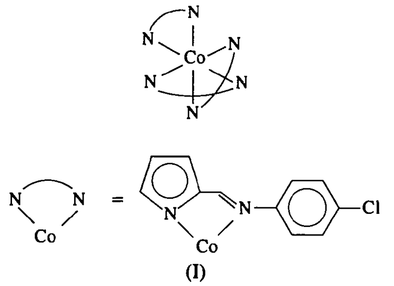
Abstract

The title compound, $[Co(C_{11}H_8ClN_2)_3]$, consists of monomeric molecules in which the central CoN_6 unit has slightly distorted octahedral geometry, with bond lengths ranging from 1.900 (8) to 1.991 (7) Å. In the complex, the ligands adopt positions such that the complex can be described as the meridional isomer.

Comment

Metal complexes with Schiff base ligands containing weak acid groups can be satisfactorily synthesized following an electrochemical procedure similar to that described by Oldham & Tuck (1982). Starting from metallic cobalt as the anode of an electrochemical cell containing the Schiff base dissolved in acetonitrile, the title compound, (I), was obtained.



(I)

The Co atom is coordinated to three bidentate anionic ligands; the environment around the metal atom can be described as having slightly distorted octahedral geometry, with the angles defined by two *trans*-N atoms close to the expected value of 180° [177.8 (3), 174.7 (3) and 174.8 (3)°] and the angles determined by the Co and two *cis*-N atoms close to 90° (Fig. 1). The Co—N(pyrrole) bond distances [average 1.911 (8) Å] are shorter than the Co—N(azomethine) bond distances [average 1.965 (7) Å]. These values are similar to those of the corresponding bonds found in cobalt(III) complexes with similar ligands (Castro *et al.*, 1992). In the title complex, the ligands adopt positions such that the complex can be described as the meridional isomer. Three signals in the ^1H NMR spectrum at 7.73, 7.62 and 7.59 p.p.m., attributable to the three non-equivalent imine protons, indicate that this coordination is maintained in solution. In the complex, the chelate Co—N—C—C—N rings are almost planar, the maximum deviation being 0.053 Å, and the bond distances and angles of these rings are as expected; in particular, the average value of the C—N bond length [1.31 (2) Å] is typical for a C═N bond. Although the three ligands are very similar in terms of their bond distances and angles and the pyrrole and phenol rings are planar, the angles between the planes are 56.6 (4), 77.6 (4) and 56.6 (4) in ligands *A* (N11 and N12 donor atoms), *B* (N21 and N22 donor atoms) and *C* (N31 and N32 donor atoms), respectively. The angles between the planes of each pyrrole ring and the plane composed of atoms Co, N11, N12, N22 and N31 are 7.75 (4), 81.4 (4) and 82.5 (4)° for ligands *A*, *B* and *C*, respectively; the pyrrole ring of ligand *A* is thus almost coplanar with this coordination plane, while the pyrrole rings of the *B* and *C* ligands are almost perpendicular to it. It is interesting to note that only the *A* ligand can influence the *fac*/*mer* isomerization (by exchange of N-atom positions).

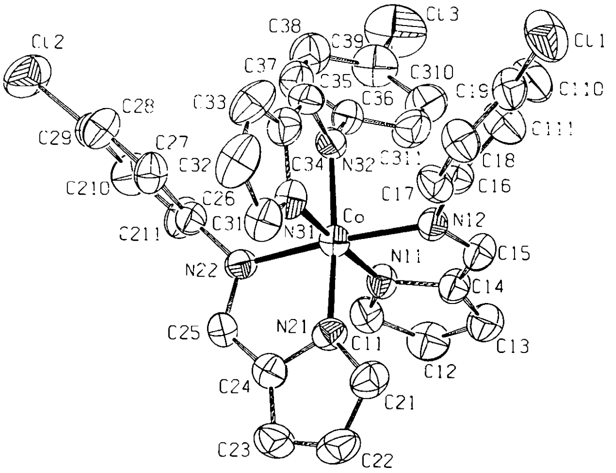


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

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Experimental

The electrochemical oxidation of a cobalt anode in an acetonitrile solution (50 ml) containing the Schiff base (0.46 g) and tetramethylammonium perchlorate (*ca.* 10 mg) for 2 h at 24 V and 20 mA, resulted in the loss of 46.8 mg of cobalt from the anode and formation of a deep-red solution. After filtration to remove any solid impurities, a well crystallized solid was obtained upon evaporation of the solvent at room temperature. The compound is diamagnetic, this being consistent with a low-spin d^6 octahedral complex.

