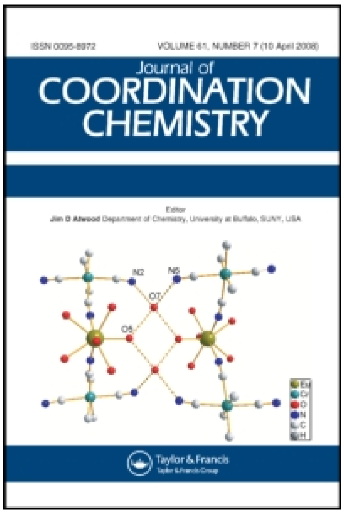

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SYNTHESIS AND STRUCTURAL STUDIES OF (1, 10-PHENANTHROLINE)(THIOCYANATE-N)-(TRIPHENYLPHOSPHINE)COPPER(I)

Antonio E. Mauro[a]; Carlos C. Porta[a]; Sandra R. Ananias[a]; Vagner Sargentelli[ab]; Regina Helena De A. Santos[c]; M. Teresa Do[c]; P. Gambardella[c]
[a] Instituto de Quimica de Araraquara, UNESP, Araraquara, Brazil [b] Universidade de Marilia, UMMAR, Marilia, Brazil [c] Instituto de Quimica de São Carlos, USP, Sao Carlos, Brazil

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SYNTHESIS AND STRUCTURAL STUDIES OF (1,10-PHENANTHROLINE)(THIOCYANATE-N)-(TRIPHENYLPHOSPHINE)COPPER(I)

ANTONIO E. MAURO[a,*], CARLOS C. PORTA[a],
SANDRA R. ANANIAS[a], VAGNER SARGENTELLI[a,†],
REGINA HELENA DE A. SANTOS[b] and
M. TERESA DO P. GAMBARDELLA[b]

[a]*Instituto de Química de Araraquara, UNESP, C.P. 355, 14801-970, Araraquara, Brazil;* [b]*Instituto de Química de São Carlos, USP, C.P. 780, 13560-970, São Carlos, Brazil*

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The compound (1,10-phenanthroline)(thiocyanate-N)(triphenylphosphine)copper(I), was synthesized and studied by IR spectroscopy and X-ray diffraction techniques. It is monomeric with the thiocyanate acting as a N-donor ligand. The copper atom shows a distorted tetrahedral coordination geometry.

Keywords: Copper(I); thiocyanato; triphenylphosphine; infrared spectroscopy;
X-ray diffraction; tetrahedral coordination

INTRODUCTION

Copper(I) complexes have been the subject of considerable research in recent years. Among the reasons for the increasing interest in such species is the diversity of their structural chemistry,[1] which is well illustrated by copper(I) compounds containing phosphines. Such compounds are useful in organic synthesis[2] and copper(I) centers are present at the active sites of a number of proteins.[3] In addition, triphenylphosphine copper(I) derivatives

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[*] Corresponding author. Tel.: 55 016 232 2022. Fax: 55 016 222 7932.
E-mail: mauro@iq.unesp.br.

[†] Present address: Universidade de Marília, UNIMAR, C.P. 525, 17525-902, Marília, Brazil.

have been receiving attention due to their potential applications in microelectronic technology.[4] For copper(I) thiocyanato complexes a further interest exists as SCN is a versatile ligand which can coordinate to the copper atom in a monodentate or bridging fashion.[5,6] As a part of a more extensive investigation into the chemistry of both Cu(I) and Cu(II) complexes, we report in this paper the results of studies on the synthesis and structural characterization of $[Cu(NCS)(phen)(PPh_3)]$.

EXPERIMENTAL

Synthesis of $[Cu(NCS)(phen)(PPh_3)]$

All operations described herein, except the weighings, were performed in an atmosphere of purified nitrogen in a Schlenk apparatus. The compound $[Cu(SCN)(PPh_3)_2]_2$ was prepared by an appropriate method described in the literature.[7] To a solution containing $[Cu(SCN)(PPh_3)_2]_2$ (0.15 g, 0.12 mmol) in diethylether (15 mL) was added 1,10-phenanthroline (0.05 g, 0.25 mmol). The mixture was stirred for 6 h at room temperature. The yellow solid that formed was filtered off, washed thoroughly with acetone and diethylether and then dried *in vacuum*. Recrystallization from acetone gave yellow crystals suitable for X-ray analysis. The elemental analysis results were in agreement with the proposed formula.

