

A New Conformation and Co-ordination Mode for 1,4,7-Trithiacyclononane (9S3): Structure of $[\text{Cu}_2(9\text{S3})_3](\text{BF}_4)_2 \cdot \text{H}_2\text{O}$

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Complex $[\text{Cu}_2(9\text{S3})_3]^{2+}$ contains two $\{\text{Cu}(\text{I})(9\text{S3})\}$ units bound to a third, exodentate 9S3, in the first example of monodentate co-ordination by this ligand.

Among crown thioethers, 1,4,7-trithiacyclononane (9S3) stands alone for the remarkable strength and breadth of its chelating ability.^{1,2,3} Because 9S3 binds so strongly, metal complexes in unfavourable geometries or oxidation states (e.g., monomeric Rh^{II} , Pd^{III} , and Pt^{III} , as well as octahedral Ag^{I} , Hg^{II} , and low-spin Co^{II} cations^{1,2,3}) nevertheless often have sufficient robustness to permit isolation. Thus the rich co-ordination chemistry of 9S3 arises ultimately from its exceptional ligating properties.

The strong ligating ability of 9S3 in turn derives from its unique conformational suitability for co-ordination. Most crown thioethers adopt 'inside-out' (i.e., exodentate^{4,5,6}) conformations with the S atoms pointing out of the macrocyclic cavity. Free 9S3, however, adopts a conformation⁷ closely resembling that required for tridentate co-ordination. Complexation accordingly requires negligible conformational change.⁸ In effect, the enthalpic price of arranging the donor atoms for co-ordination has been paid during synthesis of the ligand.

Conformational congruence between free and bound forms (often at the cost of an unusual co-ordination geometry) typifies 9S3 complexes. Such observations invite the conclusion that 9S3 lacks sufficient flexibility to accommodate other conformations. Our structural, electrochemical, and n.m.r. studies of $[\text{Cu}_2(9\text{S3})_3]^{2+}$, however, demonstrate that this impression is incorrect, and that 9S3 has considerably greater flexibility than has heretofore been appreciated.

Reaction of 9S3 in MeOH^\dagger with $[\text{Cu}(\text{MeCN})_4](\text{X})$ gives different products, depending on the identity of X. Use of the PF_6^- , BF_4^- , and ClO_4^- salts of $[\text{Cu}(\text{MeCN})_4]^+$ gives respectively $[\text{Cu}(9\text{S3})_2](\text{PF}_6)$ (1), $[\text{Cu}_2(9\text{S3})_3](\text{BF}_4)_2 \cdot \text{H}_2\text{O}$ (2), and $[\text{Cu}_3(9\text{S3})_3](\text{ClO}_4)_3$ (3).⁹ X-Ray diffraction[‡] shows that (2) contains a binuclear $\{[\text{Cu}(9\text{S3})_2(9\text{S3})]^{2+}$ cation with two structurally different types of 9S3 (Figure 1). Facially bound tridentate 9S3 occurs in the two independent $\{\text{Cu}(9\text{S3})^+\}$ units, where ligand torsional angles closely parallel those in the free ligand⁷ ($\Delta\tau_{\text{max}}$ 5.4°). Both of these units contain a local idealized C_3 axis perpendicular to the S_3 plane, with all the carbon atoms lying on the same side of this plane.

On the other hand, the unique bridging 9S3 adopts a conformation unlike that in any previously reported complex. Two of the S atoms co-ordinate to $\{\text{Cu}(9\text{S3})\}^+$ moieties in a monodentate fashion, while the third remains free. In this macrocycle a local idealized C_2 axis passes through S(1) and bisects the C(5)–C(6) bond, with carbon atoms lying on both sides of the S_3 plane. Adoption of this conformation requires that torsional angles of free 9S3 (with one exception) change by 60 to 120°.

This novel ring conformation bears kinetic and thermodynamic implications for 9S3 co-ordination chemistry. Its accessibility provides a likely mechanism for ligand exchange. Moreover, in its conformation the bridging ligand probably resembles the first step in co-ordination of 9S3 to a metal ion.¹⁰ If so, the bidentate co-ordination found in $[\text{Pt}(9\text{S3})_2]^{2+}$ ¹¹ may represent the second step. In addition, it generates an exodentate 9S3 that acts as a 'platform' for aggregation of $\{\text{Cu}(9\text{S3})\}^+$ units to give $\{[\text{Cu}(9\text{S3})]_n(9\text{S3})\}^{n+}$ ($n = 1-3$) (Scheme 1).

