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Structure of of *Bis*(O,O'-dialkyldithio-phosphato) Dimeric Silver(I) with *Bis*(1,10-phenanthroline): $Ag_2[(PhO)_2PS_2]_4(Phen)_2$ and $Ag_2[(PrO)_2PS_2]_4(Phen)_2$

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The crystal and molecular structures of $Ag_2[(PhO)_2PS_2]_4(Phen)_2$ and $Ag_2[(PrO)_2PS_2]_4(Phen)_2$ (Phen = 1,10-phenanthroline) have been determined by X-ray crystallography. The crystal structures in two complexes are difference. The former crystallizes in the monoclinic system, space group P2(1)/c, with lattice parameters a = 11.140(2), b = 10.044(2), c = 23.006(6) Å, β = 113.36(3)° and Z = 4. The latter crystallizes in triclinic, P-1, with a = 9.875(2), b = 10.992(2), c = 11.232(2) Å, α = 68.32(3), β = 99.55(3), γ = 65.16(3)° and Z = 2. The molecular structures of them are similar. They all display distorted tetrahedral geometry around the central silver atom. The two dialkyldithiophosphato ligands bridge two silver atoms to form an eight-membered $Ag_2S_4P_2$ ring, while the 1,10-phenanthroline molecule coordinates to a silver atom to complete the local tetrahedral geometry. The Ag···Ag separation in the two dimer are 3.185(2) and 3.207(1) Å, respectively.

Key Words: Dimeric silver(I) complexes, 1,10-Phenanthroline, Dialkyldithiophosphate.

INTRODUCTION

Dialkyl dithiophosphate complexes of transition metals have received increasing attention in recent years owing to their extensive applications in lubrication engineering and in the plastics industry[1,2]. In addition to their syntheses and various physico-chemical investigations, the crystal structures of many of these compounds and their adducts with nitrogen bases have been reported[3,4]. Metal chelates in which the metal ion is coordinately unsaturated can act as electron acceptors and yield adducts with the neutral molecules being electron donors[5]. Adducts and their formation reactions have also been found useful in a wide variety of ways. The amines in lubricating oil have a great influence on the properties of metal dialkyl dithiophosphate additives[6]. It is interesting to investigate further the interaction between metal dialkyl dithiophosphate and amines. When 1,10-phenanthroline reacts with bis(dialkyldithiophosphato) silver(I) in EtOH, we obtained two new dinuclear silver(I) complex; bis(1,10-phenanthroline) bis(diphenyldithiophosphato) disilver(I) $[Ag_2[(PhO)_2PS_2]_4(Phen)_2]$ and bis(1,10-phenanthroline) bis(dipropyldithiophosphato) disilver(I) $[Ag_2[(PrO)_2PS_2]_4(Phen)_2]$. Here we report the crystal structure for these two new complexes.

EXPERIMENTAL

All chemicals used were of analytical reagent grade and used directly without further purification. $Na[RO]_2PS_2$ (R = Ph, Pr) was prepared according to literature method[7].

$Ag[(RO)_2PS_2]_2$ (1): Stoichiometric amounts of silver(I) nitrate and sodium O,O-dialkyldithiophosphates in de-ionized water were stirred together for 20 min. The brown precipitate was collected by filtering, washed with water and then dried over P_4O_{10}. The complexes were collected and submitted for elemental analysis. [Anal. (%) Calcd. for $Ag[PhO]_2PS_2]_2$: C, 37.04; H, 2.59. Found: C, 36.82, H, 2.67; Anal.(%) Calcd. for $Ag[(PrO)_2PS_2]_2$: C, 22.44; H, 4.39. Found: C, 22.21, H, 4.27].

$Ag_2[(RO)_2PS_2]_4(Phen)_2$ (2): The metal complexes (**1**) (2.0 mmol) were dissolved in hot ethanol (50 mL), a slight excess of phenanthroline was added, and the resulting solution was refluxed for 4-5 h. The colourless mixture were cooled to room temperature, then filtered off and the filtrate were left to stand undisturbed. Upon slow evaporation at room temperature, the colourless crystalline solid (**2**) appeared several days later and were separated by filtration. The C, H and N contents were determined by elemental analysis [Anal. (%) Calcd. for $Ag_2[(PhO)_2PS_2]_4(Phen)_2$: C, 50.63; H, 3.19; N, 4.92. Found: C, 50.15; H, 3.06; N, 4.43; Anal. (%) Calcd. for $Ag_2[(PrO)_2PS_2]_4(Phen)_2$: C, 43.47; H, 3.65; N, 5.63. Found: C, 42.92; H, 3.48; N, 5.26].

