Octanuclear Cu(I) cubic complex decorated with six peripheral chelates

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Received (in Durham, UK) 13th March 2006, Accepted 16th May 2006
First published as an Advance Article on the web 31st May 2006
DOI: 10.1039/b603733j

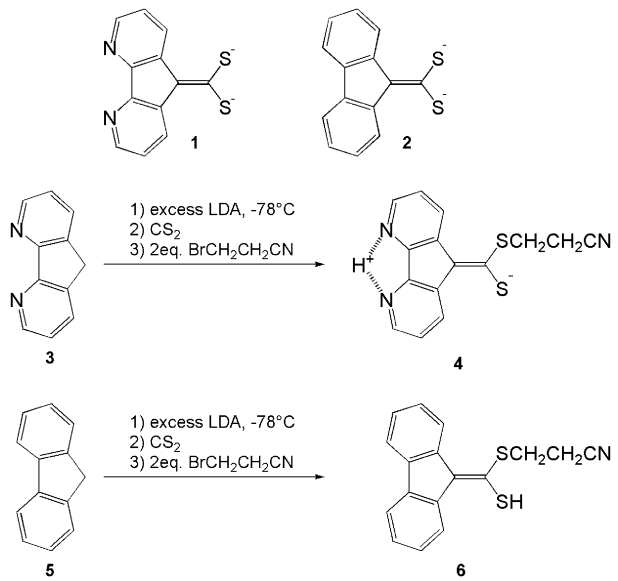
A new ligand bearing an anionic methanedithiolate unit as the primary coordination pole and a neutral chelate based on 4,5-diazafluorene as secondary pole leads to the formation of an air-stable octanuclear Cu(I) cubic complex presenting six peripheral coordinating sites.

Introduction

The strategy based on the self-assembly of molecular units into finite or infinite entities offers a wealth of possibilities in terms of design of new molecular architectures.[1,2] In particular, owing to their diverse tunable physical properties (magnetic, optical, electrochemical), metal cations or complexes[3] have been used as metallatectons (metal based building blocks) for the generation of coordination networks[4] and expanded porous solids.[5] However, the majority of reported examples is based on homometallic assemblies obtained upon combining the same metal cation or complex with organic tectons. A further approach of interest for the formation of heterometallic infinite architectures may be based on ligands bearing two different coordination poles (a primary and a secondary pole). Thus, upon coordination of their primary pole to a metallic centre, metallatectons presenting in turn coordination sites located at their periphery (secondary pole) are obtained. These construction entities may be further used for the generation of heterometallic coordination networks using other metal centres or complexes. Differentiation between the two coordination poles may be achieved either by the nature of the donor atoms comprising each pole (for example N, O, S, P) or by the use of different coordinating atoms along with the introduction of a charge on one of the two poles. For the latter strategy, we designed the unreported bischelate ligand **1** (Scheme 1) bearing one neutral pole based on 4,5-diazafluorene and one anionic pole based on the dithiolate unit.

Dithiolate and dithiolene based ligands[6] have been shown to stabilize metallic complexes with a variety of oxidation states, geometries and nuclearities, hence providing many interesting molecular materials[7] and coordination networks.[8] In particular, it has been demonstrated that the combination of copper with the iso-maleonitriledithiolate ligand (i-mnt)[9] leads to the formation of monomeric, tetranuclear, hexanuclear Cu(II) as well as octanuclear cubic Cu(I) complexes.[10] In agreement with Gompper's early predictions,[9] the syntheses of **2** based on the fluorene backbone (Scheme 1) and its gold and platinum complexes have recently been reported.[11]

We report herein on the synthesis of **1**, the preparation of its octanuclear cubic Cu(I) complex as well as its monomeric Cu(II) complex (see Experimental section).



