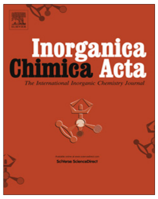
Inorganica Chimica Acta 407 (2013) 31–36

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica



# Syntheses and structural studies of heterobimetallic thiocarboxylate complexes containing zinc and silver

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A R T I C L E  I N F O

*Article history:*
Received 12 April 2013
Received in revised form 9 July 2013
Accepted 10 July 2013
Available online 26 July 2013

*Keywords:*
Zinc
Silver
Thiocarboxylate
Heterobimetallic
Density functional calculations

A B S T R A C T

Novel heterobimetallic complexes, $[(PPh_3)_2Ag(\mu\text{-}SCOth)_2Zn(SCOth)(H_2O)]$ (**1**) and $\{[(PPh_3)_2Ag(\mu\text{-}SCOPh)_2Zn(SCOPh)(H_2O)][(PPh_3)_2Ag(\mu\text{-}SCOPh)Zn(SCOPh)_2]\}$ (**2**) have been prepared and characterized by FTIR, $^1H$, $^{13}C$ and $^{31}P$ NMR spectroscopy. Molecular structures of the complexes have been determined by single crystal X-ray diffraction technique. In these complexes the two metal atoms (Ag and Zn) are held together by bridging (μ-S or μ-O,S) thiocaboxylate groups. The terminal thiocarboxylate ligand binds monodentately (through S) in **1**. Structure of **2** is unique as two different molecules, $[(PPh_3)_2Ag(\mu\text{-}SCOPh)Zn(SCOPh)_2]$ and $[(PPh_3)_2Ag(\mu\text{-}SCOPh)_2Zn(SCOPh)H_2O]$ co-crystallize in the same lattice. The terminal thiocarboxylate ligand is monodentate (S) in the latter while bidentate (O,S) in the former molecule. Electronic spectral behaviors of the complexes have been explained by TDDFT calculations. Luminescence properties of both have been studied in solid state.

## 1. Introduction

Syntheses and studies of heterobimetallic complexes have gained a lot of attention because of the exceptional physicochemical properties and functions exhibited by these complexes arising from a pair of different metal ions in close proximity [1–9]. Apart from the tuned properties such heterobimetallic systems are extremely useful as precursors of electronic materials [10–13]. During recent years, heterobimetallic complexes containing sulfur donor ligands are being utilized to prepare ternary metal sulfides by soft chemical routes which are more energy efficient as compared to conventional sintering methods [14,15].

Some times back we had reported [16] the synthesis and structure of the complex anion $[In(SCOPh)_4]^-$ which has been used to prepare a number of heterobimetallic complexes useful as single source precursors of binary and ternary metal sulfides [14]. Very recently, we have also used thiocarboxylate complexes containing lead–copper and lead–silver metal ions to prepare the corresponding ternary oxides [17].

A search of literature revealed the fact that though mononuclear Zn(II) thiocarboxylates [18–21] are known heterobinuclear thiocarboxylate containing a Zn(II) metal are rare. Moreover, complexes containing a pair of atoms one each from group 11 and 12 are limited and those with a sulfur ligand are scanty [14].

In view of these facts we have taken up the synthesis and characterization of Zn/Ag thiocarboxylate complexes. We have chosen thiophene-2-thiocarboxylate because of the fact that it contains an additional sulfur atom which could affect the structure and bonding of the complexes [22].

## 2. Experimental

### 2.1. Reagents and general procedures

All the solvents were dried according to standard procedures and distilled before use. Thiophene-2-thiocarboxylic acid was prepared by reported procedure [22]. Sodium salt of thiophene-2-thiocarboxylic acid was obtained by reacting the acid with sodium methoxide in stoichiometric ratio. Thiophene-2-carbonyl chloride and thiobenzoic acid (Sigma–Aldrich) were used as received.

### 2.2. Instrumentation

IR Spectra was recorded using Varian-3100 FTIR instruments. NMR spectra (Figs. S1–S4, Supporting information) were obtained using a JEOL AL300 FT NMR spectrometer. Electronic absorption spectral measurements were carried out using a Shimadzu UV-1700 PharmaSpec Spectrometer. Absorption spectra of the complexes have been recorded in chloroform solution ($2 \times 10^{-4}$ M). The solid state absorption spectra of **1** and **2** have also been recorded. Elemental analyses were performed by the EAT Exeter Analytical Inc. CE-440, elemental analyzer.