A summary of the key crystallographic information is given in Table-1. Reflection data and reflections for the unit cell determination were measured at 20°C using Mo K_α radiation ($\lambda = 0.71073$ Å) with a graphite monochromator. The technique used was ω-scan with θ limits $1.93 < \theta < 24.98°$ for $Ag_2[(PhO)_2PS_2]_4(Phen)_2$ and $1.97 < \theta < 27.54°$ for $Ag_2[(PrO)_2PS_2]_4(Phen)_2$. Intensities were corrected for Lorentz and polarization effects and empirical absorption and the data reduction using SADABS program[8].

The structures of $Ag[(RO)_2PS_2]_4(Phen)_2$ were solved by direct methods and refined by least squares on F^2_{obs} by using the SHELXTL software[9] package. All non-H atoms were anisotropically refined. The hydrogen atoms were located by difference synthesis and refined isotropically. For $Ag_2[(PhO)_2PS_2]_4(Phen)_2$, final conventional R(F) = 0.0961 and $wR(F^2) = 0.2885$ for $I > 2\sigma(I)$ with weighting scheme, $w = 1/[\sigma^2(F^2) + (0.0512P)^2 + 0.0000P]$, where $P = (F^2)+2Fc^2]/3$. For $Ag_2[(PrO)_2PS_2]_4(Phen)_2$, final conventional R(F) = 0.0493 and wR(F^2) = 0.1137 for I > 2σ(I) with weighing scheme, $w = 1/[\sigma^2(Fo^2) + (0.0710P)^2 + 0.0000P]$, where $P = (F^2) + 2Fc^2]/3$. The molecular graphics were plotted using SHELXTL[9]. Atomic scattering factors and anomalous dispersion corrections were taken from International tables for X-ray crystallography[10].

TABLE-1
CRYSTALLOGRAPHIC DATA FOR TWO COMPOUNDS

Compound	$Ag_2[(PhO)_2PS_2]_4(Phen)_2$	$Ag_2[(PrO)_2PS_2]_4(Phen)_2$
m.f.	$C_{24}H_{18}N_2O_2PS_2Ag$	$C_{18}H_{18}N_2O_2PS_2Ag$
m.w.	569.36	497.30
Crystal system	Monoclinic	triclinic
Space group	P2(1)/c	P-1
Unit cell dimensions (Å, °)	*a* = 11.140(2) *b* = 10.044(2) β = 113.36(3) *c* = 23.006(6)	*a* = 9.875(2) α = 68.32(3) *b* = 10.992(2) β = 74.93(3) *c* = 11.232(2) γ = 65.16(3)
V (Å^3)	2363.1(9)	1020.2(4)
Z	4	2
$D_{calc.}$ (mg/m^3)	1.600	1.619
μ (mm^{-1})	1.121	1.285
F(000)	1144	500
θ ranges (°)	1.93 to 24.98	1.97 to 27.51
h/k/l	$0 \le h \le 13$, $-11 \le k \le 0$, $-27 \le l \le 25$	$-12 \le h \le 11$, $-14 \le k \le 0$, $-14 \le l \le 12$
Reflections collected	4344/4117 [R(int) = 0.0302]	3377/3377 [R(int) = 0.0000]
Data/restraints/parameters	4117/0/290	3377/2/236
GOF	1.346	1.021
Final R indices [I > 2σ(I)]	R1 = 0.0961, wR2 = 0.2885	R1 = 0.0493, wR2 = 0.1137
R indices (all data)	R1 = 0.1385, wR2 = 0.3461	R1 = 0.0824, wR2 = 0.1260
Largest peak and hole (e·Å^{-3})	1.362 and -2.329	0.435 and -0.399

RESULTS AND DISCUSSION

The molecular structures of compounds $Ag_2[(PhO)_2PS_2]_4(Phen)_2$ and $[Ag_2[(PrO)_2PS_2]_4(Phen)_2$ are illustrated in Figs. 1 and 2, respectively. Fig. 3 shows a perspective view of the crystal packing in the unit cell for $Ag_2[(PhO)_2PS_2]_4(Phen)_2$. Selected bond distances and angles of these two compounds are listed in Table-2.