Scheme 1

Results and discussion

The synthesis of **1** (Scheme 1) was achieved starting from 4,5-diazafluorene **3**. A dry THF solution of **3** was treated with an excess of LDA followed by CS_2. Subsequent addition of 3-bromopropionitrile allows the isolation of the stable mono *S*-protected derivative **4** in acceptable 67% yield. The formation of this intermediate results from the tautomerism of **1**. Compound **4** exists in the zwitterionic form as supported by both the chemical shift of the carbon in the CS_2 group at 192.4 ppm, suggesting an anionic character of the sulfur atom, and the broadening of the signal of protons on the carbon atoms in *ortho* positions with respect to the nitrogen atoms. The biprotected derivative may also be isolated, however in lower yield. The desired ligand **1** is obtained upon treatment with an excess *n*-alkylammonium hydroxide in methanol.

Theoretical calculations have shown that the existence of Cu_8(dithiolato)$_6$ cubic complexes is mainly driven by the chelating effect of the ligands and to a lesser extent by weak d^{10}–d^{10} interactions.[12] Therefore, in a first step, we have investigated the synthesis of the $[Cu_8(\mathbf{2})_6]^{4-}$ cubic complex using the ligand **2** as a structural model (Fig. 1). Although the synthesis of **2** was reported,[11] we have followed the same

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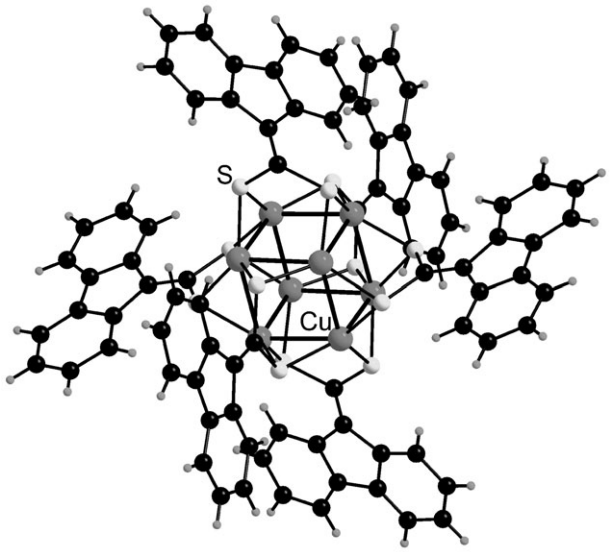

Fig. 1 Structure of the $[Cu_8(\mathbf{2})_6]^{4-}$ anion. Cations and solvent molecules are not represented for clarity. For bond distances and angles see text.

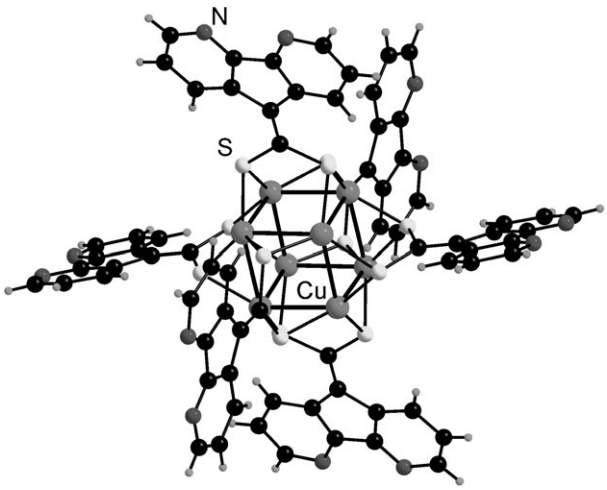

Fig. 2 Structure of the $[Cu_8(\mathbf{1})_6]^{4-}$ anion. Cations and solvent molecules are not represented for clarity. For bond distances and angles see text.

