

Co-ordination chemistry of Cu^I with 1,3,5-tris[bis(pyridin-2-ylmethyl)aminomethyl]-2,4,6-triethylbenzene, a conformationally constrained trinucleating ligand

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The new ligand 1,3,5-tris[bis(pyridin-2-ylmethyl)aminomethyl]-2,4,6-triethylbenzene (L) was prepared from 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene (TriBr) and bis(pyridin-2-ylmethyl)amine. In the crystal state TriBr adopts a conformation with the substituents alternately pointing to opposite sides of the plane of the benzene ring. Compound L adopts a similar conformation. With its donor sets thus coming together on the same side of the benzene ring L can co-ordinate three copper(I) species in a defined and close proximity. This is illustrated by the crystal structures of L, [(CuI)₃L] and [(CuNCMe)₃L][PF₆]₃. The electrochemical interdependence of the copper centres in [(CuI)₃L] and [(CuBr)₃L] has been investigated by cyclic voltammetry. With weaker and harder terminal ligands such as acetonitrile the [Cu^I₃L]³⁺ species in CH₂Cl₂ are liable to oxidation by the solvent to give Cu^{II}Cl⁺ species. In one such degradation product L co-ordinates besides an isolated Cu^I, a Cu^I and a Cu^{II} bridged by a single chloride. The Cu^{II} is further co-ordinated by an oxygen from a perchlorate anion. From the reaction of only two equivalents of [Cu(NCMe)₄]BF₄ with L a dinuclear compound was obtained, in which both copper atoms experience a distorted trigonal co-ordination from three pyridine nitrogen atoms each.

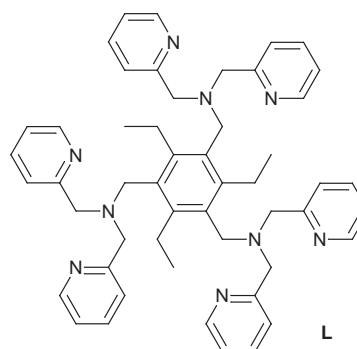
This study deals with an approach to use acyclic but conformationally constrained multidentate ligands to co-ordinate three metal centres in an effort to keep them in a geometrically defined arrangement. Besides their inherent appeal such compounds deserve interest as building blocks for supramolecular assemblies or bioinorganic model compounds. For example, trinuclear metal centres play an important role in the active sites of various enzymes.¹ A prominent example is ascorbate oxidase that plays some role in oxygenation reactions and contains a close assembly of three copper atoms with distances of 4 to 5 Å besides a fourth copper atom that is farther apart.² A variety of trinuclear copper model compounds have been obtained by self-assembly reactions.^{1,3,4} In an alternative approach trinucleating ligands have been introduced, but most of these are rather flexible and fail to impose a well defined arrangement of the metals.³ In this regard it has been noted that “the small molecule derived ligand cleft has a greater degree of conformational freedom than the more highly defined proteinaceous clefts and so the need to design in features to constrain this mobility is apparent”.¹ In different contexts a constrained mobility and preorganisation of tripodal ligands has been founded on a conformational pattern typical of certain hexa-substituted derivatives of benzene.^{5,6} Such derivatives with six substituent groups that are linked to the benzene ring *via* a methylene group tend to adopt an overall *ababab* conformation⁷ with the side chains pointing alternately to opposite sides, *a*(bove) and *b*(elow), of the benzene plane. Thereby donor groups attached to the substituent groups in 1-, 3- and 5-position are pregrouped on the same side of the benzene plane. 1,3,5-Tris(bromomethyl)-2,4,6-triethylbenzene (TriBr) is a versatile precursor to such tripodal ligands, where the presence of the ethyl substituents keeps the co-ordinating groups anchored in 1, 3 and 5 position on the same side of the benzene ring.⁵ We have now adapted this approach to the synthesis of conformationally constrained trinucleating ligands. 1,3,5-Trimethylenylbenzene groups have been used as spacers in

trinucleating ligands intended to ensure interdependent or co-operative behaviour of three metal centres;^{3,8} the use of the 1,3,5-trimethylenyl-2,4,6-triethylbenzene group as an alternative spacer instead could induce a closer and better defined arrangement of the metal centres and thus enhance such effects.

