

Acta Cryst. (1974). B30, 487

Structural Researches on Metal Complexes of Polydentate Ligands containing Carbonyl and α -Diimine Moieties. II.* Crystal Structure of Di- μ -thiocyanato(*S,N*)-diisothiocyanatobis-[2-(2'-pyridyl)-3-(*N*-2-picolylimino)-4-oxo-1,2,3,4-tetrahydroquinazoline]dicobalt(II)

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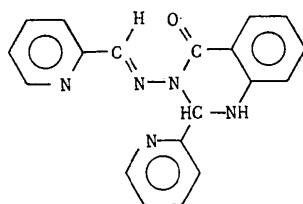
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(Received 27 July 1973; accepted 8 October 1973)

The crystals are monoclinic, space group $P2_1/c$, with unit-cell dimensions: $a = 10.58$ (1), $b = 15.66$ (1), $c = 27.58$ (1) Å, $\beta = 111.9$ (2)°, $Z = 4$. The structure has been refined to $R = 6.3$ for 1249 independent reflexions. The structure is dimeric with the presence of SCN groups in both bridging and terminal positions, as suggested by the infrared spectrum. The coordination around the two independent cobalt atoms is distorted octahedral and involves five nitrogen atoms, three from the organic ligand [Co(1)-N = 2.107, 2.153, 2.133; Co(2)-N = 2.141, 2.172, 2.171 Å] and two from SCN groups [Co(1)-N = 2.019, 2.036; Co(2)-N = 2.046, 2.116 Å], and a sulphur atom from a bridging SCN ion [Co(1)-S = 2.867; Co(2)-S = 2.787 Å].

Introduction

In connexion with our program of research on transition metal complexes of polydentate ligands containing carbonyl and α -diimine moieties, the crystal structure of the title compound has been determined, in which the tridentate ligand 2-(2'-pyridyl)-3-(*N*-2-picolylimino)-4-oxo-1,2,3,4-tetrahydroquinazoline (herein after PPQ)



is present. Results for $\text{Cu}(\text{PPQ})\text{Cl}_2$ have already been published (Mangia, Nardelli, Pelizzi & Pelizzi, 1974).

Experimental

2-Picolinaldehyde (60 m mole), anthranilhydrazide (30 m mole), cobalt (II) chloride hexahydrate (30 m mole) and sodium thiocyanate (60 m mole) in ethanol solution were refluxed for two hours; the solution was then allowed to stand at room-temperature until a red-brown crystalline product was formed. The compound was filtered off, washed with ether portions, and dried *in vacuo*.

Analysis for $\text{C}_{21}\text{H}_{15}\text{CoN}_7\text{OS}_2$: calculated, C = 50.0, Co = 11.7, H = 3.0, N = 19.4%; found, C = 49.6, Co = 11.8, H = 3.2, N = 18.9%.

Crystal data

$M = 513.3$; $a = 10.58 \pm 1$, $b = 15.66 \pm 1$, $c = 27.58 \pm 1$ Å, $\beta = 111.9 \pm 2^\circ$; $U = 4238$ Å³; $Z = 8$; $D_m = 1.60$ g

cm^{-3} , $D_c = 1.61$ g cm^{-3} ; $F(000) = 2156$; $\mu = 9.7$ cm^{-1} (Mo $K\alpha$); Mo $K\alpha$ radiation, $\lambda = 0.7107$ Å. Space group $P2_1/c$ (from systematic extinctions).

The unit-cell dimensions were first determined from Weissenberg photographs and then refined by least-squares calculations from the optimum angular settings of 11 reflexions measured on a single-crystal automated Siemens AED diffractometer.

A very small prismatic crystal, with a mean cross-sectional radius of 0.032 mm, was aligned with its c axis along the φ axis of the instrument and all the reflexions with $2\theta \leq 48^\circ$ were collected using Mo $K\alpha$ radiation and the ω - 2θ scanning technique. Of the 6595 independent reflexions recorded only 1249, corresponding to 19%, were coded as 'observed', having $I \geq 2\sigma(I)$, and considered in further calculations. The high percentage of unobserved reflexions is primarily due to the very small dimensions of the sample. All attempts to improve the quality of crystals by several recrystallizations were unsuccessful. The 5346 reflexions omitted from the calculations also included eight low-angle ($\theta < 3.0^\circ$) reflexions.

A standard reflexion was periodically measured after every 20 reflexions to check the stability of the instrument and the crystal.

Lorentz and polarization corrections were applied to the structure amplitudes as usual. Corrections for absorption effects were not considered necessary in view of the small size of the specimen and of the low μr value (0.03). The observed structure amplitudes were brought on to an absolute scale by comparison with the corresponding calculated values.

