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Structural and Spectroscopic Studies of a New Cyclohexyldithiocarbonatio-S, S' Bis (Triphenylphosphine) Copper(I) Complex.

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ABSTRACT

Chemical preparation, crystal structure, and spectroscopic studies of a new coordination compound, $[(PPh_3)_2Cu(C_6H_{11}CS_2]$, are given. This new compound crystallizes in the monoclinic system, with the space group $P2_1/n$ and the following parameters: a = 13.315 (2), b = 15.540 (3), c = 19.169 (3) Å, β = 107.04 (1)°, V = 3792 (1)° $Å^3$ and Z = 4. The crystal structure has been determined and refined to R = 0.043 and Rw = 0.064 using 8355 independent reflections. In this monomeric complex, the central Cu(I) atom is in a distorted tetrahedral environment and chelated by two phosphorus atoms of the two triphenylphosphine (TRIPHOS) ligands and two sulfur atoms from the cyclohexyldithiocarbonatio-S,Ś (CHDTC) ligand. The cyclohexyl ring adopts a chair conformation. IR and NMR results supported the crystal structure.

Keywords: coordination compound; monomeric complex; IR spectroscopy; NMR spectroscopy; X-ray diffraction.

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INTRODUCTION

The ability of the alkyldithiocarbonate, R—CS_2^-, ligand (xanthate) to bind the metal has been Known [1]. It forms a chelate with virtually all transition elements and has proven to be a versatile chelating agent for the separation and extraction of metals in analytical chemistry and mineral floating [2, 3]. In this area, there has been a growing interest in the study of the xanthate complexes toward several phosphine ligands [4, 5]. Thus, the study of a series of tri-phenylphosphine adducts of copper(I) thioacetate and copper(I) thiobenzoate has been recently described [6]. These adduct compounds are monomers or dimmers. As a contribution to the investigation of the above materials, we report here the crystal structure of one such compound, $[(PPh_3)_2Cu(C_6H_{11}CS_2]$, formed by the reaction between $C_6H_{11}CSSNa$, CuCl and tri-phenylphosphine.

RESULTS AND DISCUSSION

Structure Description

The crystal structure of the title compound (I) is illustrated in Fig. 1. Fig.2 shows that in the title monomeric complex, the central Cu atom assumes a highly distorted tetrahedral environment. This is due to the small bite of the cyclhexyldithiocarbonatio-S, Ś ligand and the large steric bulk of the TRIPHOS ligands. The coordination around the Cu(I) cation is formed by two S atoms from the bidentate CHDTC ligand and two P atoms from two TRIPHOS ligands (P_2CuS_2 core), a common bonding mode was also observed in dithiocarboxylate systems [7]. Regarding the geometrical features of tetrahedral coordination around the copper atom (Table 1) shows that the Cu—S1 and the Cu—S2 distances of [2.4535 (7) and 2.3893 (8) Å] are comparable to those [2.368 (3) and 2.463 (3) Å] observed in the complex $[(PPh_3)_2Cu(C_6H_{11}OCS_2]$ [8]. Similarly, the Cu—P1 and the Cu—P2 distances of 2.2480 (7) and 2.2462 (8) Å are comparable to those [2.258 (2) and 2.2462 (8) Å] observed in $[(Ph_3P)_2Cu(S_2C—C_6H_4—CH_3)]$ [9]. The two C—S distances [1.690 (2) and 1.678 (2) Å] agree with the literature data indicating that the normal range of the C—S distances in similar compounds is 1.640–1.790 Å. In the title compound, the two C—S distances are almost equal and fall in the lower end of the normal range. These values indicate partial double-bond character owing to the delocalization of the electrons. Thus, the S1S2C1C2 group is planar to a very good approximation, well supported by the sum of the bond angle values around the C1 carbon atom of 359.8 (2) °, close 360°. The P1—Cu—P2 and the S1—Cu—S2 angles are 124.50 (2) and 73.85 (2) °, respectively. The P—Cu—S angles range from 103.11 (2) to 117.53 (2) °, with an average value of 107.61 (2), slightly less larger than 107.99 (4) related to $(C_{18}H_{15}P)_2 1.5C_7H_8$ [10]. These angles clearly illustrate the extent of distortion in the tetrahedral geometry around the copper metal atom. The S—Cu—S bond angle, 73.85 (2) °, is in a good agreement with the bit angle observed in $[(Ph_3P)_2Cu(S_2C—C_6H_4—CH_3)]$ [73.5 (1) °] [9]; such a bite angle is common in dicarboxylate compounds. Examination of the geometrical features of the organic entities shows that the cyclohexyl ring exhibits a regular chair conformation with normal distances and angles [11]. For the phenyl rings, the values of the C—C bond length distances and the C—C—C bond angles are close to that indicated in stereochemical dictionary [12]. No π-π stacking interactions between the phenylene rings or C—H···π interactions towards them are observed.

