

Aquachlorobis(1,10-phenanthroline)-
cobalt(II) chloride dimethylformamide
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Key indicators

Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$
Disorder in solvent or counterion
R factor = 0.048
wR factor = 0.133
Data-to-parameter ratio = 17.6For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The Co ion in the title compound, $[\text{CoCl}(\text{phen})_2(\text{H}_2\text{O})]\text{Cl}\cdot\text{DMF}$ [phen = 1,10-phenanthroline ($\text{C}_{12}\text{H}_8\text{N}_2$) and DMF is dimethylformamide ($\text{C}_3\text{H}_7\text{NO}$)], exists in a distorted octahedral coordination environment. The cations and anions are linked by $\text{O}-\text{H}\cdots\text{Cl}$ hydrogen-bond interactions across a center of inversion, forming a dimeric entity. A supramolecular network structure is consolidated by $\pi-\pi$ stacking interactions and hydrogen bonds.

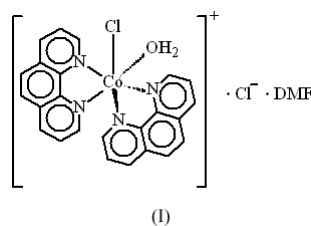
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Comment

The crystal structures of compounds containing the $[\text{Co}(\text{phen})_2]^{2+}$ fragment have been reported (Russell *et al.*, 2001; Hazell *et al.*, 1997; McAuliffe *et al.*, 1992). The compound aquachlorobis(phen)cobalt thiourea chloride dihydrate (Kon *et al.*, 1982) has also been reported and contains the above $[\text{Co}(\text{phen})_2\text{Co}]^{2+}$ motif, together with disordered thiourea and water molecules. In the present study, the reaction of cobalt dichloride hexahydrate, disodium benzene-1,4-dioxyacetate and 1,2-phenanthroline (phen) in DMF–water occasionally gave the title Co^{II} complex, $[\text{CoCl}(\text{phen})_2(\text{H}_2\text{O})]\text{Cl}\cdot\text{DMF}$, (I).



As shown in Fig. 1, the asymmetric unit of (I) is composed of a Co^{II} cation, *viz.* $[\text{CoCl}(\text{phen})_2(\text{H}_2\text{O})]^+$, a Cl anion and one DMF molecule, the DMF being disordered. Four N atoms of two phen ligands, one Cl anion and one water molecule are

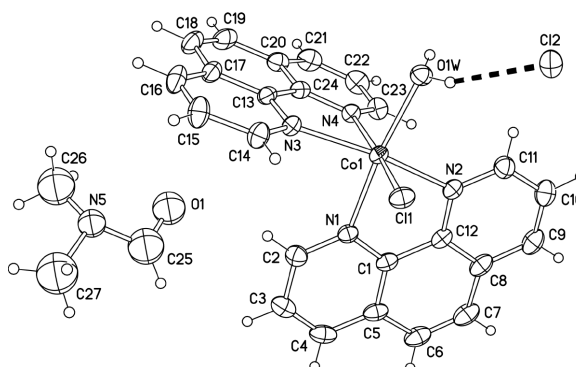


Figure 1

Plot of (I) with ellipsoids at the 30% probability level. Only one disorder component of DMF is shown.

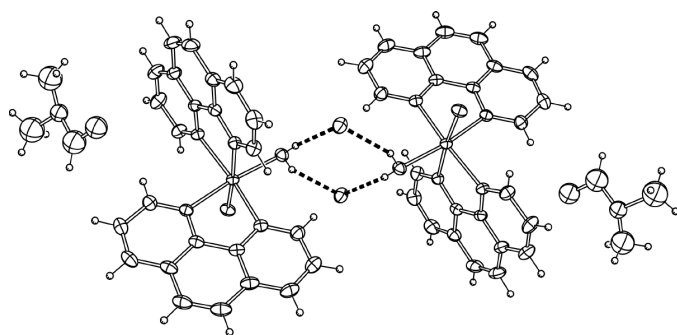


Figure 2
The dimer of (I), with hydrogen bonds shown as dashed lines.

coordinated to the Co^{II} ion, in a distorted octahedral arrangement. Atoms N4 and Cl1 occupy the apical sites [Co–N4 = 2.192 (2) Å and Co–Cl1 = 2.391 (1) Å; N4–Co–Cl1 = 172.20 (6)°]. The Co–N distances, ranging from 2.141 (2) to 2.192 (2) (1) Å, are somewhat larger than the Co–O1W distance of 2.087 (2) Å. The cations and anions are linked by pairs of O–H...Cl hydrogen bonds (Fig. 2 and Table 2) to form a centrosymmetric dimer. The closest Co...Co distance is 7.966 Å. The phen ligands are nearly perpendicular to each other [dihedral angle = 87.6 (5)°]. There are π – π stacking interactions between adjacent phen ligands of 3.781 and 3.526 Å. These π – π stacking interactions and hydrogen bonds lead to a supramolecular network structure.