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http://dx.doi.org/10.1016/j.ica.2013.07.016

**Table 1**
Crystal data and structure refinement of complexes.

| | 1 | 2 |
|---|---|---|
| Empirical formula (CCDC No.) | $C_{51}H_{41}O_4S_6P_2Zn_1Ag_1$ (772371) | $C_{114}H_{92}O_7S_6P_4Zn_2Ag_2$ (772370) |
| $T$ (K) | 293 | 150 |
| Crystal system | orthorhombic | monoclinic |
| Space group | *Pccn* | $P2_1/c$ |
| $a$ (Å) | 14.103(5) | 14.036(5) |
| $b$ (Å) | 39.571(5) | 39.376(5) |
| $c$ (Å) | 18.141(5) | 18.194(5) |
| $\beta$ (°) | 90 | 91.500(5) |
| $V$ (Å$^3$) | 10124(5) | 10052(5) |
| $Z$ | 8 | 4 |
| $\mu$ (Mo K$\alpha$) (mm$^{-1}$) | 1.215 | 1.101 |
| Reflections collected/unique | 28090/11524 | 47399/22942 |
| $R_{int}$ | 0.0525 | 0.0590 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.1109$,<br>$wR_2 = 0.2343$ | $R_1 = 0.0678$,<br>$wR_2 = 0.1120$ |
| $R$ indices (all data) | $R_1 = 0.1847$,<br>$wR_2 = 0.2811$ | $R_1 = 0.1349$,<br>$wR_2 = 0.1376$ |
| Goodness-of-fit (GOF) on $F^2$ | 1.033 | 1.020 |

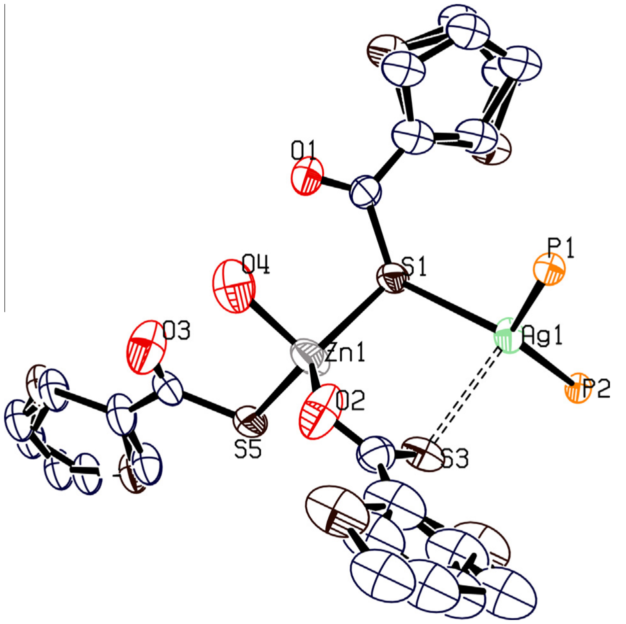


**Fig. 1.** Thermal ellipsoid plot of **1** at 30% probability level. Thiophene rings are disordered. (Hydrogens and phenyl rings of triphenylphosphine are omitted for clarity.)

### 2.3. Single crystal X-ray analysis

Single crystal X-ray data of all complexes were collected on a Xcalibur Eos Oxford Diffractometer using graphite monochromated Mo K$\alpha$ radiation ($\lambda = 0.7107$ Å). Data collections for all complexes were carried out at room temperature. Structures were solved by the direct method and then refined on $F^2$ by the full matrix least square technique with SHELX-97 software [23] using the WINGX program package [24]. Crystal data of complexes are given in Table 1 The crystals of both the complexes showed some disorders. In **1**, all the three th rings were disordered. The disordered atoms of the th rings were split in two parts and then some geometrical restraints were applied (if necessary) for refinement. Similarly disorders in rings of other structures were also refined.

