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Silver(I) Complexes Containing Diphosphine and *Bis*(Phosphine) Disulphide Ligands

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In this study, the reactions of $AgNO_3$ and $AgClO_4$ with diphosphine [$Ph_2P(CH_2)_2PPh_2$(dppe)] and *bis*(phosphine)-disulphide ligands (L-L) (L-L = $Ph_2P(S)(CH_2)$n $P(S)Ph_2$; n = 2, $dppeS_2$; n = 3, $dpppS_2$) have been investigated. The reaction of $AgClO_4$ with dppe was resulted the bridging complex $[Ag(\mu\text{-}OClO_3)(dppe)]_2$ (**1**). The reactions of $AgNO_3$ with the ligands (L-L) (L-L = $dppeS_2$, $dpppS_2$), gave two new dimeric $[Ag_2(\mu\text{-}L\text{-}L)_2](NO_3)_2$ complexes (**2**) and (**3**), respectively. The products were characterized by elemental analysis, IR, $^{31}P\{^1H\}$ NMR, electrospray mass and FAB mass spectrometry. It has been found that the complexes (**1**) and (**2**) have shown moderately antimicrobial activity against some gram (+) and gram (-) bacteria.

Key Words: Phosphine sulphide, Silver complexes, Diphoshpine, Antimicrobial activity.

INTRODUCTION

Synthesis and structure of transition metal complexes containing monodentate and bidentate tertiary phosphine chalcogenides as ligands have been investigated for many years[1-6]. Because the lability of the chalcogen-metal bonds can give rise to dynamic processes, these render ligands appropriate for catalytic applications[7]. For example, the complexes of rhodium are used for hydroformilation of alkenes, aldehydes and carbonylation of methanol[8]. 1,1'-*bis*(Diphenylphosphino)ferrocene silver complexes have been widely exploited in coordination chemistry[9], due to the fact that, the resulting complexes find applications in homogeneous catalysis, manuplation of materials and production of fine chemicals[9,10]. Despite 1,1′-*bis*(diphenylphosphino)ferrocene silver complexes, only limited number of silver(I) complexes contain dppe ligands have been investigated. It has only been reported that silver(I) complex of dppe, $[Ag(dppe)_2]NO_3$, (dppe = $Ph_2P(CH_2)_2PPh_2$) had antitumour activity[11].

In this study, three dimeric silver(I) complexes of dppe, $dppeS_2$ and $dpppS_2$ ligands (1, 2 and 3, respectively) were reported. The complexes have been characterized by $^{31}P\{^1H\}$ NMR, IR, positive ion electrospray mass spectra (ESMS), positive ion FAB mass spectra and elemental analyses.

EXPERIMENTAL

Solvents were dried by refluxing with suitable drying agents (calcium hydride for dichloromethane, molecular sieves or K_2CO_3 for acetone, phosphorus pentaoxide for acetonitrile and sodium/benzophenone for diethyl ether) and were distilled under argon prior to use. All the syntheses were carried out using standard Schlenk tube techniques under argon atmosphere. $AgNO_3$, $AgClO_4$, dppe, dppp, diethylether, acetonitrile and acetone were purchased from Merck Chemicals; dichloromethane was purchased from Lab-Scan.

$dppeS_2$ and $dpppS_2$ ligands were synthesized by the methods given in the literature[12].

Elemental analyses were performed by Midwest Microlab in Indianapolis, USA. Electrospray Mass Spectrometry (ESMS) was performed at Wayne University, Central Instrumentation Facility Mass Spectrometry Laboratory by electrospray MS system (Micromass QuattroLC), at Detroit, USA. The FAB Mass Spectrometry by Jeol JMS-700 equipment, was performed at University of Heidelberg, Faculty of Chemistry and Earth Sciences, Intitute of Organic Chemistry, in Heidelberg, Germany. The $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian AS400 + Mercury instrument, chemical shifts, in ppm, are relative to external 85 % H_3PO_4. Coupling constants are in Hz. IR spectra were recorded on Perkin Elmer 1600 Series FTIR Spectrometer by using KBr disks and melting points were determined by electrothermal melting point detection apparatus.

Preparation of $[Ag(\mu\text{-}OClO_3)(dppe)]_2$ (1): $AgClO_4$ (0.849 mmol, 0.176 g) and dppe (0.849 mmol, 0.338 g) were placed in 10 mL acetone and stirred. After 24 h the solvent was removed *in vacuo* and the residue was washed with acetone, white product was obtained. m.p. 165 °C (decomp). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.9 MHz) δ: 10.3; IR (KBr, ν_{max}, cm^{-1}): (ClO_4^-): 1109 (b), 1055 (b), 1009 (w) and 932 (m). FAB-MS m/z (%): 1109.03, 1111.03, 1113.03, 1115.03 $[Ag(dppe)]_2(OClO_3)]^+$ Anal. calcd. (%) for $C_{52}H_{48}O_8P_4Cl_2Ag_2$: C 51.55, H 3.99; found C 51.29, H 4.08.

