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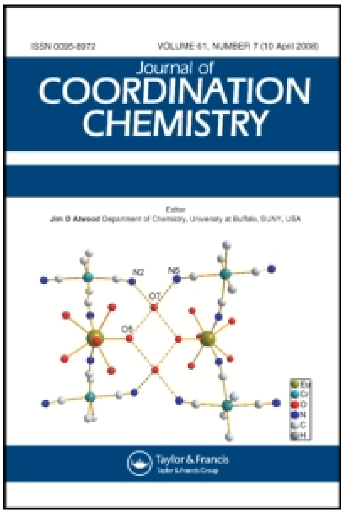

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THE CRYSTAL AND MOLECULAR STRUCTURE OF BIS(TRIPHENYLPHOSPH1NE)-(*O*-ETHYLDITHIOCARBONATO)SILVER(I)

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THE CRYSTAL AND MOLECULAR STRUCTURE OF BIS(TRIPHENYLPHOSPHINE)-(*O*-ETHYLDITHIOCARBONATO)SILVER(I)

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The crystal structure of the title compound, $Ag(PPh_3)_2(S_2COEt)$ is reported. The silver atom exists in a distorted tetrahedral environment defined by two PPh_3 ligands [Ag–P 2.469(4), 2.470(3) Å, P–Ag–P 115.6(1)°] and two S atoms derived from a chelating S_2COEt ligand [Ag–S 2.686(4), 2.601(4) Å, S–Ag–S 68.0(1)°]. Crystals are orthorhombic, space group $P2_12_12_1$ with unit cell parameters $a = 9.401(3)$, $b = 18.691(4)$, $c = 20.114(3)$ Å and $Z = 4$. The structure was refined by a full-matrix least-squares procedure to final $R = 0.047$ for 1790 reflections with $I \geq 2.5\sigma(I)$.

Keywords: Silver, triphenylphosphine, xanthate, complex, structure, X-Ray

INTRODUCTION

The addition of various bases to suspensions of polymeric xanthates, $[M^{m}(xan)_m]_n$(xan = $^{-}S_2COR$), often results in the ready dissolution of the xanthate and the subsequent isolation of a monomeric base adduct in which the coordination number of the central atom may be increased. Thus for example the insoluble $[Cu(xan)]_n$ compounds may be made soluble by the addition of PPh_3 and from such solutions, complexes of the form $Cu(xan)(PPh_3)_2$ may be isolated.[1,2] Similarly the polymeric structures of $[Cd(S_2COPr^i)_2]_n$[3] and $[Hg(S_2COPr^i)_2]_n$[4], which feature 16-membered rings as a result of bridging xanthate ligands and tetrahedral metal centres, react with PPh_3 to yield the 1 : 1 adducts $M(S_2COPr^i)_2PPh_3$, for which crystallographic studies have shown the central atom geometries to be five coordinate with chelating xanthate ligands.[5] Further changes in the mode of coordination of the xanthate ligand have been noted in other mixed xanthate/PPh_3 compounds for which X-ray crystal structures are available. Thus, the five coordinate $Ni(S_2COEt)_2PPh_3$ species features asymmetrically chelating and bidentate xanthate ligands[6] and, in the linear system $PPh_3Au(S_2COMe)$[7], a monodentate mode of coordination is found for the xanthate ligand.

The Ag(I) xanthates are thought to be polymeric due to their low solubility; however, their 1 : 2 PPh_3 adducts have been reported.[8,9] The addition of excess (4 : 1) PPh_3 to a suspension of freshly prepared $Ag(S_2COEt)$ (made from $AgNO_3$ and $[K][S_2COEt]$ in aqueous solution[8]) in acetone solution resulted in the dissolution of the Ag complex and, when left to stand overnight, the filtered solution deposited well-formed, pale yellow crystals with composition corresponding to the known compound $Ag(PPh_3)_2(S_2COEt)$; m.p. 184–186, lit.[8] 188–189°. The crystal structure analysis of this compound, reported herein, was investigated in order to determine the nature of the Ag atom geometry and the mode of coordination of the xanthate ligand.

