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Note

Syntheses and structural studies of heterobimetallic thiocarboxylate complexes containing zinc and copper

Suryabhan Singh, Jyotsna Chaturvedi¹, A.S. Aditya, N. Rajasekhar Reddy, Subrato Bhattacharya*

Department of Chemistry, Banaras Hindu University, Varanasi 221005, India

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ABSTRACT

Anionic zinc(II) complexes, $[Zn(SCOR)_3]^-$ [R = th (1)] have been used for the synthesis of heterobimetallic complexes, $[(PPh_3)Cu(\mu-SCOR)_3Zn(PPh_3)]$ [R = Ph (2) and th (3)]. All the three complexes have been characterized by FTIR, ¹H and ¹³C NMR spectroscopy. The synthetic reactions involved phosphine migration from Cu(I) to Zn(II) in the cases of 2 and 3. Molecular structures of the complexes have been determined by single crystal X-ray diffraction and the structural features have been explained on the basis of NBO calculations. The Cu–Zn distance in these molecules are shorter than the sum of their covalent radii indicating the existence of a bond between the metals. Electronic spectral behavior of the complexes have been explained by TDDFT calculations. Luminescence properties of **3** has also been studied in solid state. © 2012 Elsevier B.V. All rights reserved.

For more than past two decades heterobimetallic complexes have been of interest as they find applications in different fields of research and development because of the fact that the different metal centers could exhibit cooperative behavior [1,2]. Apart from the tuned reactivities such heterobimetallic systems have been found extremely useful as precursors of electronic and spintronic materials [3–6]. During recent years, heterobimetallic complexes containing sulfur/selenium ligands are being explored to prepare ternary metal sulfides/selenides by energy efficient soft chemical routes [7].

Very recently, we have reported the synthesis and structures of two Cd/Cu heterobimetallic thiocarboxylate complexes, $(PPh_3)_2$ Cu(μ -SCOR)₂Cd(SCOR) [8]. Surprisingly, our attempts to crystallize analogous heterobimetallic complex containing Cu and Hg led to disproportionation of the complex into several monometallic thiocarboxylates depending on the solvent used for crystallization [9].

A search of literature revealed the fact that though mononuclear Zn(II) thiocarboxylates [10–13] are known no heterobinuclear thiocarboxylate containing a Zn(II) atom has ever been reported.

In view of these facts we have taken up the synthesis and characterization of Zn/Cu thiocarboxylate complexes. We have chosen thiophene-2-thiocarboxylate because of the fact that it contains an additional sulfur atom at the peripheral part of the ligand which could also affect the structure and bonding of the complexes [14].

E-mail address: s_bhatt@bhu.ac.in (S. Bhattacharya).

Complex anions, *tris*(thiocarboxylato)zincate(II) were used as the precursors for all the complexes reported here. The *tris*(thiophen-2-thiocarboxylato)zincate(II) (1) was however, isolated by the cation exchange of sodium *tris*(thiophene-2-thiocarboxylato)zincate(II) with tetraphenylphosphonium bromide. The complexes **2** and **3** were synthesized by reacting the nitrate salt of *bis*(triphenylphosphine)copper(I) with *tris*(thiobenzoato)zincate and *tris*(thiophene-2-thiocarboxylato)zincate complexes, respectively (Scheme 1).

The formation of complexes **2** and **3** is quite interesting as there is migration of triphenylphosphine ligand from Cu(I) to Zn(II). It is also worth mentioning here that a number of Zn(II)/Cu(I) complexes are reported in the literature but Zn(II)/Cu(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)/Cu(I) complexes are those in which a (N-donor) macrocyclic complex of Zn(II) is bounded to Cu(I) [15,16] through the sulfur atoms present in the pendent arms of the macrocyclic ligand.

Complex **1** crystallized in trigonal system with P_{3_1} space group (Table S1, Supporting information). The molecular structure is depicted in Fig. 1. It has discrete cations and anions in the lattice. One of the phenyl rings of the tetraphenylphosphonium cation and all the three thiophene rings of the thiocarboxylate ligand are disordered. As there is no unusual feature in the cationic part its structural details will not be discussed further. At a glance the structure of the anion is similar to that of the reported complex, $[Zn(SCOPh)_3]^-$ [11], however, a closer look revealed a few significant differences between the two. In the anionic thiobenzoate





^{*} Corresponding author. Tel.: +91 542 6702451.

¹ Present address: IPC Department, I.I.Sc., Bangalore 560012, India.



Scheme 1.



