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Tris(3,5-dimethyl-1*H*-pyrazole-1-thiocarboxamidato-κ^2N^2,*N*)cobalt(III)

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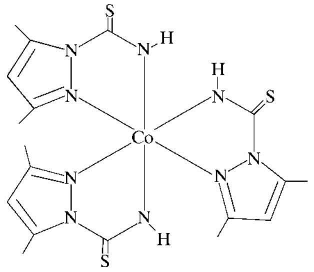
In the crystal structure of the title complex, $[Co(C_6H_8N_3S)_3]$, the Co^{III} atom is octahedrally coordinated by three monodeprotonated bidentate 3,5-dimethyl-1*H*-pyrazole-1-thiocarboxamide ligands with two thiocarboxamide N atoms in axial positions. The asymmetric unit contains two molecules (*A* and *B*) and these molecules are arranged in chains in an alternating fashion connected by N—H···S interactions.

Comment

The complexing properties of pyrazole (py) derivatives have been the subject of extensive research (Trofimenko, 1972, 1993). Much of this interest stems from the biological activity of these molecules, which has been attributed to their chelating properties. This has stimulated research into the mode of coordination and the factors which influence it, especially with regard to the ambidentate nature of some of these molecules. Also as part of these investigations, the supramolecular structures of complexes containing pyrazole moieties are being studied. The rigidity of the pyrazole ring and the possibility of attaching different groups to the base fragment have made these molecules a convenient choice in attempts to control the manner of association of molecules in the solid state. Thus, pyrazole-based ligands containing hydrogen-bond donor and acceptor sites in the same molecule have been used to mediate intermolecular interactions (Smithson *et al.*, 2003), and particularly to influence the metal–metal distance (Meyer *et al.*, 1998). As part of our research on the coordination chemistry of pyrazole-derived ligands (Jaćimović *et al.*, 1999; Tomić *et al.*, 2000), the present paper reports the crystal structure of a new cobalt(III) complex, (I), of the ligand 3,5-dimethyl-1*H*-pyrazole-1-thiocarboxamide. Recently, the crystal structures of the Co^{III} (Barik *et al.*, 2000), (II), and Ni^{II} (Barik & Bandyopadhyay, 1999) complexes of the closely related ligand 1-(*N*-ethylthiocarbamoyl)-3,5-dimethylpyrazole have been reported. In the Co^{III} complex (II), three molecules of the ligand coordinate to the metal atom in a bidentate manner, giving an octahedral coordination and a *trans* arrangement of the ligands. In the square-planar Ni^{II} complex, the ligands are *cis* coordinated *via* the ring N and thione S atoms. Thus, the ambidentate nature of the ligand has been confirmed and the mode of binding has been explained in terms of the HSAB model (Pearson, 1963, 1987). The difference between the ligand in (I) and (II) is to do with the different atom attached to the coordinated thiocarboxamide N atom; in (I), the attached atom is an H atom, while in (II) it is the C atom of an ethyl group. The aim of the present work is to investigate how a variation in the type and disposition of hydrogen-bond donors/acceptors in novel complex (I) and its counterpart (II) influence the packing of the molecules, when the ligands otherwise have similar structural characteristics and overall shape.



(I)

The asymmetric unit of (I) consists of two complex molecules. Three monodeprotonated molecules of the thiocarboxamide (thiocarb) ligand coordinate to the Co^{III} atom through the pyrazole-ring N atoms (N3, N6 and N9) and the thiocarboxamide N atoms (N1, N4 and N7). The coordination can be best described as distorted octahedral with thiocarboxamide atoms N1 and N4 in the axial (ax) positions (Fig. 1). Each type of N-donor atom, *viz*. amide or pyrazole, is in a meridional arrangement. The two independent molecules (*A* and *B*) have similar bond distances and angles around the metal atom, indicating a similar overall shape of the two coordination polyhedra (Table 1). Comparison of the bond distances (Å) in the coordination polyhedron of compound (I) (Table 1) with the distances observed in (II) [Co—N$_{ax}$ = 1.933 (2) and 1.933 (2) Å, and Co—N$_{eq}$ = 1.922 (2)/1.937 (2) and 1.933 (2)/1.937 (2) Å] shows that in (I) the octahedron is more compressed along the axial bonds. In the equatorial plane of (I), the Co—N$_{py}$ bond which is *trans* to the Co—N$_{thiocarb}$ bond is significantly longer than the other bonding distances in the polyhedron. In (II), where all coordinated pyrazole and thiocarboxamide N atoms are in *trans* positions, the difference in the bond distances is not so pronounced. If we look at the orientation of the ethyl group in (II) and consider the possible alternative disposition of the amide and pyrazole N atoms in the coordination polyhedron, it is obvious