IR Spectrum

The IR spectrum was recorded as KBr pellets on a Nicolet 730-FT spectrophotometer.

Crystal Structure Determination of $[Cu(NCS)(phen)(PPh_3)]$

A crystal of the title compound was mounted in the Enraf-Nonius CAD4 diffractometer, at room temperature and using 25 reflections automatically centered, the cell parameters were obtained and refined. Table I shows the data collection and refinement conditions. The intensity data were reduced to F_o and corrected by absorption factors $[\mu(\mathrm{MoK}_\alpha) = 0.999\,\mathrm{mm}^{-1}]$. The structure was solved by Patterson function, difference Fourier syntheses, and refined on F^2 by full matrix least squares, using the SHELXL-97.[8] The hydrogen atoms were calculated and placed in their ideal positions and not

TABLE I Summary of data collection and refinement for [Cu(NCS)-(phen)(PPh_3)]

Molecular formula	$CuSPN_3C_{31}H_{23}$
Molecular weight	564.09
Crystal system	Monoclinic
Space group	C2/c
Z (molec/unit cell)	8
D_c ($g \cdot cm^{-3}$)	1.429
a (Å)	24.706(2)
b (Å)	11.331(1)
c (Å)	19.423(2)
β (°)	105.28(1)
V (Å^3)	5245(1)
F(000)	2320
Crystal size (mm)	0.10 × 0.08 × 0.12
λ (Å)	0.71073
μ (mm^{-1})	0.999
Scan mode	ω–2θ
Scan rate (° min^{-1})	2–10
Scan range (°)	0.80
Check reflection	337
θ range (°)	0–24.92
Range in *hkl*	
Min	−29, 0, 0
Max	28, 9, 23
Unique reflections	4606
Reflections used ($I \geq 2\sigma(I)$)	1545
No. of variables	334
Goodness of fit	0.978
R, R_w	0.066, 0.13
Rall	0.217
Max. shift/e.s.d.	0.01
Max. density in diff. map (e · Å^3)	0.71
Min. density in diff. map (e · Å^3)	−0.59
Minimized function	$\sum w(F_o\vert - \vert F_c\vert)^2$
Weight system (w) for: observed	$1/[\sigma^2(F_o^2) + (0.0707P)^2]$ $P = (F_o^2 + 2F_c^2)/3$

refined, using d(C–H) = 0.93 Å, and thermal vibration equal to 1.2 times the isotropic equivalent B of the attached carbon. All non-hydrogen atoms were refined anisotropically, and the atomic scattering factors were those from Cromer and Mann[9] with anomalous dispersion from Cromer and Liberman[10] and for the hydrogen atoms from Stewart *et al.*[11] Table II shows the fractional atomic coordinates of the non-hydrogen atoms. The hydrogen coordinates, anisotropic thermal parameters, and observed and calculated structure factors have been deposited with the editor as Supplementary Material. The maximum and minimum electron density observed at the end of refinement (0.71 and −0.59) are both around the copper atom (distance Cu to peak equal to 1.08 and 1.06 Å respectively).

TABLE II Fractional atomic coordinates and isotropic equivalent displacement parameters [Å^2], with e.s.d.'s in parenthesis