procedure as the one we developed for the preparation of **1** starting from fluorene **5** (Scheme 1). Upon treatment of the *S*-protected precursor **6** under Ar and at −78 °C in THF, with an excess of $(Et_4N)OH$ in MeOH followed by addition of 1.33 equiv. of $Cu(CH_3CN)_4PF_6$ in CH_3CN, and stirring at rt for 3 days, a brown–red powder was obtained. The latter was dissolved in DMSO and, upon slow vapour diffusion of THF, large red crystalline blocks were obtained (19% yield). A shorter reaction period affords the target compound in lower yields along with an uncharacterised insoluble dark-brown material. The structure of the $[Cu_8(\mathbf{2})_6]^{4-}$ complex was investigated by single-crystal X-ray diffraction (Fig. 1)†. The crystal (monoclinic, $P2_1/c$) is composed of $[Cu_8(\mathbf{2})_6]^{4-}$ anionic complex on an inversion centre, 4 Et_4N^+ cations and 6 THF molecules both in general positions. The Cu(I) atoms are organized in a cubic arrangement with Cu–Cu distances in the range of 2.74–2.83 Å. Each sulfur atom bridges an edge of the cube and each Cu(I) centre is trigonally coordinated to 3 sulfur atoms belonging to different ligands **2** with Cu–S distances in the 2.24 to 2.26 Å range. These distances are in the same range as those reported for the $[Cu_8(i\text{-}mnt)_6]^{4-}$ analogue.[10] Since the cubic units are separated by cations and solvent molecules, no π–π interaction is observed between the fluorene moieties.

Under the same reaction conditions as for **2**, a red–brown powder was again obtained with **1**. The anionic cubic octanuclear complex $[Cu_8(\mathbf{1})_6]^{4-}$ was obtained as large red crystals in *ca.* 40% yield upon crystallisation by slow diffusion of THF into a concentrated DMSO solution containing the mixture. The structure of $([Cu_8(\mathbf{1})_6]^{4-},(Et_4N^+)_4)$ was studied by single-crystal X-ray diffraction (Fig. 2).

The crystal (monoclinic, $C2/c$) is composed of $[Cu_8(\mathbf{1})_6]^{4-}$ anionic complex on an inversion centre, 4 Et_4N^+ cations and 6 DMSO molecules both in general positions. As in the case of **2**, the eight Cu(I) centres occupy the apices of a cube (Fig. 2) with Cu–Cu distances in the range 2.74 to 2.81 Å. The Cu–S distances vary between 2.23 and 2.27 Å. Again, owing to the presence of Et_4N^+ cations and DMSO molecules, no π–π interaction is observed between the 4,5-diazafluorene moieties. The overall disposition of the metallic centres and organic moieties is almost identical to the above mentioned cubic complex obtained with **2**. However, a slight difference in the dihedral angle between the CS_2 and the aromatic moiety is observed. Indeed, angles of 4.61, 8.37 and 13.48° are observed for $[Cu_8(\mathbf{2})_6]^{4-}$ whereas they are 6.58, 7.86 and 14.77° for $[Cu_8(\mathbf{1})_6]^{4-}$. This difference is probably due to packing effects in the crystal.

In DMF solution, the two cubic complexes ($[Cu_8(\mathbf{1})_6]^{4-}$, $(Et_4N^+)_4$) and ($[Cu_8(\mathbf{2})_6]^{4-}$, $(Et_4N^+)_4$) display the same UV-vis absorption spectra with two intense bands at 361 and 484 nm and at 364 and 479 nm, respectively.

Interestingly, if instead of using Cu(I) in 8 : 6 Cu : **1** ratio, Cu(II) as its chloride salt ($CuCl_2$, $2H_2O$) is used as the metal source in 1 : 2 ratio, a mixture of the octanuclear $[Cu_8(\mathbf{1})_6]^{4-}$ cubic complex and a monomeric Cu(II) paramagnetic complex, $[Cu(\mathbf{1})_2]^{2-}$, is obtained. This suggests the existence of a redox process between Cu(II) and the ligand **1** leading to the reduction of the metal centre. Because of the lack of a suitable preparative procedure, the monomeric complex could not be isolated in large quantities. However, its crystal structure could be determined by X-ray diffraction on a single crystal obtained by slow Et_2O vapour diffusion into a concentrated MeCN solution of the crude powder. The crystal (monoclinic, $P2_1/c$) is composed of $[Cu(\mathbf{1})_2]^{2-}$, 2 Et_4N^+ and 2 CH_3CN molecules (Fig. 3). The complex $[Cu(\mathbf{1})_2]^{2-}$ lies on an inversion centre with Cu–S distances of 2.30 and 2.31 Å, these distances are similar to those reported for $[Cu(i\text{-}mnt)_2]^{2-}$.[10] The overall geometry of the complex is planar with a dihedral angle between the CuS_4 and the 4,5-diazafluorene planes of 3.5°. In the crystal, the complexes are isolated by the *n*-Bu_4N^+ cations and MeCN solvent molecules and consequently no