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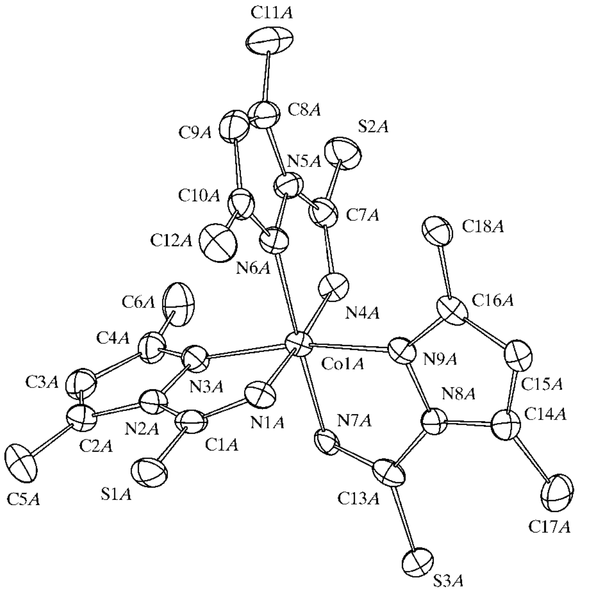

Figure 1
View of one of the molecules of the asymmetric unit of (I), showing the atom-numbering scheme.

that the ligands are oriented in such way as to avoid close contact of the ethyl groups. This suggests that while in (II) it is the steric effects which govern the configuration of the complex, in (I) there is no such influence and it could be supposed that the electronic properties of the ligand and the metal atom are the main factors in determining the mode of coordination. Following location of all the atoms of the cobalt complex, residual electron density was observed, suggesting the presence of solvent molecules. However, attempts to refine the positions of these molecules failed. To correct for the contribution of the solvent molecules, the SQUEEZE procedure of *PLATON* (van der Sluis & Spek, 1990) was used and the solvent-free model was used in the final refinement.

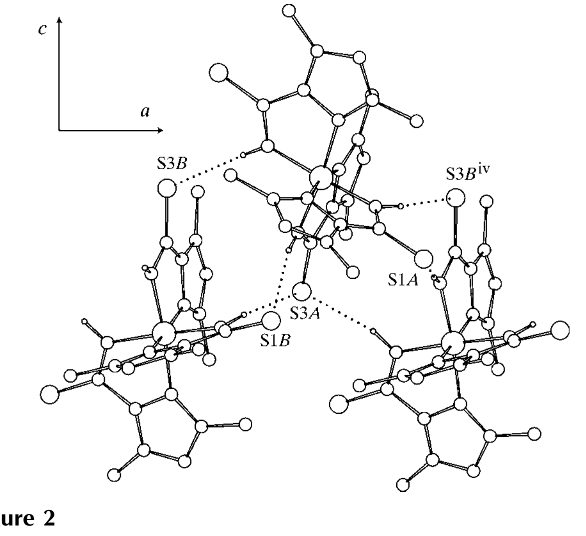

Figure 2
The association of molecules into a chain running along the *a* axis. H atoms not involved in hydrogen bonds have been omitted for clarity. [Symmetry code: (iv) $-x, y+\frac{1}{2}, -z+\frac{1}{2}$.]

