

Bis(3,5-dimethyl-1-phenylpyrazole)bis(isothiocyanato)cobalt(II)

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Abstract. $[\text{Co}(\text{C}_{11}\text{H}_{12}\text{N}_2)_2(\text{NCS})_2]$, $\text{C}_{24}\text{H}_{24}\text{CoN}_6\text{S}_2$, monoclinic, $P2_1/c$, $a = 14.612$ (7), $b = 9.016$ (5), $c = 22.39$ (2) Å, $\beta = 118.85$ (5)°, $V = 2584$ (4) Å³, $Z = 4$, $D_m = 1.34$ (floatation), $D_x = 1.33$ Mg m⁻³. The final R was 0.067 for 1898 observations. The Co^{2+} is coordinated to the thiocyanate ions and the organic ligands in an irregular tetrahedral arrangement.

Introduction. Dark-blue needle crystals of the title compound were prepared by Dr A. C. Massabni and co-workers (Institute of Chemistry of Araraquara, UNESP). Chemical analysis showed a composition ratio of 1:2:2 for the Co^{II} ions, thiocyanate and organic ligand (Massabni, 1979). The structure determination was undertaken in order to study the coordination around Co^{2+} and the interaction between Co^{2+} and NCS^- . Cell dimensions were refined by a least-squares fit to the setting angles of 25 reflections on a CAD-4 automatic diffractometer. Intensity measurements were carried out up to 30° in θ with graphite-monochromated $\text{Mo } K\alpha$ radiation and a crystal in the form of a needle, $0.6 \times 0.4 \times 0.2$ mm. Lorentz and polarization corrections were applied but no absorption correction [$\mu(\text{Mo } K\alpha) = 0.87$ mm⁻¹] was made. Of the 3160 measured unique reflections, 1898 were considered observed [$F^2 \geq 3\sigma(F^2)$] and retained for use in the structure analysis* and refinement.

The structure was solved by direct methods, using the program *MULTAN* (Germain, Main & Woolfson, 1971) and difference Fourier calculations. Refinement was by a full-matrix least-squares method minimizing $\sum w(k|F_o| - |F_c|)^2$ where $w = [\sigma(F)^2 + 6 \times 10^{-4}(F_o)^2]^{-1}$ for observed and $w = 0$ for unobserved reflections, until all the atomic parameter shifts were smaller than each standard deviation. The final unweighted R factor omitting unobserved reflections was 0.067 and including them 0.069. Anisotropic temperature factors were assigned to all non-hydrogen atoms. Complex neutral-atom scattering factors were

* Lists of structure factors, anisotropic thermal parameters, hydrogen atom parameters and bond distances and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34764 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates for the non-hydrogen atoms ($\times 10^4$; for Co $\times 10^5$) with their e.s.d.'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
Co	25872 (8)	53310 (10)	47621 (5)
S(1)	2383 (2)	9493 (3)	3443 (1)
S(2)	3682 (2)	6342 (4)	7065 (1)
N(1)	2525 (5)	7109 (8)	4239 (3)
N(2)	3173 (5)	5890 (9)	5717 (3)
N(3)	1108 (4)	4592 (7)	4450 (3)
N(4)	3461 (4)	3835 (8)	4587 (3)
N(5)	891 (4)	3253 (7)	4648 (3)
N(6)	3326 (5)	3548 (7)	3943 (3)
C(1)	2460 (6)	8088 (10)	3913 (4)
C(2)	3372 (6)	6078 (11)	6278 (4)
C(3)	46 (7)	6619 (10)	3654 (5)
C(4)	170 (5)	5146 (10)	3995 (4)
C(5)	-151 (6)	2991 (10)	4316 (4)
C(6)	-613 (6)	4169 (9)	3900 (4)
C(7)	-625 (7)	1608 (11)	4459 (5)
C(8)	1713 (5)	2338 (9)	5168 (3)
C(9)	2121 (7)	2669 (10)	5844 (4)
C(10)	2842 (8)	1771 (12)	6332 (4)
C(11)	3164 (7)	497 (11)	6139 (5)
C(12)	2774 (6)	173 (10)	5468 (5)
C(13)	2042 (6)	1094 (10)	4964 (4)
C(14)	4789 (7)	3213 (12)	5789 (4)
C(15)	4348 (6)	3121 (10)	5016 (4)
C(16)	4748 (6)	2389 (11)	4644 (4)
C(17)	4071 (6)	2657 (11)	3956 (4)
C(18)	4121 (7)	2136 (13)	3335 (4)
C(19)	2437 (6)	4095 (10)	3346 (4)
C(20)	1455 (6)	3557 (10)	3184 (4)
C(21)	592 (6)	4128 (11)	2621 (4)
C(22)	722 (8)	5190 (12)	2229 (5)
C(23)	1687 (8)	5689 (12)	2384 (5)
C(24)	2568 (7)	5123 (11)	2949 (4)