† CCDC reference numbers 294746–294748. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b603733j

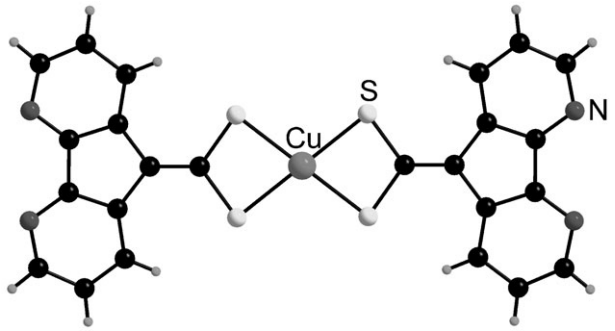

Fig. 3 Structure of the $[Cu(\mathbf{1})_2]^{2-}$ anionic mononuclear complex. $Et_4N^+$and CH_3CN solvent molecules are not represented for clarity. For bond distances and angles see text.

short intermolecular Cu–S and S–S contacts are observed. Although in the case of (2,7-di-*tert*-butylfluoren-9-ylidene)-methanedithiolate an oxidative process leading to the formation of a Cu(III) complex was reported,[13] in the case of **1** no such process was detected in MeCN for several days in the presence of air.

Conclusions

In conclusion, we have demonstrated that both dithiolate-type ligands **1** and **2**, based on fluorene and 4,5-diazafluorene, respectively, lead to the formation of octanuclear cubic Cu(I) $[Cu_8(\mathbf{1})_6]^{4-}$ and $[Cu_8(\mathbf{2})_6]^{4-}$ complexes. Interestingly, in the case of **1**, by varying the metal–ligand ratio a mononuclear Cu(II) complex could also be generated. Owing to the design of ligand **1** based on two differentiated chelate units, both the mononuclear and octanuclear cubic complexes present in their periphery additional chelating sites. This peculiar feature is currently under investigation for the formation of coordination networks bearing two different metal centres as well as the construction of finite heteropolymetallic assemblies.

Experimental

Syntheses

THF was distilled prior to use. 4,5-diazafluorene **3** was prepared as described.[14] Lithium diisopropylamide, 3-bromopropionitrile, CS_2 and fluorene were obtained from commercial sources and used as received.

Ligand 6. Lithium diisopropylamide (10 mL, 1.8 M in THF–heptane–ethylbenzene) was added to fluorene **5** (1.05 g, 6.02 mmol) dissolved in dry THF (50 mL) at −78 °C under Ar. After stirring for one hour, CS_2 (1.1 mL, 18.2 mmol) was added, causing the precipitation of an orange solid. The mixture was stirred for an additional hour. After addition of 3-bromopropionitrile (1.1 mL, 13.2 mmol), the mixture turned brown and was slowly brought to room temperature where it was stirred for 4 hours. The mixture was concentrated to dryness and purified by column chromatography (SiO_2, CH_2Cl_2–MeOH (97 : 3)). Recrystallization from hot $CHCl_3$–cyclohexane afforded **6** (500 mg, 27%) as a fluffy yellow solid. δ_H(300 MHz, $CDCl_3$) 8.77 (1H, d), 8.67 (1H, d), 7.61 (2H, t), 7.35 (1H, td), 7.27 (2H, m), 7.10 (H, td), 3.26 (2H, t), 2.53 (2H, t). Found: C, 68.23; H, 4.01; N, 4.70. $C_{17}H_{13}NS_2$ requires C, 69.12; H, 4.44; N, 4.74.

