Inorganica Chimica Acta, 142 (1988) 301–303

Reactions of Metal Dialkyl Dithiophosphates
Part IV. The Crystal Structure of $[Ag\{S_2P(OEt)_2\}_2]_2^{2-}$ a Silver Anion containing Monodentate and Tridentate Dialkyl Dithiophosphate Groups

MICHAEL G. B. DREW, RICHARD J. HOBSON, PETER P. E. M. MUMBA and DAVID A. RICE

The Department of Chemistry, The University, Whiteknights, Reading RG6 2AD, U.K.

(Received June 9, 1987)

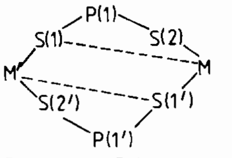
Abstract

The reaction between $Ag\{S_2P(OEt)_2\}$ and $[Me_4N][S_2P(OEt)_2]$ yields $[Me_4N][Ag\{S_2P(OEt)_2\}_2]$ (**1**), crystals of which are monoclinic, space group $P2_1/c$, with $a = 12.966(11)$, $b = 16.159(14)$, $c = 12.898(15)$ Å, $\beta = 106.0(1)°$, $Z = 2$; 2545 significant reflections were measured on a diffractometer and the structure was refined to $R = 0.068$ ($R_w = 0.088$). **1** contains the centrosymmetric species $[Ag\{S_2P(OEt)_2\}_2]_2^{2-}$ in which two dialkyldithiophosphate ligands bridge the two metal centres while the other two dialkyldithiophosphate residues are monodentate. The two sulphur atoms of the bridging dialkyldithiophosphate ligands bond very differently; thus while S(1) bridges two silver atoms [2.679(3) and 2.868(3) Å], S(2) is only bonded to one metal atom [2.728(3) Å]. Thus the ligands in the ring act simultaneously as bridging and chelating ligands. The four coordinate geometry around the metal is completed by S(3) [Ag–S(3) 2.517(3) Å] which is from the monodentate ligand.

Introduction

Single crystal studies have revealed that a number of metal dialkyl dithiophosphinates and dialkyl dithiophosphates exist as dimeric species, with either C_1 or approximate C_2 symmetry, in which eight-membered rings of the type M–S(2)–P(1)–S(1)–M′–S(2′)–P(1′)–S(1′) are present (Scheme 1) [1–5].

It has been suggested [1–6] that the formation of these dimeric units, which are also found in zinc and cadmium dialkyl dithiocarbamates, is favoured because there is less angular strain about the metal atom than would be present in a monomeric species with two chelating ligands.



Scheme 1. Schematic representation of the eight-membered ring. The dotted lines represent an interaction defined as type (a) in the text. Type (b) has a similar ring but with no across the ring interaction.

The rings can be divided into two types, dependent upon whether the metal [M] and S(1) atoms [and M′–S(1′)] across the ring (shown dotted in Scheme 1) are either within bonding distance (type a) or not (type b). Examples of type b include the cadmium and zinc diisopropyl dithiophosphates [1] [approximate C_2 symmetry, Zn···S 3.347(6), Cd···S 3.194(8) Å] and $[Cu\{S_2P(OEt)_2\}\cdot bipy]_2$ [C_1 symmetry, Cu···S 3.692(3) Å] [2]. Until recently examples of type a, where the cross ring distances are indicative of bonding interactions, were restricted to the zinc and cadmium dialkyl dithiocarbamates, for example $[Zn\{S_2CN(Et)_2\}_2]_2$ [7] and $[Cd\{S_2CN(Et)_2\}_2]_2$ [8] [C_1 symmetry, Zn···S 2.815(2), Cd···S 2.800(3) Å].

However we have recently found [5] a ring of type a in the structure of $[Ag\{S_2P(OEt)_2\}\cdot PPh_3]_2$, which has a centrosymmetric eight-membered ring with Ag–S(1) cross-ring interactions of 2.821(2) Å. The diethyl dithiophosphate residue acts as a chelate as well as having a short across the ring interaction. Thus it is acting in a unique tridentate manner in being both chelating and bridging. This unusual structure may have arisen through the steric requirements of the bulky $[S_2P(OEt)_2]^-$ and PPh_3 ligands or because of a lack of available donor atoms; as there are only three donor atoms in monomeric $Ag\{S_2P(OEt)_2\}\cdot PPh_3$ one of them has to act as a bridge between two silver atoms for these to be four coordinate. To investigate the situation further we have prepared $[Me_4N][Ag\{S_2P(OEt)_2\}_2]$ (**1**), which contains four donor atoms per silver atom, and determined its structure using single crystal X-ray methods.

