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Structures and Spectral Properties of (O-*sec*.-Butyldithiocarbonatio-S,S′) Bis(triphenylphosphine) Copper(I) and Silver(I) Complexes

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New complexes $(PPh_3)_2M(S_2COR)$ [R = *sec*.-butyl, M = copper **(1)**, silver **(2)**] were synthesized by the reaction of excessive triphenylphosphine and copper(II) or silver(I) xanthate, and characterized using IR, EA, ^{1}H NMR and TG. Their crystal structures have been determined by X-ray diffraction. The light yellow crystal of the complex **(1)** is triclinic of space group $P\bar{1}$, with parameters a = 10.300(2) Å, b = 13.120(3) Å, c = 14.570(3) Å, α = 89.53(3), β = 72.81(3), γ = 78.61(3)°, and Z = 2. The yellow crystal of the complex **(2)** is triclinic of space group $P\bar{1}$, with parameters a = 10.330(2) Å, b = 13.410(3) Å, c = 14.420(3) Å, α = 88.61(3), β = 73.60(3), γ = 78.93(3)°, and Z = 2. In the two complexes, the central Cu or Ag atom is in a distorted tetrahedral environment and chelated by two phosphorus atoms from the triphenylphosphine groups and two sulfur atoms from the O-alkyldithiocarbonate. IR and ^{1}H NMR results supported the structures. The thermal analytical data indicate that the complex **(1)** began to decompose at 122.3° and decomposition was complete at 370.9°, leaving Cu_2S, while the complex **(2)** began to decompose at 133.3° and decomposed completely at 290.3° to Ag_2S.

Key words: copper complex, silver complex, triphenylphosphine, xanthate, synthesis, crystal structure, IR, NMR-spectra

The ability of the O-alkyldithiocarbonate, $ROCS_2^-$ ligand (xanthate) to bind to metal has been known for many years [1,2]. It forms a chelate with virtually all transition elements and has proven to be a versatile chelating agent for the separation and extracting of metals in analytical chemistry and mineral floating [3,4]. A review described in detail salts, complexes, free acids and esters as well as the reaction of xanthate [5]. Most of the bidentate complexes containing dithiolates such as dithiocarbamate and carbonadithiolate according to Singh *et al.* can react with Lewis bases [triphenylphosphine, phenanthroline, pyridine *et al.*] yielding the mono-, bis- and tetrakis-(Lewis base) adducts [6,7]. There have been many reports about the studies of the xanthate complexes towards several mono-, bi- and polydentate phosphine ligands [8–12].

Complexes of IB group metals of the general formula (Rxant)ML_n (with Rxant = O-alkylxanthate ion, L = PPh_3; n = 2 when M = Cu, Ag) have been synthesized and characterized by many workers [13,14]. The crystal structures of L_2Cu(MeXant) and L_2Cu(EtXant) have been reported [15–17]. However, the structures of L_2Ag(RXant) have not been proved by the X-ray diffraction, and the complexes L_2Cu(RXant) reported were prepared from copper(I) salts with overelaborated procedures. In this paper, (O-*sec*.-butyldithiocarbonatio-S,S′) bis(triphenylphosphine) copper(I) and silver(I) complexes were conveniently prepared and their crystal structures were presented. The IR, ^{1}H NMR and TG spectra of the complexes have also been determined.

EXPERIMENTAL

Preparation of the complexes. Synthesis of complex $(PPh_3)_2Cu(S_2COR)$. To an aqueous solution of $C_4H_9OCSSNa$ (0.17 g, 1.0 mmol) was added an aqueous solution of $CuSO_4$ (0.16 g, 0.5 mmol) with stirring. A yellowish brown precipitate (*sec*.-butylxanthato copper) was collected by filtration, washed with water, and dried under vacuum (yield 0.35 g, 96%). The dried precipitate was dissolved in ethanol and an excess of triphenylphosphine (0.84 g, 3.0 mmol) was added at 343–353K with stirring. The solution was then refluxed for 1–2 h. Upon cooling, the light-yellow solution obtained was filtered and left to evaporate. After a few days, a light-yellow solid had separated out and was recrystallized from EtOH/$CHCl_3$. Single crystals suitable for X-ray analysis were obtained by slow evaporation of an EtOH solution at room temperature.