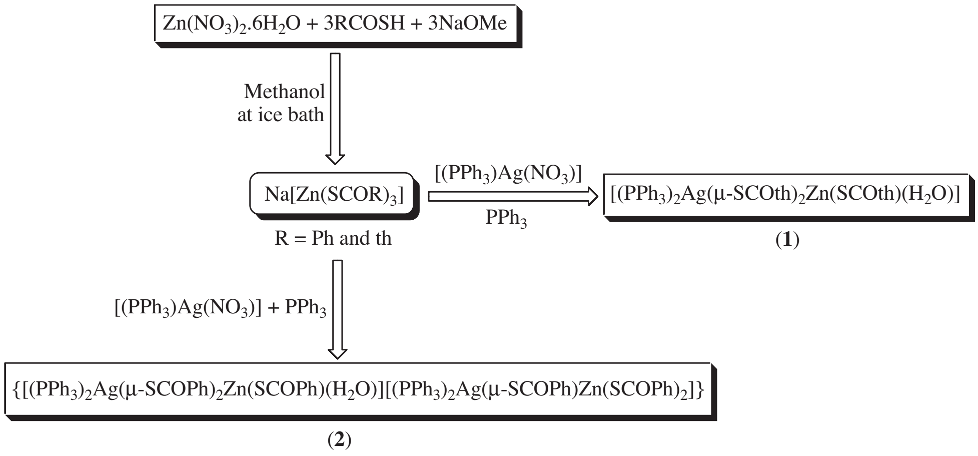
### 2.4. Computational details

All the calculations performed using GAUSSIAN 03W software [25]. As the final $R$ indices for **1** were rather high the molecular geometry was optimized using B3LYP correlation functional. The optimized atomic coordinates were used for TDDFT [26] calculations. All time dependent calculations were performed using CEP-121G basis set [27,28] for Ag atom and 6-31G** for rest of the atoms at PBE1 level [29,30]. All the molecular orbital plots were generated by MOLDEN program [31].

### 2.5. Syntheses

#### 2.5.1. Synthesis of [$(PPh_3)_2Ag(SCOth)_2Zn(SCOth)(H_2O)$], (**1**)

To the stirred methanolic solution (5.0 ml) of sodium thiophene-2-thiocarboxylate (0.240 g, 1.45 mmol) a methanolic solution (5 ml) of $Zn(NO_3)_2{\cdot}6H_2O$ (0.143 g, 0.48 mmol) was added to get a light yellow colored solution of Na[$Zn(SCOth)_3$]. In this stirred reaction mixture added $PPh_3Ag(NO_3)$ (0.208 g, 0.48 mmol) (prepared by addition of 1:1 $PPh_3$ and $AgNO_3$ in acetonitrile) in 5 ml of $CH_2Cl_2$ followed by $PPh_3$ (0.126 g, 0.48 mmol) in 5 ml of $CH_2Cl_2$ then the reaction mixture was stirred for 2 h. The solvent was evaporated under reduced pressure and the residue was dissolved in $CHCl_3$ (20 ml) and filtered off to separate out $NaNO_3$. The filtrate was evaporated under reduced pressure. The yellow colored product was dried under vacuum for 1 h. Light yellow rod shaped



**Scheme 1.**

**Table 2**
Selected bond lengths and bond angles of complexes.

| Complex | Bond length (in Å) | | Bond angle (in °) | |
|---|---|---|---|---|
| **1** | Zn1–S1 | 2.369(3) | S1–Zn1–$S_3$ | 89.14(11) |
| | Zn1–S3 | 2.794(4) | S1–Zn1–S5 | 113.46(15) |
| | Zn1–S5 | 2.319(4) | S3–Zn1–S5 | 98.73(12) |
| | Zn1–O2 | 2.178(11) | S1–Zn1–O4 | 101.4(3) |
| | Zn1–O4 | 2.071(10) | S3–Zn1–O4 | 147.0(3) |
| | Ag1–S1 | 2.709(3) | S5–Zn1–O4 | 105.5(3) |
| | Ag1–S3 | 2.722(3) | S1–Zn1–O2 | 125.5(4) |
| | Ag1–P1 | 2.450(2) | S3–Zn1–O2 | 59.1(3) |
| | Ag1–P2 | 2.475(2) | S5–Zn1–O2 | 114.6(3) |
| | | | O2–Zn1–O4 | 90.0(4) |
| | | | S1–Ag1–S3 | 84.07(10) |
| | | | S1–Ag1–P1 | 112.78(9) |
| | | | S1–Ag1–P2 | 106.65(9) |
| | | | S3–Ag1–P1 | 118.15(9) |
| | | | S3–Ag1–P2 | 93.46(9) |
| | | | P1–Ag1–P2 | 130.89(8) |
| **2** | Zn1–S1 | 2.3461(16) | S1–Zn1–S3 | 116.50(6) |
| | Zn1–S3 | 2.2979(15) | S1–Zn1–O2 | 118.83(11) |
| | Zn1–O2 | 2.004(4) | S3–Zn1–O2 | 112.72(12) |
| | Zn1–O4 | 2.061(4) | S1–Zn1–O4 | 102.35(15) |
| | Ag1–S1 | 2.7440(14) | S3–Zn1–O4 | 105.59(15) |
| | Ag1–S2 | 2.6530(15) | O2–Zn1–O4 | 97.03(16) |
| | Ag1–P1 | 2.4487(14) | S1–Ag1–S2 | 81.98(5) |
| | Ag1–P2 | 2.4814(14) | S1–Ag1–P1 | 113.25(5) |
| | Zn2–S4 | 2.333(2) | S1–Ag1–P2 | 105.41(5) |
| | Zn2–S5 | 2.341(2) | S2–Ag1–P1 | 124.23(5) |
| | Zn2–S6 | 2.3733(18) | S2–Ag1–P2 | 93.59(5) |
| | Zn2–O7 | 2.196(4) | P1–Ag1–P2 | 128.08(5) |
| | Ag2–S4 | 2.6224(18) | S4–Zn2–S5 | 124.32(7) |
| | Ag2–P3 | 2.4734(14) | S4–Zn2–S6 | 111.74(7) |
| | Ag2–P4 | 2.4471(15) | S5–Zn2–S6 | 118.28(8) |
| | | | S4–Zn2–O7 | 115.04(12) |
| | | | S5–Zn2–O7 | 105.26(12) |
| | | | S6–Zn2–O7 | 68.03(11) |
| | | | S4–Ag2–P3 | 104.68(5) |
| | | | S4–Ag2–P4 | 120.42(5) |
| | | | P3–Ag2–P4 | 130.03(5) |