Results and discussion

Synthesis and structure of the ligand L

As a suitable ligand for our purpose we decided to synthesize 1,3,5-tris[bis(pyridin-2-ylmethyl)aminomethyl]-2,4,6-triethylbenzene (L) which is accessible in a simple one-step procedure from TriBr and bis(pyridin-2-ylmethyl)amine and purified by recrystallisation. It provides three potentially tridentate donor sets to co-ordinate a single metal each. The NMR spectrum of L in CDCl₃ exhibits sharp lines and is in agreement with the C₃ symmetry of an *ababab* conformation in solution. In the crystal structure (Fig. 1) the anticipated conformation with all the bis(pyridin-2-ylmethyl)amino groups on one side and the ethyl groups pointing to the opposite side of the benzene ring is retained.



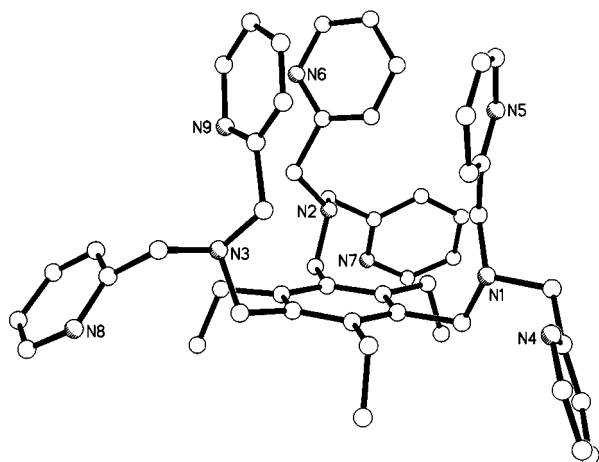


Fig. 1 The crystal structure of compound L.

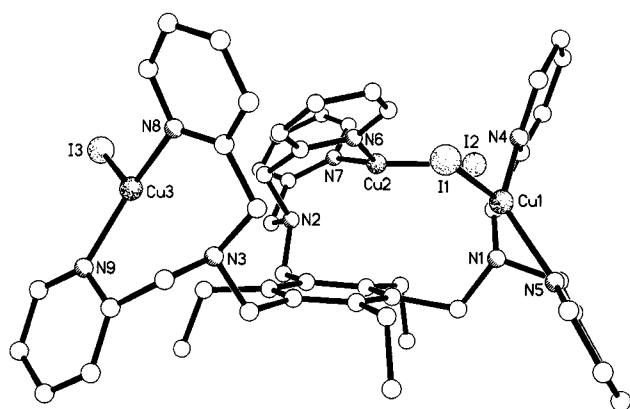


Fig. 2 Crystal structure of $[(\text{CuI})_3\text{L}]$ with H atoms omitted for clarity. Selected interatomic distances (Å) and angles ($^\circ$): Cu(1)–N(4) 1.990(5), Cu(1)–N(5) 2.002(6), Cu(2)–N(6) 1.991(5), Cu(2)–N(7) 2.002(5), Cu(3)–N(8) 1.990(6), Cu(3)–N(9) 2.005(6), Cu(1)–I(1) 2.519(1), Cu(2)–I(2) 2.5335(9), Cu(3)–I(3) 2.511(1), Cu(1)···Cu(2) 7.162(1), Cu(1)···Cu(3) 7.949(2), Cu(2)···Cu(3) 7.823(2), Cu(1)···N(1) 2.520(5), Cu(2)···N(2) 2.570(5) and Cu(3)···N(3) 2.548(5); N(4)–Cu(1)–N(5) 125.4(2), N(4)–Cu(1)–I(1) 115.9(2), N(5)–Cu(1)–I(1) 111.5(2), N(6)–Cu(2)–N(7) 125.4(2), N(6)–Cu(2)–I(2) 118.3(2), N(7)–Cu(2)–I(2) 111.0(2), N(8)–Cu(3)–N(9) 127.8(2), N(8)–Cu(3)–I(3) 117.7(2) and N(9)–Cu(3)–I(3) 111.1(2).