EXPERIMENTAL

Intensity data for a crystal 0.10 × 0.10 × 0.63 mm were measured at room-temperature up to maximum Bragg angle of 25°, on an Enraf-Nonius CAD4 diffractometer fitted with Mo*Kα* radiation (graphite monochromator, λ 0.7107 Å) with the use of the $\omega : 2\theta$ scan technique. No significant decomposition of the crystal occurred during the data collection. Corrections were applied for Lorentz and polarization effects and for absorption (analytical procedure[10]); max./min. transmission factors were 0.9503 and 0.9112, respectively. The orthorhombic space group was uniquely determined from the systematic absences as $P2_12_12_1$. Of the 6572 reflections measured 4671 were unique (R_{int} 0.036) and of these, 1790 satisfied the $I \geq 2.5\sigma(I)$ criterion and were used in the subsequent analysis.

Crystal Data $C_{39}H_{35}AgOP_2S_2$, $M = 753.6$, orthorhombic, space group $P2_12_12_1$ (D_2^4, No. 19), $a = 9.401(3)$, $b = 18.691(4)$, $c = 20.114(3)$ Å, $U = 3534.3$ Å^2, $D_x = 1.43$, $Z = 4$, $D_c = 1.416\ \mathrm{g\,cm^{-3}}$, $\mu = 7.61\ \mathrm{cm^{-1}}$, $F(000) = 1544$.

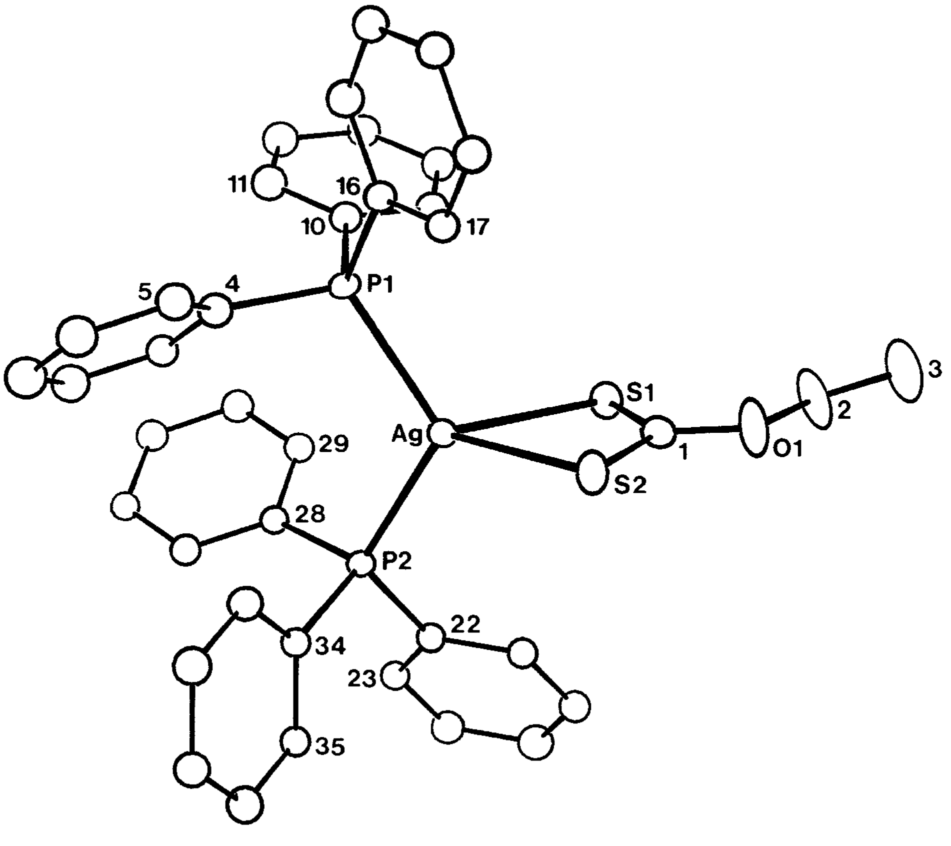

FIGURE 1 Molecular structure and numbering scheme for $Ag(PPh_3)_2(S_2COEt)$. Note that atoms otherwise not indicated are carbon atoms.