The molecular structures of both the compounds are similar and consist of discrete molecules of $Ag_2[(PhO)_2dtp]_4(Phen)_2$ and $Ag_2[(PrO)_2PS_2]_4(Phen)_2$, respectively. They are all built up of centrosymmeric dimeric entities. The coordination sphere of the silver(I) ion is best described as a distorted tetrahedral geometry. The two dialkyldithiophosphato ligands each bridge two silver atoms to form an eight-membered $Ag_2S_4P_2$ ring, while two 1,10-phenanthroline molecules coordinate to a silver to form a five-membered chelate ring, respectively. The (Ag-N) bond lengths are 2.338(10) and 2.443(8) Å for $Ag_2[(PhO)_2PS_2]_4$-$(Phen)_2$ and 2.366(3) and 2.471(3) Å for $Ag_2[(PrO)_2PS_2]_4(Phen)_2$ are comparable with those of 2.332(2), 2.342(2) and 2.419(2) Å found in other

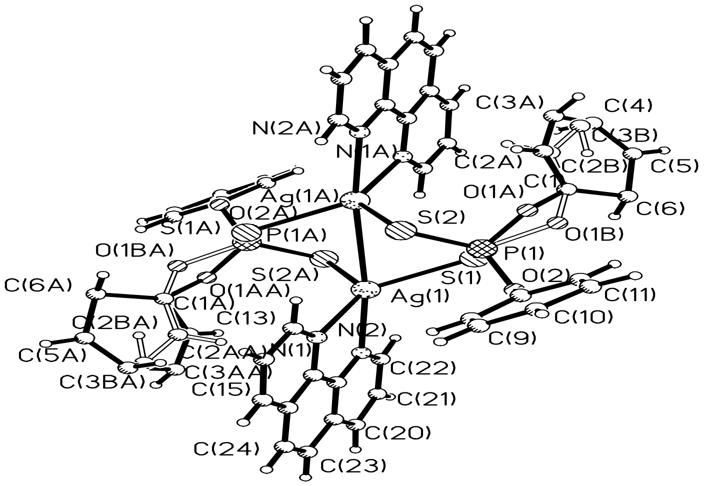

Fig. 1. Molecular structure of $Ag_2[(PhO)_2PS_2]_4(Phen)_2$ showing the atom labelling scheme. Atoms are represented as thermal ellipsoids at 50% level

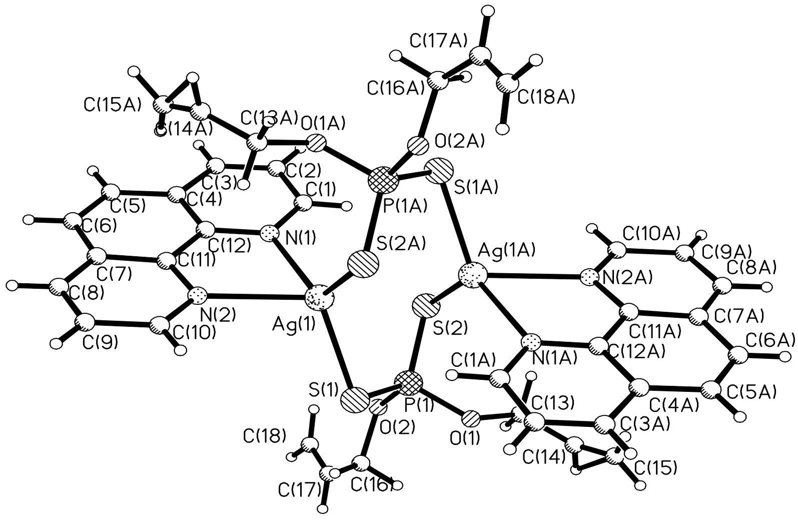

Fig. 2. Molecular structure of $Ag_2[(PrO)_2PS_2]_4(Phen)_2$ showing the atom labelling scheme

silver(I) complexes with tetrahedral coordination geometry[11-13]. There are obvious difference of the Ag-S bond distances between these two compounds. In the compound of $Ag_2[(PrO)_2PS_2]_4(Phen)_2$, the (Ag-S) bond lengths [2.559(1) and 2.567(1) Å] are observed compared with those of similar tetrahedral structure [2.507-2.644 Å][5,14]. However, there are one longer (Ag-S) bond distance [2.705(3) Å] and one shorter ones [2.482(3) Å] in the compound of $Ag_2[(PhO)_2PS_2]_4(Phen)_2$. It is apparent that the steric and electronic effects of the phenyl group can destabilize the (Ag-S) bond.

It is possible to interpret these results on the basis of a simple electrostatic model. The π conjugated system between O atom and phenyl ring reduces the net positive charge on the O atom and increases the net negative charge

