Acta Cryst. (1984). C**40**, 1313–1315

(2,3,9,10-Tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene)(thiocyanato-*N*)copper(II) Hexafluorophosphate, $[Cu(NCS)(C_{14}H_{24}N_4)](PF_6)$

By Andri E. Elia,* E. C. Lingafelter and V. Schomaker

*Department of Chemistry, BG-*10, *University of Washington, Seattle, Washington* 98195, *USA*

(*Received* 20 *August* 1982; *accepted* 19 *December* 1983)

Abstract. $M_r = 514{\cdot}96$, $Pnam$, $a = 12{\cdot}003$ (4), $b = 15{\cdot}365$ (6), $c = 11{\cdot}500$ (6) Å, $V = 2121$ Å^3, $Z = 4$, $D_m = 1{\cdot}62$ (3), $D_x = 1{\cdot}612$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 1{\cdot}2$ mm^{-1}, $F(000) = 1052$, room temperature, final $R = 0{\cdot}091$ and $R_w = 0{\cdot}041$, with 2424 F values in the *hkl* octant. The Cu atom is square-pyramidal with the N atoms of the macrocycle forming the basal plane and the NCS$^-$ nitrogen atom the apex. An S atom from another cation is 3·31 (6) Å from the Cu atom, at the sixth coordination site, and the Cu atom is displaced out of the coordination plane toward the NCS$^-$ nitrogen atom by 0·07 Å.

Introduction. The crystal and molecular structure of the title compound, [Cu(NCS)(tim)](PF$_6$), has been determined (see Fig. 1). The deep-purple crystals were provided by M. J. Maroney. The cation is five-coordinated square-pyramidal, the apical ligand being a thiocyanate ion.

Experimental. Precession photographs indicated orthorhombic symmetry, systematic absences, $0kl$ for $k + l = 2n + 1$, and $h0l$ for $h = 2n + 1$, suggesting space groups $Pna2_1$ and $Pnam$. $Pnam$ chosen on the basis of Wilson statistics, performed by the program *NORMSF*. Unit cell: least squares on 12 reflections, '$\pm 2\theta$', $15 < 2\theta < 30°$. Density measured by flotation in a solution of chloroform and 1,3-dibromopropane. Intensity data: crystal 0·3 × 0·5 × 0·2 mm; $+h$ $+k$ $+l$ octant to 55° in 2θ, 2424 reflections; four-circle, computer-controlled Picker FACS-1 diffractometer; step scans of 10 steps each at 5·4 s per step, 10 s each background count; Nb-filtered Mo $K\alpha$ radiation; instability constant $P = 0{\cdot}30\%$; no corrections for deterioration (2% overall), coincidence loss (negligible), or absorption [$\mu = 1{\cdot}2$ mm^{-1}, A(max.) 0·79, A(min.) 0·65]. All programs for the determination and refinement of the structure from the *XRAY* system (Stewart, Machin, Ammon, Dickinson, Heck & Flack, 1976). Data reduction performed in *Pnam* by the program *DATRDN*. Atomic scattering factors from Cromer & Mann (1968). From symmetry considerations, the Cu atom must be located in the mirror plane at $z = 0{\cdot}25$ or 0·75; 0·25 was chosen, and the x, y coordinates obtained from a Patterson map (using the program *FOURR*): (0·13, 0·16, 0·25). Phased initially on the Cu atom, the remainder of the structure, except F atoms, was revealed on a Fourier map (program *FOURR*), with the thiocyanate ion and the P atom in the mirror plane, and the C(1)–C(1′) and C(2)–C(2′) bonds bisected by it, see Fig. 1. After two cycles of F_o least squares with unit weights (program *CRYLSQ*), refining x, y, z, U of all these atoms, brought R to 0·300, the F atoms were located on a difference electron density map, four in the mirror plane and two on a line roughly perpendicular to it, but obviously disordered. At R 0·136, the methyl H atoms were emplaced tetrahedrally at C–H = 1·0 Å (program *BONDAT*). The other H atoms were located on a difference electron density map. With the H atoms included in the calculation and with $1/\sigma^2(F)$ weights, the structure refined to R_w 0·049. Anomalous-dispersion factors, both real and imaginary, from *International Tables for X-ray Crystallography* (1974) then included; the structure refined to R_w 0·045. From a series of structure factor calculations (program F_c) and difference electron density maps, a disordered model for the anion was obtained, which consists of two octahedra, F(1)–F(6) and F(11)–F(61) [and their

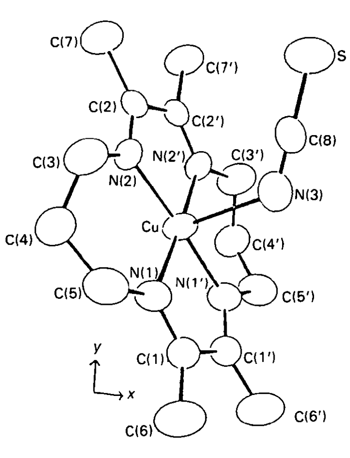

Fig. 1. The cation of [Cu(NCS)(tim)](PF$_6$).