Structure determination and refinement

The structure was solved by the heavy-atom method. The unit cell contains eight formula units $\text{Co}(\text{C}_{19}\text{H}_{15}\text{N}_5\text{O})(\text{SCN})_2$ which must occupy two independent positions as required by the symmetry of the space group

* Part I: *Acta Cryst.* (1974), B30, 17-22.

Table 1. Final atomic fractional coordinates ($\times 10^4$) and thermal parameters (\AA^2), with estimated standard deviations in parenthesesAnisotropic thermal parameters are in the form $\exp[-\frac{1}{3}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co(1)	3819 (1)	1749 (1)	1076 (1)	2.43 (5)	2.06 (5)	2.11 (5)	0.32 (5)	0.74 (4)	0.20 (5)
Co(2)	8797 (1)	2045 (1)	2880 (0)	2.30 (5)	2.37 (6)	2.37 (5)	-0.14 (6)	0.92 (4)	-0.06 (5)
S(1)	6882 (3)	756 (2)	2752 (1)	4.4 (2)	4.0 (1)	3.1 (1)	0.6 (1)	1.1 (1)	0.5 (1)
S(2)	68 (3)	-107 (2)	745 (1)	3.7 (2)	3.7 (2)	9.2 (2)	0.0 (1)	2.6 (2)	-0.8 (2)
S(3)	5697 (2)	3150 (2)	1308 (1)	3.4 (1)	3.4 (1)	3.0 (1)	0.1 (1)	0.4 (1)	0.1 (1)
S(4)	12085 (3)	4348 (2)	3258 (1)	3.5 (1)	3.2 (1)	3.9 (1)	-0.7 (1)	1.7 (1)	-0.4 (1)
O(1)	3565 (6)	4172 (4)	187 (2)	5.3 (4)	3.1 (3)	3.4 (3)	-1.8 (3)	2.8 (3)	-1.3 (3)
O(2)	8988 (6)	409 (4)	4250 (2)	5.7 (4)	1.8 (3)	4.0 (3)	-0.5 (3)	3.1 (3)	-0.3 (3)
N(1)	2775 (7)	2458 (4)	1459 (2)	3.3 (4)	1.7 (3)	0.8 (3)	0.5 (3)	-0.6 (3)	-0.5 (3)
N(2)	2719 (7)	2704 (4)	516 (2)	3.1 (4)	2.0 (4)	1.0 (3)	-1.0 (3)	0.3 (3)	-0.5 (3)
N(3)	2930 (6)	2811 (4)	48 (2)	1.5 (3)	1.8 (4)	2.7 (3)	-0.3 (3)	1.0 (3)	0.8 (3)
N(4)	2696 (6)	2157 (4)	-745 (2)	2.2 (3)	3.0 (4)	1.3 (3)	0.3 (3)	-0.2 (3)	0.0 (3)
N(5)	4880 (7)	1375 (4)	587 (2)	4.8 (4)	2.9 (4)	1.5 (3)	0.5 (3)	1.5 (3)	1.5 (3)
N(6)	5023 (7)	1148 (4)	1734 (3)	2.0 (4)	2.7 (4)	2.7 (4)	-0.8 (3)	-0.8 (3)	0.5 (3)
N(7)	2333 (7)	848 (4)	801 (3)	4.5 (4)	0.9 (3)	3.3 (4)	-0.9 (3)	1.0 (3)	-0.8 (3)
N(8)	10089 (8)	1085 (4)	2758 (2)	6.1 (5)	1.1 (3)	1.9 (4)	-0.1 (3)	1.9 (4)	-0.1 (3)