TABLE I
Fractional atomic coordinates for $Ag(PPh_3)_2(S_2COEt)$.

Atom	*x/a*	*y/b*	*z/c*
Ag	−0.20373(12)	−0.01864(6)	−0.35002(5)
S(1)	−0.3234(5)	−0.1442(2)	−0.3832(2)
S(2)	−0.1034(5)	−0.0684(2)	−0.4613(2)
P(1)	−0.0600(3)	−0.0238(2)	−0.2474(2)
P(2)	−0.3776(4)	0.0803(2)	−0.3559(2)
O(1)	−0.1979(13)	−0.1924(5)	−0.4905(6)
C(1)	−0.2067(17)	−0.1397(7)	−0.4476(7)
C(2)	−0.2830(21)	−0.2572(8)	−0.4839(10)
C(3)	−0.2265(24)	−0.3110(9)	−0.5214(11)
C(4)	−0.0157(9)	0.0648(5)	−0.2136(4)
C(5)	0.1181(9)	0.0947(5)	−0.2249(4)
C(6)	0.1438(9)	0.1660(5)	−0.2085(4)
C(7)	0.0356(9)	0.2075(5)	−0.1807(4)
C(8)	−0.0982(9)	0.1776(5)	−0.1694(4)
C(9)	−0.1238(9)	0.1063(5)	−0.1858(4)
C(10)	−0.1524(8)	−0.0722(4)	−0.1813(4)
C(11)	−0.1674(8)	−0.0488(4)	−0.1158(2)
C(12)	−0.2444(8)	−0.0897(4)	−0.0703(4)
C(13)	−0.3065(8)	−0.1540(4)	−0.0903(4)
C(14)	−0.2915(8)	−0.1774(4)	−0.1558(4)
C(15)	−0.2145(8)	−0.1365(4)	−0.2013(4)
C(16)	0.1114(8)	−0.0679(4)	−0.2526(3)
C(17)	0.1760(8)	−0.0771(4)	−0.3144(3)
C(18)	0.3109(8)	−0.1078(4)	−0.3186(3)
C(19)	0.3812(8)	−0.1294(4)	−0.2609(3)
C(20)	0.3166(8)	−0.1203(4)	−0.1991(3)
C(21)	0.1817(8)	−0.0896(4)	−0.1949(3)
C(22)	−0.5392(8)	0.0643(4)	−0.4036(3)
C(23)	−0.6682(8)	0.0961(4)	−0.3864(3)
C(24)	−0.7896(8)	0.0829(4)	−0.4244(3)
C(25)	−0.7818(8)	0.0380(4)	−0.4797(3)
C(26)	−0.6528(8)	0.0062(4)	−0.4969(3)
C(27)	−0.5314(8)	0.0193(4)	−0.4589(3)
C(28)	−0.4415(8)	0.1040(4)	−0.2722(4)
C(29)	−0.4747(8)	0.0469(4)	−0.2303(4)
C(30)	−0.5073(8)	0.0596(4)	−0.1637(4)
C(31)	−0.5067(8)	0.1293(4)	−0.1390(4)
C(32)	−0.4735(8)	0.1864(4)	−0.1809(4)
C(33)	−0.4409(8)	0.1737(4)	−0.2475(4)
C(34)	−0.3021(7)	0.1631(4)	−0.3882(4)
C(35)	−0.3768(7)	0.2071(4)	−0.4320(4)
C(36)	−0.3126(7)	0.2686(4)	−0.4575(4)
C(37)	−0.1738(7)	0.2860(4)	−0.4392(4)
C(38)	−0.0992(7)	0.2421(4)	−0.3953(4)
C(39)	−0.1633(7)	0.1806(4)	−0.3698(4)