The presence of both hydrogen-bond donors and acceptors makes the title molecule potentially suitable for the formation of an extended three-dimensional structure. However, due to omission of the solvent molecules it was not possible to analyse the hydrogen-bonding interactions fully. In (I), both independent molecules form the same pattern of intermolecular hydrogen bonds (Table 2). As was expected, the association of molecules is governed by N—H···S interactions and results in the formation of a chain consisting of alternating *A* and *B* molecules (Fig. 2). A weak C—H···S interaction [C11*B*—H30···S2A^{ii} = 2.82 Å and 154°; symmetry code: (ii) $x-1, y, z$] connects neighbouring chains. To gain additional insight into the factors important for the supramolecular arrangement of this kind of complex, we will compare the present structure with that of compound (II). In (II), all H atoms are bonded to pyrazole or to a methyl C atom. Such an arrangement of donor and acceptor atoms leads to the formation of an extended structure, which could be described as an association of molecules into sheets along the *bc* plane, and the connection of these sheets along the *ab* plane [C11—H16···S3^{v} = 2.84 Å and 154°; C3—H4···S2^{vi} = 2.84 Å and 143°; symmetry codes: (v) $x, -1+y, z$; (vi) $x, y, -1+z$]. Only H atoms bonded to pyrazole C atoms participate in these interactions. Fig. 3 shows part of the unit cell with the designated contacts leading to the association of molecules. With regard to the difference in the structure of the ligand in (I) and (II), it is interesting to note that, as a consequence of the stronger N—H···S bonds and the absence of sterically more demanding ethyl groups, in the title complex, molecules are packed more tightly. The distances between the closest Co atoms are 6.802 and 11.797 Å for (I) and (II), respectively.

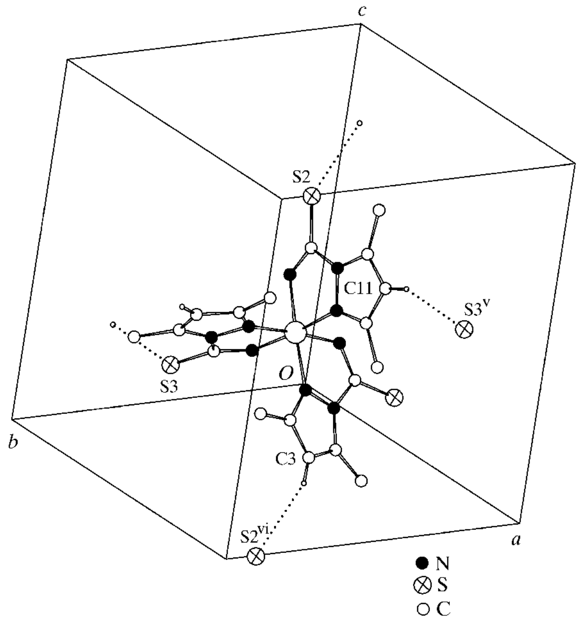

Figure 3
Part of the crystal structure of (I), showing the intermolecular contacts which govern the association of molecules. Ethyl groups and H atoms not involved in hydrogen bonds have been omitted for clarity. [Symmetry codes: (v) $x, -1+y, z$; (vi) $x, y, -1+z$.]

Experimental

The title complex was synthesized by mixing hot methanol solutions of $Co(OAc)_2 \cdot 4H_2O$ (0.124 g, 0.5 mmol) and 3,5-dimethylpyrazole-1-thiocarboxamide (0.16 g, 1 mmol). The reaction mixture, which had an intense red colour, was warmed and allowed to crystallize. After 10 h, the resulting solution was filtered and the pink crystals obtained were washed with methanol. Found/calculated (%): C 41.30/41.45, H 4.38/4.78, N 22.60/24.17.

Crystal data

$[Co(C_6H_8N_3S)_3]$
$M_r = 521.60$
Monoclinic, $P2_1/c$
$a = 8.750$ (2) Å
$b = 18.390$ (4) Å
$c = 30.485$ (6) Å
$\beta = 91.49$ (3)°
$V = 4903.8$ (18) Å^3
$Z = 8$

$D_x = 1.413$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 96 reflections
$\theta = 3.9$–25.4°
$\mu = 0.98$ mm^{-1}
$T = 293$ (2) K
Prism, pink
0.31 × 0.25 × 0.22 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
16 028 measured reflections
9487 independent reflections
6904 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.024$
$\theta_{\rm max} = 26.4°$
$h = -10 \rightarrow 10$
$k = -22 \rightarrow 19$
$l = -37 \rightarrow 37$