crystals were obtained from chloroform solution (15 ml) layered with diethyl-ether at room temperature. Yield: 0.436 g, (79%). m.p. 154–156 °C. Elemental *Anal.* Calc. for $C_{51}H_{41}O_4S_6P_2ZnAg$: C, 53.48; H, 3.61. Found: C, 53.48; H, 3.70%. IR spectra (KBr, $cm^{-1}$): 1560, 1510 *v*(CO), 1228 *v*(th–C), 912, 870 *v*(C–S). NMR ($CDCl_3$, *δ*ppm): $^1H$ NMR; 6.79–7.60 (Ph and th ring), 2.21 ($H_2O$). $^{13}C$ NMR; 127.38–146.99 (Ph and th ring), 197.29 (COS). $^{31}P$ NMR; 8.39.

### 2.5.2. Synthesis of {[$(PPh_3)_2Ag(\mu\text{-}SCOPh)_2Zn(SCOPh)(H_2O)$][$(PPh_3)_2Ag(\mu\text{-}SCOPh)Zn(SCOPh)_2$]}, (**2**)

To the stirred methanolic solution (5.0 ml) of sodium thiobenzoate [PhCOSH (0.414 g, 3.0 mmol in 5 ml of MeOH) and deprotonated by sodium methoxide (0.162 g, 3.0 mmol)], a methanolic solution (5 ml) of $Zn(NO_3)_2{\cdot}6H_2O$ (0.297 g, 1.0 mmol) was added to get a light yellow colored solution of $Na[Zn(SCOPh)_3]$. In this stirred reaction mixture added $PPh_3Ag(NO_3)$ (0.432 g, 1.0 mmol) (prepared by addition of 1:1 $PPh_3$ and $AgNO_3$ in acetonitrile) in 5 ml of $CH_2Cl_2$ followed by $PPh_3$ (0.262 g, 1.0 mmol) in 5 ml of $CH_2Cl_2$ then the reaction mixture was stirred for 2 h. The solvent was evaporated under reduced pressure and the residue was dissolved in $CHCl_3$ (20 ml) and filtered off to separate out $NaNO_3$. The filtrate was evaporated under reduced pressure. The yellow product was dried under vacuum for 1 h. Light yellow colored rod shaped crystals were obtained from chloroform solution (15 ml) layered with diethyl-ether at room temperature. Yield: 1.047 g (93%). Elemental *Anal.* Calc. for $C_{114}H_{92}O_7S_6P_4Zn_2Ag_2$: C, 61.21; H, 4.15. Found: C, 61.17, H, 4.19%. IR spectra (KBr, $cm^{-1}$): 1591, 1562 *v*(CO), 1203 *v*(Ph–C), 931, 910 *v*(C–S). NMR ($CDCl_3$, *δ*ppm): $^1H$ NMR; 7.11–7.91 (Ph ring), 2.89 ($H_2O$). $^{13}C$ NMR; 127.53–140.19 (Ph ring), 205.45 (COS). $^{31}P$ NMR; 8.63.