Fig. 1. Thermal ellipsoid plot of **1** at 30% probability level. One of the phenyl rings and all the thiophene rings are disordered (hydrogen atoms are omitted for clarity). Selected metric data (bond lengths in Å and angles in °): Zn1–S1 2.488(2), Zn1–S3 2.404(2), Zn1–S5 2.425(3), Zn1–O1 2.251(5), Zn1–O2 2.434(4), Zn1–O3 2.370(5). S1–Zn1–S3 105.89(8), S1–Zn1–S5 105.91(8), S3–Zn1–S5 114.51(9), O1–Zn1–O2 92.00(15), O1–Zn1–O3 87.13(17), O2–Zn1–O3 87.07(15), S1–Zn1–O1 64.50(11), S3–Zn1–O1 98.67(12), S5–Zn1–O1 146.75(12), S1–Zn1–O2 153.32(14), S3–Zn1–O2 63.35(12), S5–Zn1–O2 100.71(14), S1–Zn1–O3 103.25(13), S3–Zn1–O3 149.91(13), S5–Zn1–O3 63.28(14).



Fig. 2. Thermal ellipsoid plot of **2** at 30% probability level (hydrogen atoms are omitted for clarity). Selected metric data (bond lengths in Å and angles in °): Zn1–S 1 2.2823(24), Zn1–O2 1.976(3), Zn1–O3 1.965(3), Zn1–P2 2.5385(14), Zn1–Cu1 2.9415(8), Cu1–S1 2.4153(13), Cu1–S2 2.3159(13), Cu1–S3 2.2925(12), Cu1–P1 2.2885(12). S1–Zn1–O2 112.11(11), S1–Zn1–O3 124.47(9), S1–Zn1–P2 123.41(5), O2–Zn1–O3 103.95(15), O2–Zn1–P2 90.38(10), O3–Zn1–P2 96.14(9), S1–Zn1–Cu1 53.28(3), O2–Zn1–Cu1 86.88(10), O3–Zn1–Cu1 89.66(9), P2–Zn1–Cu1 174.05(4), S1–Cu1–S2 104.32(5), S1–Cu1–S3 111.14(5), S2–Cu1–S3 116.61(5), S1–Cu1–P1 112.18(5), S2–Cu1–P1 104.69(4), S3–Cu1–P1 107.82(4), S1–Cu1–Zn1 49.24(4), S2–Cu1–Zn1 83.74(3), S3–Cu1–Zn1 83.06(3), P1–Cu1–Zn1 161.40(4).



Fig. 3. Thermal ellipsoid plot of **3** at 30% probability level. Thiophene rings are disordered (hydrogen atoms are omitted for clarity). Selected metric data (bond lengths in Å and angles in °): Zn1–S1 2.3162(12), Zn1–O2 1.961(3), Zn1–O3 1.979(3), Zn1–P1 2.4568(11), Zn1–Cu1 2.9140(8), Cu1–S1 2.4191(11), Cu1–S3 2.2772(12), Cu1–S5 2.2917(13), Cu1–P2 2.2606(11). S1–Zn1–O2 129.23(8), S1–Zn1–O3 109.80(9), S1–Zn1–P1 109.48(4), O2–Zn1–O3 98.98(12), O2–Zn1–P1 99.91(8), O3–Zn1–P1 107.52(8), S1–Zn1–Cu1 53.63(3), O2–Zn1–Cu1 86.34(8), O3–Zn1–Cu1 90.45(8), P1–Zn1–Cu1 159.59(3), S1–Cu1–S3 112.68(4), S1–Cu1–S5 104.07(5), S3–Cu1–S5 116.01(5), S1–Cu1–P2 107.93(4), S3–Cu1–P2 108.36(5), S5–Cu1–P2 107.40(5), S1–Cu1–Zn1 50.44(3), S3–Cu1–Zn1 83.18(4), S5–Cu1–Zn1 82.31(4), P2–Cu1–Zn1 158.34(3).

complex, Zn(II) lies in the plane constituted by the three sulfur atoms where as in **1** the zinc atom is tipped above (0.838 Å) the S3 plane. All the three Zn-S distances are comparable to those found in [Zn(SCOPh)₃]⁻. In contrast to [Zn(SCOPh)₃]⁻ where the Zn-O distances are unequal the three Zn-O distances in 1 are comparable with one another. These are slightly longer than the sum of the covalent radii of Zn and O atoms (1.90 Å), however, the angles subtended at Zn by the three sulfur and three oxygen atoms reveal a six coordination environment around Zn. The structure can possibly be best described as octahedral with considerable distortion due to small ligand bite. It may be noted that in the [Zn(SCOPh)3]complex the Zn-O distances are larger than those found in 1 ranging between 2.328 and 3.156 Å and the geometry has been described as trigonal bipyramidal with ZnS₃O₂ core. Vittal and Dean have calculated [11] Bond-valence parameters for [Zn(SCOPh)₃]⁻ complex and found the contributions of Zn-S bond 82.6% and Zn-O bond 17.4%. Similar calculations on 1 about ZnS₃O₃ unit revealed that the total bond valence is 1.707 in which Zn-S and Zn-O bonds contributions are 68.83% and 31.17% respectively. The latter evinces the significance of the Zn–O bonds in 1.

