Aerobic oxidation of a disulfide to its sulfonate leading to supramolecular pyridine-2-sulfonato Cu(II) and Zn(II) complexes

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A one-dimensional copper(II) complex with pyridine-2-sulfonate donors, [{Cu(3-mpSO$_3$)$_2$}$_n$] (3-mpSO$_3$ = 3-methylpyridine-2-sulfonate), is formed *via* the air oxidation of 3-mpds (2,2′-bis(3-methylpyridyl)disulfide) in the presence of CuBr$_2$, and a mononuclear zinc complex, [Zn(3-mpSO$_3$)$_2$(H$_2$O)$_2$], which has two-dimensional H-bonded networks and luminescent properties in solid state, is prepared by the reaction of ZnBr$_2$ with 3-mpSO$_3$H.

A variety of complexes with pyridine derivatives have been extensively investigated as a motif in supramolecular architecture.[1] On the other hand, one of the pyridine derivatives, pyridine-2-sulfonate, has been used for studies on ligand effects on GoAgg^{II} oxidation and chromic acid oxidation,[2] which can be expected to serve as a simple chelating ligand. Luminescent complexes of pyridine-2-sulfonate with several lanthanoids have also been prepared.[3] However, except for a silver(I) complex preliminarily reported by Charbonnier *et al.*[4] and a cobalt(III) complex recently reported by Murata *et al.*,[5] there is no report on the crystal structures of pyridine-2-sulfonato complexes.

In the present work, a supramolecular entity with a pyridine-2-sulfonate donor has been unexpectedly found in the reaction of 2,2′-bis(3-methylpyridyl)disulfide (3-mpds) with CuBr$_2$ under aerobic conditions, where the air oxidation of 3-mpds to 3-methylpyridine-2-sulfonate (3-mpSO$_3$) took place to afford a one-dimensional copper(II) complex, [{Cu(3-mpSO$_3$)$_2$}$_n$] **1**. By using the sulfonato ligand we have also synthesized a photoluminescent complex, [Zn(3-mpSO$_3$)$_2$(H$_2$O)$_2$] **2**, which is assembled by intermolecular hydrogen bonds in the solid state.†

Addition of a methanolic suspension of 3-mpds[6,7] in air to a methanol solution of CuBr$_2$ immediately afforded brown and red crystals, which were removed by filtration after 2 days.‡ The filtrate was allowed to stand for a month, yielding green crystals of sulfonato complex [{Cu(3-mpSO$_3$)$_2$}$_n$] **1**.§

As shown in Fig. 1, the molecular structure of **1** consists of an infinite one-dimensional chain of octahedrally co-ordinated centrosymmetric copper atoms, bridged by 3-mpSO$_3$ ligands. Two 3-mpySO$_3$ ligands are co-ordinated to the Cu ion to form a basal plane with two five-membered chelate rings in a *trans* fashion. The apical sites are occupied by two oxygen atoms of the 3-mpSO$_3$ ligands bridging to the adjacent Cu centres; the axial Cu–O bond lengths are longer than the corresponding equatorial ones by 0.44 Å.

Oxidation of 2,2′-dipyridyl disulfide to pyridine-2-sulfinate in the presence of the Cu(II) ion and water under both aerobic and anaerobic conditions has already been reported by Seff *et al.*[8] In general, further oxidation of disulfides or sufinate compounds to the corresponding sulfonates requires a strong oxidizing agent such as hydrogen peroxide or halogen.[5,9] Surprisingly, in the present experiment, 3-mpds was oxidized to 3-mpSO$_3$ even under relatively mild oxidative conditions. Such an oxidation phenomenon is considered to be a preceding process of oxidative desulfurization and to be a mimic of the metabolism of sulfur *in vivo*.[10]

The sulfonato zinc complex, [Zn(3-mpSO$_3$)$_2$(H$_2$O)$_2$] **2**, was obtained from the reaction of ZnBr$_2$ with 3-mpSO$_3$H[6,11] in water, and the molecular structure is shown in Fig. 2.¶ The zinc ion is co-ordinated by two 3-mpSO$_3$ ligands through the aromatic nitrogens in *trans* positions and sulfonate oxygens in *cis* positions and by two water molecules *cis* to each other. This N$_2$O$_4$ donor set forms the octahedral co-ordination geometry around the Zn atom. As depicted in Fig. 3, all of the co-ordinated water molecules and the unco-ordinated sulfonate oxygens are used for intermolecular hydrogen bonds (O(2)···O(4) 2.818(2) Å, O(3)···O(4) 2.723(2) Å), forming two-dimensional H-bonded networks parallel to the *bc* plane. Interestingly, the zinc complex **2** in the solid state displays luminescence with maximum peaks at 345 and 490 nm at room temperature when excited at 311 nm (Fig. 4). The higher energy emission is presumably a fluorescence. On the other hand, the