Preparation of $[Ag_2\mu\text{-}(dppeS_2)_2](NO_3)_2$ (2): $AgNO_3$ (0.400 mmol, 0.068 g) and $dppeS_2$ (0.400 mmol, 0.185 g) were placed in 10 mL acetonitrile and stirred. After 24 h the solvent was removed *in vacuo* and the residue was dissolved with dichloromethane and filtered off, the solute was dried *in vacuo* and white product was obtained. m.p. 112 °C (decomp). $^{31}P\{^1H\}$ NMR (DMSO, 161.9 MHz) δ: 53.43; IR (KBr, ν_{max}, cm^{-1}): (P=S): 592(m).

ESMS (29 V) m/z (%): 1200.1, 1202.2, 1204.1 ($(dppe)_2Ag_2NO_3^+$). Anal. calcd. (%) for $C_{52}H_{48}N_2O_6P_4S_4Ag_2$: C 49.38, H 3.83, S 10.14; found C 48.99, H 3.84, S 10.09.

Preparation of $[Ag_2(\mu\text{-}dpppS_2)_2](NO_3)_2$ (3): $AgNO_3$ (0.240 mmol, 0.040 g) and $dpppS_2$ (0.240 mmol, 0.114 g) were placed in 15 mL acetonitrile and stirred. After 24 h the solvent was removed *in vacuo*, the complex was recrystallized from dichloromethane/diethylether to give white crystals (1:3 v/v). m.p. 108 °C (decomp). $^{31}P\{^1H\}$ NMR (DMSO, 161.9 MHz) δ: 4.75; IR (KBr, ν_{max}, cm^{-1}): (P=S): 592(m). ESMS (30 V) m/z (%): 1227.9, 1229.9, 1231.9 ($(dppp)_2Ag_2NO_3^+$). Anal. calcd. (%) for $C_{54}H_{52}N_2O_6P_4S_4Ag_2$: C 50.16, H 4.05, S 9.92; found C 49.08, H 4.00, S 9.91.

Antimicrobial studies: The Kirby-Bauer technique was used to determine the antimicrobial activities[13-16]. The complexes (**1**) and (**2**) were dissolved in DMSO (1 µg/mL). 20 mL of solutions were absorbed onto sterile 6 mm discs (oxoid antibacterial susceptibility blank tests disc) under aseptic conditins to obtain 20 µg complex/disc. Discs were transferred with a sterile forceps onto plates containing test microorganisms. The control disc contained 20 mL of sterile DMSO. Agar plates containing bacteria were incubated at 37 °C for 24 h. The antibacterial agents, ceftazidime (20 µg/disc) and SAM 20 (20 µg/disc) (SAM 20: Sulbactam (10 µg)/ampicilin (10 µg)) were used as a positive controls for the bacteria. DMSO was used as a negative control. Zone of inhibition were measured as mm. All experiments were done in triplicate.

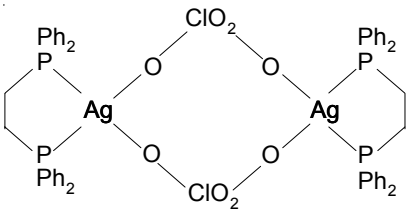
RESULTS AND DISCUSSION

Silver(I) ion can give complexes which are two, three and four coordinated. In this study, three new Ag(I) complexes containing dppe, $dppeS_2$, $dpppS_2$ ligands, were synthesized which have four coordinated Ag(I) ion. The colours of all the three complexes are white. Their analytical data are in accordance with the proposed formulation.

The IR spectrum of (**1**) shows bands at 1109 (b), 1055 (b), 1009 (w) and 932 (m) cm^{-1} arising from covalent perchlorate[17]. $^{31}P\{^1H\}$ NMR spectrum of this complex shows a doublet at 10.3 ppm consistent with the abundance and gyromagnetic ratio for ^{107}Ag and ^{109}Ag. The coupling constant value of Ag-P interaction is 533 Hz. This value is in accordance with the value of $Ag(TfO)(PFe_2Ph)(PPh_3)$ complex[18] and $[Ag(OClO_3)(dppf)]_2$[17] and also the dppe ligand resonance is shifted downfield on complexation. In the ^1H NMR spectrum shows, apart from the multiplet for the phenyl protons, a singlet for the protons of $-CH_2$ groups at 2.62 ppm. The positive ion FAB mass spectrum of (**1**) exhibit a peak, which corresponding to the fragment $\{[Ag(dppe)]_2(OClO_3)\}^+$ at m/z 1109.03, 1111.03, 1113.03, 1115.03. These peaks show that the silver (^{107}Ag, ^{109}Ag) and chlorine (^{35}Cl and ^{37}Cl) atoms

isotope patterns[19]. Other fragments correspond to $[Ag(dppe)_2]^+$ and $[Ag(dppe)]^+$ show peaks at m/z 903.5, 905.5 and 505.3, 507.3, respectively.

