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Reaction of Thiocyanogen with Chloro-tris(triphenylphosphine)–Copper(I) and Crystal Structure of μ-Dithiocyanato-tetrakis(triphenylphosphine)dicopper(I)

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Many attempts have been made to synthesize metal complexes containing the thiocyanogen entity as a neutral ligand. Fernandez and co-workers reacted $SnCl_4$ [1], $MoCl_5$ [2] and CrO_2Cl_2 [3] with $(SCN)_2$ and obtained $Sn_2Cl_7(SCN)_3$, $MoCl_5(SCN)_2$ and $[CrO_2Cl_2(SCN)_3]_2$, respectively. They suggested the following structures: $Cl_4Sn{-}NCS{-}SCN{-}SnCl_3NCS$ with $(SCN)_2$ as a bridging ligand (based on IR and Raman spectroscopy), $Cl_5MoNCS{-}SCN$ with $(SCN)_2$ boned to $MoCl_5$ through one nitrogen atom (based on IR and ESR spectroscopy), and $(SCN)_2Cl_2O_2Cr{-}NCS{-}SCN{-}CrO_2Cl_2(SCN)_2$ (based on IR and Raman spectroscopy). However, no X-ray structures have been reported.

$CuCl(PPh_3)_3$ seemed to be a good substrate for the formation of an $(SCN)_2$ complex. Instead of complexation, reduction of $(SCN)_2$ with Cl/SCN exchange was observed. The white crystalline product is shown by X-ray structure determination to be $[CuSCN(PPh_3)_2]_2$ with bridging SCN groups. The structure is compared with that of $[CuSCN(PMePh_2)_2]_2$ [4].

Experimental

A 0.65 g (5.6 mmol) sample of freshly prepared $(SCN)_2$ in 80 ml CH_2Cl_2 was added dropwise to a solution of 5.0 g (5.6 mmol) of $CuCl(PPh_3)_3$ in 80 ml CH_2Cl_2 at –50 °C. The reaction mixture was allowed to come slowly to room temperature. After stirring for 3 h the white precipitate was separated from the yellow-orange solution by filtration, dried in vacuum, and recrystallized from CH_2Cl_2.

TABLE 1. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$).

	x	*y*	*z*
Cu	3445(1)	4453(1)	3054(1)
P(1)	3209(1)	6152(1)	2985(1)
P(2)	2196(1)	2688(1)	1791(1)
S	5803(1)	4517(2)	3082(1)
N	3318(4)	4737(4)	4660(4)
C	6329(5)	4954(5)	4416(5)
C(11)	1715(5)	6604(4)	3500(4)
C(12)	1608(7)	7727(5)	4032(6)
C(13)	405(7)	8000(7)	4328(6)
C(14)	–696(7)	7145(7)	4117(6)
C(15)	–628(7)	6025(7)	3601(6)
C(16)	570(6)	5745(5)	3289(5)
C(21)	4582(5)	7388(5)	3845(4)
C(22)	5167(6)	7397(5)	4800(5)
C(23)	6227(7)	8281(5)	5466(5)
C(24)	6720(6)	9157(5)	5207(5)
C(25)	6148(7)	9181(5)	4264(5)
C(26)	5083(6)	8292(5)	3582(5)
C(41)	2675(6)	1390(5)	1753(4)
C(42)	3971(6)	1291(5)	1635(5)
C(43)	4355(7)	288(6)	1517(6)
C(44)	3458(7)	–590(6)	1560(5)
C(45)	2163(6)	–494(5)	1722(5)
C(46)	1770(6)	495(5)	1801(5)
C(51)	474(5)	2490(4)	2058(4)
C(52)	247(6)	2909(5)	3156(5)
C(53)	–1036(6)	2811(6)	3426(5)
C(54)	–2124(6)	2301(5)	2598(6)
C(55)	–1921(6)	1878(5)	1501(5)
C(56)	–648(5)	1965(5)	1229(5)
C(31)	3098(5)	6235(4)	1659(4)
C(32)	4206(6)	6167(5)	1098(5)
C(33)	4128(7)	6174(5)	68(5)
C(34)	2948(7)	6214(5)	–434(5)
C(35)	1849(6)	6274(5)	104(5)
C(36)	1910(6)	6288(5)	1143(5)
C(61)	2047(5)	2362(5)	312(4)
C(62)	2053(7)	1282(5)	–515(5)
C(63)	1930(8)	1089(6)	–1613(5)
C(64)	1800(7)	1939(6)	–1905(5)
C(65)	1773(7)	3016(6)	–1104(5)
C(66)	1892(6)	3220(5)	2(5)

