Synthesis and characterization of tris(2-pyridylthio)methanido Zn complex with a Zn–C bond and DFT calculation of its one-electron oxidized species†

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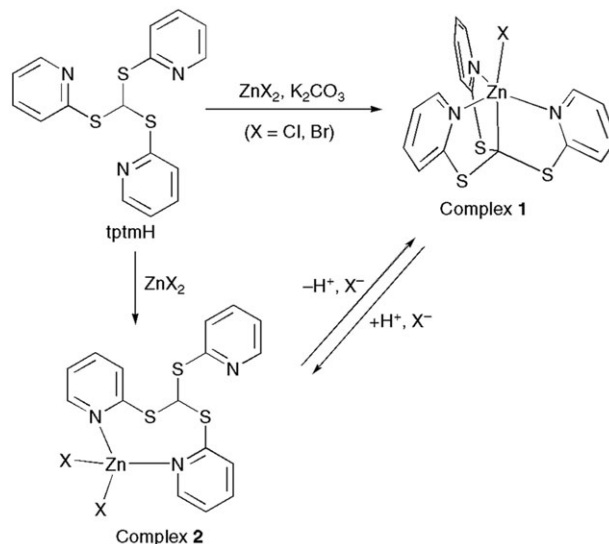**Tris(2-pyridylthio)methane (tptmH) reacts with ZnCl$_2$ producing the Zn–C containing complex of [ZnCl(tptm)], whose cyclic voltammogram shows an irreversible oxidation peak at 0.2 V *vs.* $E^{0\prime}(Fc^{+/0})$. DFT calculations suggested that $1e^-$ oxidation should occur at the tptm ligand resulting in the cleavage of the Zn–C bond, leading to decomposition of the complex.**

Tripodal ligands based on substituted pyridines have attracted considerable attention in inorganic chemistry.[1] We have recently found copper(II) complexes with the tris(2-pyridylthio)methanido (tptm) ligand. Each complex of [Cu^{II}X(tptm)] (X = F, Cl, Br, I) with trigonal bipyramidal structure shows a reversible oxidation process at +0.1 V (*vs.* $E^{0\prime}(Fc^{+/0})$) in dichloromethane for all the halogeno complexes. Not only that, the chloro complex, [Cu^{II}Cl(tptm)], is oxidized to [Cu^{III}Cl(tptm)]$^+$ without large structural change, which is the first example of the trigonal bipyramidal structure for copper(III) complexes.[2] Such invariance in oxidation potential for all [Cu^{II}X(tptm)] arouses suspicions whether the ligand or the metal centre is oxidized. The oxidation–reduction chemistry of the first transition metal complexes lacks zinc complexes, which can possibly become the standard for evaluation of coordination compounds containing redox-suspicious ligands. To explore this point, we have synthesized a zinc(II) complex containing the tptm ligand (Scheme 1).

[ZnCl(tptm)] (**1-Cl**) was synthesized by the reaction of ZnCl$_2$ and tptmH in acetonitrile under an aerobic condition in the presence of K$_2$CO$_3$. Crystals of **1-Cl** suitable for X-ray analysis were obtained from a solution in CH$_2$Cl$_2$–cyclohexane in a 30% yield. During some trials to obtain single crystals of the corresponding bromo complex that was prepared in the same manner using ZnBr$_2$, we obtained crystals of the different complex [ZnBr$_2$(tptmH)] (**2-Br**). Interestingly, the recrystallization of [ZnX(tptm)] (X = Cl, Br) causes the contamination with [ZnX$_2$(tptmH)] indicating the presence of trigonal bipyramidal (tbp)–tetrahedral (Td) equilibrium with H$_2$O as a proton source. Although some tbp[3a,b] and Td[3c] zinc complexes with tripodal ligands were reported, such equilibrium was not mentioned.

Both Td and tbp complexes have been structurally analyzed by X-ray crystallography (Fig. 1).‡ For the crystal of the tbp complex, [ZnCl(tptm)] (**1-Cl**), two crystallographically independent complex molecules are positionally disordered almost at the same place and are overlapped to each other in the asymmetric unit with 0.8 and 0.2 occupancies (see ESI†). Both of the complex molecules have tbp structure with the equatorial plane formed by three N atoms of pyridines and the axial positions occupied by the chloro ligand and the C atom of the carbanion. The Zn–C bond lengths are 2.213(6) and 2.19(2) Å, which are considerably longer than those of the Cu–C bond in [CuCl(tptm)] (2.01(1)–2.04(1) Å) and the Zn–C bond in the zinc-alkyl caged cobalt(III) complex (2.049(4) Å).[4] The Zn–N lengths are 2.111(7), 2.137(5), 2.155(6), 2.05(3), 2.11(2) and 2.12(2) Å. The Zn–Cl lengths are 2.341(2) and 2.334(7) Å. Unlike the Zn–C bond, the Zn–N and Zn–Cl bond lengths are not so different from those in the copper(II) complex. The Zn–N(py) and Zn–Cl bond lengths are significantly longer than those in the corresponding tris(pyridylmethyl)amine (tpa) complex.[3a] These longer Zn–N and Zn–Cl bonds were