used (*International Tables for X-ray Crystallography*, 1974). Final positional parameters for the H atoms were calculated assuming standard C—H lengths and the trigonal angle with the isotropic temperature factors assumed to be 6.0 Å². Final positional parameters for non-hydrogen atoms are shown in Table 1.

Discussion. The coordination around Co is distorted tetrahedral. The pyrazole rings are coordinated to the Co through atoms N(3) and N(4). The thiocyanate groups, which are linear within the standard deviations,

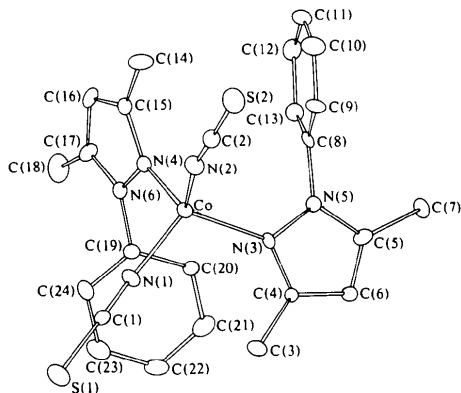


Fig. 1. Molecular structure and numbering scheme.

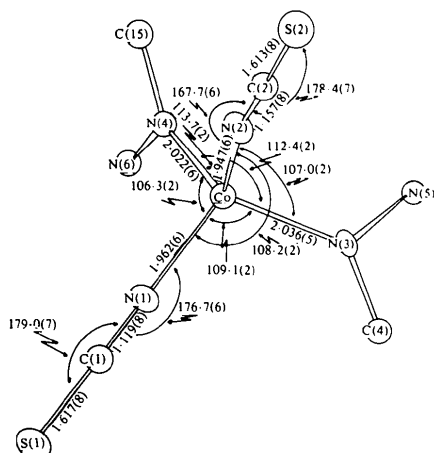


Fig. 2. Interatomic distances (Å) and angles (°) around the central ion, with their e.s.d.'s.

are coordinated to the Co through N(1) and N(2), completing a distorted tetrahedron. The coordination around the Co atom is shown in Fig. 1. All relevant distances and angles are shown in Fig. 2. The two rings

of each organic ligand are planar within one e.s.d. The mean value of the dihedral angle between phenyl and pyrazole rings is 72.95° . In the complex $[\text{Ag}(\text{C}_{11}\text{H}_{12}\text{N}_2)_3]\text{NO}_3$ (Francisco, Mascarenhas & Lechat, 1979) which contains the same ligand, the value for the dihedral angle is 57.4° . The difference is probably due to the shorter coordination radius of Co which brings the ligand molecules closer together than in the Ag complex causing greater steric hindrance. All other distances and angles agree within 3σ with the values found in tris(3,5-dimethyl-1-phenylpyrazole)silver(I) nitrate, and in bis(3,5-dimethyl-1-phenylpyrazole)-dinitratocopper(II) (Francisco, Lechat & Mascarenhas, 1979).

All computer calculations were performed using the *Enraf-Nonius Structure Determination Package*. The figure was drawn with the *ORTEP* program (Johnson, 1965).

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Potassium Dicyanoaurate(I)–2,2'-Bipyridyl

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Abstract. $\text{K}[\text{Au}(\text{CN})_2] \cdot \text{C}_{10}\text{H}_8\text{N}_2$, $M_r = 444.29$, monoclinic, $P2_1$, $a = 3.789(1)$, $b = 18.871(6)$, $c = 9.293(3)$ Å, $\beta = 101.73(2)^\circ$, $U = 650.6$ Å³, $Z = 2$, $D_x = 2.27$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 11.6$ mm⁻¹. $R = 5.4\%$ for 2140 unique reflexions. The structure consists

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of K^+ and linear $[\text{Au}(\text{CN})_2]^-$ ions and bipyridyl molecules which are not coordinated to Au.

Introduction. Dohie, Llewellyn, Wardlaw & Welch (1939) prepared single crystals of a compound which

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