N(9)	9795 (6)	1480 (4)	3648 (2)	1.3 (3)	3.1 (4)	1.5 (3)	-0.1 (3)	0.9 (3)	-0.1 (3)
N(10)	9542 (6)	1734 (4)	4075 (2)	2.9 (4)	2.5 (3)	1.7 (3)	-0.1 (3)	0.8 (3)	-0.4 (3)
N(11)	9654 (6)	2891 (4)	4636 (2)	2.0 (3)	1.9 (3)	1.0 (3)	-1.2 (3)	-0.7 (2)	-0.1 (3)
N(12)	7489 (7)	2734 (4)	3193 (2)	3.8 (4)	2.9 (4)	0.1 (3)	0.4 (3)	0.4 (3)	0.4 (3)
N(13)	7809 (7)	2393 (5)	2116 (3)	4.2 (4)	3.7 (4)	2.6 (4)	-1.4 (4)	1.5 (4)	0.1 (3)
N(14)	10208 (7)	3065 (5)	3045 (3)	3.4 (4)	5.3 (5)	4.7 (4)	0.0 (4)	1.9 (3)	-0.4 (4)
C(1)	2675 (9)	2266 (6)	1936 (3)	4.3 (6)	5.1 (6)	3.0 (5)	-1.2 (5)	2.3 (4)	-0.6 (5)
C(2)	1997 (10)	2793 (6)	2141 (4)	5.5 (6)	3.1 (5)	4.2 (5)	0.2 (5)	2.4 (5)	-0.1 (5)
C(3)	1309 (10)	3495 (6)	1886 (3)	6.4 (6)	3.3 (6)	1.7 (4)	0.6 (5)	2.5 (4)	1.3 (4)
C(4)	1352 (9)	3678 (6)	1397 (4)	3.9 (5)	2.8 (5)	3.6 (5)	1.0 (4)	1.7 (4)	0.5 (4)
C(5)	2144 (8)	3122 (5)	1209 (3)	3.4 (5)	2.0 (5)	1.8 (4)	0.1 (4)	0.9 (3)	-0.5 (4)
C(6)	2198 (8)	3318 (5)	694 (3)	2.4 (4)	2.3 (4)	2.7 (4)	0.1 (4)	1.5 (4)	-0.1 (4)
C(7)	3503 (7)	3536 (4)	-80 (3)	1.1 (4)	0.8 (4)	0.7 (3)	0.4 (3)	0.5 (3)	0.0 (3)
C(8)	3816 (8)	3502 (5)	-537 (3)	2.5 (4)	2.8 (5)	2.0 (4)	-0.1 (4)	0.9 (4)	1.0 (4)
C(9)	4519 (9)	4168 (6)	-655 (3)	2.5 (5)	2.8 (5)	3.4 (5)	-0.8 (4)	1.2 (4)	0.4 (4)
C(10)	4803 (9)	4140 (6)	-1123 (3)	2.8 (5)	3.3 (5)	3.9 (5)	0.3 (4)	1.5 (4)	0.6 (4)
C(11)	4388 (9)	3453 (6)	-1434 (3)	3.6 (5)	2.8 (5)	3.5 (5)	0.8 (4)	2.0 (4)	0.2 (4)
C(12)	3715 (7)	2773 (5)	-1324 (3)	1.9 (4)	1.5 (4)	1.1 (4)	1.1 (3)	0.3 (3)	0.6 (3)
C(13)	3434 (8)	2797 (5)	-877 (3)	2.3 (4)	2.8 (5)	2.5 (4)	0.8 (4)	1.5 (3)	0.1 (4)
C(14)	3049 (7)	1960 (4)	-198 (3)	1.1 (3)	0.3 (4)	1.3 (3)	0.3 (3)	0.4 (3)	0.2 (3)
C(15)	4449 (8)	1536 (5)	76 (3)	2.7 (4)	1.8 (5)	2.1 (4)	0.0 (4)	1.3 (4)	0.7 (3)
C(16)	5174 (8)	1220 (5)	-217 (3)	2.4 (4)	1.3 (4)	2.6 (4)	-0.4 (3)	1.0 (4)	0.3 (4)
C(17)	6323 (9)	746 (6)	45 (3)	3.3 (5)	2.5 (5)	3.3 (5)	1.5 (4)	1.4 (4)	0.5 (4)
C(18)	6812 (8)	590 (6)	549 (3)	2.9 (5)	2.3 (5)	2.6 (4)	0.8 (4)	1.0 (4)	0.2 (4)