Experimental

To a solution of $[Me_4N][OH]\cdot 5H_2O$ (1.24 g in CH_3OH, 15 cm^3) was added a solution of $[NH_4]$-

0020-1693/88/$3.50

$[S_2P(OEt)_2]$ (1.40 g in CH_3OH, 3 cm^3). The mixture was stirred until the evolution of NH_3 ceased when $Ag\{S_2P(OEt)_2\}$ (2.00 g) dissolved in CH_2Cl_2/propan-2-ol (1:1 *v/v*, 5 cm^3) was added. Removal of the solvent *in vacuo* gave a white powder which on recrystallization from CH_2Cl_2/toluene (1:1 *v/v*) gave crystals suitable for a single crystal X-ray study.

Crystal Data for $[Me_4N]_2[Ag\{S_2P(OEt)_2\}_2]_2$ *(1)*

$C_{24}H_{64}N_2O_8P_4S_8Ag_2$, $M = 1104.94$, monoclinic, $a = 12.966(1)$, $b = 16.159(14)$, $c = 12.898(15)$ Å, $\beta = 106.0(1)^\circ$, $U = 2597.75$ Å^3, $D_m = 1.46$ g cm^3 (flotation), $D_c = 1.41$ g cm^3, $Z = 2$, $F(000) = 1136$, Mo Kα radiation, $\lambda = 0.7107$ Å, $\mu = 12.00$ cm^{-1}, space group $P2_1/c$. Data were collected as previously described [9]. 3999 independent reflections with $2\theta < 50^\circ$ were measured of which 2545 with $I > 3\sigma(I)$ were used in the subsequent refinement. The structure was solved by normal heavy atom methods. All atoms in the anion except hydrogen were refined anisotropically. The tetramethylammonium ion was disordered and 2 positions were refined for each carbon atom but hydrogen atoms were not included. The non-chelating sulphur atom S(4) was disordered and three different positions were refined. In the anion hydrogen atoms were placed in tetrahedral positions and those bonded to the same carbon atoms were given a common refined thermal parameter. The weighting scheme used was $w = 1/[\sigma(F) + 0.002F^2]$ where $\sigma(F)$ was taken from counting statistics. Calculations were carried out using SHELX-76 [10] and some of our own programs on the University of Reading Amdahl V7 computer. The final R value was 0.068 (R_w 0.088). Atomic coordinates are given in Table I and selected bond lengths and angles in the anion are given in Table II.

TABLE I. Atomic Coordinates ($\times 10^4$) [a]

Atom	*x*	*y*	*z*
Ag(1)	1346(1)	80(1)	547(1)
S(2)	909(2)	1440(2)	1604(3)
P(1)	−54(2)	707(2)	2176(2)
S(1)	−305(2)	−410(2)	1511(2)
P(2)	3768(3)	−572(3)	2592(3)
S(3)	3131(2)	−647(2)	965(3)
S(4A)	5146(6)	−1104(6)	3195(6)
S(4B)	4858(11)	−1508(10)	3154(12)
S(4C)	5457(9)	−747(8)	3090(10)
N(60)	−1415(8)	3068(7)	−672(10)
C(61)	−1773(15)	2758(9)	341(14)
C(62)	−1024(28)	3920(17)	−545(29)
C(63)	−674(12)	2508(9)	−949(10)
C(64)	−2393(12)	3200(11)	−1671(11)
C(65)	−2060(21)	3611(18)	−1528(19)
C(66)	−1045(16)	2247(11)	−1106(13)
C(67)	−594(17)	3670(13)	−86(18)
C(68)	−2216(24)	2707(15)	− 73(24)
O(21)	−1206(7)	1188(5)	2040(8)
C(22)	−2064(7)	911(7)	2421(10)
C(23)	−2880(9)	1334(8)	2300(12)
O(31)	410(10)	542(6)	3469(8)
C(32)	979(13)	1182(15)	4147(9)
C(33)	1299(16)	978(8)	5313(9)
O(41)	3858(15)	422(11)	2876(17)
C(42)	4362(10)	791(6)	3679(11)
C(43)	4161(17)	1730(9)	3628(11)
O(51)	2812(15)	−955(16)	3064(17)
C(52)	2761(12)	−1380(9)	4032(18)
C(53)	1907(15)	−1594(12)	4202(14)

[a] E.s.d.s given in parentheses.