Evidence for this latter contention comes from electrochemical studies, which show that (1) and (2) exist in a mobile equilibrium in MeNO_2 at room temperature. Both complexes exhibit a single quasi-reversible cyclic voltammetric process centred at +0.59 V vs. standard calomel electrode (S.C.E.) ($E_p = 86$ mV; $v = 50$ mV s⁻¹); $[\text{Cu}(9\text{S3})_2]^{2+}$ behaves similarly.¹² Addition of 9S3 to solutions of (2) nearly doubles the peak currents of this couple, consistent with an increase in concentration of $[\text{Cu}(9\text{S3})_2]^{2+}$. This observation shows that oxidation of both (1) and (2) occurs *via* (1), and that the two complexes interconvert rapidly on the cyclic voltammetric time scale. Similarly, ¹H n.m.r. investigation indicates that (1) and (2) also interconvert rapidly on the n.m.r. time scale (singlet, δ 3.14, at 310 K). Apparently the unusual conforma-

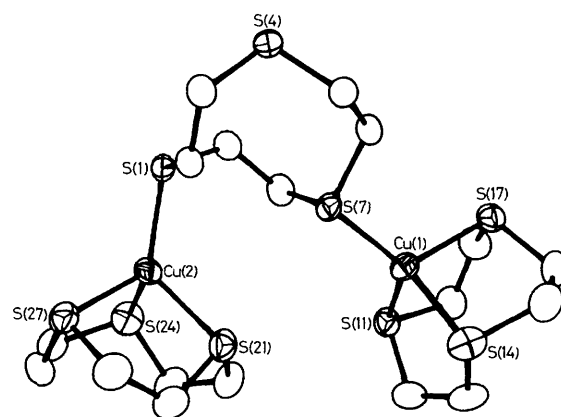
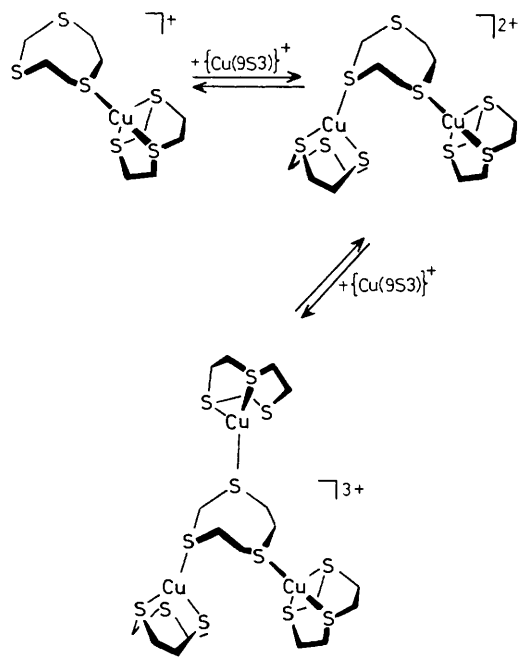


Figure 1. ORTEP view of $[\text{Cu}_2(9\text{S3})_3]^{2+}$, showing thermal ellipsoids at 50% probability level. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): average Cu–S (non-chelating ligand) 2.238(1); average Cu–S (chelating ligands) 2.320(1); average S–Cu–S (inter-ligand) 122.11(5); average S–Cu–S (intra-ligand) 94.21(5).

[†] Experimental procedure: to a solution of $[\text{Cu}(\text{MeCN})_4](\text{BF}_4)$ (0.112 g, 0.36 mmol) in dry MeOH (5 ml) under N_2 was added 9S3 (0.110 g, 0.58 mmol). The solution was stirred for 2 h and the resulting white solid (2) (50% yield) was recrystallised from MeOH . ¹H N.m.r. (CD_3NO_2 vs. Me_4Si) δ 3.14 (s). Complex (1) was prepared by a similar procedure from $[\text{Cu}(\text{MeCN})_4](\text{PF}_6)$, and gave an n.m.r. spectrum identical to that of (2). Satisfactory microanalysis was obtained for both complexes. Diffraction quality crystals of (2) were grown from MeOH solution. Electrochemical measurements were made in MeNO_2 solution, at a glassy carbon electrode, with 0.1 M NEt_4BF_4 as support electrolyte.

[‡] Crystal data for (2): space group $P\bar{1}$, $a = 10.856(3)$, $b = 15.198(4)$, $c = 11.464(2)$ Å; $\alpha = 109.18(3)$, $\beta = 95.15(3)$, $\gamma = 109.22(2)^\circ$; $Z = 2$; $D_c = 1.736$ g cm⁻³; Enraf-Nonius CAD4 diffractometer, $\text{Cu-K}\alpha$ radiation; 4854 unique reflections with $F^2 > 3\sigma(F^2)$, $R = 4.33\%$, $R_w = 4.49\%$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Scheme 1

tion of the bridging 9S3 allows it to bind to one, two, or (possibly) three $[Cu(9S3)]^+$ units. It thereby promotes both the facile co-ordinative equilibrium and the rapid interconversion of the various Cu^I-9S3 complexes.

In conclusion, the results presented here establish that the

structural chemistry of 9S3 encompasses greater conformational diversity than hitherto supposed. In particular they show that 9S3 can adopt a conformation commensurate with monodentate co-ordination. Lastly, they provide a model for intermediates in the formation and dissociation of 9S3 complexes.

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