## 3. Results and discussion

### 3.1. Syntheses

Complex anions, *tris*(thiocarboxylato)zincate(II) was used as the precursor for all the complexes reported here. For the synthesis of heterobimetallic complexes these precursors were generated *in situ* and used as such without any attempt for their purification

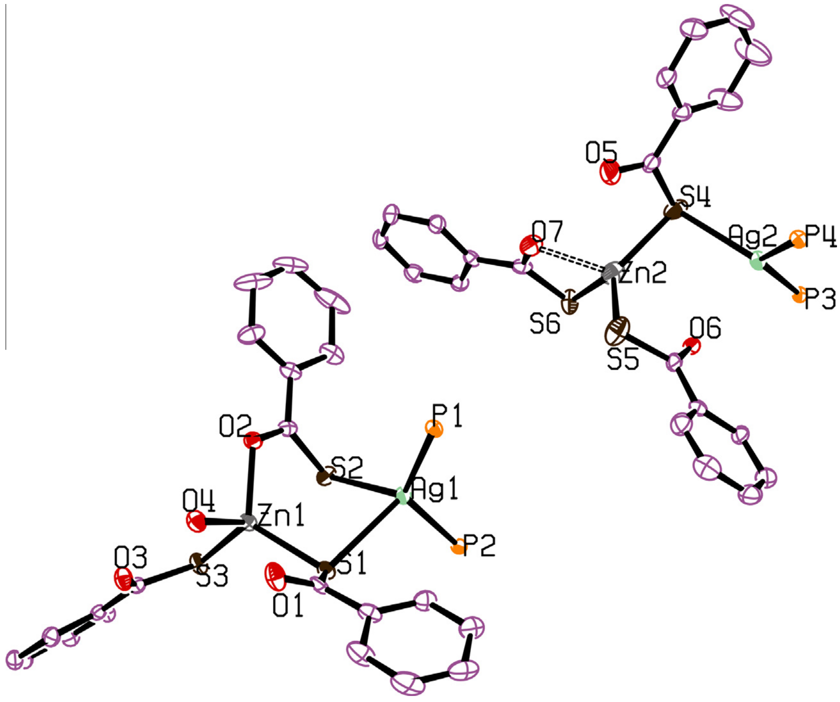


**Fig. 2.** Thermal ellipsoid plot of **2** at 30% probability level (Hydrogens and phenyl rings of triphenylphosphine are omitted for clarity.)