$(Et_4N)_4[Cu_8(\mathbf{2})_6](THF)_6$. To a THF (7 mL) solution of **6** (100 mg, 0.33 mmol) at −78 °C unded Ar, tetraethylammonium hydroxide (1 mL, 25% in MeOH) was added. The solution was gently warmed to room temperature. It was then cooled down again to −78 °C and $Cu(CH_3CN)_4PF_6$ (168 mg, 0.45 mmol) in degassed CH_3CN (1 mL) was added. The mixture was gently warmed to room temperature and stirred for 3 days. The red precipitate was recovered by filtration and washed with THF. Recrystallization by slow THF vapor diffusion into a concentrated DMSO solution afforded $(Et_4N)_4[Cu_8(\mathbf{2})_6](THF)_6$ as large crystalline red blocks (31.5 mg, 19%). δ_H(300 MHz, DMSO-d_6) 9.28 (12H, d, J = 8.1 Hz), 7.82 (12H, d, J = 6.9 Hz), 7.29 (24H, m), 3.18 (32H), 1.13 (48H); δ_C(75 MHz, DMSO-d_6) 168.7, 140.4, 136.8, 129.6, 127.3, 125.9, 123.5, 118.6, 51.9, 7.5 ppm. ES-MS: 1104.89 $[(Et_4N)_2[Cu_8(\mathbf{2})_6]]^{2-}$, 1039.81 $[(Et_4N)[Cu_8(\mathbf{2})_6]]^{2-}$, 649.82 $[Cu_8(\mathbf{2})_6]^{3-}$. λ_{max}(DMF)/nm 361 (ε/dm^3 mol^{-1} cm^{-1} 51200), 484 (159000).

Ligand 4. Lithium diisopropylamide (10 mL, 1.8 M in THF–heptane–ethylbenzene) was added to a suspension of 4,5-diazafluorene **3** (1.06 g, 6.3 mmol) in dry THF (50 mL) at −78 °C under Ar. The solution immediately turned purple and was stirred for one hour. CS_2 (1.1 mL, 18.2 mmol) was then added, causing the precipitation of an orange solid which redissolved upon stirring. The mixture was stirred for an additional hour. After addition of 3-bromopropionitrile (1.1 mL, 13.2 mmol), the mixture turned brown and was slowly brought to room temperature where it was stirred for 4 hours. The mixture was filtered and washed with $CHCl_3$. After concentration of the filtrate and washings, the compound was purified by column chromatography (SiO_2, CH_2Cl_2–MeOH (97 : 3)) and recrystallized as purple crystalline blocks from hot $CHCl_3$–MeOH–cyclohexane (1.25 g, 67%). δ_H(300 MHz, DMSO-d_6) 10.30 (1H, br s), 9.25 (1H, br s), 8.50 (2H, dd, J = 1.8, 4.8 Hz,), 7.70 (2H, dd, J = 4.8, 8.4 Hz), 3.70 (2H, t, J = 6.9 Hz), 3.00 (2H, t, J = 6.9 Hz); δ_C (75 MHz, DMSO-d_6) 192.4, 139.4, 138.1, 134.8, 123.5, 120.1, 119.0, 114.7, 28.5, 18.5 ppm. Found: C, 60.78; H, 3.78; N, 14.17%. $C_{15}H_{11}N_3S_2$ requires C, 60.58; H, 3.73; N, 14.13%.

$(Et_4N)_4[Cu_8(\mathbf{1})_6](DMSO)_6$. To a THF (7 mL) solution of **4** (100 mg, 0.33 mmol) at −78 °C unded Ar, tetraethylammonium hydroxide (1 mL, 25% in MeOH) was added. The solution was gently warmed to room temperature. It was then cooled down again to −78 °C and $Cu(CH_3CN)_4PF_6$ (168 mg, 0.45 mmol) in degassed CH_3CN (1 mL) was added. The mixture was gently warmed to room temperature and stirred for 3 days. The red precipitate was recovered by filtration and washed with THF. Recrystallization by slow THF vapor diffusion into a concentrated DMSO solution afforded $(Et_4N)_4[Cu_8(\mathbf{1})_6](DMSO)_6$ as large crystalline red blocks (65.9 mg, 40%). δ_H(300 MHz, DMSO-d_6) 9.46 (12H, d, J = 7.8 Hz), 8.42 (12H, d, J = 4.0 Hz,), 7.29 (12H, dd, J = 4.0, 7.8 Hz,), 3.18 (32H), 1.13 (48H); δ_C (75 MHz, DMSO-d_6) 173.1,

