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Dichlorobis(thiourea)cobalt(II) di(4,5-diazafluoren-9-one)

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.004 Å
R factor = 0.033
wR factor = 0.099
Data-to-parameter ratio = 15.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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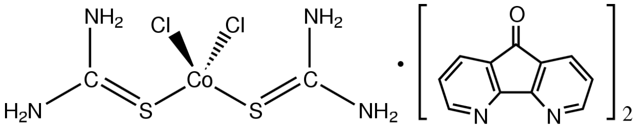
The title compound, $[CoCl_2(CH_4N_2S)_2].2C_{11}H_6N_2O$, consists of the tetrahedral cobalt(II) complex and free 4,5-diazafluoren-9-one (dafone). Dafone links to the complex through hydrogen bonding between N atoms. The carbonyl bridge in dafone distorts the bipyridine moiety. The longer N···N separations of 3.068 (3) and 3.064 (3) Å in dafone are considered to be the reason for the weaker chelating ability of dafone.

Comment

As 4,5-diazafluoren-9-one (dafone) is structurally similar to phenanthroline (phen), dafone has been used as a chelating reagent in the preparation of metal complexes. However, most of metal complexes involving dafone show that it is not a good chelating reagent (Menon & Rajasekharan, 1998). In the structure of the title compound, (I), dafone does not coordinate to the Co^{II} ion, but forms a 1:2 cocrystal with the cobalt–thiourea complex.



(I)

The molecular structure of (I) is illustrated in Fig. 1. Selected geometric parameters and hydrogen-bonding geometry are listed in Tables 1 and 2, respectively. The crystallographic asymmetric unit consists of one Co^{II} complex and two free dafone molecules. The Co^{II} atom has a tetrahedral coordination geometry. The coordination plane formed by Cl1, Cl2 and Co is approximately perpendicular to that formed by S1, S2 and Co, the dihedral angle being 88.02 (3)°. Dafone links to the Co^{II} complex through hydrogen bonding between N atoms. The bridge carbonyl in dafone distorts the bipyridine moiety. The larger bond angles of N6—C12—C13, N5—C13—C12, N8—C23—C24 and N7—C24—C23 (see Table 1) result in larger N···N separations of 3.068 (3) and 3.064 (3) Å in dafone, compared to the value of 2.724 Å in free phenanthroline (Nishigaki *et al.*, 1978). This is considered to reduce the overlap of nitrogen–metal orbitals and result in dafone having weaker chelating ability than phen.

Experimental

Dafone was prepared according to the reported methods (Henderson *et al.*, 1984). 0.060 g (0.25 mmol) $CoCl_2{\cdot}6H_2O$, 0.038 g (0.5 mmol) thiourea and 0.091 g (0.5 mmol) dafone were mixed in 10 ml ethanol. The blue solution was refluxed for 1 h, then 15 ml benzene was added to the solution. The mixed solution was filtered and the filtrate was allowed to stand at room temperature. Blue crystals were obtained after 4 d. C, H and N were analysed using a Carlo–Erba 1160 instrument. Analysis calculated for $C_{24}H_{20}Cl_2CoN_8O_2S_2$: C 44.59, H 3.12, N 17.33%; found: C 44.78, H 3.02, N 17.34%.

Crystal data

$[CoCl_2(CH_4N_2S)_2]\cdot 2C_{11}H_6N_2O$
$M_r = 646.45$
Triclinic, $P\overline{1}$
$a = 7.3902$ (11) Å
$b = 12.9763$ (12) Å
$c = 15.1615$ (18) Å
$\alpha = 89.111$ (10)°
$\beta = 78.107$ (11)°
$\gamma = 80.045$ (10)°
$V = 1401.0$ (3) Å^3
$Z = 2$
$D_x = 1.532$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 20 reflections
$\theta = 4.5$–10.2°
$\mu = 0.99$ mm^{-1}
$T = 298$ (2) K
Prism, blue
0.56 × 0.32 × 0.14 mm

