

A novel alkoxide bridging motif between boron trifluoride and copper(II) in a crown thioether complex

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Received (in Cambridge, UK) 3rd November 1999, Accepted 19th January 2000

Reaction of 6-hydroxy-1,4,8,11-tetrathiacyclotetradecane (LH) with $\text{Cu}(\text{BF}_4)_2$ in THF yields $[\text{Cu}(\text{LH})](\text{BF}_4)_2$; crystallisation of the complex from $\text{MeNO}_2/\text{Et}_2\text{O}$ gives brown crystals of $[\text{Cu}(\text{LBF}_3)](\text{BF}_4)$, the first example of alkoxide bridging between BF_3 and a metal centre.

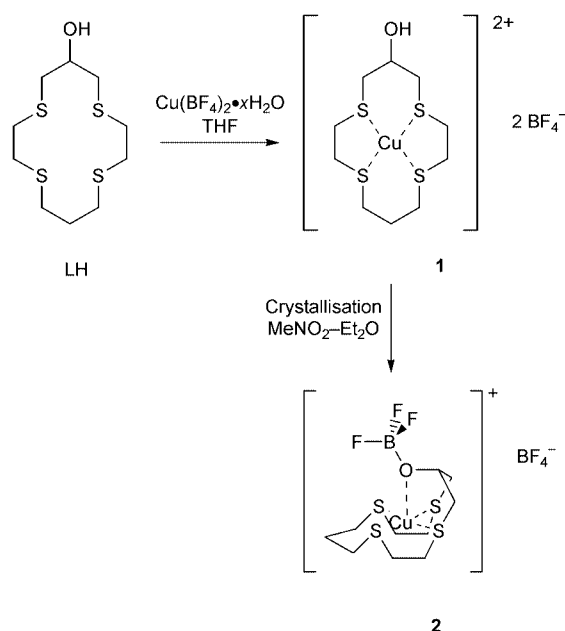
The synthesis and coordination chemistry of crown thioethers has become well established over the past two decades¹ with many complexes of the transition metals, from titanium to mercury, having been reported.² We have been interested in the functionalisation of thioether crowns³ in order to couple their coordination behaviour to desirable physical and/or chemical properties, with a particular interest in developing macrocyclic metallomesogens.⁴ Because such modification must take place on the carbon backbone we have been studying the organic and coordination chemistry of a number of functionalised crown thioethers including 6-hydroxy-1,4,8,11-tetrathiacyclotetradecane (LH)⁵ so that we might better understand the interplay between the macrocyclic core and the pendant functionality.

Addition of a colourless solution of LH in THF to a pale green solution of a slight excess of $\text{Cu}(\text{BF}_4)_2$ hydrate in THF immediately affords a fine dark green precipitate which was isolated in 85% yield (Scheme 1). IR spectroscopic, FAB mass spectrometric and microanalytical data for this product are in accord with the stoichiometry $[\text{Cu}(\text{LH})](\text{BF}_4)_2$, **1**.[†] Compound **1** appears to be unstable in MeCN and MeNO_2 to give very dark brown solutions. Deep brown crystals suitable for X-ray diffraction were formed over several days by the diffusion of Et_2O vapour into a solution of **1** in MeNO_2 and a single crystal structural determination[‡] was undertaken in order to confirm the structure of the product. The single crystal X-ray structure

determination (Fig. 1) confirms the formation of $[\text{Cu}(\text{LBF}_3)]\text{BF}_4$, **2**, in which one of the BF_4^- anions from **1** has condensed with the $[\text{Cu}(\text{LH})]^{2+}$ cation, eliminating HF. Presumably, HF goes on to combine with the glass walls of the vials used for crystallisation forming Si–F bonds which provide the thermodynamic driving force for the reaction. Interestingly, attempted crystallisation of $\text{Ni}(\text{BF}_4)_2$ with LH from $\text{MeOH}-\text{Et}_2\text{O}$ resulted in the quantitative formation of $[\text{Ni}(\text{MeOH})_6]\text{SiF}_6$ (confirmed by single crystal X-ray structural analysis) supporting the mechanism postulated.