C(19)	6100 (8)	959 (6)	831 (4)	1.5 (5)	4.6 (6)	4.1 (5)	0.5 (4)	1.5 (4)	1.0 (4)
C(20)	5775 (9)	979 (5)	2147 (3)	3.0 (5)	2.7 (5)	2.5 (4)	1.0 (4)	0.9 (4)	-0.1 (4)
C(21)	1355 (8)	468 (5)	747 (3)	1.5 (4)	2.3 (4)	2.7 (4)	1.1 (3)	0.6 (4)	0.1 (3)
C(22)	10255 (8)	905 (5)	2311 (3)	3.2 (5)	1.4 (4)	2.1 (4)	-1.2 (4)	1.0 (4)	-0.3 (4)
C(23)	11221 (9)	261 (5)	2293 (3)	2.2 (4)	2.9 (5)	2.9 (5)	-0.4 (4)	1.5 (4)	-0.7 (4)
C(24)	11955 (10)	-156 (6)	2729 (4)	4.1 (6)	4.0 (6)	5.6 (6)	0.1 (5)	2.6 (5)	0.2 (5)
C(25)	11642 (10)	12 (6)	3175 (4)	4.6 (6)	2.8 (5)	4.4 (6)	1.1 (4)	1.5 (5)	-0.3 (5)
C(26)	10761 (8)	613 (6)	3173 (3)	1.7 (4)	3.3 (5)	2.1 (4)	-0.2 (4)	0.3 (4)	-0.2 (4)
C(27)	10598 (8)	801 (5)	3666 (3)	1.8 (4)	1.9 (4)	3.1 (4)	-0.4 (4)	1.3 (4)	-1.4 (4)
C(28)	9089 (9)	1173 (6)	4347 (4)	3.3 (5)	2.9 (5)	4.5 (6)	0.3 (4)	1.8 (4)	1.1 (1)
C(29)	8692 (8)	1506 (5)	4769 (3)	1.7 (4)	1.5 (4)	2.1 (4)	0.3 (3)	0.9 (3)	-0.5 (3)
C(30)	8027 (8)	1050 (5)	5037 (3)	2.9 (5)	1.7 (4)	2.3 (4)	-0.7 (4)	1.0 (4)	1.0 (4)
C(31)	7839 (9)	1385 (5)	5463 (3)	3.7 (5)	2.4 (5)	2.7 (5)	-0.3 (4)	1.5 (4)	0.2 (4)
C(32)	8211 (9)	2221 (6)	5607 (3)	3.3 (5)	2.9 (5)	3.6 (5)	0.1 (4)	1.4 (4)	0.1 (4)
C(33)	8840 (9)	2727 (5)	5350 (3)	2.8 (4)	1.9 (5)	3.2 (5)	-0.5 (4)	1.0 (4)	-0.1 (4)
C(34)	9045 (8)	2388 (5)	4910 (3)	2.6 (4)	1.5 (4)	3.0 (4)	0.0 (4)	0.9 (4)	0.2 (4)
C(35)	9392 (7)	2648 (4)	4098 (3)	1.2 (4)	0.9 (4)	1.5 (4)	0.4 (3)	0.9 (3)	0.2 (3)
C(36)	7913 (8)	2932 (6)	3716 (3)	3.0 (5)	2.7 (5)	3.3 (4)	-0.4 (4)	1.9 (4)	0.3 (4)
C(37)	7074 (9)	3473 (6)	3884 (3)	3.9 (5)	3.3 (5)	3.5 (5)	1.1 (4)	1.9 (4)	0.3 (4)
C(38)	5927 (8)	3816 (5)	3522 (3)	2.5 (5)	3.1 (5)	1.4 (4)	0.0 (4)	0.9 (3)	0.8 (4)
C(39)	5480 (8)	3583 (5)	3006 (3)	2.9 (5)	3.0 (5)	1.7 (4)	-0.2 (4)	1.3 (4)	0.0 (4)
C(40)	6302 (7)	3055 (5)	2859 (3)	1.4 (4)	1.8 (4)	1.9 (4)	0.4 (3)	0.6 (3)	0.9 (3)
C(41)	6921 (9)	2706 (6)	1761 (3)	2.9 (5)	3.5 (5)	3.4 (5)	0.2 (4)	1.9 (4)	-0.1 (4)
C(42)	11006 (9)	3629 (5)	3137 (3)	3.4 (5)	2.4 (5)	2.4 (5)	0.6 (4)	1.7 (4)	0.0 (4)