---

* From a dissertation submitted to the Graduate School, University of Washington, Seattle, Washington, in partial fulfillment of the requirements for the PhD degree in Chemistry.

0108-2701/84/081313-03$01.50

reflections through the mirror plane, F(1′)–F(6′) and F(11′)–F(61′), a total of four octahedra], one of occupancy 0·35 and the other of occupancy 0·15. Group refinement was used to refine the partial F atoms, with each octahedron (including the P atom) entered as a group and refined separately. When all four groups were refined, the Gaussian amplitudes of the P atom and the partial F atoms of 0·35 occupancy were refined anisotropically. Subsequently, the Gaussian amplitudes of the partial *F* atoms of 0·15 occupancy were refined isotropically. With the anion refined to convergence, the cation was also refined to convergence (average last-cycle Δ/σ: 0·04), see Table 1:* $R = 0{\cdot}091$, $R_w = 0{\cdot}041$, goodness of fit 2·24. Total number of reflections 2424, 1070 of which were excluded from the last least-squares cycle, based on a 3σ cut-off. All 2424 reflections used in the *R*-factor calculation.

Table 1. *Fractional atomic coordinates* ($\times 10^4$), *isotropic, equivalent isotropic Gaussian amplitudes* ($\times 10^3$), *and partial populations when different from* 1·0

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	p.p.	U_{eq}(Å^2)	U(Å^2)
Cu	1266 (2)	1564 (1)	2500		48 (1)	
N(3)	3119 (10)	2121 (9)	2500		65 (10)	
C(8)	3315 (13)	2867 (11)	2500		50 (12)	
S	3552 (5)	3891 (3)	2500		86 (4)	
N(1)	1611 (7)	638 (5)	3620 (7)		43 (6)	
N(2)	837 (7)	2443 (6)	3600 (6)		39 (6)	
C(1)	2004 (8)	−59 (8)	3171 (8)		46 (7)	
C(2)	538 (8)	3160 (6)	3165 (8)		44 (8)	
C(3)	907 (10)	2333 (8)	4834 (10)		65 (10)	
C(4)	685 (10)	1420 (8)	5197 (9)		66 (9)	
C(5)	1555 (11)	736 (7)	4866 (10)		66 (10)	
C(6)	2453 (10)	−825 (7)	3790 (9)		75 (10)	
C(7)	210 (10)	3971 (7)	3786 (10)		68 (9)	
P	3808 (4)	1632 (3)	7500		52 (3)	
F(1)	3122 (29)	808 (23)	7254 (33)	0·35	164 (20)	
F(2)	4917 (30)	1198 (20)	7205 (27)	0·35	162 (17)	
F(3)	4458 (22)	2452 (18)	7788 (22)	0·35	156 (21)	
F(4)	2711 (27)	2072 (21)	7796 (25)	0·35	101 (16)	
F(5)	3952 (36)	1274 (25)	8779 (36)	0·35	93 (17)	
F(6)	3672 (34)	1996 (22)	6223 (34)	0·35	57 (12)	
F(11)	3028 (31)	908 (32)	7228 (34)	0·15		102 (14)
F(21)	3192 (30)	2314 (29)	6704 (34)	0·15		185 (23)
F(31)	4624 (32)	2357 (30)	7751 (36)	0·15		122 (16)
F(41)	4476 (36)	974 (30)	8294 (32)	0·15		59 (12)
F(51)	4379 (36)	1341 (30)	6335 (29)	0·15		73 (13)
F(61)	3267 (34)	1926 (29)	8660 (30)	0·15		64 (13)