Atom	*x*	*y*	*z*	U_{eq}
Cu	0.84977(5)	0.08518(11)	0.01553(7)	0.0406(4)
S	0.92573(13)	0.4045(3)	0.16347(17)	0.0638(9)
P	0.85895(10)	0.1078(2)	− 0.09287(13)	0.0329(7)
N	0.8717(4)	0.2231(8)	0.0799(5)	0.051(3)
N1	0.7751(3)	0.0096(7)	0.0267(4)	0.033(2)
N2	0.8826(3)	−0.0604(7)	0.0794(4)	0.037(2)
C	0.8941(4)	0.2984(9)	0.1148(6)	0.040(3)
C1	0.7223(5)	0.0450(10)	0.0017(5)	0.049(3)
C1b	0.7924(4)	0.1257(8)	−0.1600(5)	0.032(2)
C1c	0.8951(4)	−0.0026(8)	−0.1306(5)	0.031(2)
C1a	0.8973(4)	0.2399(9)	−0.1035(5)	0.036(3)
C2b	0.7578(4)	0.2196(11)	−0.1528(6)	0.052(3)
C2a	0.8837(5)	0.3138(10)	−0.1632(6)	0.049(3)
C2c	0.9066(4)	0.0092(10)	−0.1967(6)	0.047(3)
C2	0.6778(5)	−0.0211(13)	0.0124(6)	0.070(4)
C3a	0.9156(5)	0.4100(11)	−0.1671(7)	0.060(3)
C3	0.6871(5)	−0.1249(11)	0.0482(6)	0.061(4)
C3c	0.9341(4)	−0.0798(11)	−0.2239(6)	0.057(3)
C3b	0.7058(5)	0.2330(11)	−0.2024(7)	0.055(3)
C4b	0.6877(5)	0.1536(14)	−0.2569(7)	0.075(5)
C4a	0.9610(5)	0.4407(10)	−0.1126(7)	0.058(3)
C4	0.7417(5)	−0.1676(11)	0.0740(6)	0.050(3)
C4c	0.9513(5)	−0.1804(11)	−0.1845(7)	0.058(3)
C5a	0.9743(5)	0.3715(11)	−0.0529(6)	0.059(3)
C5b	0.7212(5)	0.0599(12)	−0.2625(7)	0.071(4)
C5c	0.9416(5)	−0.1903(11)	−0.1180(7)	0.058(4)
C5	0.7554(6)	−0.2763(11)	0.1110(6)	0.063(4)
C6	0.8088(6)	−0.3099(12)	0.1369(6)	0.068(4)
C6c	0.9140(4)	−0.1040(9)	−0.0918(5)	0.041(3)
C6a	0.9423(4)	0.2734(9)	−0.0473(6)	0.044(3)
C6b	0.7729(5)	0.0453(10)	−0.2155(6)	0.051(3)
C7	0.8549(5)	−0.2397(9)	0.1289(5)	0.043(3)
C8	0.9122(5)	−0.2694(11)	0.1556(5)	0.056(3)
C9	0.9526(5)	−0.1935(11)	0.1454(6)	0.059(4)
C10	0.9352(4)	−0.0919(11)	0.1068(5)	0.048(3)
C11	0.8413(4)	−0.1323(8)	0.0905(5)	0.033(2)
C12	0.7844(4)	−0.0938(9)	0.0622(4)	0.034(2)

RESULTS AND DISCUSSION

Taking into account the interesting aspects of the coordination chemistry of the thiocyanato ligand, as well as the structural features that emerged from our previous studies[12–16] of copper complexes, we were motivated to perform the reaction of $[Cu(NCS)(PPh_3)_2]_2$ with 1,10-phenanthroline. At room temperature a cleavage of the dimeric species was observed, affording the compound $[Cu(NCS)(phen)(PPh_3)]$. The IR spectrum of $[Cu(NCS)(phen)(PPh_3)]$ showed a number of absorption bands, but the most characteristic ones were those assigned to the coordinated thiocyanato group at 2081 s, νCN; 751 w, νCS and 488 w, δNCS, cm^{-1}.[17] The νCN stretching vibration indicated terminally-bonded thiocyanate, while in [Cu(SCN)(PPh$_3$)$_2$]$_2$ the νCN mode was present at 2098 cm^{-1}, characteristic of bridging coordination. Spectroscopic results alone are not sufficient to answer unambiguously the question whether thiocyanato is N or S bonded to the copper atom in the complex [Cu(NCS)(phen)(PPh$_3$)$_2$]. In order to clarify this point and provide the structural features of the compound [Cu(NCS)(phen)(PPh$_3$)$_2$] we undertook its full X-ray crystallographic analysis.

The X-ray diffraction study confirmed that the title compound is monomeric with a terminal thiocyanato group N-coordinated to copper atom. The structure of the compound with the labeling scheme is presented in Figure 1. Selected interatomic bonding distances and angles are given in Table III. The molecular structure shows that the copper atom is bonded to the phosphorus atom of the thriphenylphosphine, to the nitrogen atom of