Synthesis, structure and electrochemistry of $[(\text{CuI})_3\text{L}]$ and $[(\text{CuBr})_3\text{L}]$

In our first experiments to study the co-ordination chemistry of L with Cu^{I} we employed CuBr and CuI since the soft Lewis bases Br^- and especially I^- stabilise Cu^{I} and reduce both the air-sensitivity and the potential problem of disproportionation of copper(I) compounds. The reaction of L with three equivalents of CuBr or CuI in hot dmf gives the trinuclear complexes $[(\text{CuBr})_3\text{L}]$ and $[(\text{CuI})_3\text{L}]$ that are isolated as yellow crystalline solids. While the crystals of $[(\text{CuBr})_3\text{L}]$ rapidly lost solvated solvent to give a powder, those of $[(\text{CuI})_3\text{L}]$ were suitable for crystallography. The crystal structure is depicted in Fig. 2. All three bis(pyridin-2-ylmethyl)amino groups co-ordinate a single Cu^{I} each. The copper atoms are further co-ordinated by terminal iodide ligands to give overall distorted trigonal geometries. The tertiary amino groups do not participate in co-ordinating the copper atoms, corresponding $\text{Cu} \cdots \text{N}$ distances being 2.52 to 2.57 Å. However, all three copper atoms are slightly displaced by 0.23 to 0.33 Å out of the least squares planes described by the iodine and the two pyridine nitrogen atoms of their donor sets towards the tertiary amino groups, and this may reflect a weak electrostatic interaction. In general, Cu^{I} prefers tetrahedral co-ordination, but trigonal geometries

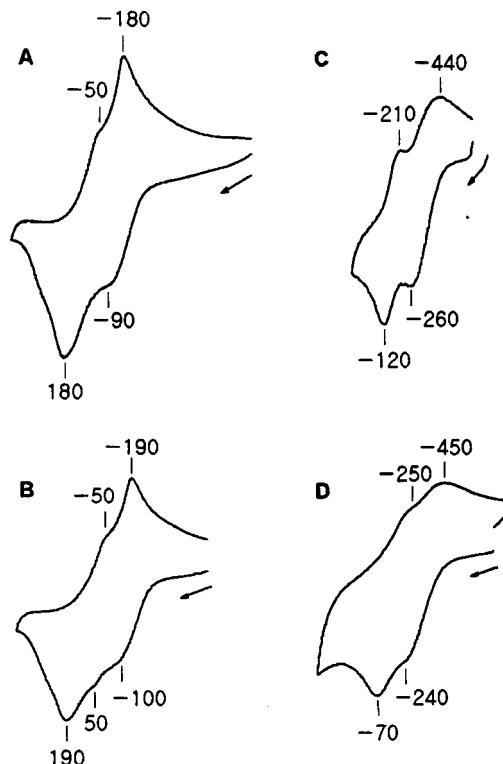


Fig. 3 Cyclic voltammograms in dichloromethane (potentials are given in mV vs. Fc/Fc^+): (A) $[(\text{CuI})_3\text{L}]$, scan rate 100 mV s^{-1} ; (B) $[(\text{CuI})_3\text{L}]$, scan rate 200 mV s^{-1} ; (C) $[(\text{CuBr})_3\text{L}]$, scan rate 50 mV s^{-1} ; (D) $[(\text{CuBr})_3\text{L}]$, scan rate 1 V s^{-1} .

are also common.⁹ Moreover, Cu^{I} is notorious for its remarkable tolerance of rather severe distortions from these ideal geometries.¹⁰ In the case of L the co-ordination geometry is biased by the chelate bite of the bis(pyridin-2-ylmethyl)aminomethyl groups. As tridentate ligands these groups are confined to narrow chelate angles. They cannot afford tetrahedral co-ordination, but rather support higher co-ordination numbers. Since higher co-ordination numbers are not favourable for Cu^{I} and no further auxiliary ligands are available, anyway, the observed bidentate co-ordination of the bis(pyridin-2-ylmethyl)aminomethyl groups is reasonable. The *ababab* conformation around the central benzene ring in the ligand's backbone is retained and governs the overall conformation. The copper centres are therefore kept on the same side of the central benzene ring with distances of 7.16 to 7.95 Å.