153.4, 145.5, 134.6, 133.4, 123.9, 122.3, 51.9, 7.5 ppm. Found: C, 46.89; H, 5.35; N, 7.24%. $C_{116}H_{152}Cu_8N_{16}O_6S_{18}$ requires C, 47.20; H, 5.19; N, 7.59%. ES-MS: 1111.86 $[(Et_4N)_2[Cu_8(\mathbf{1})_6]]^{2-}$, 653.80 $[Cu_8(\mathbf{1})_6]^{3-}$. λ_{max}(DMF)/nm 364 (ε/dm^3 mol^{-1} cm^{-1} 76500), 479 (212200).

X-Ray crystallography†

Data were collected on a Bruker SMART CCD diffractometer with Mo-Kα radiation. The structures were solved using SHELXS-97 and refined by full matrix least-squares on F^2 using SHELXL-97. The hydrogen atoms were introduced at calculated positions and not refined (riding model). In $(Et_4N)_4[Cu_8(\mathbf{2})_6](THF)_6$, the THF molecules display severe positional disorder which was modelled accordingly. In $(Et_4N)_4[Cu_8(\mathbf{1})_6](DMSO)_6$, the DMSO molecules show as well positional disorder.

Crystal analysis for $(Et_4N)_4[Cu_8(2)_6](THF)_6$. $C_{138}H_{176}Cu_8N_4O_6S_{12}$, M = 2879.87 monoclinic, space group $P2_1/c$ (No. 14), a = 16.0263(5), b = 22.3943(7), c = 19.7820(8) Å, β = 112.7590(10)°, V = 6546.9(4) Å^3, T = 173(2) K, Z = 2, D_c = 1.461 g cm^{-3}, μ = 1.521 mm^{-1}, 58035 collected reflections, 14973 independent (R_{int} = 0.0849), GooF = 1.039, $R1$ = 0.0674, $wR2$ = 0.1757 for $I > 2\sigma(I)$ and $R1$ = 0.1370, $wR2$ = 0.2115 for all data.

Crystal analysis for $(Et_4N)_4[Cu_8(1)_6](DMSO)_6$. $C_{116}H_{152}Cu_8N_{16}O_6S_{18}$, M = 2951.94, monoclinic, space group $C2/c$ (No. 15), a = 39.0401(13), b = 17.3267(6), c = 24.2754(8) Å, β = 124.138(2)°, V = 13591.3(8) Å^3, T = 173(2) K, Z = 4, D_c = 1.443 g cm^{-3}, μ = 1.558 mm^{-1}, 77661 collected reflections, 11777 independent (R_{int} = 0.0581), GooF = 1.068, $R1$ = 0.0666, $wR2$ = 0.2064 for $I > 2\sigma(I)$ and $R1$ = 0.1233, $wR2$ = 0.2466 for all data.

Crystal analysis for $(n\text{-}Bu_4N)_2[Cu(1)_2](CH_3CN)_2$. $C_{60}H_{90}CuN_8S_4$, M = 1115.18, monoclinic, space group $P2_1/c$ (No. 14), a = 18.6672(7), b = 8.7381(3), c = 18.9133(7) Å, β = 101.396(2)°, V = 3024.24(19) Å^3, T = 173(2) K, Z = 2, D_c = 1.225 g cm^{-3}, μ = 0.543 mm^{-1}, 29283 collected reflections, 6879 independent (R_{int} = 0.0635), GooF = 1.044, $R1$ = 0.0584, $wR2$ = 0.1500 for $I > 2\sigma(I)$ and $R1$ = 0.1040, $wR2$ = 0.1727 for all data.

Acknowledgements

We thank the Université Louis Pasteur, the Institut Universitaire de France, the Ministry of Education and Research and CNRS for financial support.

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