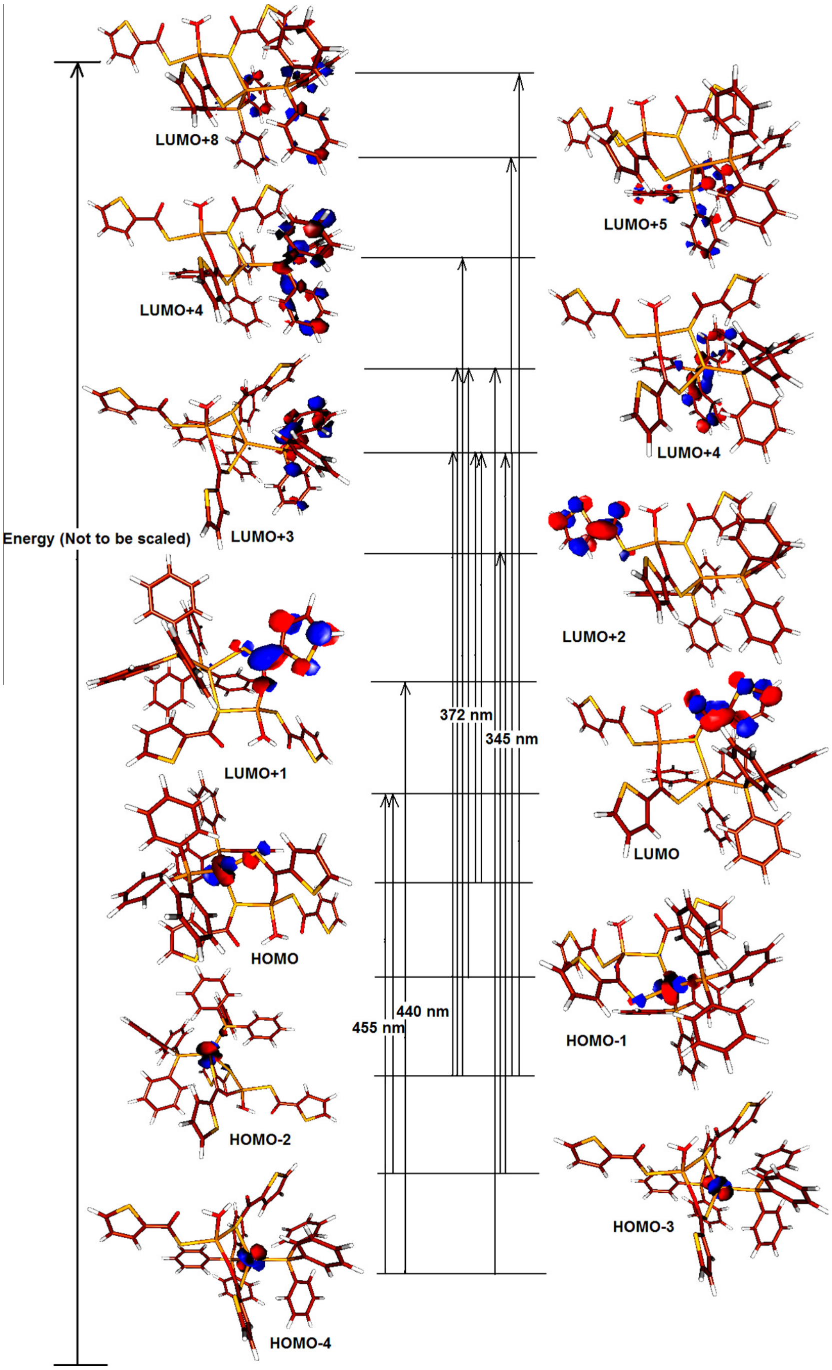


**Fig. 3.** Selected orbital transitions in **1** (orbital contour value 0.05).

or isolation. Both the complexes were synthesized by addition of chloroform solution of triphenylphosphine silver to a methanolic solution containing the thiocarboxylato zincate anion followed by addition of one equivalent of triphenylphosphine (chloroform solution) with stirring at room temperature (Scheme 1).

It may be noted that the complex **2** has two different molecules in the solid state. However, in solution their individual identity is not retained. As a result only one signal (at 8.63 ppm) is observable in the $^{31}$P NMR spectrum of the complex.

It is also worth mentioning that Zn(II)/Ag(I) complexes are uncommon and there are only a few such compounds that contain a sulfur ligand. To the best of our knowledge the only structurally characterized Zn(II)/Ag(I) complexes are those in which a (N-donor) macrocyclic complex of Zn(II) is bounded to Ag(I) [32,33] through the sulfur atoms present in the pendent arms of the macrocyclic ligand.

Both the complexes were soluble in common organic solvents such as chloroform, benzene etc. The compounds in solid state were found to be fairly stable, under ambient conditions.

### 3.2. Crystal and molecular structures

Complex **1** crystallized in orthorhombic system with *Pccn* space group. The molecular structure with atom labeling scheme is depicted in Fig. 1 and slected bond lengths and bond angles are gi-

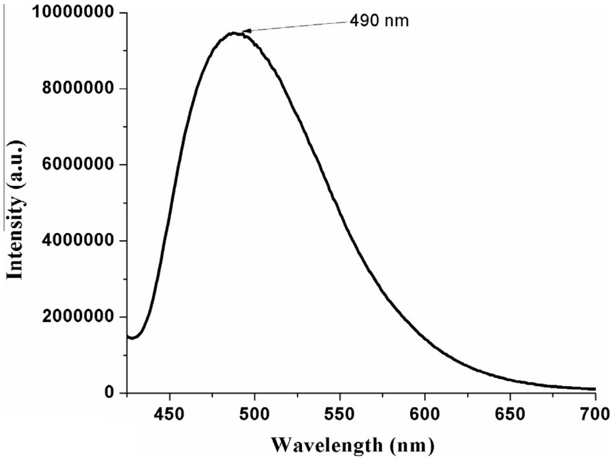


**Fig. 4.** Emission spectrum of **2** in solid state.

ven in Table 2. In this case all three thiophene rings and two phenyl rings of triphenylphosphine are distorted.

The three thiocarboxylate ligands exhibit three different coordination modes. One of the ligands binds monodentately to Zn(II) through the sulfur atom (S5) and the other two form bridges between Zn and Ag atoms. The bridging in one case is μ-S while it is (μ-O,S) in the other. The Zn(II) being harder as compared to Ag(I) is bounded by O2 atom of the (μ-O,S) bridging ligand. The fourth coordination site of Zn is occupied by the oxygen atom of a water molecule. A look at the various angles subtended at Zn1 by the donor atoms also reveals a distorted tetrahedral geometry around it. However, the presence of S3 atom affects the geometry to some extent by capping the S1, S5, O2 face of tetrahedron. Geometry around Ag1 is also tetrahedral with significant distortion which is possibly a consequence of large steric demands of the two triphenylphosphine ligands.