The synthesis procedure of complex $(PPh_3)_2Ag(S_2COR)$ was similar to the complex **(1)**. The C and H contents of four compounds [$Cu(S_2COR)_2$, $(PPh_3)_2Cu(S_2COR)$, $Ag(S_2COR)$ and $(PPh_3)_2Ag(S_2COR)$] were determined by elemental analysis. Anal. Calcd. for $C_{10}H_{18}CuO_2S_4$: C, 33.15; H, 4.97. Found: C, 33.06; H, 5.14. for $C_{41}H_{39}CuOP_2S_2$: C, 66.73; H, 5.29. Found: C, 66.78; H, 5.28. for $C_5H_9AgOS_2$: C, 23.35; H, 3.50. Found: C, 23.48; H, 3.42. for $C_{41}H_{39}AgOP_2S_2$: C, 62.98; H, 5.01. Found: C, 62.89; H, 5.11.

Physical measurement. Elemental analysis was performed on PE-240 elemental analyzer. IR spectra were measured in KBr discs using a Brucker Vector 22 spectrophotometer. ^{1}H NMR spectra were obtained in $CDCl_3$ solution at 300 K on Bruker DRX 300 MHZ spectrophotometer. Thermal analyses were performed in nitrogen gas with a Shimadzu TGA-50(10°C/min).

Crystallographic data collection and solution of structure. A summary of the key crystallographic information is given in Table 1. The selected crystals of the title compounds were mounted on a Bruker P4 diffractometer. Reflection data and reflections for the unit cell determination were measured at 293 K using MoKα radiation ($\lambda = 0.071073$ nm) with a graphite monochromator. Intensities were corrected for Lorentz and polarization effects and empirical absorption correction was applied using SHELXTL5 [18]. The structures were solved by direct methods using SHELXS97 [19]. Nonhydrogen atoms were refined on F^2 anisotropically by full-matrix least squares method [20]. The hydrogen atoms were located from the difference map and refined isotropically. The final least-square cycle gave $R_1 = 0.0636$ and $wR_2 = 0.1465$ for 6465 reflections with $I > 2\sigma(I)$; the weighing scheme, $w = 1/[\sigma^2(F_o^2) + (0.1000P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$ for the complex **(1)**, and $R_1 = 0.0468$ and $wR_2 = 0.0854$ for 6593 reflections with $I > 2\sigma(I)$; the weighing scheme, $w = 1/[\sigma^2(F_o^2) + (0.0300P)^2 + 0.3000P]$, where $P = (F_o^2 + 2F_c^2)/3$ for the complex **(2)**. Atomic scattering factors and anomalous dispersion correction were taken from the International Tables for X-ray Crystallography [21]. The crystal structures for the title compounds have been deposited at the CCDC (CCDC-210337 for the complex **(1)**, and CCDC-211071 for the complex **(2)**). These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Table 1. Crystal data and data collection details for the title compounds.

	Complex **(1)**	Complex **(2)**
Empirical formula	$C_{41}H_{39}CuOP_2S_2$	$C_{41}H_{39}AgOP_2S_2$
Formula weight	737.32	781.65
Wavelength, Å	0.71073	0.71073
Crystal system, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
Unit cell dimensions	a = 10.300(2) Å α = 89.53(3)° b = 13.120(3) Å β = 72.81(3)° c = 14.570(3) Å γ = 78.61(3)°	a = 10.330(2) Å α = 88.61(3)° b = 13.410(3) Å β = 73.60(3)° c = 14.420(3) Å γ = 78.93(3)°
Volume, $Å^3$	1841.3(6)	1879.7(7)
Z	2	2
Calculated density, Mg m^3	1.330	1.381
Absorption coefficient, mm^{-1}	0.825	0.763
F(000)	768	804
Crystal size, mm	0.3× 0.2×0.1	0.35×0.26×0.30
Theta range for data collection	1.47 to 24.97°	1.47 to 24.97
Limiting indices	$0 \le h \le 12, -15 \le k \le 15, -16 \le l \le 17$	
Reflections collected/unique	6861/6465 [R(int) = 0.0517]	6997/6593 [R(int) = 0.0405]
Data/restraints/parameters	6465/0/424	6593/1/424
Goodness-of-fit on F^2	0.907	1.016
Final R indices [I>2sigma(I)]	R1 = 0.0636, wR2 = 0.1465	R1 = 0.0468, wR2 = 0.0854
R indices (all data)	R1 = 0.1991, wR2 = 0.2010	R1 = 0.1516, wR2 = 0.1066
Largest diff. peak and hole, e. $Å^{-3}$	0.476 and –0.416	0.510 and –0.496

RESULTS AND DISCUSSION

Analytical data. EA results for $Cu(S_2COR)_2$, $(PPh_3)_2Cu(S_2COR)$, $Ag(S_2COR)$ and $(PPh_3)_2Ag(S_2COR)$ are listed in the experimental section. These data are in good agreement with the calculated ones from the deduced molecular formula.