NMR Results

The proton spectrum of the title compound is shown in Fig. 3. The resonance at 3 ppm is assigned to the H atom attached to The C2 carbon atom of the cyclohexyl ring. The set of the peaks centered at 1.6 ppm corresponds to the remaining hydrogen atoms of the cyclohexyl ring. The series of the peaks at about 7.3 ppm is attributed to the aromatic hydrogen atoms.

The proton-decoupled ^{13}C spectrum of the title compound is shown in Fig. 4. The peak at 64.3 ppm is assigned to the C2 carbon atom of the cyclohexyl ring. The peak at 26.4 ppm is attributed to the C5 carbon atom, while the one at 26.7 ppm correspond to and C3 and C7 carbon atoms. The set of signals at about 132 ppm is related to the aromatic carbon atoms. The peak having the highest chemical shift, at 269 ppm, corresponds to the carbon atom of the CS_2 group.

Fig. 5 shows the proton-decoupled ^{31}P spectrum of the title compound .This spectrum is in good agreement with the molecular structure. Indeed, it exhibits only one resonance at - 4.1 ppm, proving the presence of only one phosphorous environment in this complex. This chemical shift value agrees with that in similar compounds [13].

IR Absorption Spectroscopy

The IR spectrum of the crystalline complex $[(PPh_3)_2Cu(C_6H_{11}CS_2]$ is shown in Fig. 6. The characteristic vibrational modes of the title compound can be compared to those of similar materials [14].

The bands between 3100 and 2850 cm^{-1} correspond to the ν(CH)⍰and⍰⍰(CH_2) stretching modes of the organic groups [15]. The band at 1031 cm^{-1} is characteristic absorption of ν(C-S). The bands at 1592, 1486 and 1442 cm^{-1} belong to ν(C=C) of benzene ring [16]. The two bands at 751 and 700 cm^{-1} correspond to the out of plan bending modes γ(C_{aryl} -H) and γ(Caryl-C), respectively of a monosubstituted benzene [17]. The bands observed between 1314 and 1100 cm^{-1} are assigned to the waging, twisting and rocking modes of the cyclohexyl CH_2 groups [18].

EXPERIMENTAL

Chemical Preparation

A mixture of copper (I)-cyclohexylperthiocarboxylate (0.25 g, 0.001 mol) and PPh_3 (0.52 g, 0.002 mol) in 200 ml of acetone was refluxed. After 30 min the red reaction mixture was filtered in air and the filtrate was transferred to a stoppered flask and allowed to stand undisturbed for four days. Small orange crystals of Copper(I) triphenylphosphino-cyclohexyl-dithiocarboxylate slowly formed and used for X-ray diffraction work.

Investigation Techniques

X-ray Diffraction

The experimental parameters used for data collection and determination of the structure are given in Table 1. All nonhydrogen atoms were refined anisotropically. The hydrogen atom positions were located by difference Fourier syntheses and were not refined. The drawings were made with Diamond. Crystallographic Data (CIF) for the structure reported in this article have been deposited in to the Cambridge Crystallographic Data Center as supplementary publication No. ……… Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB 12EZ, UK (Fax: +44(1223)336-033; e-mail:deposit@ccdc.cam.ac.uk).

