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은(I) 화합물: 비스(디프로필디싸이오포스페이토)비스(1,10-펜안트로린) 이온(I); $Ag_2[Phen]_2[S_2P(OPr)_2]_2$

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Dimeric Silver(I) Complex: Bis(dipropyldithiophosphato) bis(1,10-phenanthroline) Disilver(I); $Ag_2[phen]_2[S_2P(OPr)_2]_2$

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요 약. 이핵 화합물, $Ag_2[Phen]_2[S_2P(OPr)_2]_2$ (Phen=1,10-phenanthroline; Pr=propyl)은 비스(디프로필디싸이오포스페이토) 은(I)화합물과 1,10-펜안트로린 리간드 반응에 의하여 합성되었고, 그 화합물 구조는 X-ray에 의하여 규명되었다. 두 디프로필디싸이오포스페이토 리간드는 두 개의 은 원자를 연결하여 팔각형 $Ag_2S_4P_2$ 고리를 형성하였고, 1,10-펜안트로린 리간드는 은 이온과 결합하여 사면체구조를 이루었다. Ag-S 결합거리는 2.471(1)와 2.567(1) Å이었고, Ag-N 결합 거리는 2.366(3)와 2.471(3) Å이었다.

주제어: Phen Ligand, Crystal Structure, Dimeric Silver(I), Dithiophosphate

ABSTRACT. The dinuclear complex, $Ag_2[phen]_2[S_2P(OPr)_2]_2$ (phen=1,10-phenanthroline; Pr=propyl), was prepared by the reaction of bis(dipropyldithiophosphato) silver(I) complex with 1,10-phenanthroline ligand, and its structure was determined by X-ray crystallography. The two dipropyldithiophosphato ligands each 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 for the metal ion. The Ag-S bond distances are 2.559(1) and 2.567(1) Å, and the Ag-N bond distances are 2.366(3) and 2.471(3) Å.

Key words: Phen Ligand, Crystal Structure, Dimeric Silver(I), Dithiophosphate

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] 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.[3] 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.[4] Also, it is well-known that metal thiolate complexes adopt geometries of variable nuclearities and great structural complexity. Theses features are the result of the tendency of thiolate ligands to bridge metal centers to yield oligomeric

or polymeric species.[5] On the other hand, the presence of coligands, such as 2,2-bipyridine, 1,10-phenanthroline, bis(diphenylphosphino)methane, *etc*. might modify such aggregation processes producing binuclear or polynuclear thiolate complexes.[6] When 1,10-phenanthroline reacts with bis(dipropyldithiophosphato) silver(I) in EtOH, we obtained a new dinuclear silver(I) complex, bis(1,10-phenanthroline) bis(dipropyldithiophosphato) disilver(I). Here we report the crystal structure for this new complex.

EXPERIMENTAL SECTION

All chemicals used were of analytical reagent grade and used directly without further purification. Na[(n-PrO)$_2$dtp] (dtp=dithiophosphate) was prepared according to literature method.[7] IR spectra were recorded with a Nicolet 510P FT-IR spectrophotometer as KBr pellets in the range 4000~400 cm^{-1}.

Preparation of Ag[(n-PrO)$_2$dtp] (1). Stoichiometric amounts of Ag(I) nitrate and sodium dipropyldithiophosphates in deionized water were stirred for 20 min. The precipitate was collected by filtration, washed with water, and then dried over P_4O_{10}. The complexes were collected and submitted for elemental analysis. [Anal. Calcd. For $C_6H_{14}O_2PS_2Ag$: C, 22.44%; H, 4.39%. Found: C, 22.21%, H, 4.27%.]

Preparation of $Ag_2[phen]_2[S_2P(OPr)_2]_2$ (2). To a stirred complex (**1**) (2 mmol) dissolved in hot ethanol (50 ml), a slight excess of phenanthroline was added. The mixture was cooled to room temperature, then filtered off, and the filtrate was left to stand undisturbed. Upon slow evaporation at room temperature, the colorless crystalline solid **(2)** appeared several days later and was separated by filtration. [Anal. Calcd. For $C_{18}H_{18}N_2O_2PS_2Ag$ Found: C, 42.92; H, 3.48; N, 5.26%. Calc.: C, 43.47; H, 3.65; N, 5.63%.]