IR and NMR spectra properties. Table 2 lists three frequencies of four compounds. The IR spectra of four compounds exhibit characteristic strong bands at 1198–1177 cm^{-1} for υ(C–O–R) and 1101–1090 cm^{-1} for υ(C–O). The bands at 1037–1015 cm^{-1} are the characteristic absorption of υ(C=S) of the dithioformate group [12,14]. The IR spectra data show that the values of υ(C–O–R) are lower and υ(C=S) are higher when copper or silver xanthate are coordinated by triphenylphosphine.

The ^{1}H NMR spectra of two title complexes, triphenylphosphine and *sec.*-butylxanthato silver are listed in Table 2. As found previously from the ^{1}H NMR signals, there were not significant differences when xanthate coordinated to triphenylphosphine except for a small increase of the δ values [22]. Similar phenyl resonance of two complexes shows that the P–Cu–P angle is close to the P–Ag–P angle. All these findings support the crystal structures.

Table 2. IR and ^{1}H NMR spectroscopic data for the compounds[a].

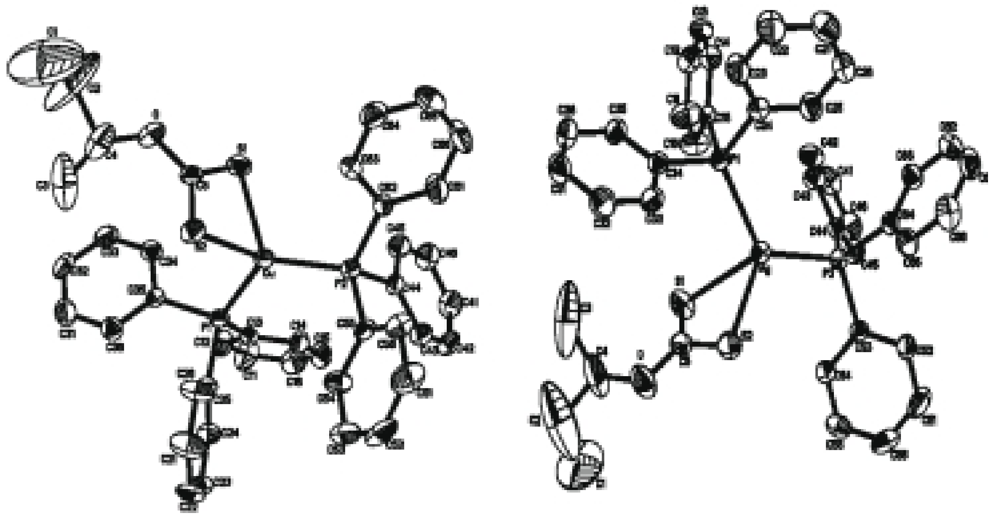
Compound	IR (cm^{-1}) data		
	v(C–O–R)	v(C–O)	v(C=S)
$Cu(S_2COR)_2$	1198	1101	1015
$L_2(S_2COR)Cu$	1190	1090	1035
$Ag(S_2COR)$	1177	1093	1037
$L_2(S_2COR)Ag$	1198	1095	1022

	^{1}H NMR (δ ppm)				
Compound	L	CH_3–[b]	CH_2–	CH_3–	CH–
$L_2(S_2COR)Cu$	7.2583	0.9158t	1.7386	1.2478d	5.2258
$L_2(S_2COR)Ag$	7.3205	0.9771t	1.8356	1.3433d	5.2662
$Ag(S_2COR)$		0.8906t	1.6286	1.1838d	4.1032
L	7.2653				

[a] L = PPh_3; R = sec.-butyl. [b] end methyl group. d = doublet; t = triplet.

Thermal gravimetric analyses. In order to examine the thermal stability of the title complexes, thermal gravimetric analyses were carried out from 20°C to 600℃ in nitrogen gas. The TGA curve of the complex **(1)** displays a weight loss of 87.568% between 122℃ to 370℃, which corresponds to the decomposition of the complex, leaving Cu_2S (calculated: 89.145%). For the complex **(2)**, between 133.3°C and 290.3°C, there is a weight loss of 83.142% corresponding to the decomposition to Ag_2S (calculated: 84.121%).