Experimental

Cobalt dichloride hexahydrate (4.76 g, 20 mmol), phen (3.98 g, 20 mmol) and disodium benzene-1,4-dioxyacetate (5.40 g, 20 mmol) were dissolved in a 1:1 DMF–water solution (25 ml). Pink crystals separated from the filtered solution at room temperature in a few days. Analysis calculated for $\text{C}_{27}\text{H}_{25}\text{Cl}_2\text{CoN}_5\text{O}_2$: C 55.78, H 4.33, N 12.05%; found: C 55.97, H 4.49, N 11.89%.

Crystal data

[CoCl(C ₁₂ H ₈ N ₂) ₂ (H ₂ O)]Cl·C ₃ H ₇ NO	$Z = 2$
$M_r = 581.35$	$D_x = 1.491 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 9.632$ (4) Å	Cell parameters from 5907 reflections
$b = 11.612$ (4) Å	$\theta = 3.1$ – 27.5°
$c = 12.777$ (5) Å	$\mu = 0.91 \text{ mm}^{-1}$
$\alpha = 66.97$ (3)°	$T = 293$ (2) K
$\beta = 85.63$ (3)°	Prism, pink
$\gamma = 79.87$ (3)°	$0.36 \times 0.24 \times 0.19 \text{ mm}$
$V = 1294.6$ (9) Å ³	

Data collection

Rigaku R-Axis RAPID diffractometer	5881 independent reflections
ω scans	4687 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	$R_{\text{int}} = 0.032$
$T_{\text{min}} = 0.737$, $T_{\text{max}} = 0.847$	$\theta_{\text{max}} = 27.5^\circ$
9430 measured reflections	$h = -12 \rightarrow 12$
	$k = -14 \rightarrow 15$
	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.133$
 $S = 1.05$
 5881 reflections
 334 parameters

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0902P)^2]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.64 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.61 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Co1–Cl1	2.391 (1)	Co1–N2	2.169 (2)
Co1–N3	2.141 (2)	Co1–N4	2.192 (2)
Co1–N1	2.148 (2)	Co1–O1W	2.087 (2)
N1–Co1–Cl1	93.81 (6)	N3–Co1–N4	76.72 (8)
N1–Co1–N2	77.14 (8)	N4–Co1–Cl1	172.20 (6)
N1–Co1–N4	89.16 (8)	O1W–Co1–Cl1	91.10 (6)
N2–Co1–Cl1	95.74 (6)	O1W–Co1–N1	169.97 (8)
N2–Co1–N4	91.95 (8)	O1W–Co1–N2	93.68 (8)
N3–Co1–Cl1	95.94 (6)	O1W–Co1–N3	96.15 (8)
N3–Co1–N1	92.04 (8)	O1W–Co1–N4	87.10 (8)
N3–Co1–N2	164.56 (8)		

Table 2

Hydrogen-bonding geometry (Å, °).

D –H... A	D –H	H... A	D ... A	D –H... A
O1W–H1W1...Cl2	0.84 (1)	2.35 (2)	3.131 (2)	154 (3)
O1W–H1W2...Cl2 ⁱ	0.84 (1)	2.24 (1)	3.077 (2)	172 (3)

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

The DMF molecule is disordered, and the disorder was assumed to be a 50:50 disorder. For each half-molecule, the non-H atoms were restrained to be coplanar. Corresponding bond distances were restrained to be equal within 0.01 Å, and the displacement parameters of the atoms of the two components were set equal to each other. The displacement parameters were not restrained. H atoms on C and O atoms were placed in calculated positions, with C–H = 0.93 (aromatic) or 0.97 Å (aliphatic), O–H = 0.85 Å (water) and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{O})$ in the riding-model approximation.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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