Scheme 1 Formation of Zn complexes with tris(2-pyridylthio)methane (tptmH) and tris(2-pyridylthio)methanido (tptm) ligands.

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† Electronic supplementary information (ESI) available: syntheses and characterization of the complexes and the results of the DFT calculation for the oxidized chloro complex. See DOI: 10.1039/b715996j
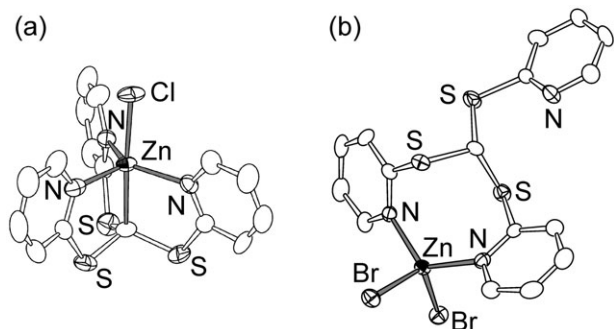
Fig. 1 Structures of (a) one of the disordered molecules with higher occupancy **1-Cl** and (b) **2-Br**.

attributed to the compensation for the formation of the strong Zn–C bond in the tptm complex. Similar compensation was also observed in the (6-R-2-pyridylmethyl)-bis-(2-pyridyl-methyl)amine zinc chloro complexes (R = NHCO^{t}Bu or NH$_2$) with tbp structure showing the longer Zn–N(py) and Zn–Cl bonds with the shorter Zn–N(amine) bond.[5]

[ZnBr$_2$(tptmH)] (**2-Br**) has tetrahedral structure with two bromo ligands and two of three pyridyl groups in the neutral tptmH forming an eight-membered chelate ring with the metal centre. The Zn–N bond lengths are 2.073(5) and 2.077(6) Å, and the Zn–Br bond lengths are 2.3702(12) and 2.3734(11) Å. The proton of the CH group in the tptmH ligand probably came from a small amount of water in the solvent used for crystallization. In addition, **2-Br** was separately prepared by the reaction of ZnBr$_2$ and tptmH in acetonitrile.

Noteworthy, each of the complexes, [ZnX(tptm)], shows a sharp irreversible oxidation peak at 0.2 V vs. $E^{0\prime}$(Fc$^{+/0}$) (Fig. 2). The potential of the oxidation peak is very close to those potentials observed for [CuX(tptm)] in the cyclic vol-tammograms in dichloromethane, which indicates that the oxidation occurs at the tptm ligand moiety. The free proto-nated ligand, tptmH, also gives an irreversible oxidation peak at considerably positive potential of 1.1 V vs. $E^{0\prime}$(Fc$^{+/0}$).

Of course, it is impossible to oxidize zinc(II) to zinc(III) at such potential around the $E^{0\prime}$(Fc$^{+/0}$) couple. The initial oxida-tion for the {Zn(tptm)} unit occurred at the tptm ligand and the resulting ligand radical should be unstable, which proceeds to a successive decomposition.