Physical Measurements

Table 1: Experimental details

Crystal data	
Chemical formula	$C_{43}H_{41}CuP_2S_2$
M_r	747.41
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	566
a, b, c (Å)	13.315 (2), 15.540 (3), 19.169 (3)
β (°)	107.04 (1)
V (Å^3)	3792 (1)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	2.85
Crystal size (mm)	0.20 × 0.18 × 0.12
Data collection	
Diffractometer	CAD-4 diffractometer
Absorption correction	–
No. of measured, independent and observed [$I > 3.00\sigma(I)$] reflections	8355, 8355, 5966
R_{int}	0.00000
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.626
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.043, 0.064, 1.55
No. of reflections	5966
No. of parameters	433
H-atom treatment	H-atom parameters not refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.54, −0.60
Computer programs:	TEXSAN [19]

NMR spectroscopy. All NMR spectra were recorded on a Bruker DSX-300 spectrometer operating at 300 MHz for ^{1}H, 75.49 MHz for ^{13}C and 121.51 MHz for ^{31}P using $CDCl_3$ as the solvent. ^{1}H and ^{13}C NMR chemical shifts are given relative to tetramethylsiline and ^{31}P one relative to 30% H_3PO_4.

IR spectroscopy. Infrared spectrumwas recorded in the range 4000–400 cm^{-1} using a sample dispersed in spectroscopically pure KBr pellet.

Table 2: Selected geometric parameters (Å, º)

Cu—S1	2.4535 (7)	Cu—P2	2.2462 (8)
Cu—S2	2.3893 (8)	S1—C1	1.690 (2)
Cu—P1	2.2480 (7)	S2—C1	1.678 (2)
S1—CU—S2	73.854 (7)	S1—CU—P2	117.526 (7)
S2—CU—P2	111.050 (9)	S2—CU—P1	115.655 (9)
P2—CU—P1	124.501 (9)	Cu—S1—C1	82.21 (7)
P1—CU—S1	103.108 (8)	Cu—S2—C1	84.45 (7)

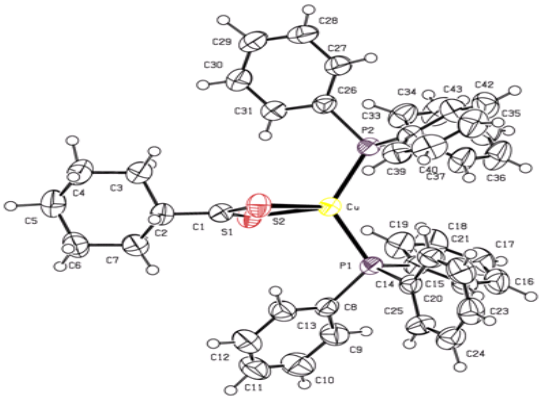

Figure 1: A view of the title compound, showing 50% probability displacement ellipsoids and spheres for the H atoms.

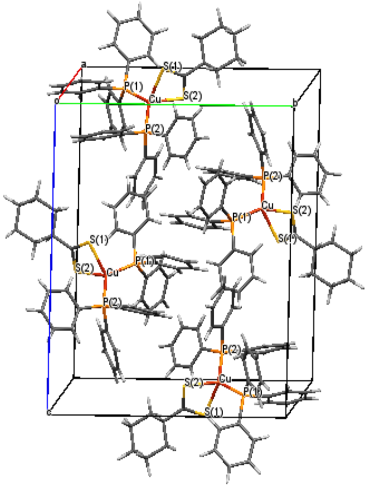

Figure 2: A perspective view of the $[(PPh_3)_2Cu(C_6H_{11}CS_2]$ packing.

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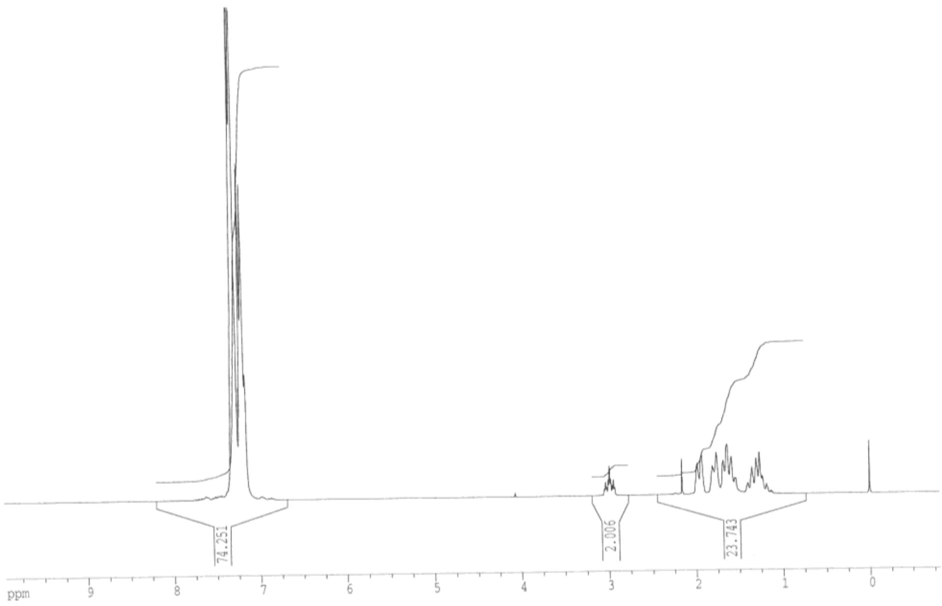