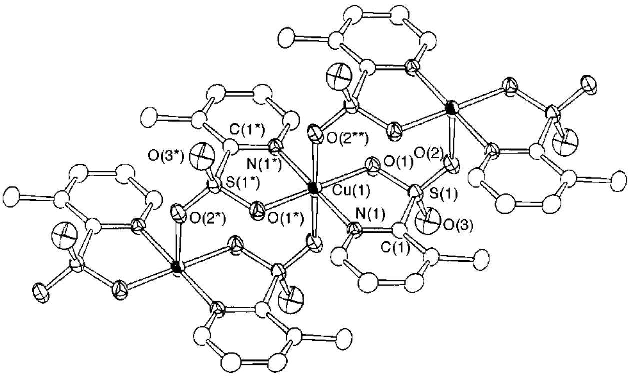

Fig. 1 One-dimensional infinite structure of [{Cu(3-mpSO$_3$)$_2$}$_n$] **1** along the *c* axis, showing three of the copper centres. Selected bond lengths (Å) and angles (°): Cu(1)–O(1) 1.977(2), Cu(1)–N(1) 1.985(2), Cu(1)–O(2**) 2.419(2), O(1)–Cu(1)–N(1) 94.74(7), O(1)–Cu(1)–O(1*) 180.0, N(1)–Cu(1)–N(1*) 180.0, Cu(1)–O(1)–S(1) 119.1(1), O(1)–S(1)–C(1) 102.0(1), S(1)–C(1)–N(1) 114.0(2), Cu(1)–N(1)–C(1) 117.8(2).

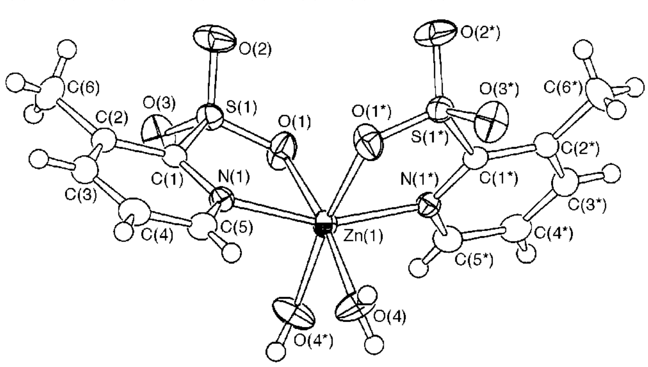

Fig. 2 The molecular structure of [Zn(3-mpSO$_3$)$_2$(H$_2$O)$_2$] **2**. Selected bond lengths (Å) and angles (°): Zn(1)–O(1) 2.155(1), Zn(1)–O(4) 2.095(1), Zn(1)–N(1) 2.109(1), O(1)–Zn(1)–N(1) 79.90(5), O(4)–Zn(1)–O(4*) 83.51(9), Zn(1)–O(1)–S(1) 120.37(7), O(1)–S(1)–C(1) 104.82(8), S(1)–C(1)–N(1) 114.6(1), Zn(1)–N(1)–C(1) 120.0(1).

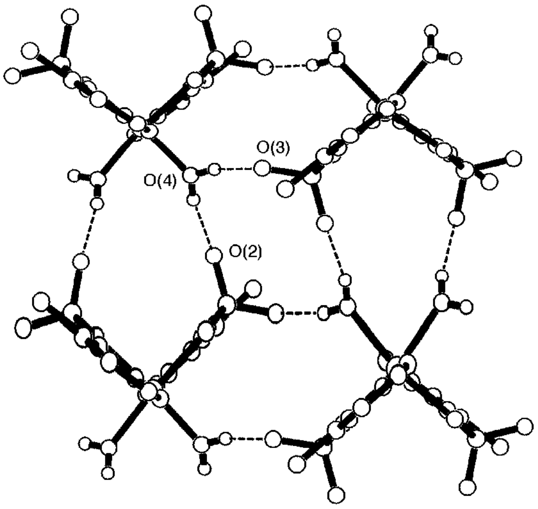

Fig. 3 H-Bonded network of complex **2** parallel to the *bc* plane. The intermolecular H-bonds are drawn as dashed lines. All hydrogen atoms except for the co-ordinated H_2O are omitted for clarity. H-bond lengths (Å): O(2)···O(4) 2.818(2), O(3)···O(4) 2.723(2).