In order to investigate the degree of interaction between the three copper centres we have performed the electrochemistry of both $[(\text{CuBr})_3\text{L}]$ and $[(\text{CuI})_3\text{L}]$. The cyclic voltammogram of $[(\text{CuBr})_3\text{L}]$ is shown in Fig. 3. At a scan rate of 50 mV s^{-1} two separate anodic responses are seen at -260 and -120 mV . At moderate scan rates (100 mV s^{-1}) the voltammogram of $[(\text{CuI})_3\text{L}]$ is similar to that of $[(\text{CuBr})_3\text{L}]$, but the corresponding potentials are more positive than with the latter. This is reasonable since the softer iodide compared to bromide better stabilises Cu^{I} . In both cases the redox waves are somewhat broadened, but the overall processes are chemically reversible as the intensities of oxidative and reductive peak currents are the same, and there is no decrease of wave heights in successive cycles. Since the relative heights of the overlapping waves are difficult to estimate we have carried out controlled potential coulometry to find out the overall number of electrons transferred. In these experiments charges corresponding to 3 electrons have been transferred within about 2 h. In each of the cyclic voltammograms, by sight, the first oxidation wave appears to be twice as large as the second one. It is reasonable to assume the first two Cu^{I} should be oxidised at lower potential than the remaining third one. Since any two of the three Cu^{I} in

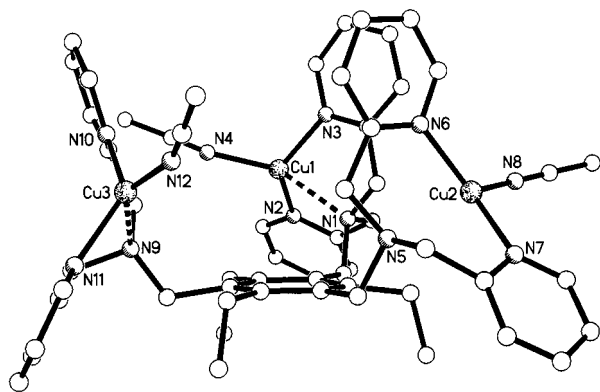


Fig. 4 The complex cation in the crystal structure of $[(\text{CuNCMe})_3\text{L}][\text{PF}_6]_3 \cdot 7\text{CH}_2\text{Cl}_2$ with H atoms omitted for clarity. Selected interatomic distances (Å) and angles (°): Cu(1)⋯N(1) 2.372(4), Cu(1)–N(2) 2.028(4), Cu(1)–N(3) 1.991(4), Cu(1)–N(4) 1.930(4), Cu(2)⋯N(5) 2.510(4), Cu(2)–N(6) 1.975(4), Cu(2)–N(7) 2.015(5), Cu(2)–N(8) 1.966(5), Cu(3)⋯N(9) 2.429(4), Cu(3)–N(10) 1.992(4), Cu(3)–N(11) 2.027(4), Cu(3)–N(12) 1.942(5), Cu(1)⋯Cu(2) 7.2371(9), Cu(1)⋯Cu(3) 7.3418(9) and Cu(2)⋯Cu(3) 7.8659(9); N(2)–Cu(1)–N(3) 126.0(2), N(2)–Cu(1)–N(4) 108.1(2), N(3)–Cu(1)–N(4) 116.2(2), N(1)–Cu(1)–N(2) 78.9(2), N(1)–Cu(1)–N(3) 77.7(2), N(1)–Cu(1)–N(4) 150.2(2), N(6)–Cu(2)–N(7) 133.1(2), N(6)–Cu(2)–N(8) 114.1(2), N(7)–Cu(2)–N(8) 107.2(2), N(5)–Cu(2)–N(6) 76.0(2), N(5)–Cu(2)–N(7) 77.1(2), N(5)–Cu(2)–N(8) 153.2(2), N(10)–Cu(3)–N(11) 126.2(2), N(10)–Cu(3)–N(12) 116.2(2), N(11)–Cu(3)–N(12) 110.4(2), N(9)–Cu(3)–N(10) 77.9(2), N(9)–Cu(3)–N(11) 78.5(2) and N(9)–Cu(3)–N(12) 145.8(2).

$[(\text{CuI})_3\text{L}]$ may enhance their co-ordination number by bridging and sharing their halide ligands, whereas any third one would be left aside and less easily oxidised. At higher scan rates ($>150 \text{ mV s}^{-1}$) a small additional anodic peak appears in the cyclic voltammogram of $[(\text{CuI})_3\text{L}]$. This could be interpreted in terms of a relatively slow rearrangement of the first two copper centres to share their iodide ligands. The compound $[(\text{CuBr})_3\text{L}]$ did not show any additional oxidation peak even at a scan rate of 1 V s^{-1} . A similar reversible bridging of chloride ligands has recently been postulated for another trinuclear copper(II) complex.¹¹ Alternatively, the higher potential of the third copper centre may simply result from positive charge accumulation after the first two copper centres have been oxidised.