X-ray structure determination. The selected crystals of the complexes of $Ag_2[phen]_2[S_2P(OPr)_2]_2$ was mounted on an Rigaku Raxis-IV diffractome-

Table 1. Crystal data and structure refinement

Empirical formula	$C_{18}H_{18}AgN_2O_2PS_2$
Formula weight	497.30
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	triclinic, P-1
Unit cell dimensions	a=9.875(2) Å α=68.32(3) deg.
	b=10.992(2) Å β=74.93(3) deg.
	c=11.232(2) Å γ=65.16(3) deg.
Volume	1020.2(4) Å^3
Z, Calculated density	2, 1.619 Mg/m^3
Absorption coefficient	1.285 mm^{-1}
F(000)	500
Crystal size	0.30 × 0.30 × 0.20 mm
Theta range for data collection	1.97 to 27.51 deg.
Limiting indices	-12≤h≤11, -14≤k≤0, -14≤l≤12
Reflections collected / unique	3377 / 3377 [R(int) = 0.0000]
Completeness to theta = 27.51	72.1%
Max. and min. transmission	0.7831 and 0.6991
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3377 / 2 / 236
Goodness-of-fit on F^2	1.021
Final R indices [I>2sigma(I)]	R_1=0.0493, wR_2=0.1137
R indices (all data)	R_1=0.0824, wR_2=0.1260
Extinction coefficient	0.0068(8)
Largest diff. peak and hole	0.435 and -0.399 e. Å^{-3}

ter. Reflection data were measured at 293 K, using graphite monochromated Mo-K_a (λ=0.71073 Å) radiation ω-2θ scan mode. Intensities were corrected for Lorentz.

The structures of $Ag_2[phen]_2[S_2P(OPr)_2]_2$ was solved by direct methods and refined by least squares on F_{obs}^2 by using the *SHELXTL*[8] software package. All non-H atoms were anisotropically refined. The hydrogen atoms were located by difference synthesis and refined isotropically. The final conventional R(F)= 0.0493 and $wR(F^2)$=0.1137 for $I>2\sigma(I)$ with weighting scheme, $w=1/[\sigma^2(F^2)+(0.0710P)^2+0.0000P]$, 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]

Details on crystal data, intensity collection, and structure refinements are given in *Table* 1. Final atomic coordinates and some selected bond distances and bond angles are shown in Table **2** and **3**, respectively.

RESULT AND DISCUSSION

Preparation. The title compound has been prepared by the reaction $Ag[S_2P(OPr)_2]$ with Phen in EtOH. The colorless solution was filtered and the filtrate was left to stand undisturbed. The colorless prisms of the complex suitable for X-ray measurements were obtained by slow evaporation at room temperature for one week. It is air- and moisture-stable and is soluble in common organic solvents.

$$2Ag[S_2P(OPr)_2]+2Phen \rightarrow Ag_2[phen]_2[S_2P(OPr)_2]_2$$

The IR spectrum showed the characteristic strong bands at 1586 (C=C), 1523, 1425 (C=N), 852 (n_{C-H}

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^4$)

x	y	z	U	(eq)
Ag(1)	9294(1)	6671(1)	-5278(1)	65(1)
S(1)	9975(1)	5992(1)	-3012(1)	73(1)
S(2)	8325(1)	3857(1)	-3101(1)	75(1)
P(1)	9121(1)	4493(1)	-2087(1)	59(1)
O(1)	10423(3)	3251(3)	-1290(3)	72(1)
O(2)	7762(3)	4950(3)	-1016(3)	71(1)
N(1)	6886(3)	7393(3)	-5881(3)	66(1)
N(2)	8176(4)	9255(3)	-6121(3)	78(1)
C(1)	6268(4)	6465(5)	-5803(5)	84(1)
C(2)	4858(5)	6860(6)	-6140(5)	104(2)
C(3)	4028(5)	8222(6)	-6497(5)	104(2)
C(4)	4551(5)	9235(5)	-6586(5)	88(2)
C(5)	3734(6)	10686(7)	-6989(5)	113(2)
C(6)	4326(6)	11613(6)	-7087(5)	105(2)
C(7)	5859(7)	11221(5)	-6852(5)	98(2)
C(8)	6514(9)	12108(6)	-6978(6)	141(3)
C(9)	7975(7)	11678(6)	-6748(6)	130(2)
C(10)	8770(6)	10172(5)	-6287(6)	110(2)
C(11)	6724(5)	9758(4)	-6416(4)	71(1)
C(12)	6057(4)	8767(4)	-6268(4)	65(1)
C(13)	10279(6)	1932(6)	-575(6)	123(2)
C(14)	11618(7)	923(7)	-43(8)	166(4)
C(15)	12759(9)	261(11)	-68(9)	254(5)
C(16)	7960(5)	5440(5)	-61(4)	88(1)
C(17)	6534(6)	5985(5)	730(6)	106(2)
C(18)	5306(7)	6228(6)	589(7)	125(2)

Table 3. Selected bond lengths [A] and angles [°]

