

First metal-encapsulating star polysulfoxide incorporating 2-amino-1,3,4-thiadiazole

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The first star polysulfoxide **2** is synthesized by selective oxidation of a new hexaaminohexathioether **1**, which gives a novel binuclear bis-tripodant species by encapsulating a pair of Cu^{II} ions.

Suitably hexa-substituted benzene derivatives as new hosts and complex-forming ligands with a great underlying potential have received considerable attention in recent years.¹ A series of such macromolecules with specific enclathration properties have been uncovered, which are related to octopus,² hexa-host,³ hexa-pedals,⁴ aromatic propeller⁵ and star polymers.⁶ In particular, octopus polythioethers fitted with numerous donor atoms show unusual complexing tendency to metal cations owing to their conformational mobility being impeded by spatial crowding.⁷ The binding of Cu^{II} to polythioethers has led to a great understanding of Cu–S interactions in copper enzymes.⁸ However, no report has yet appeared on the synthesis of octopus polysulfoxide or solid metal complexes of octopus ligands. We now report the synthesis and properties of novel Cu^{II} complexes with a novel octopus polythioether **1** and the first star polysulfoxide **2**.

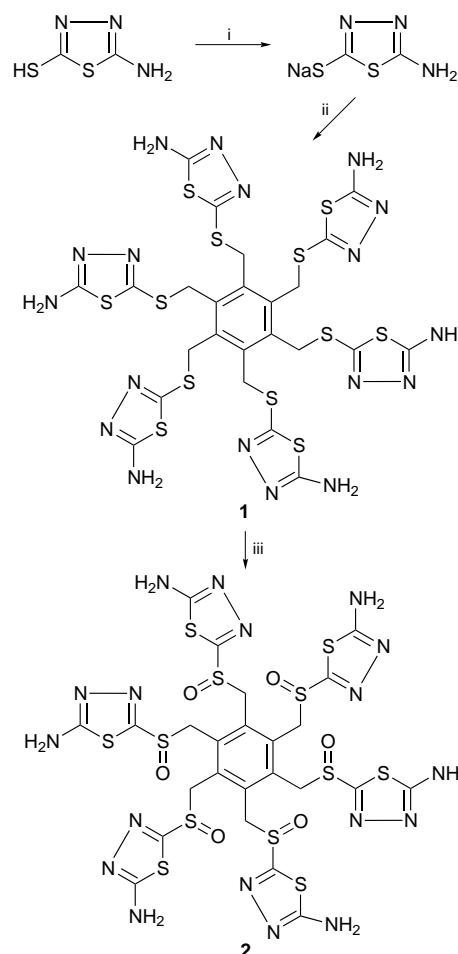
Synthesis of **1** was both straightforward and high yielding. Refluxing of hexakis(bromomethyl)benzene with the sodium salt of 2-amino-5-sulfanyl-1,3,4-thiadiazole gave **1** in >93% yield.[†] Mild and selective oxidation of **1** with an excess of dilute hydrogen peroxide in dilute HCl solution at ambient temperature for 18 h afforded **2** in high yield (>90%),[†] with amino groups preserved and no over oxidation (see Scheme 1). Octopus compounds **1** and **2** can form inclusion compounds with DMF and Me₂SO with host:guest = 1:1 and 1:2, respectively.

The hexasubstituted benzene octopus may form two possible types of metal complexes directed by suitable metal ions based on their preferential conformations: (a) a mononuclear species with the six arms of an octopus encapsulating a metal ion; (b) a binuclear bis-tripodant species with three arms of an octopus at 1,3,5-positions located above the phenyl plane encapsulating a metal ion, and the remaining three arms at 2,4,6-positions located below the plane encapsulating another metal ion. Copper(II) complexes of **1** and **2** were prepared in hot HCl solution in quantitative yield, giving a mononuclear species of **1**·CuCl₂ **3**,[†] and a binuclear species **2**·Cu₂Cl₄ **4**.[†] The FAB⁺ mass spectrum of **3** which exhibits a peak at *m/z* 1011 ([Cu^I]²⁺) is clearly indicative of the formation of a 1:1 complex. The presence of the characteristic molecular peak at *m/z* (FAB⁺ MS) 1171 ([Cu₂]⁴⁺) unambiguously shows complexation of two Cu^{II} ions per molecule of **2** in **4**. The IR spectra suggest that the amino groups and exocyclic sulfur do not coordinate to the metal ions, only the 1,3,4-thiadiazole rings participate in coordination.⁹ Thus, it is highly possible that in **3** one Cu^{II} ion is encapsulated by six arms of **1**, and in **4**, two Cu^{II} ions are each encapsulated by three arms of **2**.

Mononuclear complex **3** shows broad ¹H NMR peaks as usual for paramagnetic copper(II) complexes. In contrast, binuclear complex **4** produces very narrow ¹H NMR peaks, such an observation is similar to those found for some

magnetically coupled dimeric copper(II) complexes.¹⁰ The anisotropic X-band EPR spectrum of polycrystalline **3** at 100 K (*g*_⊥ = 2.263, *g*_∥ = 2.061) exhibits the usual line shape for mononuclear copper(II) complexes with a d_{x²-y²} ground state. The EPR spectrum of **4** shows a unique quasi-isotropic, broad absorption centered at *g* = 2.072 (100 K) with a half-weight width of ca. 300 G; the broadness of this EPR signal is typical of weak metal–metal interaction, and hence implies a dimeric structure.¹¹ Thermogravimetry of **4** shows a total mass loss of 87.1%, which correlates well with the expected loss of 87.9% for a metal:ligand molar ratio of 2:1.