Crystal data

$[Co(C_{11}H_8ClN_2)_3]$
$M_r = 669.89$
Monoclinic
$P2_1/n$
$a = 9.166\ (2)$ Å
$b = 35.341\ (4)$ Å
$c = 10.101\ (3)$ Å
$\beta = 110.65\ (1)°$
$V = 3061.8\ (7)$ Å^3
$Z = 4$
$D_x = 1.453$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 4.9–10.0°$
$\mu = 0.86$ mm^{-1}
$T = 293$ K
Prism
0.65 × 0.25 × 0.20 mm
Amber

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
$T_{min} = 0.37$, $T_{max} = 0.85$
8649 measured reflections
7727 independent reflections

2103 observed reflections $[I > 3\sigma(I)]$
$R_{int} = 0.033$
$\theta_{max} = 29°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 48$
$l = -13 \rightarrow 13$
2 standard reflections frequency: 120 min intensity decay: none

Refinement

Refinement on F
$R = 0.052$
$wR = 0.059$
$S = 2.92$
2103 reflections
389 parameters
H atoms: see below
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}
Extinction correction: Zachariasen (1963)
Extinction coefficient: 2.085×10^{-8}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Co	0.0887 (1)	0.11226 (3)	0.1201 (1)	0.0320 (5)
Cl1	0.0450 (4)	0.26468 (8)	−0.3917 (3)	0.089 (2)
Cl2	0.8431 (3)	0.02892 (9)	0.5312 (3)	0.074 (2)
Cl3	0.5604 (4)	0.2057 (1)	0.7830 (3)	0.097 (2)
N11	0.0041 (8)	0.1218 (2)	0.2663 (7)	0.035 (3)
N12	−0.0217 (8)	0.1603 (2)	0.0421 (7)	0.038 (4)
N21	−0.0899 (8)	0.0814 (2)	0.0305 (7)	0.036 (4)
N22	0.1808 (7)	0.0648 (2)	0.2031 (7)	0.035 (4)
N31	0.1697 (8)	0.1048 (2)	−0.0270 (7)	0.038 (4)
N32	0.2840 (8)	0.1408 (2)	0.2063 (7)	0.038 (4)
C11	−0.002 (1)	0.1052 (3)	0.3811 (9)	0.044 (5)
C12	−0.107 (1)	0.1249 (3)	0.4295 (9)	0.056 (5)
C13	−0.168 (1)	0.1552 (3)	0.339 (1)	0.053 (5)
C14	−0.096 (1)	0.1518 (3)	0.2355 (9)	0.041 (4)
C15	−0.105 (1)	0.1730 (3)	0.1158 (9)	0.046 (5)
C16	0.003 (1)	0.1846 (3)	−0.0597 (9)	0.042 (4)
C17	−0.020 (1)	0.1722 (3)	−0.1960 (9)	0.049 (5)
C18	−0.006 (1)	0.1963 (3)	−0.297 (1)	0.057 (6)
C19	0.032 (1)	0.2332 (3)	−0.2621 (9)	0.053 (5)
C21	−0.238 (1)	0.0854 (3)	−0.0559 (9)	0.047 (5)
C22	−0.317 (1)	0.0513 (3)	−0.066 (1)	0.057 (6)
C23	−0.210 (1)	0.0251 (3)	0.016 (1)	0.059 (5)
C24	−0.069 (1)	0.0445 (3)	0.0791 (9)	0.042 (4)
C25	0.0844 (9)	0.0364 (2)	0.1713 (9)	0.039 (4)
C26	0.341 (1)	0.0568 (2)	0.2838 (9)	0.040 (5)
C27	0.448 (1)	0.0525 (3)	0.2160 (9)	0.041 (5)
C28	0.602 (1)	0.0445 (3)	0.2937 (9)	0.050 (6)
C29	0.649 (1)	0.0408 (3)	0.436 (1)	0.043 (5)
C31	0.130 (1)	0.0861 (3)	−0.149 (1)	0.051 (5)
C32	0.245 (1)	0.0923 (4)	−0.213 (1)	0.075 (7)
C33	0.353 (1)	0.1171 (4)	−0.124 (1)	0.071 (6)
C34	0.306 (1)	0.1243 (3)	−0.0084 (9)	0.048 (5)
C35	0.366 (1)	0.1429 (3)	0.1230 (9)	0.048 (5)
C36	0.3477 (9)	0.1566 (3)	0.3447 (8)	0.035 (4)
C37	0.494 (1)	0.1453 (3)	0.433 (1)	0.047 (5)
C38	0.562 (1)	0.1599 (3)	0.569 (1)	0.054 (6)
C39	0.477 (1)	0.1852 (3)	0.6158 (9)	0.054 (6)
C110	0.061 (1)	0.2468 (3)	−0.129 (1)	0.070 (6)
C111	0.049 (1)	0.2225 (3)	−0.027 (1)	0.061 (6)
C210	0.548 (1)	0.0456 (3)	0.508 (1)	0.054 (6)
C211	0.393 (1)	0.0540 (3)	0.4304 (9)	0.048 (5)
C310	0.330 (1)	0.1963 (3)	0.531 (1)	0.059 (6)
C311	0.266 (1)	0.1817 (3)	0.396 (1)	0.059 (6)