To clarify this point, DFT calculations were employed for the chloro complex (**1-Cl**) and the one-electron oxidized species, [ZnCl(tptm)]$^+$.[6] The Gaussian 03 result for **1-Cl** afforded reasonably assumed C_3 symmetry with Zn–C (2.18 Å), Zn–Cl (2.39 Å) and Zn–N (2.14 Å) bond lengths. All these values are consistent with the experimental ones. The calcula-tion of the virtual cationic complex of [ZnCl(tptm)]$^+$ was also performed along with its structural optimization (Fig. 3). Interestingly, the energy difference between [ZnCl(tptm)]$^{+/0}$ with the same tbp structural frameworks is 6.69 eV. This difference is 0.24 eV larger than that between [CuCl(tptm)]$^{+/0}$ obtained by the similar calculations. The electrochemical measurement showed an irreversible oxidation wave at 0.2 V vs. $E^{0\prime}$(Fc$^{+/0}$), which was also fairly consistent with the calculations. The optimized structure maintains the C_3 sym-metry with elongation of the Zn–C bond to 2.69 Å. Whereas,
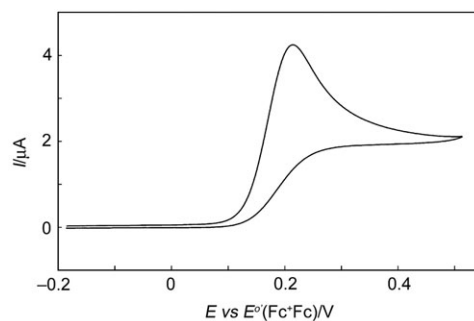
the Zn–Cl and Zn–N bonds are 2.25 and 2.08 Å, respectively, which are shortened more than 0.05 Å. The coordination geometry of the zinc(II) center becomes closer to tetrahedral. The charge density on the sulfur atoms mainly increased, whereas the charge on the zinc atom is unchanged. The spin analysis indicates that the spin density is mainly located on the central carbon causing the bond rupture between the zinc and carbon atoms. The resulting radical is probably unstable and it decomposes via C–S bond cleavage. Actually, 2,2′-dipyridyl-disulfide was detected in the reaction mixture of oxidative decomposition of the tptm complex by electrospray ionization mass measurement (see ESI†). Such behavior presumably re-flects the irreversible wave for the oxidation process in the cyclic voltammogram. So, in the case of the copper complex, succes-sive rearrangement of the electron configuration after the re-moval of an electron from the ligand causes the stable copper(III) complex, whereas it is impossible for the zinc complex to give zinc(III) through such a process. Another possibility is the formation of a tetracoordinated zinc center with liberation of the chloro ligand. Because of the disadvantage of liberation of the chloro ligand, this process may not proceed.

Conclusively, it is now clear that the tptm ligand conveni-ently coordinates to a zinc(II) ion with the formation of a Zn–C bond. From the DFT calculations, the oxidation of [ZnCl(tptm)] results in the formation of [ZnCl(tptm)]$^+$ produ-cing the central carbon radical and presumably causes the succeeding Zn–C bond rupture.
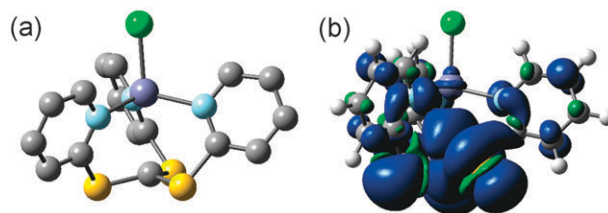
Fig. 3 (a) Optimized structure of the oxidized complex [ZnCl(tptm)]$^+$ by density functional calculation (UB3LYP) with 6-31g(d) basis set and (b) spin density on [ZnCl(tptm)]$^+$.

Notes and references

‡ *Crystal Data* for **1-Cl**: $C_{16}H_{12}ClN_3S_3Zn$, $M = 443.29$, monoclinic, $a = 15.278(4)$, $b = 9.109(2)$, $c = 15.379(4)$ Å, $\beta = 125.120(4)°$, $U = 1750.6(8)$ Å, $T = 193(2)$ K, space group Cc (no. 9), $Z = 4$, 7566 reflections measured, 3447 unique ($R_{int} = 0.0269$), $R_1 = 0.0471$ ($I > 2\sigma(I)$), $wR_2 = 0.1108$ (all data), GOF = 1.052.
Crystal Data for **2-Br**: $C_{18}H_{16}Br_2N_4S_3Zn$, $M = 609.72$, triclinic, $a = 7.8742(16)$, $b = 11.738(2)$, $c = 12.500(2)$ Å, $\alpha = 77.213(8)°$, $\beta = 82.363(9)°$, $\gamma = 84.516(9)°$, $U = 1114.1(4)$ Å, $T = 193(2)$ K, space group $P\bar{1}$ (no. 2), $Z = 2$, 11 100 reflections measured, 4993 unique ($R_{int} = 0.0411$), $R_1 = 0.0724$ ($I > 2\sigma(I)$), $wR_2 = 0.1329$ (all data), GOF = 1.049. CCDC 664489 (**1-Cl**) and CCDC 664490 (**2-Br**). For crystallographic data in CIF or other electronic format, See DOI: 10.1039/b715996j

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