TABLE II. Molecular Dimensions in the Coordination Sphere [a]

Distances (Å)	
Ag(1)···Ag(1)*	3.396(2)
Ag(1)–S(2)	2.728(3)
Ag(1)–S(1)	2.868(3)
Ag(1)–S(3)	2.517(3)
Ag(1)–S(1*)	2.679(3)
Angles (°)	
S(2)–Ag(1)–S(1)	73.90(8)
S(2)–Ag(1)–S(3)	125.03(10)
S(1)–Ag(1)–S(3)	122.02(10)
S(2)–Ag(1)–S(1*)	102.52(9)
S(1)–Ag(1)–S(1*)	104.59(8)
S(3)–Ag(1)–S(1*)	119.23(11)

[a] Starred items: symmetry element −*x*, −*y*, −*z*.

Results

The $[Ag\{S_2P(OEt)_2\}_2]_2{}^{2-}$ anion, depicted in Fig. 1 together with the atom numbering scheme, has a centrosymmetric dimeric structure containing an eight-membered Ag–S(2)–P(1)–S(1)–Ag′–S(2′)–P(1′)–S(1′) ring similar to those [1–5] in other related compounds. However there are also strong cross-ring interactions [Ag–S(1) 2.868(3) Å] like those [5] in $[Ag\{S_2P(OEt)_2\}\cdot PPh_3]_2$ [2.821(2) Å]. Thus the $[S_2P(OEt)_2]^-$ groups in the ring are both chelating and bridging. The other $[S_2P(OEt)_2]^-$ moieties are monodentate with one sulphur atom [S(4)] uncoordinated and having no long range interactions within the sum of van der Waals radii. The anion might be expected to have a structure similar to that of $[Cd\{S_2P(OPr^i)_2\}_2]_2$, which is isoelectronic and has an eight-membered ring without strong cross-ring interactions with the exocyclic $[S_2P(OPr^i)_2]^-$

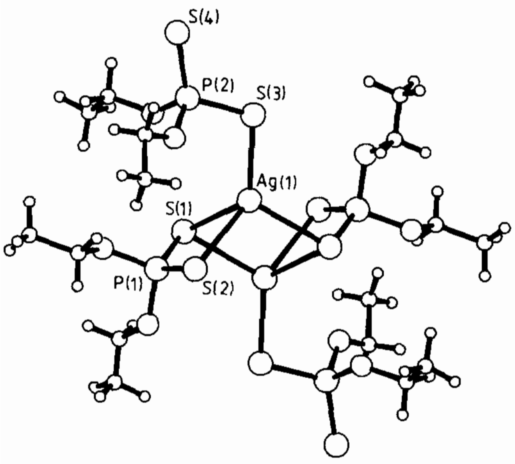


Fig. 1. The structure of the $[Ag\{S_2P(OEt)_2\}_2]_2{}^{2-}$ anion.

groups forming chelate rings [1]. However, the eight-membered ring in the latter complex has approximate C_2 symmetry, and no zinc or cadmium complex containing a ring with this symmetry [1, 4, 6] has ever been found to have significant cross-ring interactions.

The factors which determine whether the dimer is C_2 or C_1 are not clear but seem to be associated with intermolecular (*i.e.* packing) rather than intramolecular interactions. This is shown by a consideration of the structures of $[Zn\{S_2CNMe_2\}_2]_2$ [6], $[Zn\{S_2P(OPr^i)_2\}_2]_2$ [1] and $[Zn\{S_2CNEt_2\}_2]_2$ where the steric requirements of the alkyl groups are $Me < Et < Pr^i$. Thus while the first two compounds form rings with C_2 symmetry of type b the remaining compound has a ring with C_1 symmetry [7] having signficant cross-ring interactions [Zn···S 2.815(2) Å]. Thus the formation of a centrosymmetric rather than a non-centrosymmetric dimer in **1** is probably governed by packing forces, and a more valid comparison would be to $[Cd\{S_2CN(Et)_2\}_2]_2$ which contains an eight-membered ring of C_1 symmetry with significant cross-ring interactions [8].