The complex **2**, $[(PPh_3)Cu(\mu$ -SCOPh)₃Zn(PPh₃)] crystallized in the orthorhombic crystal system with the $P2_12_12_1$ space group. The molecular structure is shown in Fig. 2. In this complex two



Fig. 4. Selected orbital transitions for 2 (orbital contour value 0.05).

different types of binding modes of thiobenzoate ligands are observed; O, S (bidentate) bridging and S bridging. In the former case which represents the classical binding mode of the ligands, oxygen atom is bonded to Zn(II), a comparatively hard metal center where as the sulfur atom is bounded with the soft Cu(I) atom. Besides, the three bridging thiobenzoate ligands a strong Cu–Zn interaction is also responsible for holding the two metals together (the Cu–Zn distance [2.9415(8) Å] is slightly shorter than the sum of the covalent radii of the two metals (2.97 Å)). The coordination environment around Zn(II) seems to be distorted tetrahedral if the Zn–Cu contact is ignored. However, the angles subtended at Zn are highly deviated from ideal tetrahedral angle. Two P–Zn–O angles are closer to 90° while the two O–Zn– S angles are rather obtuse (112.11° and 124.47°). A better description of the geometry around Zn would be trigonal bipyramidal if the Cu atom is considered to be within the coordination sphere of Zn (as it appears by short Cu–Zn distance). The P–Zn–Cu axial angle (174.05°) is quite close to the ideal value of 180° while the equatorial O-Zn-S angles are closer to 120°. The geometry around Cu atom is highly deviated from that of a trigonal bipyramid. The angles subtended at the Cu center by three S and one P atoms are closer to 109°. Though two S-Cu-Zn angles are closer to 90°, the third one (S1–Zn–Cu) is very small. The Zn–Cu–P angle (161.39°) is also highly deviated from the expected value of 180°.

During recent years four papers have appeared describing compounds containing Cu(II) and Zn(II) together [17-20]. In all these compounds Zn and Cu centers are bridged by two oxygen atoms of the ligands with a Cu-Zn distance varying within a range of 2.95–3.23 Å which is very close to the sum of their covalent radii. Notably, in none of the reports there is any comment on the nature of Cu-Zn bond and the coordination geometries of the metals have been described without considering the existence of Cu-Zn bond. Possibly, the short M-M distance in these molecules is a consequence of O bridging which cannot be stretched beyond a limit. In the present case, however, the bridging are through OCS units (which can open wide to a larger extent) and through sulfur atom which has a substantially larger covalent radius than that of oxygen. One would expect the angle subtended at sulfur (Zn-S-Cu) to be larger than 90° considering its hybridization and number of bonds. In that case the Zn-Cu distance should be larger than 3.32 Å based on purely geometric considerations. Evidently, the short Cu-Zn distance in the present case is not a consequence of the strain imposed by the bridging atoms. On the contrary the acute Zn–S–Cu angle (77.48°) is possibly a consequence of strong Zn–Cu interaction. While comparing with the earlier reported data it should also be kept in mind that the present complex is the first example where Cu is in +1 oxidation state and obviously will have a larger radius than those reported in the literature having +2 oxidation state.

To get further insight into the nature of Cu-Zn interaction we have carried out density functional calculations. The results of second order perturbation theory analysis of Fock matrix (NBO) reveal that there are significant intramolecular interactions. Electron transfers from Lp*Zn to Lp*Cu and various Ry*Cu orbitals amount to 50.17 and 8.01 kcal/mol of energy lowering. Similarly, there are significant $Cu \rightarrow Zn$ charge transfers also. The total energy involved in the electron transfer from the LpCu to various antibonding orbitals of Zn is -8.80 kcal/mol while the same from Lp*Cu is -10 kcal/mol. It may therefore, be concluded that the short Cu-Zn distance is not merely a consequence of steric constrains imposed by the ligands but is a result of strong bonding interactions between the two atoms.

Complex 3 (Fig. 3) is structurally similar to 2 but there are a few significant differences between the two. The P-Zn and Cu-Zn bonds are considerably shorter than the corresponding bonds in 2. A shorter Cu–Zn distance though indicates a stronger bond between the two metals, the coordination geometries around Cu and Zn do not fit into the trigonal bipyramidal model. The bond angles subtended both at Zn and Cu are indicative of tetrahedral geometries around these metal centers, however, distortion from ideal geometry is greater around Zn as compared to that in the case of Cu. Two of the thiophene rings are disordered in 3. Notably, the thiocarboxylate ligands are show two different bridging modes in both **2** and **3**. Two ligands bridge bidentately (μ -S,O) while the third one bridges the two metals through its sulfur atom $(\mu$ -S) only. Similar bridging modes have earlier been reported in the cases of Ga/Cu and In/Cu complexes [21].