Synthesis and structure of $[(\text{CuNCMe})_3\text{L}][\text{PF}_6]_3$

After the co-ordination properties of L had been established with CuBr and CuI we were interested in trinuclear compounds with more labile auxiliary ligands to increase their reactivity and make them more liable to ligand substitution. When L is dissolved with three equivalents of $[\text{Cu}(\text{NCMe})_4]\text{PF}_6$ in dmf a yellow solution is obtained that rapidly turns green and a small amount of dark solid precipitates indicating disproportionation of Cu^{I} . When dichloromethane is used as solvent instead the yellow colour persists and chilling the solution gives yellow crystals of $[(\text{CuNCMe})_3\text{L}][\text{PF}_6]_3$ suitable for X-ray structure analysis.

The molecular structure of the cation $[(\text{CuNCMe})_3\text{L}]^{3+}$ is depicted in Fig. 4. Though no crystal symmetry is imposed, the trinuclear cation adopts near C_3 symmetry. Each copper atom is co-ordinated by two pyridine nitrogen atoms and a terminal acetonitrile molecule. The three copper centres significantly differ in the degree of interaction with the corresponding tertiary amino groups (N_{tert}). The respective interatomic distances $\text{Cu} \cdots \text{N}_{\text{tert}}$ are 2.37, 2.43 and 2.51 Å. A similar structural motif has been reported in a dinuclear copper(I) complex of the ligand 1,3-bis[bis(pyridin-2-ylmethyl)amino]benzene with a corresponding distance $\text{Cu} \cdots \text{N}_{\text{tert}}$ of 2.39 Å.¹² Compared to $[(\text{CuI})_3\text{L}]$ these distances $\text{Cu} \cdots \text{N}_{\text{tert}}$ are shorter, thus corresponding reasonably to the lower ligand strength of acetonitrile compared to iodide. However, whereas the soft base iodide

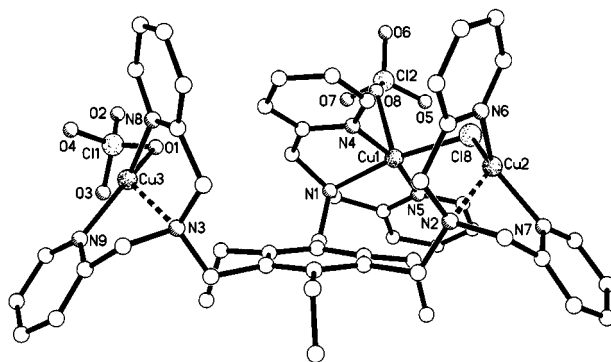


Fig. 5 The complex cation in the crystal structure of $[\text{Cu}_3\text{Cl}(\text{ClO}_4)_2\text{L}] \cdot \text{ClO}_4 \cdot 2\text{CH}_2\text{Cl}_2$ with H atoms omitted for clarity. Selected interatomic distances (Å) and angles (°): Cu(1)–N(1) 2.051(4), Cu(1)–N(4) 1.977(4), Cu(1)–N(5) 1.988(4), Cu(1)–Cl(8) 2.276(2), Cu(1)–O(8) 2.410(4), Cu(2)⋯N(2) 2.382(4), Cu(2)–N(6) 2.007(4), Cu(2)–N(7) 1.981(5), Cu(2)–Cl(8) 2.302(2), Cu(3)⋯N(3) 2.403(4), Cu(3)–N(8) 1.934(5), Cu(3)–N(9) 1.926(5), Cu(3)–O(1) 2.406(6), Cu(1)⋯Cu(2) 3.8488(9), Cu(1)⋯Cu(3) 7.542(2) and Cu(2)⋯Cu(3) 9.257(2); N(1)–Cu(1)–N(4) 83.0(2), N(4)–Cu(1)–Cl(8) 96.9(1), Cl(8)–Cu(1)–N(5) 97.3(2), N(5)–Cu(1)–N(1) 83.0(2), N(1)–Cu(1)–O(8) 91.4(2), N(4)–Cu(1)–O(8) 87.2(2), N(5)–Cu(1)–O(8) 91.0(2), Cl(8)–Cu(1)–O(8) 100.8(1), Cu(1)–Cl(8)–Cu(2) 114.44(6), N(6)–Cu(2)–N(7) 125.1(2), N(6)–Cu(2)–Cl(8) 111.8(1), N(7)–Cu(2)–Cl(8) 118.5(1), N(2)–Cu(2)–Cl(8) 137.0(1), N(2)–Cu(2)–N(6) 78.2(2), N(2)–Cu(2)–N(7) 79.7(2), N(3)–Cu(3)–N(8) 79.6(2), N(3)–Cu(3)–N(9) 82.5(2), N(3)–Cu(3)–O(1) 130.7(2), N(8)–Cu(3)–N(9) 138.8(2), N(8)–Cu(3)–O(1) 96.3(2) and N(9)–Cu(3)–O(1) 123.1(2).