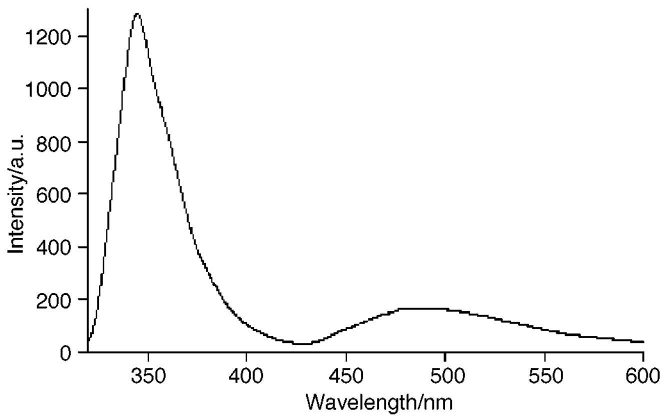

Fig. 4 Emission spectrum of complex **2** in the solid state at room temperature when excited at 311 nm.

lower energy emission can be assigned to a phosphorescence (τ = 0.15 s).

In preliminary experiments, crystals of Mn(II) and Co(II) complexes with 3-mpSO_3 ligands prepared in the same manner have proved to be isomorphous with those of complex **2**. Comparative studies of their chemical and physical properies are in progress.

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Notes and references

† *Crystal data*: intensity data were collected on a Rigaku AFC-7S diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å) at 296 K, using the ω–2θ scan technique to a maximum 2θ value of 60.0°.

[{Cu(3-mpSO_3)$_2$}$_n$] **1**: $C_{12}H_{12}CuN_2O_6S_2$, M = 407.90, green prismatic crystal (0.36 × 0.20 × 0.10 mm), triclinic, space group $P\bar{1}$, a = 7.7242(8), b = 9.7417(8), c = 4.9584(7) Å, α = 103.837(9), β = 98.12(1), γ = 93.227(8)°, V = 357.07(7) Å^3, Z = 1, D_c = 1.897 Mg m^{-3}, F(000) = 207, μ(Mo-Kα) = 1.855 mm^{-1}, 2293 reflections, of which 2069 were independent (R_{int} = 0.025). R = 0.033, R_w = 0.051, $\Delta\rho_{\max}$ = +0.28 and $\Delta\rho_{\min}$ = −0.76 e Å^{-3} (teXsan software).

[Zn(3-mpSO_3)$_2$(H_2O)$_2$] **2**: $C_{12}H_{16}N_2O_8S_2Zn$, M = 445.77, colorless prismatic crystal (0.62 × 0.34 × 0.28 mm), monoclinic, space group $C2/c$, a = 19.058(1), b = 7.381(1), c = 14.321(1) Å, β = 126.176(4)°, V = 1626.2(3) Å^3, Z = 4, D_c = 1.821 Mg m^{-3}, F(000) = 912, μ(Mo-Kα) = 1.813 mm^{-1}, 2630 reflections, of which 2556 were independent (R_{int} = 0.021). R = 0.027, R_w = 0.038, $\Delta\rho_{\max}$ = +0.30 and $\Delta\rho_{\min}$ = −0.47 e Å^{-3} (teXsan software). CCDC 182/1157. See http://www.rsc.org/suppdata/cc/1999/497/ for crystallographic files in .cif format.

‡ X-Ray diffraction analysis revealed that the brown and red products were [$CuBr_2$(3-mpds)] and [CuBr(3-mpts)] (3-mpts = 2,2′-bis(3-methylpyridyl)trisulfide), respectively.

§ Complex **1**: (Calc. for $C_{12}H_{12}CuN_2O_6S_2$: C, 35.33; H, 2.97; N, 6.87. Found: C, 35.15; H, 2.89; N, 6.82%). Although the yield of complex **1** is low (*ca.* 5%), the formation of this complex *via* the air oxidation of 3-mpds is reproducible. When $Cu(ClO_4)_2\cdot 6H_2O$ was applied to the reaction, the oxidation of 3-mpds was terminated at the formation of 3-methylpyridine-2-sulfinate as reported by Seff *et al.* for the oxidation of 2,2′-dipyridyl disulfide. The direct reaction of 3-mpSO_3H with $CuBr_2$ in aqueous methanol afforded another polymorph with complex **1** in a better yield.

¶ *Selected data* for complex **2**: (Calc. for $C_{12}H_{16}N_2O_8S_2Zn$: C, 32.33; H, 3.62; N, 6.29. Found: C, 32.30; H, 3.58; N, 6.26%). ^{1}H NMR (300 MHz, CD_3OD, TMS): δ 2.61 (s, 6H, CH_3), 7.49 (dd, 2H, ^3J = 7.7 Hz, ^3J = 4.8 Hz, β-H), 7.89 (d, 2H, ^3J = 7.7 Hz, γ-H), 8.51 (d, 2H, ^3J = 4.8 Hz, α-H).

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