Figure 3: ^1H spectrum of $[(PPh_3)_2Cu(C_6H_{11}CS_2]$.

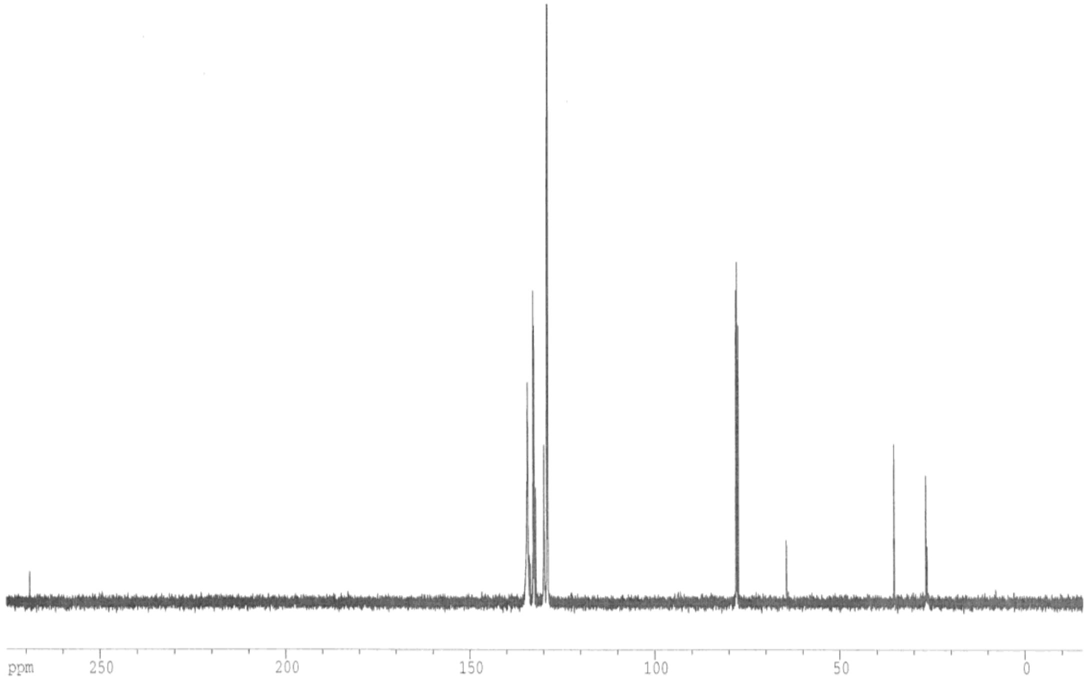

Figure 4: ^{13}C spectrum of $[(PPh_3)_2Cu(C_6H_{11}CS_2]$.