Data collection

Rigaku AFC-7*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.69$, $T_{max} = 0.87$
5748 measured reflections
5495 independent reflections
3653 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$
$\theta_{max} = 26°$
$h = -9 \rightarrow 8$
$k = -15 \rightarrow 0$
$l = -18 \rightarrow 18$
3 standard reflections every 100 reflections intensity decay: 0.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.099$
$S = 1.03$
5495 reflections
352 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0459P)^2 + 0.2616P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.50$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—N2	1.309 (3)	C2—S2	1.717 (3)
C1—N1	1.313 (3)	S1—Co	2.3387 (9)
C1—S1	1.719 (3)	S2—Co	2.3147 (8)
C2—N3	1.312 (3)	Cl1—Co	2.2330 (10)
C2—N4	1.315 (3)	Cl2—Co	2.2692 (8)
N2—C1—N1	119.1 (2)	N7—C24—C23	126.7 (2)
N2—C1—S1	121.9 (2)	C1—S1—Co	109.43 (9)
N1—C1—S1	118.9 (2)	C2—S2—Co	108.26 (9)
N3—C2—N4	119.0 (2)	Cl1—Co—Cl2	111.42 (4)
N3—C2—S2	119.3 (2)	Cl1—Co—S2	108.24 (3)
N4—C2—S2	121.7 (2)	Cl2—Co—S2	113.81 (3)
N6—C12—C13	126.8 (2)	Cl1—Co—S1	112.26 (4)
N5—C13—C12	126.6 (2)	Cl2—Co—S1	112.76 (3)
N8—C23—C24	126.8 (2)	S2—Co—S1	97.59 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···N5	0.86	2.06	2.894 (3)	164
N1—H2···S1^{i}	0.86	2.84	3.606 (3)	149
N2—H3···N6	0.86	2.14	2.993 (3)	171
N2—H4···Cl2	0.86	2.49	3.321 (2)	163
N3—H5···N7	0.86	2.10	2.944 (3)	167
N3—H6···Cl1^{ii}	0.86	2.73	3.502 (2)	150
N4—H7···N8	0.86	2.11	2.953 (3)	169
N4—H8···Cl2	0.86	2.51	3.345 (2)	165

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

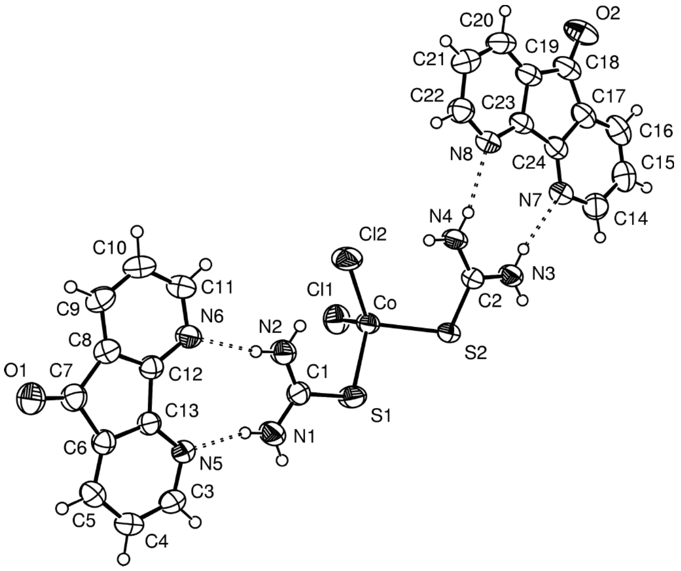


Figure 1
View of (I) (50% probability displacement ellipsoids).

H atoms were placed in calculated positions, with N—H distances of 0.86 Å and C—H distances of of 0.93 Å. All H atoms were included in the final cycles of least-squares refinement as riding on their parent non-H atoms.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1985); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*3 for Windows (Farrugia, 1997).

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