It was not been able to obtain single crystals of the complex (**1**) for X-ray crystallography, however, according to the analysis results; we have been proposing the following dinuclear structure (Fig. 1).



(1)

Fig. 1. Proposed structure for $[Ag(\mu\text{-}OClO_3)dppe]_2$ (**1**)

The reactions of neutral $dppeS_2$ and $dpppS_2$ ligands with $AgNO_3$ give dinuclear Ag(I) complexes (**2**) and (**3**) in which the ligands act as a bridge between two silver ions. The $^{31}P\{^1H\}$ NMR spectrum of complex (**2**) shows a singlet at 53.43 ppm, which is considerable deshielded when compared to the $dppeS_2$ ligand with a shift of 44.40 ppm. The similar result has been observed for (**3**) which has a signal at 45.75 ppm (δ(P) = 43.10 ppm for $dpppS_2$)[6]. On the IR spectra of these two complexes, ν(P=S) stretching vibration is present at 592 cm^{-1}, it is displaced towards lower frequencies by 13-16 cm^{-1}, respectively, as compared with the free ligands (605 and 608 cm^{-1} for $dppeS_2$ and $dpppS_2$). The NO_3^- group vibrations give rise to two intense bands: ν_{as}: 1441 and 1441 cm^{-1}; ν_s: 1395 and 1387 cm^{-1} for complexes (**2**) and (**3**), respectively. A small band separation correlated with the weak $Ag^+ \cdots\cdots NO_3^-$ interactions. Similar results have been reported for the $Ag_2(dppeS)_2(NO_3)_2$ complex[8].

ESMS spectra of the complexes (**2**) and (**3**) do not show the molecular peaks. At moderate (29 and 30 V) desolvation energy, the ESMS spectra of the complexes (**2**) and (**3**) have peak groups at m/z = 1200.1, 1202.2, 1204.1 and m/z = 1227.9, 1229.9, 1231.9, which belong to loss of one NO_3^- group, $L_2Ag_2NO_3^+$ (L = $dppeS_2$ and $dpppS_2$). These peaks reflect the isotope patterns of silver atoms. The calculated ESMS spectra of complexes (**2**) and (**3**) support these results. In two spectra, peaks at m/z 1031.1, 1033.1 and 1059.0, 1061.0 are due to the L_2Ag^+ ions and at m/z 569.0, 571.0 and 583.0, 585.0 are due to the LAg^+ ions, respectively. According to these spectral data, the proposed structures for complexes (**2**) and (**3**) are given in Fig. 2.

The antimicrobial activity of the complexes (**1**) and (**2**) were tested against to four microorganisms which are *Staphylococcus aureus* ATCC 6538-P, *Escherichia coli* ATCC 11230, *Salmonella typhimurium* CCM 5445

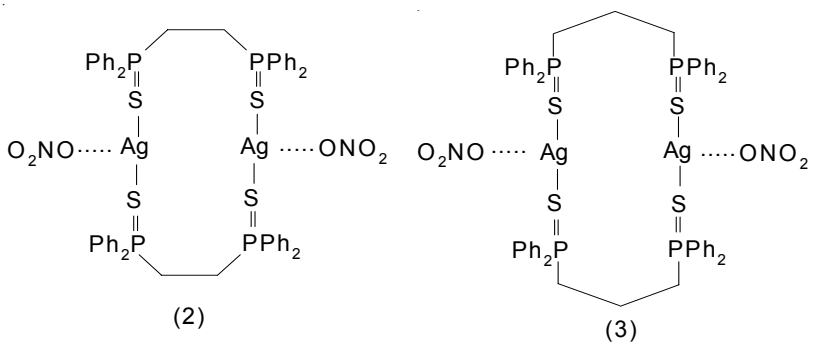


Fig. 2. Proposed structure for $[Ag_2(\mu\text{-}dppeS_2)_2(NO_3)_2]$ (**2**) and $[Ag_2(\mu\text{-}dpppS_2)_2(NO_3)_2]$ (**3**)

and *Enterococcus faecalis* ATCC 29212. The results are given in Table-1. Complexes (**1**) and (**2**) which have mixed donor atoms, oxygen, phosphorus and sulphide, have moderetly active against to four gram (+) and gram (-) bacteria. This result show that the antimicrobial activity depended on the nature of the bonding atoms to the silver(I)[20]. Because of complex (**3**) has similar structure to complex (**2**), it has not been studied on the antimicrobial activity of this complex.