M.p. = 235 °C. *Anal.* Calc. for $C_{37}H_{30}CuNP_2S$: C, 68.8; H, 4.65; N, 2.17; P, 9.60. Found: C, 69.8; H, 4.33; N, 2.28; P, 9.54. Single crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent. IR: 2100vs, 1583w, 1480s, 1463sh, 1326w, 1306w, 1260w, 1182w, 1156w, 1091m, 1070sh, 1026w, 992w, 800w, 751sh, 740s, 745s, 720sh, 695sh, 690s, 680sh, 615 w cm^{-1}. Raman: 756m, 702m, 687m, 619s, 528m, 428m, 258s, 223s, 196s, 167s, 96sh, 84vs. ^{13}C NMR: δ = 134.08 ppm (d, $^2J_{CP}$ = 15.0 Hz), 133.21 ppm (d, $^1J_{CP}$ = 27.8 Hz), 130.16 ppm (s), 128.95 ppm (d, $^3J_{CP}$ 9.2 Hz), 132.31 ppm (SCN, d, $^3J_{CP}$ = 9.4 Hz). ^{31}P NMR: δ = –2.14 ppm (s). The mass spectrum showed peaks due to PPh_3.

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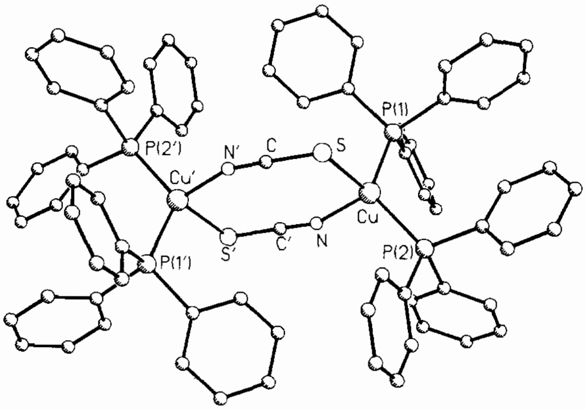

Fig. 1. The dimer unit of $[CuNCS(PPh_3)_2]_2$. Primed atoms have been generated via the crystallographic inversion centre. Principal dimensions: Cu–N 1.983(7), Cu–S 2.408(3), N–C 1.115(9), C–S 1.617(7), Cu–P (mean) 2.294(3), P–C (mean) 1.808(9) Å, N–Cu–S 98.5(2), P–Cu–P 122.5(1), Cu–S–C 102.6(3), S–C–N 179.4(8), C–N–Cu 157.1(5)°.

Crystal Data

$C_{37}H_{30}CuNP_2S$, M = 646.2, triclinic space group $P\bar{1}$, a = 10.276(4), b = 13.077(5), c = 13.041(5) Å, α = 114.71(2), β = 92.99(3), γ = 100.77(3)°, U = 1547.2 Å^3, Z = 2, d_{calc} = 1.387 g cm^{-3}, $\mu(MoK_\alpha)$ = 0.90 mm^{-1}.

Intensities for 4349 reflections were measured from a crystal of dimensions 0.3 × 0.4 × 0.5 mm^3, using a Stoe-Siemens 4-circle diffractometer and a profile-fitting procedure [5], and graphite monochromated MoK_α radiation (λ = 0.71069 Å), for $2\theta < 45°$. After Lp but not absorption corrections the 3140 unique data with $F > 3\sigma(F)$ were used for all calculations. The structure was solved by direct methods and refined with riding isotropic H-atoms [C–H 0.96 Å on external C–C–C bisectors, $U(H) = 1.2\ U_{eq}(C)$] and all other atoms anisotropic to R = 0.060 and R_w = 0.051. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0005\ F^2$, and an isotropic extinction parameter x refined to 0.0012(2) where $F_c^* = F_c/[1 + 0.002xF_c^2/\sin(2\theta)]^{0.25}$. Atomic coordinates are presented in Table I, and selected bond lengths and angles in the legend to the Fig. 1.*

Results and Discussion

The structure consists of dimeric units $[CuNCS(PPh_3)_2]_2$ with a crystallographic inversion centre in the middle of each dimer (Fig. 1). The structure is very similar to that of $[CuNCS(PPh_2Me)_2]_2$ [4]. However, the Cu–P distances are about 0.04 Å longer, possibly because of the greater steric requirements of the phenyl group compared to methyl, and the ligand S and N are both about 0.04 Å closer to Cu. The coordination of Cu(I) is distorted tetrahedral, the small N–Cu–S angle compensating for a large P–Cu–P angle. The thiocyanate group is linear at carbon, but coordinates non-linearly through N and S.

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*Tables of geometrical parameters, anisotropic temperature factors, and observed and calculated structure factors are obtainable from author GMS on request.