The structure was solved by the Patterson method and refined by a full-matrix least-squares procedure in which the function $\Sigma w\Delta^2$ was minimized,[10] where $\Delta = \| F_{obs}| - |F_{calc}\|$ and w was the weight applied to each reflection. Phenyl groups were refined as rigid hexagonal groups and the remaining non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were included in the model at their calculated positions. The C(2)–C(3) bond distance was found to be shorter than anticipated. However, no significant residual electron density peaks were found in this region of the difference map and thus this disorder was not modelled. After the inclusion of a weighting scheme, $w = k/[\sigma^2(F) + g|F|^2]$, the refinement was continued until convergence, $R = 0.047$, $R_w = 0.047$, $k = 1.017$ and $g = 0.002$. The analysis of variance showed no special features and the maximum residual electron density peak in the final difference map was 0.67 e Å^{-3} in the vicinity of a phenyl group. The absolute configuration of the compound was determined by differences in Friedel pairs included in the data set.

The refinement was performed with the SHELX program[10] established on the University of Adelaide VAX 11/750 computer system. Scattering factors for neutral Ag (corrected for f′ and f″) were from the *International Tables for X-ray Crystallography*[11] and those for the remaining atoms were from SHELX.[10] Final fractional atomic coordinates are listed in Table I, the numbering scheme used is shown in Figure 1 (drawn with ORTEP[12]) and selected interatomic parameters are given in Table II. Listings of thermal parameters, hydrogen atom parameters, all bond distances and angles and the observed and calculated structure factor tables are available from the Editor on request.

TABLE II
Selected interatomic distances (Å) and bond angles (°) for $Ag(PPh_3)_2(S_2COEt)$.

Distances			
Ag–P(1)	2.469(4)	Ag–P(2)	2.470(3)
Ag–S(1)	2.686(4)	Ag–S(2)	2.601(4)
S(1)–C(1)	1.70(2)	S(2)–C(1)	1.67(1)
C(1)–O(1)	1.31(2)		
Angles			
P(1)–Ag–P(2)	115.6(1)	P(1)–Ag–S(1)	113.7(1)
P(1)–Ag–S(2)	120.5(1)	P(2)–Ag–S(1)	111.4(1)
P(2)–Ag–S(2)	117.8(2)	S(1)–Ag–S(2)	68.0(1)
Ag–S(1)–C(1)	82.9(5)	Ag–S(2)–C(1)	86.1(5)
S(1)–C(1)–S(2)	122.7(8)	S(1)–C(1)–O(1)	120(1)
S(2)–C(1)–O(1)	117(1)		

RESULTS AND DISCUSSION

The structure determination confirms the stoichiometry of the compound as $Ag(PPh_3)_2(S_2COEt)$. The crystal structure is composed of discrete molecular units, there being no intermolecular contacts less than 3.5 Å between non-hydrogen atoms.

The Ag atom is coordinated by two PPh_3 groups and two S atoms derived from the bidentate $^-S_2COEt$ ligand. The Ag–P distances of 2.469(4) and 2.470(3) Å are equal within experimental error and lie in the range expected for Ag–PPh_3 bonds of 2.363–2.529 Å (quoted in ref.).[13] The Ag–S bond lengths of 2.686(4) and 2.601(4) Å are longer than those found in comparable Ag coordination compounds which feature a P_2S_2 donor set. Thus for example the Ag–S bond distances of 2.580(6) and 2.578(5) Å [Ag–P 2.477(6); 2.447(5) Å] are found in $PPh_3Ag(\mu\text{-}S)_2W(\mu\text{-}S)_2AgPPh_3$[14] and Ag–S distances of 2.573(4) and 2.571(5) Å [Ag–P 2.471(4); 2.470(4) Å] are found for the comparable Ag atom in the Mo analogue.[15] The lengthening of the Ag–S bonds in $Ag(PPh_3)_2(S_2COEt)$ suggests a small contribution of the ionic formulation $[Ag(PPh_3)_2]^+[S_2COEt]^-$ to the molecular structure. A similar situation has been noted in the compound $Sb(oxin)_2(S_2COEt)$, where oxin = 8-hydroxyquinolate, in which the Sb–S separations are > 3.1 Å.[16] The overall coordination about the Ag atom is a distorted tetrahedral one, the distortion being due in part to the restricted bite angle of the xanthate ligand with S–Ag–S being 68.0(1)°.