Refinement

Refinement on F^2
$R(F) = 0.051$
$wR(F^2) = 0.141$
$S = 1.08$
9487 reflections
571 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0693P)^2 + 3.7975P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.87$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.52$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co1*A*—N1*A*	1.894 (3)	Co1*B*—N1*B*	1.889 (3)
Co1*A*—N4*A*	1.904 (3)	Co1*B*—N4*B*	1.906 (3)
Co1*A*—N3*A*	1.917 (3)	Co1*B*—N7*B*	1.919 (3)
Co1*A*—N9*A*	1.923 (3)	Co1*B*—N3*B*	1.924 (3)
Co1*A*—N7*A*	1.938 (3)	Co1*B*—N9*B*	1.932 (3)
Co1*A*—N6*A*	1.951 (3)	Co1*B*—N6*B*	1.944 (3)
N1*A*—Co1*A*—N4*A*	176.13 (13)	N1*B*—Co1*B*—N4*B*	177.37 (12)
N1*A*—Co1*A*—N3*A*	81.40 (14)	N1*B*—Co1*B*—N7*B*	89.00 (13)
N4*A*—Co1*A*—N3*A*	97.19 (13)	N4*B*—Co1*B*—N7*B*	93.45 (13)
N1*A*—Co1*A*—N9*A*	90.87 (13)	N1*B*—Co1*B*—N3*B*	81.53 (13)
N4*A*—Co1*A*—N9*A*	91.06 (13)	N4*B*—Co1*B*—N3*B*	97.52 (13)
N3*A*—Co1*A*—N9*A*	168.27 (12)	N7*B*—Co1*B*—N3*B*	89.73 (12)
N1*A*—Co1*A*—N7*A*	89.85 (13)	N1*B*—Co1*B*—N9*B*	91.12 (13)
N4*A*—Co1*A*—N7*A*	93.74 (13)	N4*B*—Co1*B*—N9*B*	90.18 (13)
N3*A*—Co1*A*—N7*A*	89.49 (12)	N7*B*—Co1*B*—N9*B*	81.55 (12)
N9*A*—Co1*A*—N7*A*	81.64 (12)	N3*B*—Co1*B*—N9*B*	168.72 (12)
N1*A*—Co1*A*—N6*A*	96.10 (13)	N1*B*—Co1*B*—N6*B*	97.05 (12)
N4*A*—Co1*A*—N6*A*	80.29 (13)	N4*B*—Co1*B*—N6*B*	80.52 (12)
N3*A*—Co1*A*—N6*A*	90.84 (13)	N7*B*—Co1*B*—N6*B*	173.80 (13)
N9*A*—Co1*A*—N6*A*	98.79 (13)	N3*B*—Co1*B*—N6*B*	92.45 (12)
N7*A*—Co1*A*—N6*A*	174.02 (13)	N9*B*—Co1*B*—N6*B*	96.96 (12)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4*A*—H1···S3*B*	0.85	2.57	3.414 (3)	171
N7*A*—H3···S1*B*	0.86	2.80	3.644 (3)	168
N1*A*—H2···S3*B*$^{\rm i}$	0.96	2.48	3.424 (3)	169
N1*B*—H25···S3*A*	0.93	2.50	3.410 (3)	168
N7*B*—H26···S1*A*$^{\rm ii}$	0.87	2.83	3.695 (3)	174
N4*B*—H27···S3*A*$^{\rm ii}$	0.94	2.47	3.394 (3)	165
C11*B*—H30···S2*A*$^{\rm iii}$	0.96	2.82	3.706 (5)	154

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

H atoms attached to C atoms were included in idealized positions (C—H = 0.93 Å), while those attached to N atoms were located in a difference map. All H atoms were refined using a riding model. There are two solvent-accessible voids per unit cell, with the symmetry-unique void located at 0,0,0. *PLATON* (Spek, 2003) estimated the solvent-accessible region to occupy 406 Å^3 and account for 86 e per unit cell.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996), *PLUTON* (Spek, 1991), *PLATON* (Spek, 2003) and *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97 and *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1141). Services for accessing these data are described at the back of the journal.

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