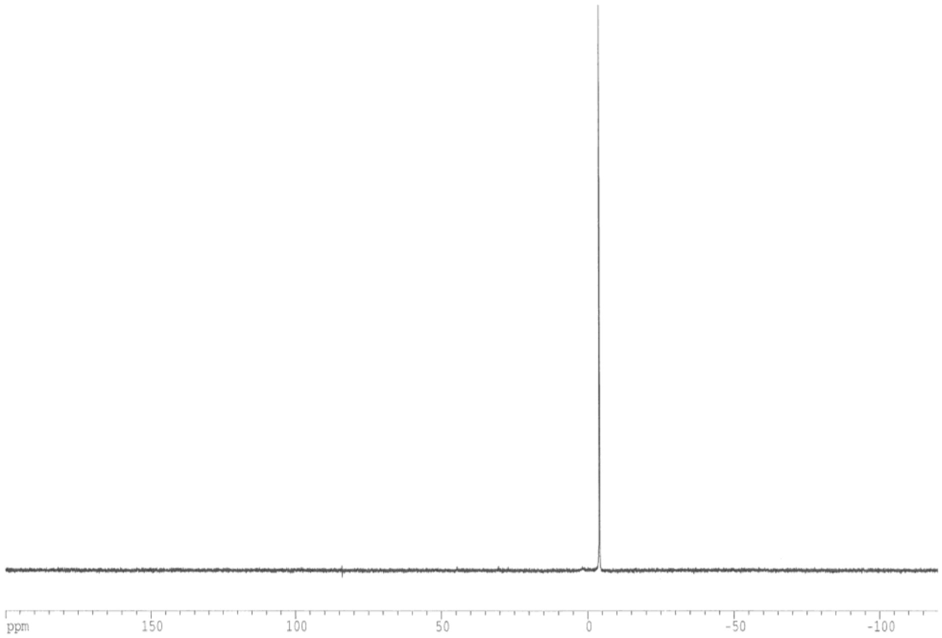

Figure 5: ^{31}P **spectrum of** $[(PPh_3)_2Cu(C_6H_{11}CS_2]$**.**

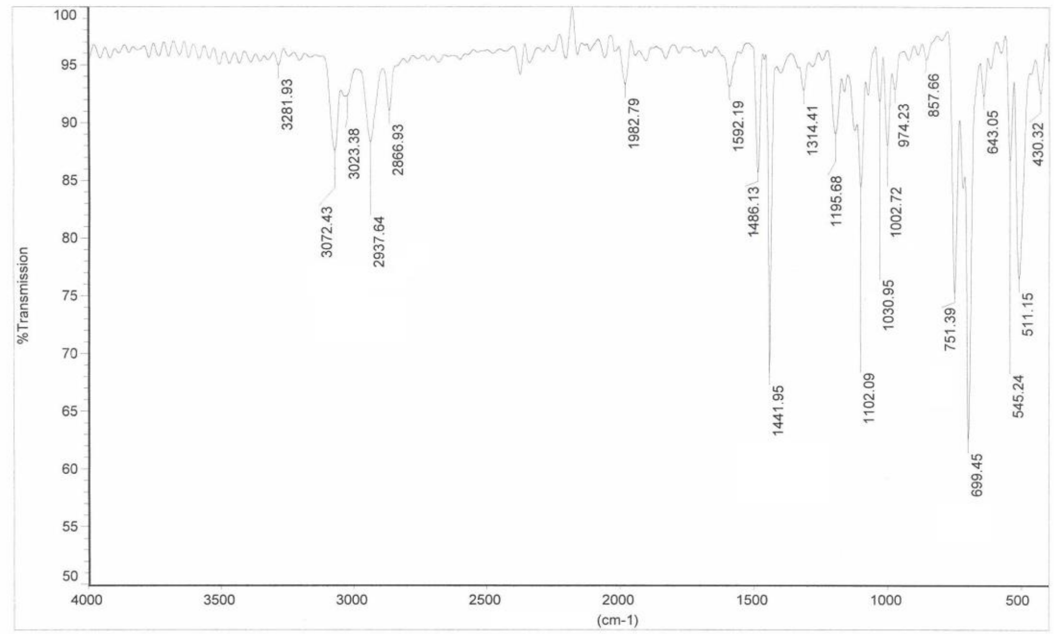

Figure 6: IR absorption spectrum of $[(PPh_3)_2Cu(C_6H_{11}CS_2]$**.**

CONCLUSION

- In the title monomeric complex, the central Cu atom assumes a highly distorted tetrahedral environment.
- The coordination around the Cu(I) cation is formed by two S atoms from the bidentate CHDTC ligand and two P atoms from two TRIPHOS ligands.
- The number of RMN components agrees with the molecular structure.
- The vibrational properties of this structure were studied by infrared spectroscopy.

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