Table 2. *Bond lengths* (Å) *and angles* (°) *of the cation*

		Intramolecular	
Cu–N(3)	2·384 (13)	N(3)–Cu–N(1)	93·6 (4)
Cu–N(1)	1·963 (8)	N(3)–Cu–N(2)	89·7 (4)
Cu–N(2)	1·920 (8)	N(1)–Cu–N(1′)	82·0 (3)
N(1)–C(1)	1·280 (13)	N(1)–Cu–N(2)	97·7 (3)
N(1)–C(5)	1·442 (13)	N(1)–Cu–N(2′)	176·5 (4)
N(2)–C(2)	1·262 (12)	N(2)–Cu–N(2′)	82·4 (4)
N(2)–C(3)	1·432 (13)	Cu–N(1)–C(1)	114·8 (6)
C(1)–C(1′)	1·543 (12)	Cu–N(1)–C(5)	124·5 (6)
C(1)–C(6)	1·477 (15)	Cu–N(2)–C(2)	115·4 (6)
C(2)–C(2′)	1·530 (13)	Cu–N(2)–C(3)	123·6 (7)
C(2)–C(7)	1·488 (14)	Cu–N(3)–C(8)	122·6 (11)
C(3)–C(4)	1·487 (16)	N(3)–C(8)–S	178·6 (15)
C(4)–C(5)	1·530 (16)	N(1)–C(1)–C(1′)	113·8 (9)
N(3)–C(8)	1·171 (21)	N(1)–C(1)–C(6)	127·4 (8)
C(8)–S	1·598 (17)	N(2)–C(2)–C(2′)	113·3 (8)
		N(2)–C(2)–C(7)	128·0 (9)
Intermolecular		N(1)–C(5)–C(4)	110·5 (9)
N(3)–Cu–S	170·6 (3)	N(2)–C(3)–C(4)	112·3 (9)
Cu–S–C(8)	88·1 (9)	C(3)–C(4)–C(5)	117·1 (9)

Primed atoms are related to the corresponding unprimed atoms by reflection through the mirror plane.

Discussion. The unit cell of [Cu(NCS)(tim)](PF_6) contains four discrete complex cations and four disordered hexafluorophosphate anions. The Cu atom is five-coordinate square-pyramidal, the four tim N atoms forming the base of the pyramid and the N atom of the thiocyanate group the apex (see Fig. 1). The equatorial Cu–N bond lengths are 1·963 (8) and 1·920 (8) Å (Table 2), within the range of other published results for equatorial imine Cu^{II}–N bond lengths, 1·917 (9) to 2·009 (5) Å. The axial Cu–N bond length is 2·384 (13) Å, considerably longer than the 1·930 (5) Å reported by Domiano, Musatti, Nardelli, Pelizzi & Predieri (1975) for the Cu–N bond in *catena-μ*-isothiocyanato-(*N*′-pyridylmethylene-*N*″-salicyloylhydrazinato-*NN*′*O*)copper(II) and any of the Cu–N bonds, 1·83 (7) to 2·10 (1) Å, reported by Norbury (1975) for bridging thiocyanates. A weak attractive interaction exists between the Cu atom of one complex and the S atom of another, at the sixth coordination site [N(3)–Cu–S = 170·6 (3)°], at distance 3·331 (6) Å, about 0·5 Å less than the Cu–S van der Waals distance, and close to 3·27 (1) Å, the Cu–S bond in the bis(ethylenediamine)copper(II) thiocyanate reported by Brown & Lingafelter (1964), which has a Cu–S–C angle similar to the present angle, 79·9 (1) *vs* 88·1 (9)°. However, the present Cu–S distance is considerably longer than the 2·709 (2) Å reported by Domiano *et al.* (1975) and other Cu–S distances, 2·46 (1) to 3·11 (4) Å, reported by Norbury, for bridging thiocyanates. The four tim N atoms are coplanar as required by symmetry, and the Cu atom deviates only 0·07 (1) Å from the coordination plane toward the axial ligand. This amount is much less than for the other pentacoordinate Cu^{II}–tim complexes (Elia, Santarsiero, Lingafelter & Schomaker, 1982; Elia, 1982), and might be due to the Cu–S interaction, combined with the fact that the axial Cu–N(3) bond is weak.

Unlike the other pentacoordinate square-pyramidal Cu^{II}–tim complexes the macrocycle of [Cu(NCS)-(tim)](PF_6) deviates very little from planarity* and

---

* Lists of structure factors and their standard deviations, the anisotropic Gaussian amplitudes of the non-hydrogen atoms, and the final coordinates and isotropic Gaussian amplitudes of the hydrogen atoms, as well as bond lengths and angles of the anion, contact distances, and distances of tim atoms from the coordination plane have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39133 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* See deposition footnote.

resembles the tetracoordinate square-planar cation of $[Cu(tim)](BPh_4)_2$ in which the macrocycle is nearly planar, excepting the C(4) atoms (Elia, 1982). The conformation assumed is by symmetry a boat, with the C(4) carbon atoms and the axial ligand on opposite sides of the coordination plane as shown in Fig. 1.