Ag(1)-N(1)	2.366(3)	Ag(1)-N(2)	2.471(3)
Ag(1)-S(1)	2.559(1)	Ag(1)-S(2)#1	2.567(1)
Ag(1)-Ag(1)#1	3.207(1)	S(1)-P(1)	1.987(2)
S(2)-P(1)	1.980(2)	P(1)-O(1)	1.594(3)
O(1)-C(13)	1.421(6)	N(1)-C(12)	1.342(5)
N(1)-Ag(1)-N(2)	68.88(13)	N(1)-Ag(1)-S(1)	127.71(9)
N(2)-Ag(1)-S(1)	109.28(10)	N(1)-Ag(1)-S(2)#1	121.04(9)
N(2)-Ag(1)-S(2)#1	100.99(9)	S(1)-Ag(1)-S(2)#1	110.75(4)
N(1)-Ag(1)-Ag(1)#1	105.66(9)	N(2)-Ag(1)-Ag(1)#1	169.06(9)
S(1)-Ag(1)-Ag(1)#1	81.60(5)	S(2)#1-Ag(1)-Ag(1)#1	73.30(5)
O(1)-P(1)-O(2)	104.68(15)	O(1)-P(1)-S(2)	112.79(13)

Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y+1,-z-1

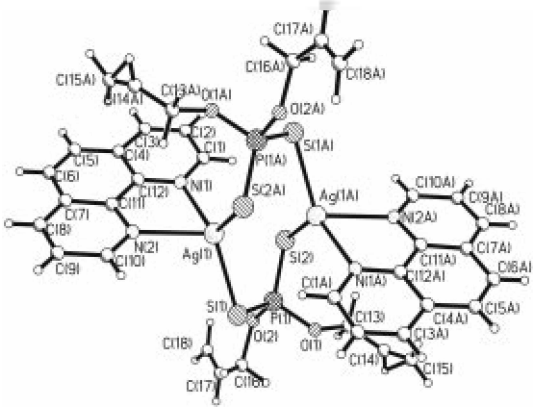

Fig. 1. Molecular structure for the title compound with the atomic numbering scheme.

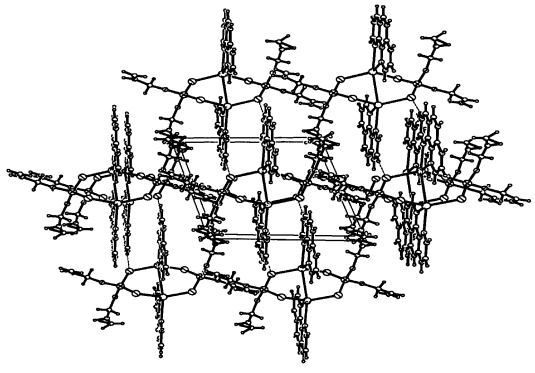

Fig. 2. A view of the crystal packing down a axis for the title compound.

benzene ring) and 720 cm^{-1} (n_{C-H} pyridine ring) for the coordinated phen ligands.[11] The shift of the two bands at 1523 and 1425 cm^{-1} compared for the free ligand (1503 and 1420 cm^{-1}) indicated the nitrogen coordination to a silver. The infrared absorption spectra of P-O in P-O-C group is at 915-1050 cm^{-1} band at 420 cm^{-1} is assigned to the n_{Ag-N} stretching mode.

Structure. *Fig.* 1 shows a perspective view of the title compound with atomic numbering scheme, and *Fig.* 2 shows a perspective view of the crystal packing in the unit cell.

Its structure contains two silver(I), bis(1,10-phenanthroline) and bis(dipropyldithiophosphato) molecules. It is built up of centro-symmeric dimeric entities. The coordination sphere of the silver(I) ion is best described as a distorted tetrahedral geometry. The two dipropyldithiophosphato ligands each bridge two silver atoms to form an eight-membered $Ag_2S_2P_2$ ring, while two 1,10-phenanthroline molecules coordinate to a silver to form a five-membered chelate ring, respectively. The Ag-N bond lengths [2.366(3) and 2.471(3) Å] are comparable with those of 2.332(2), 2.342(2) and 2.419(2) Å found in other silver(I) complexes with tetrahedral coordination.[12-14] Similarly, no significant difference of the Ag-S bond distances [2.559(1) and 2.567(1) Å] is observed compared with those of similar tetrahedral structure [2.507~2.644 Å].[5,15] The highest value for the tetrahedral angles is N(1)-Ag-S(1) [127.71(9)°]; which is 19° greater than the ideal value. The lowest value is N(1)-Ag-N(2) [68.9(1)°], which is 40° lower than the idea value. The P-S bond lengths [1.987(2) and 1.980(2) Å] are normal. The phenanthroline ligand with Ag atoms is planar, with no atom deviating from a least-sqares plane through the

fifteen atoms by as much as 0.091(2)°. The average C-C distances in the phenanthroline rings are approximately the expected mean value of 1.399 Å. The plane formed by S(2)-P(1)-O(2)-C(16) with the phenanthroline rings formed dihedral angles of 70.88(1)°. The Ag···Ag separation in the dimmer is 3.207(1) Å, which is in the range 2.93 to 3.52 Å, showing that no significant silver-silver interactions exist in the compound.[5]

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