$P2_1/c$. It was thought that the molecule could be a dimer with the presence of SCN groups both in bridging and in terminal position as suggested by the infrared spectrum.

From a three-dimensional Patterson map the positions of the two independent cobalt atoms were obtained and used as a starting point for a three-dimensional electron density synthesis which showed all the other non-hydrogen atoms. Refinement was carried out by block-diagonal least-squares techniques with anisotropic thermal parameters down to $R=6.3\%$. The quantity minimized was $\sum w(\Delta|F|)^2$ and unit weights were given to all reflexions. No attempt was made to locate the hydrogen atoms as the fraction of observed reflexions was too low.

The positional and thermal parameters with their estimated standard deviations are quoted in Table 1. The atomic scattering factors used throughout the calculations are those of Cromer & Mann (1968).*

* A table of observed and calculated structure factors has been deposited with the British Library Lending Division, as Supplementary Publication No. SUP 30246 (28 pp., 1 microfiche). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

All the calculations were carried out on the CDC 6600 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale using the programs of Immirzi (1967).

Results and discussion

As can be seen from its clinographic projection (Fig. 1) the structure is dimeric as there are two SCN⁻ anions acting as bridges between two cobalt atoms. The dimers are nearly centrosymmetrical.

Table 2 gives bond distances and angles. The two independent coordination polyhedra are practically equivalent from the chemical point of view, being both cobalt atoms surrounded by five nitrogen atoms, three from the PPQ organic ligand and two from the thiocyanate anions, and, more loosely, by a sulphur atom from a bridging SCN group, so that the two polyhedra can be described as distorted octahedra asymmetrically elongated along the Co-S direction.

The value of the room-temperature magnetic moment (4.99 B.M.) and the presence, in the visible spectrum of three bands at 550 [${}^4T_{1g}(P) \leftarrow {}^4T_{1g}$], 750 [${}^4A_{2g} \leftarrow {}^4T_{1g}$] and 1070 [${}^4T_{2g} \leftarrow {}^4T_{1g}$] nm are in agreement with the observed octahedral environment of Co(II).

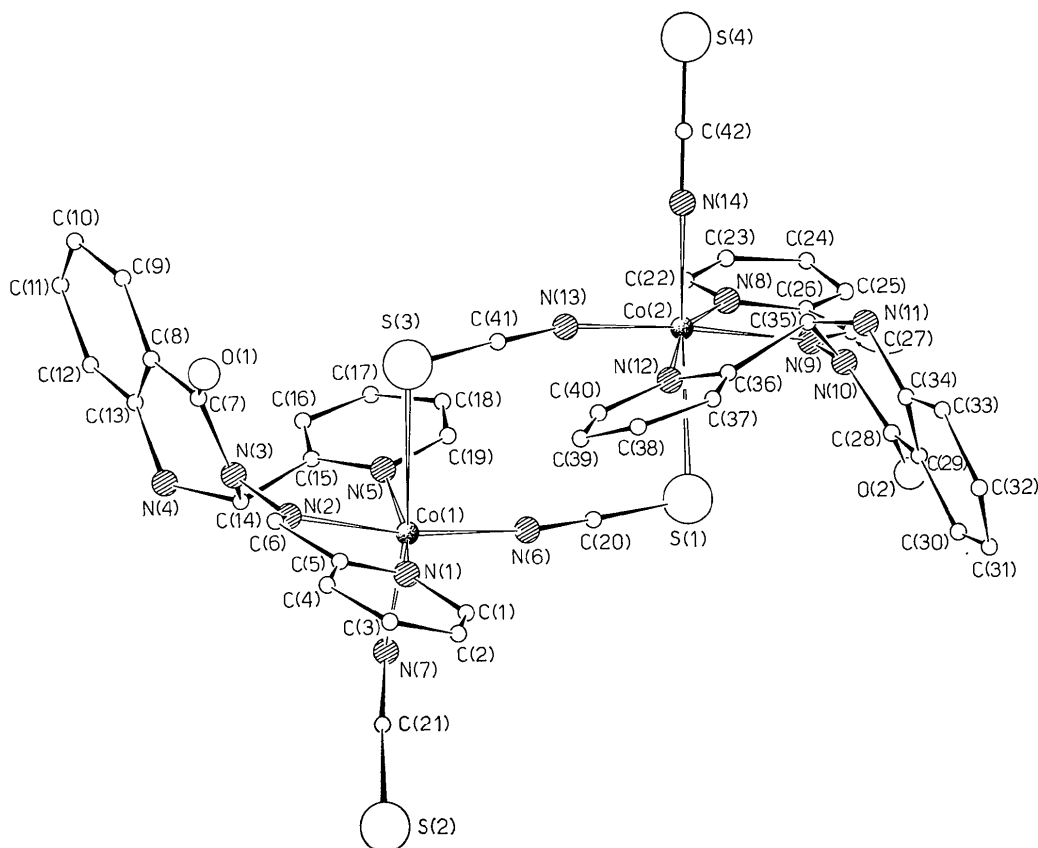


Fig.1 Clinographic projection of the structure

The values observed for all the Co-N distances are in the range 2.019–2.171 Å and are comparable with those found in other octahedral cobalt(II) complexes: 2.086, 2.171, 2.207 Å in bis(isothiocyanato)tetrakis-(4-vinylpyridine)cobalt(II) (Andreotti & Sgarabotto, 1972); 2.160 Å in hexakis(imidazole)cobalt(II) nitrate (Prince, Mighell, Reimann & Santoro, 1972); 1.99–2.16 Å in di- μ -acetato-tetrakis[μ_3 -methoxo-2,4-pentanedionatocobalt(II,III)] (Bertrand & Hightower, 1972). It is worth noting that all the Co(1)-N distances are slightly longer than the corresponding Co(2)-N distances, while for Co(1)-S and Co(2)-S the reverse is true. Moreover in both polyhedra the two Co-N distances involving the SCN groups are shorter than the other three involving the nitrogen atoms of the organic ligand.