In **1** the exocyclic ligand is monodentate, giving the silver atom a four coordinate environment, whereas in $[Cd\{S_2CN(Et)_2\}_2]_2$ it is chelating making the cadmium atom five coordinate. This difference is consistent with the known coordination geometries of the elements of groups Ib and IIb; that is the lower coordination number of Ag compared to Cd. Examination of the silver–sulphur distances in the present structure shows that those of the chelate ring [Ag–S(1) 2.868(3), Ag–S(2) 2.728(3) Å] are appreciably longer than the other two silver–sulphur bonds [Ag–S(1′) 2.679(3), Ag–S(3) 2.517(3) Å]. This contrasts with the structure of $[Cd\{S_2CN(Et)_2\}_2]_2$, where only the cross-ring bonds Cd···S 2.800(3) Å] are excessively long and the remaining four Cd–S bond lengths fall in the relatively narrow range of 2.536(4)–2.644(3) Å, suggesting that there may be considerably more strain involved in the formation of chelate rings with silver(I) than with cadmium(II) by this type of ligand. This proposal is supported by the common occurrence of bridging dialkyl dithiophosphate groups in compounds formed with the group Ib elements, for example [2, 11, 12] $Cu\{S_2P(OEt)_2\}\cdot$2,2′-bipy, $[Cu\{S_2P(OPr^i)_2\}]_4$, and $[Au\{S_2P(OPr^i)_2]_n$, and the rare occurrence of chelates. There are some exceptions, *viz.* $Cu\{S_2P(OEt)_2\}\cdot 2PPh_3$ [2] and $Cu\{S_2P(OPh)_2\}\cdot$2.9-dimethyl-phen [13], but in both cases the bulky steric effects of the other ligands may override any preference for bridges.

The coordination sphere in the present structure is more regular than that observed in $[Ag\{S_2P(OEt)_2\}\cdot PPh_3]_2$. The chelate angle S(1)–Ag–S(2) is 73.9(1)° but the other angles range from 102.5(1)–125.0(1)°. The equivalent angles in $[Ag\{S_2P(OEt)_2\}\cdot PPh_3]_2$ range from 73.7(1) to 142.8(1) for S(1′)–Ag–PPh$_3$. This disparity between the two structures may indicate that steric effects are important in establishing the exact geometry around the Ag(I) ion.

Acknowledgements

We thank the Food and Agriculture Organization of the United Nations for a grant to P.P.E.M.M. and Mr A. W. Johans for his help in the collection of the crystallographic data.

References

1 S. L. Lawton and G. T Kokotailo, *Inorg. Chem.*, *8*, 2410 (1969).
2 M. G. B. Drew, G. A. Forsyth, M. Hasan, R. J. Hobson and D. A. Rice, *J. Chem. Soc., Dalton Trans.*, 1027 (1987).
3 H. Wunderlich, *Acta Crystallogr., Sect. B*, *38*, 614 (1982).
4 M. Calligaris, G. Nardin and A. Ripamonti, *J. Chem. Soc. A*, 714 (1970).
5 M. G. B. Drew, R. J. Hobson, P. P. E. M. Mumba and D. A. Rice, *J. Chem. Soc., Dalton Trans.*, 1569 (1987).
6 H. P. Klug, *Acta Crystallogr.*, *21*, 536 (1966).
7 M. Bonamico, G. Mazzone, A. Vaciago and L. Zambonelli, *Acta Crystallogr.*, *19*, 898 (1965).
8 A. Domenicano, L. Torelli, A. Vaciago and L. Zambonelli, *J. Chem. Soc. A*, 1351 (1968).
9 M. G. B. Drew, M. Hasan, R. J. Hobson and D. A. Rice, *J. Chem. Soc., Dalton Trans.*, 1161 (1986).
10 G. M. Sheldrick, 'SHELX-76', package for crystal structure determination, University of Cambridge, 1976.
11 S. L. Lawton, W. J. Rohrbaugh and G. Kokotailo, *Inorg. Chem.*, *11*, 612 (1972).
12 S. L. Lawton, W. J. Rohrbaugh and G. Kokotailo, *Inorg. Chem.*, *11*, 2227 (1972).
13 M. G. B. Drew, G. A. Forsyth, R. J. Hobson and D. A. Rice, unpublished results.