References

BROWN, B. W. & LINGAFELTER, E. C. (1964). *Acta Cryst.* **17**, 254–259.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

DOMIANO, P., MUSATTI, A., NARDELLI, M., PELIZZI, C. & PREDIERI, G. (1975). *J. Chem. Soc. Dalton Trans.* pp. 2357–2360.

ELIA, A. E. (1982). *X-ray Crystallographic Studies of Some Copper*(II) *Coordination Complexes.* Doctoral Dissertation, Univ. of Washington.

ELIA, A. E., SANTARSIERO, B. D., LINGAFELTER, E. C. & SCHOMAKER, V. (1982). *Acta Cryst.* B**38**, 3020–3023.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

NORBURY, A. H. (1975). *Adv. Inorg. Chem. Radiochem.* **17**, 231–386.

STEWART, J. M., MACHIN, P. A., AMMON, H. L., DICKINSON, C. W., HECK, H. & FLACK, H. (1976). The *XRAY* system – version of March 1976. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Acta Cryst. (1984). C**40**, 1315–1318

Structure of Tetraphenylarsonium Bis(μ_6-carbido-2,3;4,5-di-μ-carbonyl-1,1,1,2,2,3,3,-4,4,5,5,6,6,6-tetradecacarbonyl-*octahedro*-hexaruthenio-*Ru*^{3},*Ru*^{4})thallate(1−)(4*Tl–Ru*), $[As(C_6H_5)_4][\{Ru_6C(CO)_{16}\}_2Tl]$

BY GERALD B. ANSELL* AND MICHELLE A. MODRICK

Analytical Division, Exxon Research and Engineering Company, PO Box 121, *Linden, NJ* 07036, *USA*

AND JOHN S. BRADLEY

Corporate Research Science Laboratories, Exxon Research and Engineering Company, PO Box 45, *Linden, NJ* 07036, *USA*

(*Received* 6 *July* 1983; *accepted* 23 *February* 1984)

Abstract. $M_r = 2720{\cdot}9$, triclinic, $P1$, $a = 15{\cdot}325$ (5), $b = 17{\cdot}301$ (3), $c = 17{\cdot}356$ (3) Å, $\alpha = 115{\cdot}25$ (1), $\beta = 106{\cdot}01$ (2), $\gamma = 94{\cdot}77$ (2)°, $Z = 1$, $D_x = 2{\cdot}32$ g cm^{-3}, D_m not measured, graphite-monochromatized Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71073$ Å, $\mu = 48{\cdot}1$ cm^{-1}, $T = 293$ (2) K, $F(000) = 2532$, 3634 independent reflections, for which $R = 0{\cdot}078$. The $[\{Ru_6C(CO)_{16}\}_2Tl]^-$ anion consists of a bimetallic carbonyl cluster containing two distorted Ru_6 octahedra, each linked by two edge-related Ru atoms to the central Tl atom. Each Ru_6 octahedron encapsulates a central C atom and bears 16 carbonyl ligands (14 linear, two semi-bridged). The bimetallic anion has pseudo 222 symmetry. Within the Ru_6 octahedra Ru–Ru distances range from 2·813 (4) to 2·938 (4) Å with the exception of the edges bridged by Tl, which average 3·10 Å. Average Ru–Tl distances are 2·780 (3) and 2·864 (2) Å. The four Ru Tl bonds deviate from coplanarity (torsional angle 35·9°) because of non-bonded interactions between the O atoms of the two sets of six carbonyls associated with the Ru_2TlRu_2 region of the cluster.

Introduction. The title material was synthesized as part of an investigation of oxidative activation of transition-metal carbide clusters (Bradley, Ansell & Hill, 1980; Bradley, Pruett, Hill, Ansell, Leonowicz & Modrick, 1982).

Experimental. Title compound was crystallized from toluene. Block-shaped crystal approximately 0·1 × 0·12 × 0·1 mm. Cell dimensions from the setting angles of 25 centered reflections of various intensities. Enraf–Nonius CAD-4 diffractometer. ω–2θ scan-mode. Intensities of 7172 reflections measured, $0{\cdot}0° < 2\theta < 40{\cdot}0°$. Scan begun 0·75° below the calculated 2θ position for $K\alpha_1$ and terminated 0·75° above the calculated $K\alpha_2$ angle. Total background counting time half the scan time and evenly divided on either side of the peak. 3634

---

* Present address: Exxon Research and Engineering Company, Clinton Township, Route 22 East, Annandale, NJ 08801, USA.

0108-2701/84/081315-04$01.50