There is no redox peaks observed for **1**, while cyclic voltammetry (CV) (Fig. 1) of **2** shows three quasi-reversible redox waves at *E*_{1/2} = 0.052, –0.46 and –0.425 V vs. SCE, corresponding to the successive reduction waves of the three 2-amino-5-sulfanyl-1,3,4-thiadiazole arms located at the same side of the benzene plane (*i.e.* the groups at 1,3,5-positions),



Scheme 1 Reagents and conditions: i, Na, EtOH, room temp.; ii, EtOH, 80 °C, Ar, 22 h; iii, H₂O₂, HCl–H₂O, room temp., 18 h

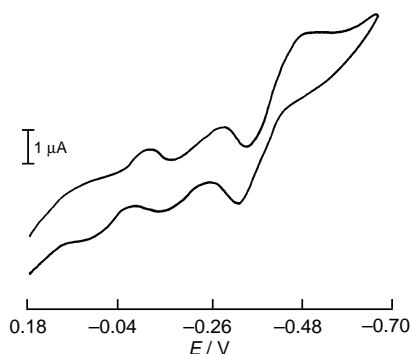
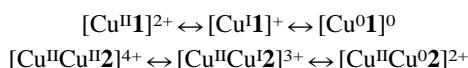


Fig. 1 Cyclic voltammetry of **2** (5×10^{-5} M) on a carbon-glass electrode with NBu_4Cl (10^{-3} M) in HCl (3 M). Sweep rate: 100 mV s^{-1} .

leading to the overall formation of a hexa-anion. The shapes of the waves are in accordance with a six-electron transfer and each wave behaving as a two-electron wave, similar to those of cryptates.¹² These results indicate that the redox process of **2** is mainly ascribed to the presence of redox-active sulfinyl groups. CV studies of **3** and **4** show two similar quasi-reversible cathodic waves at $E_{1/2} = -0.121$ and -0.225 V, and at $E_{1/2} = 0.21$ and 0.295 V (vs. $10 \text{ mm Ag}^1/\text{AgCl}$), respectively, corresponding to the following reduction:¹³



A possible reason for the observed behaviour of the binuclear species **4** is that only one Cu^{II} ion, surrounded by three arms, can approach and be adsorbed by the electrode surface at a given time, resulting in similar behaviour to that observed for **3**.

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Footnotes and References

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† *Selected data*: **1**·3HCl: Anal. Calc. for $\text{C}_{24}\text{H}_{27}\text{Cl}_3\text{N}_{18}\text{S}_{12}$: C, 27.32; H, 2.56; N, 23.91; Cl, 10.12. Found: C, 27.39; H, 2.57; N, 24.03; Cl, 10.21%; UV ($\lambda_{\text{max}}/\text{nm}$): 286; FABMS: m/z 949; IR (KBr): 1630, 1496, 1032, 800, 744, 702, 610 cm^{-1} ; $^1\text{H NMR}$ [300 MHz, $(\text{CD}_3)_2\text{SO}$, 25 °C]: δ 4.51 (br, 12 H, NH_2), 4.76 (br, 12 H, CH_2).

2·HCl: Anal. Calc. for $\text{C}_{24}\text{H}_{25}\text{ClN}_{18}\text{O}_6\text{S}_{12}$: C, 26.65; H, 2.31; N, 23.32; Cl, 3.29%. Found: C, 26.57; H, 2.33; N, 23.51; Cl, 3.31%. FABMS: m/z 1045; IR (KBr): 1609, 1496, 1321, 1124, 1039, 786, 463 cm^{-1} ; $^1\text{H NMR}$ [400 MHz, $(\text{CD}_3)_2\text{SO}$, 25 °C]: δ 5.10 (br, 12 H, NH_2), 8.14 (br, 12 H, CH_2).

3: Anal. Calc. for $\text{C}_{24}\text{H}_{26}\text{CuN}_{18}\text{O}_2\text{S}_{12}$: C, 27.53; H, 2.49; N, 24.20; Cu, 6.22; S, 36.74%. Found: C, 27.42; H, 2.50; N, 24.25; Cu, 6.16; S, 36.70%. FABMS: m/z 1011. IR(KBr): 1623, 1496, 1039, 744, 695 cm^{-1} ; $^1\text{H NMR}$ [400 MHz, $(\text{CD}_3)_2\text{SO}$, 25 °C]: δ 3.68 (br, 12 H, NH_2), 4.46 (br, 12 H, CH_2).

4: Anal. Calc. for $\text{C}_{24}\text{H}_{24}\text{Cl}_4\text{Cu}_2\text{N}_{18}\text{O}_6\text{S}_{12}$: C, 21.93; H, 1.84; N, 19.18; S, 29.27; Cu, 9.67%. Found: C, 21.82; H, 1.85; N, 18.97; Cu, 9.69%. FABMS: m/z 1172. IR (KBr): 1609, 1496, 1046, 463 cm^{-1} ; $^1\text{H NMR}$ [400 MHz, $(\text{CD}_3)_2\text{SO}$, 25 °C]: δ 5.40 (s, 12 H, NH_2), 7.88 (s, 12 H, CH_2).

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