Note

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

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ABSTRACT

Anionic zinc(II) complexes, $[Zn(SCOR)_3]^-$ [R = th (**1**)] have been used for the synthesis of heterobimetallic complexes, $[(PPh_3)Cu(\mu\text{-}SCOR)_3Zn(PPh_3)]$ [R = Ph (**2**) and th (**3**)]. All the three complexes have been characterized by FTIR, ^1H and ^{13}C 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.

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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, $(PPh_3)_2Cu(\mu\text{-}SCOR)_2Cd(SCOR)$ [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].

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(II) 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 $P3_1$ 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
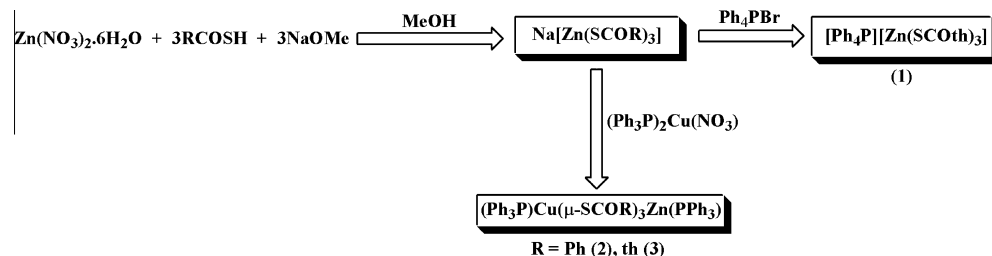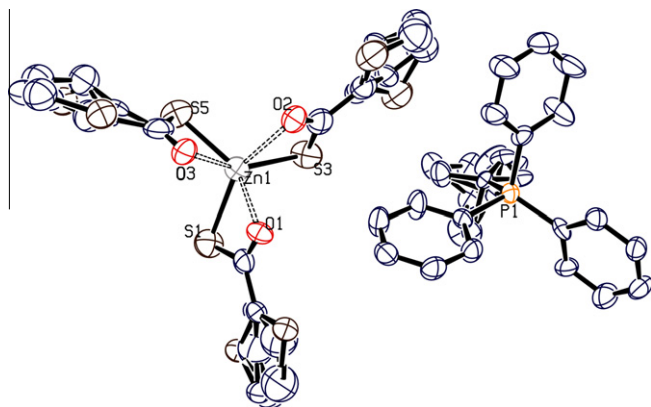
Scheme 1.

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).
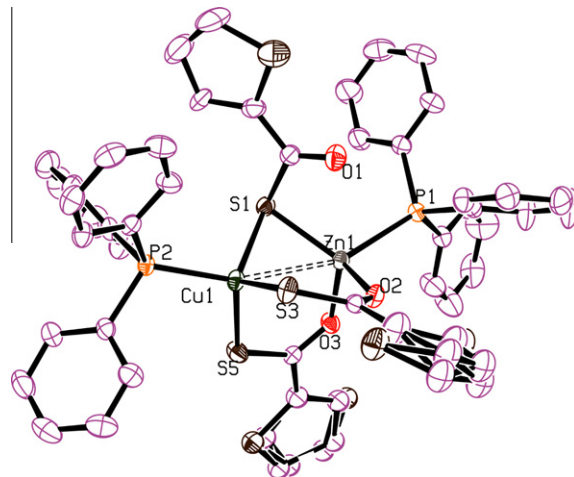

Fig. 3. Thermal ellipsoid plot of **3** at 30% probability level. Thiophene rings are disordered (hydrogen atoms are omitted for clarity). Selected metric data (bond lengths in Å and angles in °): Zn1–S1 2.3162(12), Zn1–O2 1.961(3), Zn1–O3 1.979(3), Zn1–P1 2.4568(11), Zn1–Cu1 2.9140(8), Cu1–S1 2.4191(11), 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–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).
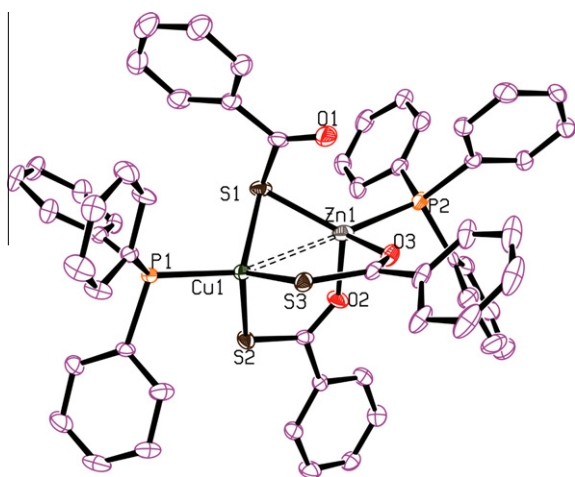

Fig. 2. Thermal ellipsoid plot of **2** at 30% probability level (hydrogen atoms are omitted for clarity). Selected metric data (bond lengths in Å and angles in °): Zn1–S1 2.2823(24), Zn1–O2 1.976(3), Zn1–O3 1.965(3), Zn1–P2 2.5385(14), Zn1–Cu1 2.9415(8), Cu1–S1 2.4153(13), Cu1–S2 2.3159(13), Cu1–S3 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).

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 ZnS_3O_2 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 ZnS_3O_3 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**, $[(PPh_3)Cu(\mu\text{-}SCOPh)_3Zn(PPh_3)]$ 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