mer-Bis(2,3-dimethyl-5-oxo-1-phenyl-2,5-dihydro-1H-pyrazole-4-carbaldehyde 4,4-dimethylthio-semicarbazonato-κ³S,N,O)cobalt(III) tetrafluoro-borate

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Key indicators

Single-crystal X-ray study
$T = 291$ K
Mean σ(C–C) = 0.006 Å
Disorder in solvent or counterion
R factor = 0.043
wR factor = 0.109
Data-to-parameter ratio = 13.6

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

In the title compound, $[Co(C_{15}H_{18}N_5OS)_2]BF_4$, the cation has a distorted octahedral geometry around the Co^{III} atom, with two 2,3-dimethyl-5-oxo-1-phenyl-2,5-dihydro-1H-pyrazole-4-carbaldehyde 4,4-dimethylthiosemicarbazonate anions coordinated as meridional tridentate ligands through the thiolate S, the antipyrine O and the imine N atoms. A tetrafluoroborate anion balances the charge of the Co^{III} complex.

Comment

The continuing interest in the chemistry of thio-semicarbazones and their metal complexes is mainly due to their interesting coordination chemistry and significant biological activity (Doron *et al.*, 2004; Belicchi-Ferrari *et al.*, 2005). Similarly, antipyrine (2,3-dimethyl-1-phenylpyrazol-5-one) and its derivatives possess a wide variety of biological activity. We have reported the preparation and characterization through elemental analysis, physical and spectral studies, of coordination compounds of Fe^{III}, Co^{II} and Co^{III} with 4-formylantipyrine $N(4)$-methyl-, $N(4)$-dimethy- and 3-pi-peridylthiosemicarbazones (El-Sawaf *et al.*, 1998). In this paper, we report the crystal structure of the Co^{III} complex, (I), with 2,3-dimethyl-5-oxo-1-phenyl-2,5-dihydro-1H-pyrazole-4-carbaldehyde 4,4-dimethylthiosemicarbazone.

(I)
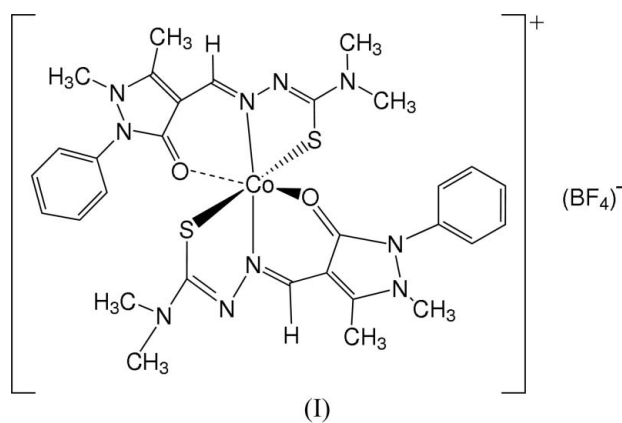
The structure of (I) is shown in Fig. 1 and selected bond lengths and angles are listed in Table 1. The geometry around the Co^{III} ion is distorted octahedral, with two thio-semicarbazonate ligands coordinated in a meridional fashion, acting as tridentate through the thiolate S, the antipyrine O and the imine N atoms. The phenyl rings in both ligands deviate from the mean plane of the remaining heavy atoms, by 70.6 (2)° for the C12–C17 ring and by 70.2 (2)° for the C27–C32 ring. The F atoms from the tetrafluoroborate anion are disordered over two positions, with occupancies of 0.53 (2) and 0.47 (2), respectively.

metal-organic papers

The cobalt complexes reported with the 2,3-dimethyl-5-oxo-1-phenyl-2,5-dihydro-1*H*-pyrazole-4-carbaldehyde 4,4-dimethylthiosemicarbazone ligand in our earlier paper (El-Sawaf *et al.*, 1998) were high-spin octahedral Co^{II} complexes. The present result indicates that, during crystalization, the Co^{II} salt was oxidized to the Co^{III} salt, as has been reported to happen with thiosemicarbazone complexes of Co^{II} with poorly coordinating anions such as BF$_4^-$ (Maichle *et al.*, 1995).

Experimental

The title compound was obtained as reported elsewhere (El-Sawaf *et al.*, 1998).