The organic molecule behaves as a tridentate ligand, as already observed in Cu(PPQ)Cl₂ (Mangia, Nardelli, Pelizzi & Pelizzi, 1974), giving rise, in both parts of the dimer, to a boat-shaped six-membered chelation ring [N(2)N(3)C(14)C(15)N(5)Co(1) and N(9)N(10)C(35)C(36)N(12)Co(2)], whose torsion angles are quoted in Table 3, and to a nearly planar five-membered chelation ring [N(1)C(5)C(6)N(2)Co(1) and N(8)C(26)C(27)N(9)Co(2)]. Each of these five-membered rings is almost parallel to the pyridine ring to which it is attached, the dihedral angles formed by their mean

planes being 4.6 and 3.7° respectively. The aromatic rings are planar, as expected, with no significant departures from the usual values for bond distances and angles. The heteroatomic ring of the quinazoline moiety is not planar in either molecule; the values of the internal rotation angles, listed in Table 3, indicate a half-chair conformation. The bonds formed by the nitrogen atoms in these rings show a pyramidal character.

Table 3. *Internal rotation angles* (°)

(a) In the six-membered chelation rings			
N(3)-C(14)	-77.0	N(10)-C(35)	-79.1
C(14)-C(15)	56.9	C(35)-C(36)	57.6
C(15)-N(5)	4.7	C(36)-N(12)	0.1
N(5)-Co(1)	-20.4	N(12)-Co(2)	26.7
Co(1)-N(2)	0.8	Co(2)-N(9)	-8.1
N(2)-N(3)	41.6	N(9)-N(10)	-39.9
(b) In the heteroatomic rings of the quinazoline parts			
N(3)-C(7)	-17.8	N(10)-C(28)	-13.5
C(7)-C(8)	6.4	C(28)-C(29)	10.1
C(8)-C(13)	2.1	C(29)-C(34)	-3.5
C(13)-N(4)	-37.0	C(34)-N(11)	25.7
N(4)-C(14)	55.8	N(11)-C(35)	-45.0
C(14)-N(3)	-45.9	C(35)-N(10)	40.5

The differences for bond distances and angles in the two independent organic molecules are not of chemical significance as the σ are probably underestimated. Com-

Table 2. *Bond distances* (Å) *and angles* (°)

(a) In the coordination polyhedra

Co(1)-N(1)	2.107 (8)	Co(1)-N(6)	2.019 (7)	Co(2)-N(8)	2.141 (8)	Co(2)-N(13)	2.046 (7)
Co(1)-N(2)	2.153 (7)	Co(1)-N(7)	2.036 (7)	Co(2)-N(9)	2.172 (7)	Co(2)-N(14)	2.116 (8)
Co(1)-N(5)	2.133 (9)	Co(1)-S(3)	2.867 (3)	Co(2)-N(12)	2.171 (8)	Co(2)-S(1)	2.787 (4)
N(1)-Co(1)-N(2)	75.5 (2)	N(2)-Co(1)-S(3)	76.9 (2)	N(8)-Co(2)-N(9)	76.2 (2)	N(9)-Co(2)-S(1)	83.9 (2)
N(1)-Co(1)-N(5)	164.6 (3)	N(5)-Co(1)-N(6)	97.8 (3)	N(8)-Co(2)-N(12)	161.8 (3)	N(12)-Co(2)-N(13)	96.9 (3)
N(1)-Co(1)-N(6)	93.9 (3)	N(5)-Co(1)-N(7)	95.1 (3)	N(8)-Co(2)-N(13)	97.8 (3)	N(12)-Co(2)-N(14)	92.4 (3)
N(1)-Co(1)-N(7)	94.4 (3)	N(5)-Co(1)-S(3)	82.4 (2)	N(8)-Co(2)-N(14)	97.1 (3)	N(12)-Co(2)-S(1)	82.5 (2)
N(1)-Co(1)-S(3)	86.2 (2)	N(6)-Co(1)-N(7)	98.8 (3)	N(8)-Co(2)-S(1)	87.0 (2)	N(13)-Co(2)-N(14)	93.9 (3)
N(2)-Co(1)-N(5)	90.5 (3)	N(6)-Co(1)-S(3)	90.2 (2)	N(9)-Co(2)-N(12)	88.0 (2)	N(13)-Co(2)-S(1)	89.7 (2)
N(2)-Co(1)-N(6)	163.6 (3)	N(7)-Co(1)-S(3)	170.9 (2)	N(9)-Co(2)-N(13)	171.4 (3)	N(14)-Co(2)-S(1)	174.1 (2)
N(2)-Co(1)-N(7)	94.5 (3)			N(9)-Co(2)-N(14)	92.9 (3)		