TABLE-1
ANTIMICROBIAL ACTIVITY OF COMPLEXES (**1**) AND (**2**)

	(**1**)*	(**2**)*	Ceftasidime	SAM 20**	DMSO
Staphylococcus aureus ATCC 6538-P	10	9	24	23	-
Escherichia coli ATCC 11230	10	9	21	13	-
Enterococcus faecalis ATCC 29212	9	8	17	19	-
Salmonella typhimurium CCM 5445	10	8	20	15	-

*Zone area is in mm; **Sulbactam (10 mg)/ampicilin (10 mg).

Conclusion

In this study, the reactions of three Ag(I) complexes with phosphine sulfide ligands are reported. The *bis*(phosphine) disulphide ligands, $dppeS_2$ and $dpppS_2$, act as a bridge between two silver ions in complexes (**2**) and (**3**), ClO_4^- ions behave as bridging ligands to silver ion in complex (**1**). Complexes (**1**) and (**2**) have been found to inhibit the growth of certain gram (-) and gram (+) bacteria.

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REFERENCES

1. C.J. Carmalt and N.C. Norman, *Polyhedron*, **14**, 1405 (1995).
2. S.O. Grim and E.D. Walton, *Inorg. Chem.*, **19**, 1982 (1980).
3. T.S. Tarlok and M.K. Sandhu, *J. Chem. Soc. Dalton Trans.*, 1401 (1988).
4. P.K. Baker, A.I. Clark, M.G.B. Drew, M.C. Durrant and R.L. Richards, *Polyhedron*, **17**, 1407 (1998).
5. T.S. Lobana, R. Verma, A. Singh, M. Shikha and A. Castineiras, *Polyhedron*, **21**, 205 (2002).
6. H. Schumann, *J. Organomet. Chem.*, **320**, 145 (1987).
7. B. Alvarez, E.J. Fernandez, M.C. Gimeno, P.G. Jones, A. Laguna and J.M. Lopez-de-Luzuriaga, *Polyhedron*, **17**, 2029 (1998).
8. E.I. Matrosov, Z.A. Starikova, A.I. Yanovsky, D.I. Lobanov and I.M. Aladzheva, O.V. Bykhovskaya, Y.T. Struchkov, T.A. Mastryukova and M.I. Kabachnik, *J. Organomet. Chem.*, **535**, 121 (1997).
9. A. Togni and T. Hayashi, Ferrocenes, Homogeneous Catalysis, Organic Synthesis and Material Science, (Ch. 1), VCH, Weinheim (1995).
10. W.R. Cullen and J.D. Woolins, *Coord. Chem. Rev.*, **39**, 1 (1981).
11. C.S.W. Harker and E.R.T. Tieknik, *J. Coord. Chem.*, **21**, 287 (1990).
12. A. Davison and D.L.T. Reger, *Inorg. Chem.*, **10**, 1967 (1971).
13. C.H. Collins and P.M. Lyne, Antibiotic Sensitivity and Assay Tests, Microbial Methods, Butterworth & Co (Publishers) Ltd., London, edn. 5 (1985).
14. H.W. Seeley and P.J. Vandemark, Sensitivity Discs in the Therapeutic Use of Antibiotics, Microbes in Action, A Laboratory Manual of Microbiology, W.H. Freeman and Company, San Fransisco, edn. 2 (1972).
15. NCCLS, Performance Standarts for Antimicrobial Disc Susceptibility Tests, Approved Standard NCCLS Publication M2-A5, Villanova, PA, USA (1993).
16. E.H. Akalin, Anitbiyotik duyarlilik testleri: Antibiyotiklere direnç mekanizmalari ve antibiyotik duyarlilik testleri. Pfizer Ilaçlari A.S. Kitaplar Serisi, Istanbul (1992).
17. M.C. Gimeno, P.G. Jones, A. Laguna and C. Sarroca, *J. Chem. Soc. Dalton Trans*, 1473 (1995).
18. M.C. Gimeno, P.G. Jones, A. Laguna and C. Sarroca, *Polyhedron*, **21**, 3681 (1998).
19. W. Henderson and G.M. Olsen, *Inorg. Chim. Acta*, **215**, 179 (1994).
20. A.A. Isab and M.I.M. Wazeer, *Spectrochim. Acta A*, **66**, 364 (2007).

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