Evidently, there is no Zn–Ag bonding in this complex as the two atoms are separated by 3.723 Å which is even larger than the sum of the van der Waals' radii of these two atoms.

The structure of complex **2** revealed an unusual co-crystallization of two different molecules in the same lattice (Fig. 2). Molecular core in one of these (containing Zn1 and Ag1) is isostructural to that of **1**. In the second molecule, the two metals Zn2 and Ag2 are held together by the sulfur ($\mu_2$-S) atom of a thiobenzoate ligand. The Zn2 atom is coordinated by O7 besides the three S atoms. The Ag2 is tricoordinated having bonded to one sulfur and two phosphorus atoms. Notably, the Ag2 atom is tipped above the $P_2S$ plane by 0.317 Å which is possibly a consequence of Ag2···O6 interaction. [The Ag2–O6 distance is 2.757 Å which is substantially shorter than the sum of the van der Waals' radii of the Ag and O atoms (3.24 Å).]

### 3.3. Electronic absorption spectra

Absorption spectrum of **1** showed absorptions at 234, 239, 255 and 312 nm. In solid state the peaks at higher frequencies appeared at 272 and 288 nm, while the lower energy absorptions were observed at 321, 342, 368 nm and a broad peak at 426 nm. Similarly, the complex **2** showed absorption peaks at 225, 234, 239, 246 and 314 nm in solution state whereas in solid state peaks were observed at 252, 305, 326, 342 and 412 (broad) nm (Figs. S5–S8, Supporting information). In general, lower energy peaks appear because of the metal to ligand (or ligand to metal) charge transfers while peaks below 300 nm are due to the inter- or intra-ligand charge transfers. Spectral behavior of both the complexes are very similar to the thiocarboxylate complexes of Cd(II)/Ag(I) [15] and Pb(II)/Ag(I) [17].

For unambiguous assignment of the absorption bands time dependent density functional theory (TDDFT) calculations have been performed at PBE1 level. The orbital transition plots of **1** are shown in Fig. 3. The calculated absorptions at 455 nm and 440 nm are due to electron transfers from lone pair of silver atom to the π* orbital of thiophene ring of the bridging thiocarboxylate. This involves transitions ($n \rightarrow \pi^*$) from HOMO−4 and HOMO−3 to LUMO, LUMO+1 orbitals. Experimentally these transitions are responsible for the broad absorption peak ranging from 400 to 450 nm (with an absorption maximum at 426 nm). Other absorption peaks at 372 and 345 nm are due to admixing of metal to ligand, intra-ligand and inter-ligand charge transfer transitions. These peaks are observed experimentally at 368 and 342 nm respectively.

### 3.4. Emission spectra

To the best of our knowledge there is no literature available on the photoluminescence properties of Zn(II)/Ag(I) heterobimetallic compounds. Emission spectra of complexes **1** and **2** have been recorded in solid state. When exited at 426 nm complex **1** showed two weak emission bands at 469 and 522 nm (broad) (Fig. S9, Supporting information). Complex **2** showed a strong and broad emission band at 490 nm (Fig. 4) when it was exited at 400 nm. In both the cases, no significant changes were observed in the emission spectrum on changing the excitation wavelengths. The emission bands observed are thus due to the excitation of electrons by metal centered charge transfer transitions [17].

## 4. Conclusions

Two new heterobimetallic complexes, $[(PPh_3)_2Ag(\mu\text{-SCOth})_2Zn(SCOth)(H_2O)]$ (**1**) and $\{[(PPh_3)_2Ag(\mu\text{-SCOPh})_2Zn(SCOPh)(H_2O)][(PPh_3)_2Ag(\mu\text{-SCOPh})Zn(SCOPh)_2]\}$ (**2**) have been synthesized and characterized by spectral and X-ray diffraction studies. Structure of **2** is unique as two different molecules, $[(PPh_3)_2Ag(\mu\text{-SCOPh})_2Zn(SCOPh)]$ and $[(PPh_3)_2Ag(\mu\text{-SCOPh})_2Zn(SCOPh)H_2O]$ co-crystallize in the same lattice. Electronic spectral behavior of the complex **1** has been explained by TDDFT calculations. The two complexes may further be explored for their application as single source precursors for Ag/Zn sulfide nanoparticles.

## Acknowledgements

The authors are grateful to Professor R.J. Butcher, Howard University, USA for his help in refining the structures (particularly of compound **1**). Financial supports in the form of a research project to S.B. by the university grants commission, India, SRF to S.S. and J.C. by the Council of Scientific and Industrial Research, India are gratefully acknowledged.