Crystal structure description. The crystal structures of the title compounds are illustrated in Fig. 1. Selected bond lengths and angles are given in Table 3. In two complexes, the copper or silver atom is tetrahedrally coordinated by two sulfur atoms from the bidentate xanthate and two phosphorus atoms from the triphenylphosphine ligand. The geometry of two complexes is highly distorted due to the small bite of the xanthate ligands, the bond angle of S1–Cu–S2 reaching the value of 73.96(9)° (range of the other angles 101.45(8)–125.99(8)°), and the angle of S1–Ag–S2 reaching the value of 67.13(6)° (range of the other angles 98.90(6)–25.65(6)°). The distortion is not restricted to the bond angles but also appears in bond distances. In the complex **(1)**, while the Cu–P bond distances (2.253(2), 2.269(2) Å), similar each to other, are in excellent agreement with those reported, the Cu–S bond distances (2.369(2), 2.484(2) Å) are not equivalent [16]. A similar arrangement is also observed in the complex **(2)**, the Ag–P1 bond distance (2.4687(18) Å) close to the bond length of Ag–P2 (2.4327(15)), and the Ag–S bond distances (2.7437(19), 2.5759(18) Å) are different. An unsymmetrical distribution around the metal atom has been proved in other monomeric copper(I) complexes and in dimeric silver(I) complex and tentatively rationalized on the basis of the well-known tendency of copper(I) or silver(I) to be three- or four-coordinated [23,24]. The P–Cu–P angle (125.99(8)°) is almost equal to the P–Ag–P angle (125.65(6)°). The reason why the mean Ag–P (2.4507 Å) and Ag–S (2.6598 Å) bond lengths are longer than the mean Cu–P (2.261 Å) and Cu–S (2.426 Å) bond distances is probably that the Ag^{1+} radius is bigger than Cu^{1+} radius.



$(PPh_3)_2Cu(S_2COR)$ $(PPh_3)_2Ag(S_2COR)$

Figure 1. ORTEP perspective of the title compounds showing the atom numbering scheme.

Table 3. Selected bond distances (Å) and angles (°) for the title compounds.

	Complex **(1)**		Complex **(2)**
Cu–P(1)	2.269(2)	Ag–P(1)	2.4687(18)
Cu–P(2)	2.253(2)	Ag–P(2)	2.4327(15)
Cu–S(1)	2.369(2)	Ag–S(1)	2.7437(19)
Cu–S(2)	2.484(2)	Ag–S(2)	2.5759(18)
S(1)–C(5)	1.664(9)		1.670(6)
S(2)–C(5)	1.677(8)		1.676(6)
C(5)–O	1.346(9)		1.344(7)
O–C(4)	1.427(12)		1.467(8)
P(1)–Cu–P(2)	125.99(8)	P(1)–Ag–P(2)	125.65(6)
P(1)–Cu–S(1)	110.80(9)	P(1)–Ag–S(1)	98.90(6)
P(2)–Cu–S(1)	115.08(9)	P(2)–Ag–S(1)	119.60(6)
P(1)–Cu–S(2)	101.45(8)	P(1)–Ag–S(2)	111.78(6)
P(2)–Cu–S(2)	117.12(8)	P(2)–Ag–S(2)	117.69(6)
S(1)–Cu–S(2)	73.96(9)	S(1)–Ag–S(2)	67.13(6)

In the complex **(1)**, Cu, P1, P2 and C35 atoms are planar, with the maximum deviation from the plane being –0.028 Å for Cu. Ag atom in the complex **(2)** lies on a plane defined by the atoms Ag, S1, S2 and C5, with the maximum deviation from the plane being –0.113 Å for C5.

The S_2CO group is planar to a very good approximation. The C(5)–O bond distance [1.346(9) Å in the complex **(1)** and 1.344(7) Å in the complex **(2)**] is shorter than C(4)–O [1.427(12) Å in the complex **(1)** and 1.467(8) Å in the complex **(2)**] bond length, which is indicative of considerable double-bond character. The C–S bond distances, 1.664(9)–1.677(8) Å and 1.670(6)–1.676(6) in complex **(1)** and **(2)**, respectively, agree well with those in related compounds [12,16,17].

The complex $(PPh_3)_2Cu(S_2COR)$ was easily synthesized here by the reaction of excessive triphenylphosphine and copper(II) xanthate, and yet similar derivatives reported were obtained by copper(I) salts [16,17]. Therefore, triphenylphosphine here acts as reducing agent that reduces Cu^{2+} to Cu^{1+} and it plays the role in stabilizing the low-valent metal as p-acid ligands as reported [25,26]. There have also been reports that $Au(S_2CNC_5H_{10})_3$ is reduced to gold(I) complex or azide reduction with triphenylphosphine [27,28].

CONCLUSIONS

The new complexes $(PPh_3)_2M(S_2COR)$ (R = *sec*.-butyl, M = copper or silver) have been synthesized and their crystal structures have been determined by X-ray diffraction. The results of IR, EA and ^1H NMR spectroscopic measurement for the complexes agree well with the crystal structures. The thermal analytical data showed that the complexes $(PPh_3)_2Cu(S_2COR)$ and $(PPh_3)_2Ag(S_2COR)$ decomposed completely at 370.9°C and 290.3°C, respectively, leaving Cu_2S and Ag_2S.

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