The structure found for $Ag(PPh_3)_2(S_2COEt)$ has a precedent in the closely related $Cu(PPh_3)_2(S_2COR)$ compounds (R = Me[1], Et[2]) which display distorted tetrahedral Cu centres. A similar geometry has also been found in the dithiocarbamate complex $Cu(PPh_3)_2(S_2CN(H)Ph)$[2] and in the dithiophosphate analogue $Cu(PPh_3)_2(S_2P(OEt)_2)$.[17] Although no other Ag or Au phosphine/dithiolate complexes of the general formula $M(PPh_3)_2$(dithiolate) have been structurally characterized, the crystal structure of the 1 : 1 adduct between $Ag(S_2P(OEt)_2)$ and PPh_3 has recently been reported.[13] This compound crystallizes as centrosymmetric dimeric units, which arise as a result of the presence of bridging dithiophosphate ligands. Thus a chelating $S_2P(OEt)_2$ group simultaneously bridges a second Ag atom *via* one of its S donor atoms [Ag–S 2.821(2); 2.810(2) Å and S–Ag′ 2.502(2) Å]. By way of contrast, the related $Au(dithiolate)PPh_3$ compounds (dithiolate = S_2COMe[7] and S_2CNEt_2[18]) are monomeric with linear P–Au–S units.

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REFERENCES

1. G. Ciani, M. Manassero, L. Naldini and M. Sansoni, *Izv. Jugosl. Cent. Kristalografiju, Ser. A*, **11**, 6 (1976).
2. C. Bianchini, C.A. Ghilardi, A. Meli, S. Midollini and A. Orlandini, *Inorg. Chem.*, **24**, 932 (1985).
3. Y. Iimura, *Sci. Pap. Inst. Phys. Chem. Res. Jpn*, **67**, 43 (1973).
4. Y. Watanabe, *Acta Cryst.*, **B37**, 553 (1981).
5. B.F. Abrahams, M. Corbett, D. Dakternieks, R.W. Gable, B.F. Hoskins, E.R.T. Tiekink and G. Winter, *Aust. J. Chem.*, **39**, 1993 (1986).
6. E.R.T. Tiekink and G. Winter, *Aust. J. Chem.*, **39**, 813 (1986).
7. E.R.T. Tiekink, *Z. Kristallogr.*, **173**, 243 (1985).
8. C. Kowala and J.M. Swan, *Aust. J. Chem.*, **19**, 999 (1966).
9. F. Cariati, M.L. Ganadu, L. Naldini and S. Seneci, *Gazz. Chim. Ital.*, **109**, 181 (1979).
10. G.M. Sheldrick, "SHELX76. Program for Crystal Structure Determination", (Univ. of Cambridge, England, 1976).
11. W.C. Hamilton and J.A. Ibers, Editors, "International Tables for X-ray Crystallography", Vol. IV, pp. 99, 149, (Birmingham, Kynoch Press, 1974).
12. C.K. Johnson, ORTEPII, *Report ORNL-3794, Oak Ridge National Laboratory, Tennessee* (1971).
13. M.G.B. Drew, R.J. Hobson, P.P.E.M. Mumba and D.A. Rice, *J. Chem. Soc., Dalton Trans.*, 1569 (1987).
14. A. Müller, H. Bögge and E. Königer-Ahlborn, *Z. Naturforsch*, **34b**, 1698 (1979).
15. A. Müller, H. Bögge and U. Schimanski, *Inorg. Chim. Acta*, **69**, 5 (1983).
16. B.F. Hoskins, E.R.T. Tiekink and G. Winter, *Inorg. Chim. Acta*, **97**, 217 (1985).
17. M.G.B. Drew, G.A. Forsyth, M. Hasan, R.J. Hobson and D.A. Rice, *J. Chem. Soc., Dalton Trans.*, 1027 (1987).
18. J.G. Wijnhoven, W.P.J.H. Bosman and P.T. Beurskens, *J. Cryst. Mol. Struct.*, **2**, 7 (1972).