## Appendix A. Supplementary material

CCDC 772371 and 772370 contains the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2013.07.016.

## References

[1] M. Yamami, H. Furutachi, T. Yokoyama, H. Okawa, Inorg. Chem. 37 (1998) 6832.

[2] F. Keller, A.J. Rippert, Helv. Chim. Acta 82 (1999) 125.
[3] H.Z. Kou, B.C. Zhou, S. Gao, R.J. Wang, Angew. Chem., Int. Ed. 42 (2003) 3288.
[4] C.N. Verani, E. Rentschler, T. Weyhermüller, E. Bill, P. Chaudhuri, J. Chem. Soc., Dalton Trans. (2000) 4263.
[5] H.-L. Gao, L. Yi, B. Ding, H.-S. Wang, P. Cheng, D.-Z. Liao, S.-P. Yan, Inorg. Chem. 45 (2006) 481.
[6] C.P. Berlinguette, K.R. Dunbar, Chem. Commun. (2005) 2451.
[7] T.I. Doukov, T.M. Iverson, J. Seravalli, S.W. Ragsdale, C.L. Drennan, Science 298 (2002) 567.
[8] P. Kalck, N. Wheatley, Chem. Rev. 99 (1999) 3379.
[9] K. Severin, Chem. Eur. J. 8 (2002) 1514.
[10] E.K. Byrne, L. Parkanyi, K.H. Theopold, Science 241 (1988) 332.
[11] S.A. Wolf, D.D. Awschalom, R.A. Buhrman, J.M. Daughton, S.V. Molnár, M.L. Roukes, A.Y. Chtchelkanova, D.M. Treger, Science 294 (2001) 1488.
[12] K. Liu, C.-L. Ho, S. Aouba, Y.-Q. Zhao, Z.-H. Lu, S. Petrov, N. Coombs, P. Dube, H.E. Ruda, W.Y. Wong, I. Manners, Angew. Chem., Int. Ed. 47 (2008) 1255.
[13] W.Y. Wong, P.D. Harvey, Macromol. Rapid Commun. 31 (2010) 671.
[14] J.J. Vittal, Acc. Chem. Res. 39 (2006) 869.
[15] J. Chaturvedi, S. Singh, S. Bhattacharya, H. Nöth, Inorg. Chem. 50 (2011) 10056.
[16] P. Singh, S. Bhattacharya, V.D. Gupta, H. Nöth, Chem. Ber. 129 (1996) 1093.
[17] J. Chaturvedi, S. Bhattacharya, R. Prasad, Dalton Trans. 39 (2010) 8725.
[18] V.V. Savant, J. Gopalakrishnan, C.C. Patel, Inorg. Chem. 9 (1970) 748.
[19] J.J. Vittal, P.A.W. Dean, Inorg. Chem. 35 (1996) 3089.
[20] J.T. Sampanthar, T.C. Deivaraj, J.J. Vittal, P.A.W. Dean, J. Chem. Soc., Dalton Trans. 22 (1999) 4419.
[21] C.V. Amburose, T.C. Deivaraj, G.X. Lai, J.T. Sampanthar, J.J. Vittal, Inorg. Chim. Acta 332 (2002) 160.
[22] S. Singh, S. Bhattacharya, H. Nöth, Eur. J. Inorg. Chem. (2010) 5691.
[23] G.M. Sheldrick, SHELX 97, Program for Crystal Structure Refinement from Diffraction Data, University of Gottingen, 1997.
[24] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837.
[25] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, GAUSSIAN 03, Revision D.01, Gaussian Inc., Wallingford, CT, 2004.
[26] J. Tomasi, B. Mennucci, E. Cances, J. Mol. Struct. (THEOCHEM) 464 (1999) 211.
[27] J.W. Stevens, H. Basch, M. Krauss, J. Am. Chem. Phys. 81 (1984) 6026.
[28] J.T. Cundari, J.W. Stevens, J. Chem. Phys. 98 (1993) 5555.
[29] P.J. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.
[30] P.J. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 78 (1997) 1396.
[31] G. Schaftenaar, J.H. Noordik, J. Comput. Aided Mol. Des. 14 (2000) 123.
[32] G. Huang, C.K. Tsang, Z. Xu, K. Li, M. Zeller, A.D. Hunter, S.S.Y. Chui, C.M. Che, Cryst. Growth Des. 9 (2009) 1444.
[33] J.A. Tainer, E.D. Getzoff, J.S. Richardson, D.C. Richardson, Nature 306 (1983) 284.