Microanalytical data obtained from the sample of **2** from which the crystal was drawn, in concert with the difference in colour of **1** and **2**, indicate that conversion of **1** to **2** occurs quantitatively.[§] Further evidence that **1** is different to **2** is provided by the powder X-ray diffraction pattern (Fig. 2) obtained from **1**, which is different to that calculated for **2**. Compound **2** is unstable in air, with hydrolysis *via* atmospheric moisture affording a product tentatively assigned as $[\text{Cu}(\text{LH})](\text{BF}_4)(\text{BF}_3\text{OH})$, which exhibits a similar electronic spectrum to **1**.

The monocation $[\text{Cu}(\text{LBF}_3)]^+$ in **2** adopts a square-pyramidal geometry at Cu(II) which is somewhat distorted by the steric restrictions imposed by the macrocyclic ligand, with Cu, B(1), O(6), C(6) and C(13) lying on a crystallographic mirror plane. The Cu–S distances of 2.2677(15) and 2.3312(15) Å in **2** are similar to those observed⁶ in $[\text{Cu}([\text{14}]\text{aneS}_4)]^{2+}$, with the Cu–O(6) distance of 2.311(5) Å in the five coordinate complex **2**.



Scheme 1

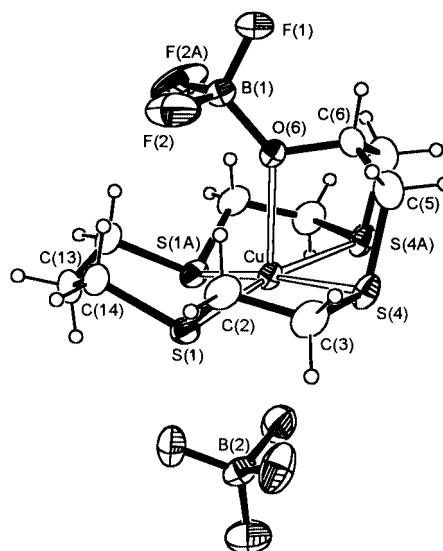


Fig. 1 View of the structure of **2** with numbering scheme adopted. Selected bond distances (Å) and angles (°): Cu–S(1) 2.2677(15), Cu–S(4) 2.3312(15), Cu–O(6) 2.311(5), B(1)–O(6) 1.441(10), O(6)–C(6) 1.419(9); S(1)–Cu–S(1A) 95.32(8), S(1)–Cu–S(4) 88.58(6), S(4)–Cu–S(4A) 86.43(8), S(1)–Cu–O(6) 103.29(9), S(4)–Cu–O(6) 83.71(10), Cu–O(6)–B(1) 139.2(4), Cu–O(6)–C(6) 100.0(4), B(1)–O(6)–C(6) 120.8(6). Minor parts of disorder omitted for clarity. Atoms carrying the suffix A are related to the corresponding unsuffixed atoms across a crystallographic mirror plane by $x, -y + 3/2, z$.

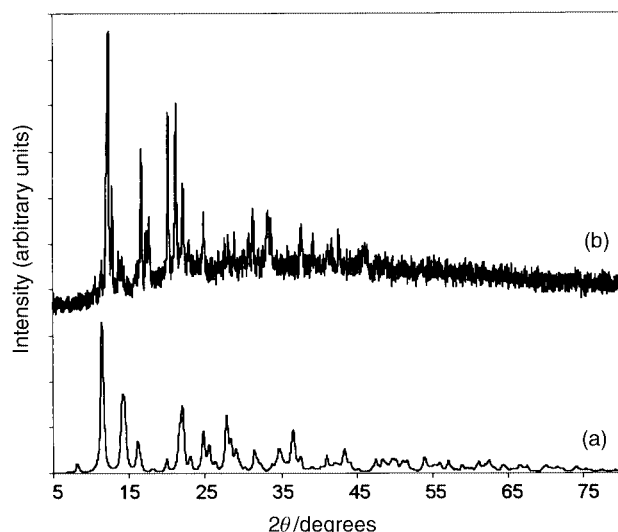


Fig. 2 Powder X-ray diffraction patterns: (a) calculated for **2** from crystal data¹³ and (b) recorded for **1** (Philips X-pert diffractometer; PW3710 diffractometer control unit; Cu-K α radiation source at 40kV/40mA; step size 0.02° (0.4 s per step); 2 θ range 5–80°; divergence slit 1° and receiving slit 2°).