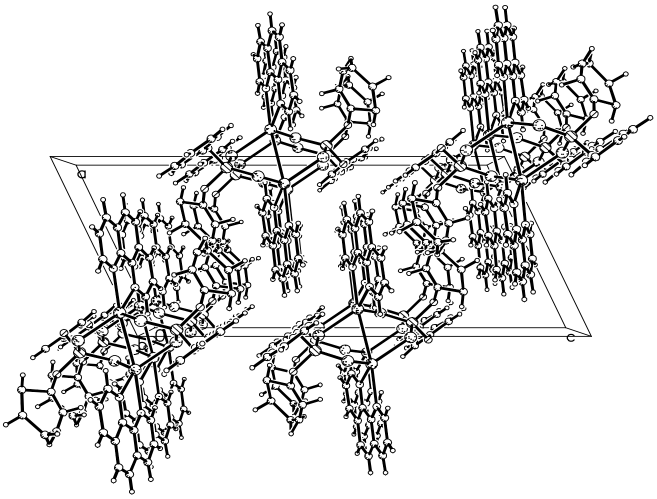

Fig. 3. View of the crystal packing down the a axis for $Ag_2[(PhO)_2PS_2]_4(Phen)_2$

TABLE-2
SELECTED BOND LENGTHS (Å) AND ANGLES (°)

$Ag_2[(PhO)_2PS_2]_4(Phen)_2$		$Ag_2[(PrO)_2PS_2]_4(Phen)_2$	
Ag(1)-N(1)	2.338(10)	Ag(1)-N(1)	2.366(3)
Ag(1)-S(1)	2.482(3)	Ag(1)-S(1)	2.559(1)
Ag(1)-Ag(1)#1	3.185(2)	Ag(1)-Ag(1)#1	3.207(1)
S(2)-P(1)	1.944(5)	S(2)-P(1)	1.980(2)
O(1A)-C(1)	1.470(2)	O(1)-C(13)	1.421(6)
Ag(1)-N(2)	2.443(8)	Ag(1)-N(2)	2.471(3)
Ag(1)-S(2)#1	2.705(3)	Ag(1)-S(2)#1	2.567(1)
S(1)-P(1)	1.963(4)	S(1)-P(1)	1.987(2)
P(1)-O(1A)	1.587(18)	P(1)-O(1)	1.594(3)
N(1)-C(13)	1.339(17)	N(1)-C(12)	1.342(5)
N(1)-Ag(1)-N(2)	68.500(3)	N(1)-Ag(1)-N(2)	68.880(13)
N(2)-Ag(1)-S(1)	120.200(2)	N(2)-Ag(1)-S(1)	109.280(10)
N(2)-Ag(1)-S(2)#1	88.900(3)	N(2)-Ag(1)-S(2)#1	100.990(9)
N(1)-Ag(1)-Ag(1)#1	114.200(2)	N(1)-Ag(1)-Ag(1)#1	105.660(9)
S(1)-Ag(1)-Ag(1)#1	65.910(9)	S(1)-Ag(1)-Ag(1)#1	81.600(5)
O(1A)-P(1)-O(2)	109.400(9)	O(1)-P(1)-O(2)	104.700(2)
N(2)-Ag(1)-S(1)	120.200(2)	N(1)-Ag(1)-S(1)	127.710(9)
N(1)-Ag(1)-S(2)#1	130.900(3)	N(1)-Ag(1)-S(2)#1	121.040(9)
S(1)-Ag(1)-S(2)#1	106.200(1)	S(1)-Ag(1)-S(2)#1	110.750(4)
N(2)-Ag(1)-Ag(1)#1	171.400(2)	N(2)-Ag(1)-Ag(1)#1	169.060(9)
O(2)-P(1)-S(2)	111.300(3)	O(1)-P(1)-S(2)	112.800(1)

on the S atoms. The latter effect results in an increase in the (S-P-S) angle [119.8(2)° for $Ag_2[(PhO)_2PS_2]_4(Phen)_2$, while the former effect lengthens the (Ag-S) distance and decreases the (S-Ag-S) angle [106.16(13)° for $Ag_2[(PhO)_2PS_2]_4(Phen)_2$. There are some disorder at O(1), C(2) and C(3) atoms in the compound of $Ag_2[(PhO)_2PS_2]_4(Phen)_2$. The occupies ratio of them are 60, 50 and 60 %, respectively.

The (P-S) bond lengths and (S-P-S) angles in both compounds are normal[15]. The phenanthroline ligand with Ag atoms are all planar. The average (C-C) distances in the phenanthroline rings are approximately the expected mean value of 1.40 Å. The Ag···Ag separations in the two dimmer are 3.185(2) Å and 3.207(1) Å, respectively, which are all in the range 2.93 to 3.52 Å, showing that no significant silver-silver interactions exist in the compound[5].

In the two title compounds, there are some π-π stacking interactions in the lattice[16,17]. The shortest center-to-center distances between the adjacent moieties are 3.469 Å and 3.603 Å for $Ag_2[(PhO)_2PS_2]_4(Phen)_2$ and $Ag_2[(PrO)_2PS_2]_4(Phen)_2$, respectively. It is obvious that they form the slightly stronger π-π stacking interaction[18]. In the solid state, all above extensive hydrogen bonds stablized the crystal structure.

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