(b) In the thiocyanate groups

S(1)-C(20)	1.68 (1)	S(2)-C(21)	1.63 (1)	S(3)-C(41)	1.59 (1)	S(4)-C(42)	1.55 (1)
C(20)-N(6)	1.15 (1)	C(21)-N(7)	1.15 (1)	C(41)-N(13)	1.18 (1)	C(42)-N(14)	1.18 (1)
S(1)-C(20)-N(6)	178.7 (8)	S(2)-C(21)-N(7)	172.9 (8)	S(3)-C(41)-N(13)	176.7 (8)	S(4)-C(42)-N(14)	178.3 (9)
C(20)-N(6)-Co(1)	165.5 (7)	C(21)-N(7)-Co(1)	159.3 (7)	C(41)-N(13)-Co(2)	155.1 (7)	C(42)-N(14)-Co(2)	179.3 (8)
C(20)-S(1)-Co(2)	100.3 (3)			C(41)-S(3)-Co(1)	97.7 (4)		

(c) In the organic ligands

N(1)-C(1)	1.39 (1)	C(7)-N(3)	1.39 (1)	N(8)-C(22)	1.34 (1)	C(28)-N(10)	1.35 (1)
C(1)-C(2)	1.35 (2)	C(7)-O(1)	1.23 (1)	C(22)-C(23)	1.45 (1)	C(28)-O(2)	1.22 (1)
C(2)-C(3)	1.36 (1)	C(8)-C(9)	1.39 (1)	C(23)-C(24)	1.33 (1)	C(29)-C(30)	1.39 (1)
C(3)-C(4)	1.40 (1)	C(9)-C(10)	1.43 (1)	C(24)-C(25)	1.41 (2)	C(30)-C(31)	1.37 (1)
C(4)-C(5)	1.43 (1)	C(10)-C(11)	1.34 (1)	C(25)-C(26)	1.32 (1)	C(31)-C(32)	1.38 (1)
C(5)-N(1)	1.29 (1)	C(11)-C(12)	1.38 (1)	C(26)-N(8)	1.32 (1)	C(32)-C(33)	1.39 (1)
C(5)-C(6)	1.48 (1)	C(12)-C(13)	1.37 (1)	C(26)-C(27)	1.46 (1)	C(33)-C(34)	1.41 (1)
C(6)-N(2)	1.29 (1)	C(14)-C(15)	1.54 (1)	C(27)-N(9)	1.35 (1)	C(35)-C(36)	1.59 (1)
N(2)-N(3)	1.40 (1)	C(15)-N(5)	1.33 (1)	N(9)-N(10)	1.36 (1)	C(36)-N(12)	1.38 (1)
N(3)-C(14)	1.52 (1)	C(15)-C(16)	1.40 (1)	N(10)-C(35)	1.44 (1)	C(36)-C(37)	1.42 (1)
C(14)-N(4)	1.45 (1)	C(16)-C(17)	1.38 (1)	C(35)-N(11)	1.46 (1)	C(37)-C(38)	1.36 (1)
N(4)-C(13)	1.40 (1)	C(17)-C(18)	1.31 (1)	N(11)-C(34)	1.40 (1)	C(38)-C(39)	1.37 (1)
C(13)-C(8)	1.41 (1)	C(18)-C(19)	1.39 (1)	C(34)-C(29)	1.45 (1)	C(39)-C(40)	1.37 (1)
C(8)-C(7)	1.42 (1)	C(19)-N(5)	1.38 (1)	C(29)-C(28)	1.47 (1)	C(40)-N(12)	1.35 (1)