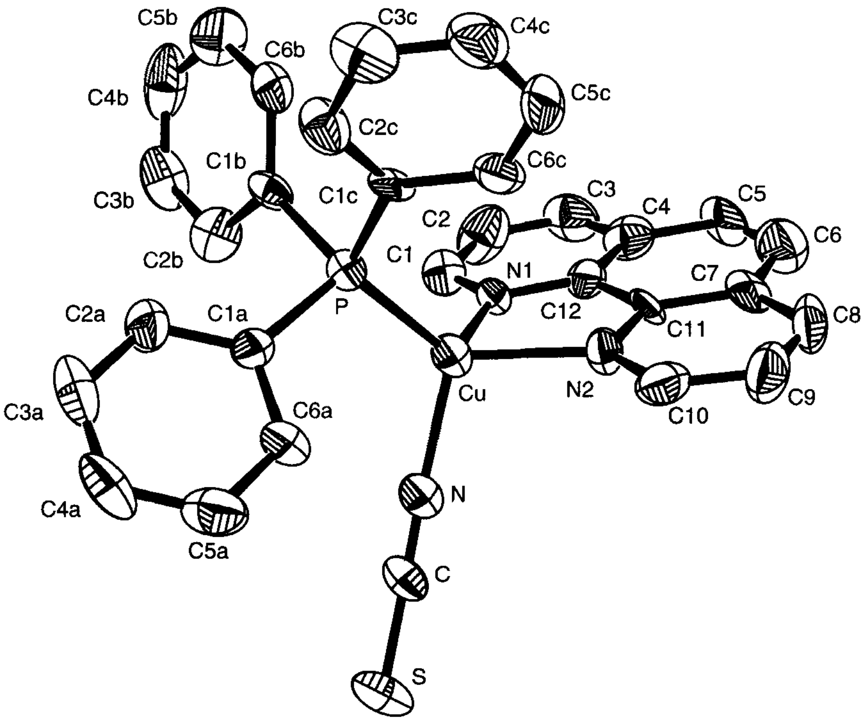

FIGURE 1 ORTEP drawing of [Cu(NCS)(phen)(PPh$_3$)] showing the labeling of atoms.

TABLE III Selected distances (Å) and angles (°) for [Cu(NCS)(phen)(PPh$_3$)]

Cu-N	1.985(9)	N-Cu-N1	111.0(3)
Cu-N1	2.096(8)	N-Cu-N2	104.4(3)
Cu-N2	2.095(8)	N-Cu-P	115.6(3)
Cu-P	2.191(3)	N1-Cu-N2	80.3(3)
N-C	1.139(12)	N1-Cu-P	117.6(2)
C-S	1.600(11)	N2-Cu-P	122.6(2)
P-C1a	1.813(10)	Cu-N-C	166.9(10)
P-C1b	1.821(10)	N-C-S	179.6(11)
P-C1c	1.801(9)		

the thiocyanato and is also chelated by two nitrogen atoms of the phenanthroline ligand. The coordination geometry around the metal is that of a distorted tetrahedron with an N_3P donor set, in which the bond angle N1-Cu-N2 of 80.3(3)° differs significantly from the ideal value of 109°48′. The dihedral angle between the [N1CuN2] and [NCuP] planes is 95.0(3)°.

The N-C and S-C bonds of the thiocyanato group in [Cu(NCS)(phen)-(PPh$_3$)] have normal values and are co-linear, since the angle N-C-S is 179.6(11)°. However, the NCS ligand is not quite co-linear with the copper atom, since the angle Cu-N-C is 166.9(10)°. The Cu-P distance equals to 2.191(3) Å is within the range of those found[1] in a number of copper(I) complexes containing triphenylphosphine. In addition an interesting observation can be inferred by comparing the Cu-P bond length to that of [Cu(SCN)(PPh$_3$)$_2$]$_2$, whose mean value[18] is 2.294(3) Å. Hence it is verified that the Cu-P bond becomes stronger when the number of phosphine ligands coordinated to copper decreases. This is suggestive of an increase in the π component of the Cu-P bond of the species [Cu(NCS)(phen)(PPh$_3$)] compared to [Cu(SCN)(PPh$_3$)$_2$]$_2$.

The N1-Cu-P and N2-Cu-P angles of 117.6(2)° and 122.6(2)° compared to 111.0(3)° and 104.4(3)° for the N-Cu-N1 and N-Cu-N2 angles, respectively, reflect the greater steric bulk of the triphenylphosphine and phenanthroline ligands compared to the thiocyanato group.

Various explanations[5,6] have been given to account for the influence of neutral ligands on the coordination mode of the thiocyanato group. In the title compound the N coordination probably arises from a fine interplay of electronic and steric effects associated with the bulky molecules of triphenylphosphine and phenanthroline. Other related compounds are being investigated in order to better understand the factors that govern the conversion of the dimeric into monomeric species as well as the mode of coordination of the thiocyanato group to the copper atom. The thermal behavior of this class of copper(I) complexes is also underway. Our first thermogravimetric

(TG) results obtained under dynamic flow of dry synthetic air have clearly indicated that [Cu(NCS)(phen)(PPh_3)] has a higher thermal stability than [Cu(SCN)$(PPh_3)_2]_2$.

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