Absorption spectrum of 1 shows bands at 245, 294, 315 348 and 416 nm. The spectrum of 2 shows absorptions at 255, 301 and a shoulder at 339 nm. In solid state the peaks at higher frequencies exhibit a blue shift and appear at 225 and 250 while the lower energy absorption band is broad and appear between 287 and 425 nm. Complex 3 also shows similar spectral pattern (Figures S1–S3, Supporting information). In general, lower energy peaks appear because of the metal to ligand (or ligand to metal) charge transfers while peak below 300 nm are due to the inter- or intraligand charge transfers.

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 2 are shown in Fig. 4. The calculated absorptions at 427 nm and 419 nm are due to electron transfers from sulfur and copper atoms to the bridging thiobenzoate phenyl ring $(n \rightarrow \pi^*)$ involving HOMO to LUMO, LUMO+2, LUMO+3 and HOMO-1 to LUMO and LUMO+3 orbitals of the molecule. Other absorption peaks at 368 nm, 336 nm, 333 and 325 nm are due to intra- and inter-ligand charge transfers

To the best of our knowledge there is no literature available on the photoluminescence properties of Zn(II)/Cu(I) heterobimetallic compounds. Emission spectrum of Complex **3** has been recorded in solid state. When exited at 400 nm the complex **3** shows a strong emission at 423 nm due to inter-ligand transitions (Figure S4, Supporting information). The weak intensity emissions at 485 and 546 nm are possibly due to ligand centered (involving thiocarboxylate ligands) charge transfer.

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Appendix A. Supplementary material

Experimental details, Figures S1-S4, Table S1 and the crystallographic data in CIF format. CCDC 772374, 772372 and 772373 contains the supplementary crystallographic data for compounds 1-3, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://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.2012.11.022.

References

- [1] P. Kalck, N. Wheatley, Chem. Rev. 99 (1999) 3379.
- K. Severin, Chem. Eur. J. 8 (2002) 1514.
- [3] E.K. Byrne, L. Parkanyi, K.H. Theopold, Science 241 (1988) 332.
- 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.
- [5] 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.
- W.Y. Wong, P.D. Harvey, Macromol. Rapid Commun. 31 (2010) 671.
- [7] J.J. Vittal, Acc. Chem. Res. 39 (2006) 869.
- [8] J. Chaturvedi, S. Singh, S. Bhattacharya, H. Nöth, Inorg. Chem. 50 (2011) 10056.
- S. Singh, J. Chaturvedi, S. Bhattacharya, Inorg. Chim. Acta 385 (2012) 112.
- [10] V.V. Savant, J. Gopalakrishnan, C.C. Patel, Inorg. Chem. 9 (1970) 748.
- [11] J.J. Vittal, P.A.W. Dean, Inorg. Chem. 35 (1996) 3089.
- [12] J.T. Sampanthar, T.C. Deivaraj, J.J. Vittal, P.A.W. Dean, J. Chem. Soc., Dalton Trans. (1999) 4419
- [13] C.V. Amburose, T.C. Deivaraj, G.X. Lai, J.T. Sampanthar, J.J. Vittal, Inorg. Chim. Acta 332 (2002) 160.
- [14] S. Singh, S. Bhattacharya, H. Nöth, Eur. J. Inorg. Chem. (2010) 5691.
- [15] M.S. Masar III, N.C. Gianneschi, C.G. Oliveri, C.L. Stern, S.T. Nguyen, C.A. Mirkin, J. Am. Chem. Soc. 129 (2007) 10149.
- [16] C.G. Oliveri, N.C. Gianneschi, S.T. Nguyen, C.A. Mirkin, C.L. Stern, Z. Wawrzak, M. Pink, J. Am. Chem. Soc. 128 (2006) 16286.
- [17] D. Ülkü, L. Tatar, O. Atakol, S. Durmus, Acta Crystallogr., Sect. C 55 (1999) 1652. [18] E.A. Vinogradova, O.Y. Vassilyeva, V.N. Kokozay, P.J. Squattrito, J. Reedijk,
- G.A.V. Albada, W. Linert, S.K. Tiwary, P.R. Raithby, New J. Chem. 25 (2001) 949. [19] M. Hamid, A.A. Tahir, M. Mazhar, M. Zeller, A.D. Hunter, Inorg. Chem. 46 (2007)
- 4120. [20] A. Roth, E.T. Spielberg, W. Plass, Inorg. Chem. 46 (2007) 4362.
- [21] T.C. Deivaraj, J.-H. Park, M. Afzaal, P. O'Brien, J.J. Vittal, Chem. Mater. 15 (2003) 2383.