paring the present structure with that of $\text{Cu}(\text{PPQ})\text{Cl}_2$ it can be seen that the organic ligand maintains its geometry even if there is a substantial change in the environment of the metal, *i.e.* five-coordinate $\text{Cu}(\text{II})$. The dimeric character of the $\text{Co}(\text{II})$ complex is obviously due to the SCN groups which show a tendency to act as bridges. These groups show small distortions from linearity, as is usually observed. Their structural behaviour is particularly interesting as they are not all in the same situation: two of them act as bridges and two are terminal. This fact influences the infrared spectrum in which the bands of the two types of SCN are found: two strong $\nu(\text{C}-\text{N})$ bands at 2085 (bridging) and 2070 cm^{-1} (terminal), two weak $\nu(\text{C}-\text{S})$ bands at 790 (bridging) and 845 cm^{-1} (terminal) and a medium $\delta(\text{NCS})$ at 479 cm^{-1} (terminal). These assignments are made on the basis of the observation that the $\text{C}-\text{N}$ stretching frequency in a bridging thiocyanate group is higher than in a terminal one, while the reverse is observed for the $\text{C}-\text{S}$ stretching (Nardelli, Gasparri, Musatti & Manfredotti, 1966).

Packing is determined by normal van der Waals contacts, the most significant of which are quoted in Table 4. The absence of hydrogen bonds can be related with the value of $\nu(\text{N}-\text{H})$ which is higher (3260 cm^{-1}) than that observed in the $\text{Cu}(\text{II})$ complex (3160 cm^{-1}) where two rather strong $\text{N}-\text{H}\cdots\text{Cl}$ hydrogen bonds occurred.

Acta Cryst. (1974). **B30**, 491

The Crystal and Molecular Structure of Tris(cyclopentadienyl)titanium

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(Received 10 October 1973; accepted 12 October 1973)

Tris(cyclopentadienyl)titanium crystallizes in space group *Pbca* with $a = 13.468$, $b = 10.229$, $c = 17.180$ Å and $Z = 8$. The structure has been determined from four-circle diffractometer data and refined by least-squares calculations to $R = 0.052$ for 1461 reflexions. It consists of isolated $(\text{C}_5\text{H}_5)_3\text{Ti}$ molecules containing two normal $5e-\pi$ -cyclopentadienyl groups with a third cyclopentadienyl ring which is bonded to the metal by two carbon atoms only. It is suggested that this group is acting as a 3-electron ligand

It is a feature of many organotitanium(III) compounds (Coutts & Wailes, 1970) that the metal atom increases its coordination number by chelation, as in $(\text{C}_5\text{H}_5)_2\text{-Ti}(\text{O}_2\text{CR})$, by dimerization, as in $[(\text{C}_5\text{H}_5)_2\text{TiCl}]_2$, or by solvation. However, the physical properties of tris(cyclopentadienyl)titanium, first described by Fischer & Lochner (1960), suggest that it is monomeric. The structures of a number of other compounds containing more than two cyclopentadienyl rings around one metal atom, such as $(\text{C}_5\text{H}_5)_4\text{Ti}$ (Calderon, Cotton, DeBoer & Takats, 1971), $(\text{C}_5\text{H}_5)_3\text{MoNO}$ (Calderon, Cotton & Legzdins, 1969), and $(\text{C}_5\text{H}_5)_3\text{In}$ (Einstein,

Table 4. *Most significant van der Waals interactions* (Å)

Standard deviations are in the range 0.007–0.013 Å.

S(1)·····N(9)	3.348	C(20)·····C(41)	3.299
S(1)·····N(12)	3.302	O(1)·····C(30 ⁱ)	3.330
S(3)·····N(2)	3.170	N(11)·····S(2 ⁱ)	3.354
S(3)·····N(5)	3.338	C(4)·····O(2 ⁱ)	3.191
N(6)·····N(13)	3.359	N(2)·····N(11 ⁱⁱ)	3.377
N(6)·····C(41)	3.143	N(4)·····C(42 ⁱⁱⁱ)	3.179
N(13)·····C(20)	3.111	O(1)·····C(9 ⁱⁱⁱ)	3.253

Code for symmetry-related atoms:

Superscript	Atom at		
none	x ,	y ,	z
i	$1-x$,	$\frac{1}{2}+y$,	$\frac{1}{2}-z$
ii	$x-1$,	$\frac{1}{2}-y$,	$z-\frac{1}{2}$
iii	$1-x$,	$1-y$,	\bar{z}

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Gilbert & Tuck, 1972), have proved valuable in exploring the nature of the C_5H_5 ligand. The structure of tris(cyclopentadienyl)titanium has therefore been determined by single-crystal X-ray diffraction. A preliminary account of this work has appeared (Lucas, Green, Forder & Prout, 1973).

Experimental

$(\text{C}_5\text{H}_5)_3\text{Ti}$, prepared as dark green-black crystals by the reaction of $[(\text{C}_5\text{H}_5)_2\text{TiCl}]_2$ and NaC_5H_5 in tetrahydrofuran and purified by vacuum sublimation, was kindly