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

Co—N11	1.924 (8)	N21—C24	1.38 (1)
Co—N21	1.908 (7)	N22—C25	1.30 (2)
Co—N31	1.900 (8)	N31—C34	1.38 (1)
Co—N12	1.991 (7)	N32—C35	1.31 (1)
Co—N22	1.933 (7)	C14—C15	1.40 (1)
Co—N32	1.971 (6)	C24—C25	1.42 (2)
N11—C14	1.37 (1)	C34—C35	1.41 (1)
N12—C15	1.32 (1)		
N11—Co—N12	82.5 (3)	N11—Co—N21	87.3 (3)
N11—Co—N22	92.9 (3)	N11—Co—N31	177.8 (3)
N11—Co—N32	96.9 (3)	N12—Co—N21	93.9 (3)
N12—Co—N22	174.7 (3)	N12—Co—N31	95.3 (3)
N12—Co—N32	89.7 (3)	N21—Co—N22	83.1 (3)
N21—Co—N31	93.2 (3)	N21—Co—N32	174.8 (3)
N22—Co—N31	89.3 (3)	N22—Co—N32	93.6 (3)
N31—Co—N32	82.6 (3)		

The title structure was solved by Patterson and Fourier methods, and refined by a full-matrix least-squares procedure, with anisotropic displacement parameters for the non-H atoms. H atoms were placed in calculated positions.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *SDP-VAX* (Frenz, 1978). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1986). Program(s) used to refine structure: *SDP-VAX*. Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1109). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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7-Methyl-3-adeninium Trichloro(7-methyladenine-N^9)zinc(II) Hydrate

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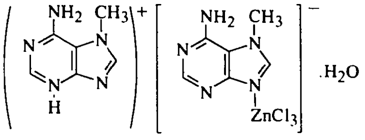
Abstract

The crystal structure of the title compound, ($C_6H_8N_5$)-[$ZnCl_3(C_6H_7N_5)$].H_2O, contains 7-methyladeninium cations protonated at the N3 atom and trichloro(7-methyladenine)zinc(II) anions, with the Zn atom tetrahedrally coordinated by the N9 atom and three chlorine ligands. Both species are present as hydrogen-bonded centrosymmetric dimers stacked alternately in columns in the crystal.

Comment

The title compound, (1), was isolated in the course of an ongoing program of research into the metal complexes of heterocyclic bases. The N7 site of adenine is favoured for coordination of zinc when it is available, *e.g.* dichlorobis(purine)zinc(II) (Laity & Taylor, 1995), trichloro(adeninium)zinc(II) (Taylor, Vilkins & McCall, 1989) and trichloro(purinium)zinc(II) (Sheldrick, 1982), although N1 can also be a binding site, *e.g.* trichloro(9-methyladeninium)zinc(II) (McCall & Taylor, 1975). In this work, the intention was to study the coordination of zinc to adenine when the favoured N7 position is blocked.



(1)

The structure of (1) consists of trichloro(7-methyladenine)zinc(II) anions and protonated 7-methyladenine cations (Fig. 1). Zinc is coordinated *via* the N9 atom and its approximate tetrahedral stereochemistry is completed by three chlorine ligands. These metal–complex anions occur in the structure as centrosymmetric hydrogen-bonded dimers, with an $\mathrm{N11—H\cdots N1^{i}}$ distance of 3.007 (3) Å [symmetry code: (i) $1-x$, $2-y$, $1-z$]. The Zn atom lies 0.382 (2) Å from the least-squares plane of the purine framework. The other 7-methyladenine moiety is protonated at the N3 position. This is a surprising result as N1 is the usual site of protonation in adenine and its derivatives, although N3 is protonated in 7-methyladenine dihydrochloride (Kistenmacher & Shigematsu, 1975). The internal angle at N3 shows an expansion of about 5° when compared with the corresponding angle in the coordinated base; this is characteristic of protonation of N in this ring (Table 2). In the crystal structure, these cations also occur as dimers, hydrogen bonded across another centre of symmetry, with an $\mathrm{N3'—H\cdots N9'^{ii}}$ distance of 2.790 (3) Å [symmetry code: (ii) $-x$, $2-y$, $1-z$]. It is possible that the occurrence of these dimers leads to the N3(H) tautomer being the stable form in the solid. Hydrogen bonds link the moieties in the structure, *e.g.* $\mathrm{N11'—H11'\cdots Cl1^{iii}}$ of length 3.492 (2) Å [symmetry code: (iii) $1-x$, $1-y$, $1-z$].

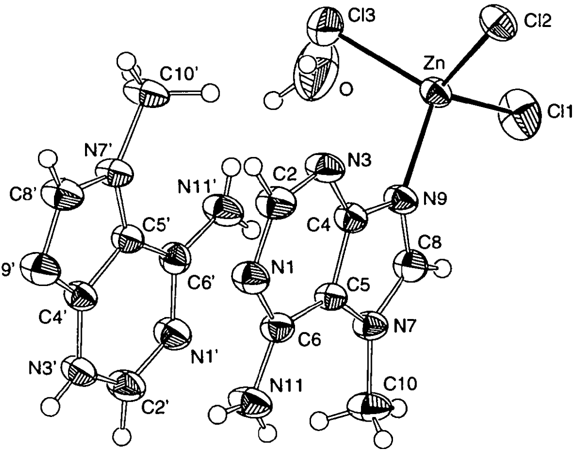


Fig. 1. A perspective drawing of the title compound showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are drawn as circles with arbitrary radii.

The dimeric cations and anions are alternately stacked in columns running parallel to the *a* axis (Fig. 2). The

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