stabilises copper as Cu^{I} even in somewhat distorted geometries, this is much less the case with acetonitrile and the observed co-ordination renders Cu^{I} liable to oxidation or disproportionation. Indeed, stabilising Cu^{I} in the given co-ordination means a dilemma. When the distance $\text{Cu} \cdots \text{N}_{\text{tert}}$ is reduced to compensate for the weak acetonitrile ligand, the bis(pyridin-2-ylmethyl)aminomethyl groups become more tridentate in character. The small five-membered chelate rings thus formed are known to destabilise Cu^{I} towards Cu^{II} .¹³

The complexes $[\text{Cu}(\text{NCMe})_4]\text{BF}_4$ and $[\text{Cu}(\text{NCMe})_4]\text{ClO}_4$ react similarly with L. However, with BF_4^- and ClO_4^- as anions the corresponding copper compounds are unstable in dichloromethane solutions that turn green within hours. Instability of certain copper(I) compounds due to oxidation by dichloromethane has been reported by Karlin and co-workers.¹⁴ Those compounds have ligands similar to the bis(pyridin-2-yl)methylamino groups of L that likewise support higher co-ordination numbers and Cu^{II} . Such species reduce CH_2Cl_2 by abstracting chlorine to give CuCl^+ species. In the present case this reaction is presumably catalysed by the weakly co-ordinating anions ClO_4^- and BF_4^- , but slow in the presence of PF_6^- only. The use of organic nitriles has been recommended in cases when oxidation by CH_2Cl_2 is a problem,¹⁵ but unfortunately the trinuclear complexes of L are insoluble in acetonitrile or thf. In consequence, the practical confinement to CH_2Cl_2 proved to be a severe handicap in studying the co-ordination chemistry of Cu^{I} with L.

$[\text{Cu}_3\text{Cl}(\text{ClO}_4)_2\text{L}]\text{ClO}_4$, A product from the oxidation of $[(\text{CuNCMe})_3\text{L}][\text{ClO}_4]_3$ by dichloromethane

While in general amorphous material is obtained from the oxidation of $[(\text{CuNCMe})_3\text{L}]^{3+}$ species by CH_2Cl_2 (see above), we have occasionally obtained some green crystals among other material from a solution of $[(\text{CuNCMe})_3\text{L}][\text{ClO}_4]_3$, prepared *in situ* from L with three equivalents of $[\text{Cu}(\text{NCMe})_4]\text{ClO}_4$, in dichloromethane after layering with diethyl ether. Crystal structure analysis revealed that is a trinuclear compound with the formula $[\text{Cu}_3\text{Cl}(\text{ClO}_4)_2\text{L}]\text{ClO}_4$. Though this compound is only a minor product and not fully characterised we briefly comment on the structure that is depicted in Fig. 5. In this compound L