some 0.131 Å shorter than in the related [Cu(*trans*-6,13-dihydroxy[14]aneS₄)](ClO₄)₂ where O atoms occupy the two axial sites of a Jahn–Teller distorted octahedral Cu(II) centre.⁷ This reflects the greater electrostatic interaction expected for the five coordinate Cu(II) centre in **2** with an apical alkoxide ligand compared to the six coordinate analogue. The apical O-donor in **2** bridges to a disordered BF₃ moiety, O(6)–B(1) 1.441(10) Å which exhibits a rigorously planar geometry. The unconstrained B(1)–O(6)–C(6) angle of 120.8(6)° and the fact that the relevant atoms lie on a crystallographic mirror plane indicate sp² hybridisation at O(6), supporting the designation of this oxygen as a bridging alkoxide.⁸

Significantly, the structure of **2** represents the first example of an alkoxide bridge between BF₃ and a metal ion to be confirmed crystallographically. Hydrolysis of BF₄[–] to give BF₃(OH)[–] is not uncommon and several examples of coordination of this anion *via* bridging hydroxide have been reported.⁹ Alcoholysis has also been observed yielding, for example, the BF₃(OEt)[–] anion, which has not been seen to coordinate further.¹⁰ A small number of adducts of BF₃ and carbonyl compounds have been isolated¹¹ due to the interest in the use of Lewis acids to activate such compounds. However, examples of trigonal oxygen in BF₃–alcohol adducts such as the MeOH·BF₃ are rare,¹² and the structure of **2** represents, to our knowledge, the first example of alkoxide bridging between BF₃ and a metal centre.

The short Cu–O(6) distance in **2** affords boat conformation for the Cu–S(4)–C(5)–C(6)–C(5A)–S(4A) chelate ring. We conclude that the stereochemistry and conformation of the complexed macrocycle is a key factor governing the formation of the novel bridging motif observed in **2**, the macrocyclic core allowing O(6) to adopt a position where stabilising interactions with both BF₃ and Cu(II) are possible. The crown thioether macrocycle, therefore, provides a covalently attached S₄-donor set which supports the close approach of Cu(II) to the alkoxytrifluoroborate O-centre, resulting in the unusual structure observed.

We thank the EPSRC for support and Dr David Rees for assistance with X-ray powder diffraction.

Notes and references

† Analytical data for **1**: found: C, 23.06; H, 3.83; N, 0.00. C₁₀H₂₀B₂CuF₃OS₄ requires C, 23.02; H, 3.86; N, 0%; $\nu_{\max}/\text{cm}^{-1}$ (KBr disc) 3441s,

2920w, 1636m, 1419m, 1294w, 1084v, 1059v, 862w, 668w, 522m; λ_{\max}/nm ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$): (DMF, 25 °C) 396 (330); m/z (FAB) 347 ($\text{M}^+ - 2\text{BF}_4$).

‡ Crystal data for **2**: C₁₀H₁₉B₂CuF₇OS₄, $M = 501.65$, monoclinic, space group $P2_1/m$ with $a = 7.6090(5)$, $b = 11.0873(10)$, $c = 10.7640(9)$ Å, $\beta = 91.687(7)^\circ$, $U = 907.7$ Å³, $Z = 2$, $\mu = 1.728$ mm^{–1}. Of 1783 reflections collected ($2\theta_{\max} = 50^\circ$, $-9 \leq h \leq 9$, $-8 \leq k \leq 13$, $-9 \leq l \leq 12$), 1688 were unique and 1432 were used in all calculations. Disorder was modelled by rotation of 60° about the B(1)–O(6) bond in *ca.* 10%, and rotation of 60° about the B(2)–F(3) vector in *ca.* 34% of the asymmetric units, similarity restraints being placed on appropriate bond lengths, angles and anisotropic displacement parameters. At final convergence, $R1[1432 F \geq 4\sigma(F)] = 0.0464$ and $wR2(F^2, \text{all data}) = 0.1325$ and the final ΔF synthesis showed no peaks above 0.81 e Å^{–3}. CCDC 182/1527. See <http://www.rsc.org/suppdata/cc/a9/a908778h/> for crystallographic files in .cif format.

§ Analytical data for **2**: found C, 24.00; H, 3.85; N, 0.00. C₁₀H₁₉B₂CuF₇OS₄ requires C, 23.94; H, 3.82; N, 0%; λ_{\max}/nm ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$) (MeCN, 25°C) 571 (1200), 392 (7200).

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Communication a908778h