Crystal data

[Co(C$_{15}$H$_{18}$N$_5$OS)$_2$]BF$_4$
$M_r = 778.55$
Monoclinic, $P2_1/c$
$a = 15.1182$ (10) Å
$b = 14.0027$ (9) Å
$c = 17.3551$ (12) Å
$\beta = 107.173$ (2)°
$V = 3510.2$ (4) Å^3
$Z = 4$

$D_x = 1.473$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5009 reflections
$\theta = 2.4–31.3°$
$\mu = 0.67$ mm^{-1}
$T = 291$ (2) K
Prism, black
$0.36 \times 0.22 \times 0.18$ mm

Data collection

Bruker SMART APEX AXS CCD area-detector diffractometer
ω scans
Absorption correction: none
28284 measured reflections
6188 independent reflections

4433 reflections with $I > 2\sigma(I)$
$R_{int} = 0.050$
$\theta_{max} = 25.0°$
$h = -17 \rightarrow 17$
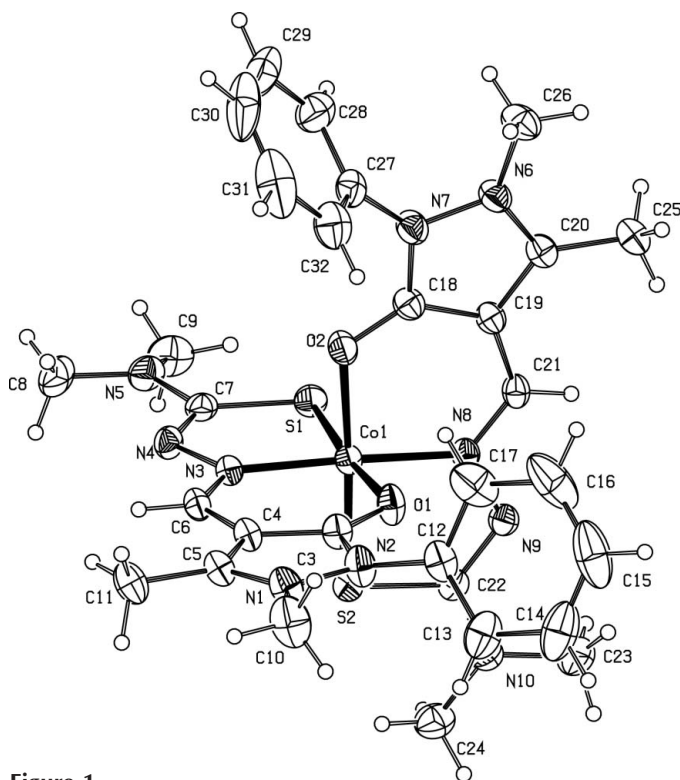$k = -16 \rightarrow 16$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.109$
$S = 0.94$
6188 reflections
456 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.06P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.027$
$\Delta\rho_{max} = 0.46$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}

Figure 1
View of the molecule of (I). Displacement ellipsoids are drawn at the 50% probability level.

H atoms were located in a difference Fourier map and refined as riding [C—H = 0.93 or 0.96 Å; $U_{iso}(H) = 1.2U_{eq}(C)$].

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

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Table 1
Selected geometric parameters (Å, °).

Co1—N8	1.921 (2)	O2—C18	1.259 (3)
Co1—N3	1.922 (2)	N3—C6	1.288 (3)
Co1—O1	1.9938 (19)	N3—N4	1.395 (3)
Co1—O2	1.995 (2)	N4—C7	1.299 (4)
Co1—S2	2.1934 (8)	N5—C7	1.365 (4)
Co1—S1	2.1937 (8)	N8—C21	1.291 (3)
S1—C7	1.750 (3)	N8—N9	1.391 (3)
S2—C22	1.746 (3)	N9—C22	1.306 (3)
O1—C3	1.258 (3)	N10—C22	1.357 (4)
N8—Co1—N3	174.52 (10)	N3—Co1—S1	86.43 (7)
N8—Co1—O1	86.20 (8)	O1—Co1—S1	174.77 (6)
N3—Co1—O1	97.44 (9)	O2—Co1—S1	91.05 (6)
N8—Co1—O2	97.60 (9)	S2—Co1—S1	92.17 (3)
N3—Co1—O2	86.80 (9)	C7—S1—Co1	95.47 (10)
O1—Co1—O2	85.66 (9)	C22—S2—Co1	95.72 (10)
N8—Co1—S2	86.36 (7)	C3—O1—Co1	117.76 (19)
N3—Co1—S2	89.43 (7)	C18—O2—Co1	118.03 (19)
O1—Co1—S2	91.40 (7)	O1—C3—N2	122.2 (3)
O2—Co1—S2	174.88 (6)	O1—C3—C4	131.1 (3)
N8—Co1—S1	90.21 (7)		