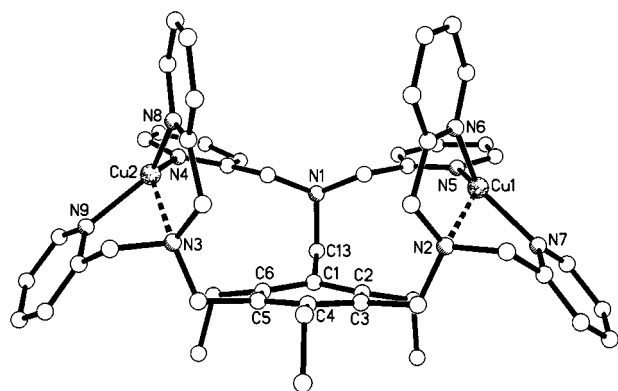


Fig. 6 The complex cation in the crystal structure of $[\text{Cu}_2\text{L}][\text{BF}_4]_2 \cdot \text{CH}_2\text{Cl}_2$ with H atoms omitted for clarity. The benzene ring is distorted; the strong deviation of C(1) and C(13) from the least-squares plane of the benzene ring is clearly visible. Selected interatomic distances (Å) and angles ($^\circ$): Cu(1)–N(5) 2.024(5), Cu(1)–N(6) 2.014(6), Cu(1)–N(7) 2.009(6), Cu(1)···N(2) 2.478(6), Cu(2)–N(4) 2.017(5), Cu(2)–N(8) 1.993(6), Cu(2)–N(9) 2.022(5), Cu(2)···N(3) 2.525(6) and Cu(1)···Cu(2) 7.986(8); N(5)–Cu(1)–N(6) 112.5(2), N(5)–Cu(1)–N(7) 117.0(3), N(6)–Cu(1)–N(7) 126.9(2), N(2)–Cu(1)–N(5) 142.1(2), N(2)–Cu(1)–N(6) 76.5(2), N(2)–Cu(1)–N(7) 76.4(2), N(4)–Cu(2)–N(8) 115.5(2), N(4)–Cu(2)–N(9) 113.0(2), N(8)–Cu(2)–N(9) 128.4(2), N(3)–Cu(2)–N(4) 138.9(2), N(3)–Cu(2)–N(8) 77.5(2) and N(3)–Cu(2)–N(9) 77.8(2).

still co-ordinates three copper nuclei but all three of them experience a different environment. One is co-ordinated by the two pyridine nitrogen atoms of a bis(pyridin-2-ylmethyl)amino group and by an oxygen atom of one perchlorate anion. The corresponding distance $\text{Cu} \cdots \text{N}_{\text{tert}}$ is 2.41 Å. The remaining two copper atoms are bridged by a single chloride. Consideration of displacement factors, interatomic distances and R values clearly precluded the refinement of this atom as an oxide or hydroxide. This implies in the presence of three ClO_4^- anions per formula the oxidation of one of the two copper atoms to Cu^{II} that is consistent with the green colour of the compound. Considering bond distances and the fact that Cu(1) is five-co-ordinated with the help of an oxygen atom from another one of the perchlorate anions we assign the oxidation state II to Cu(1). The co-ordination geometry of Cu(1) is best described as near square pyramidal with O(8) in the axial position. The τ value¹⁶ that is 0 for ideal square pyramidal and 1 for trigonal-bipyramidal co-ordination geometry is 0.03 in the present case.

The dinuclear complex $[\text{Cu}_2\text{L}][\text{BF}_4]_2$

When L is treated with $[\text{Cu}(\text{NCMe})_4]\text{BF}_4$ in a ratio of 1:2 a dinuclear compound $[\text{Cu}_2\text{L}][\text{BF}_4]_2$ is obtained. The crystal structure is depicted in Fig. 6. In this compound two of the bis(pyridin-2-ylmethyl)amino groups co-ordinate a copper each by means of the pyridine nitrogen atoms, and the copper atoms are further co-ordinated each by a third pyridine nitrogen atom from the remaining bis(pyridin-2-ylmethyl)amino group. Both copper atoms experience distorted trigonal co-ordination and are displaced by 0.2 Å out of the least squares planes formed by each of the three co-ordinating nitrogen atoms, presumably to allow weak interactions $\text{Cu}(1) \cdots \text{N}(2)$ 2.48 and $\text{Cu}(2) \cdots \text{N}(3)$ 2.53 Å. Interestingly, the framework of L is significantly distorted. The dinucleating bis(pyridin-2-ylmethyl)amino group adopts a somewhat stretched conformation and its amino group N(1) is lifted away from the plane of the benzene ring in order to enable N(4) and N(5) of its two pyridine rings to participate in co-ordination. The benzene ring is thus bent “upwards” at this corner: C(1) deviates by 0.077 and C(13) by 0.653 Å from the least-squares plane of the benzene ring. Nevertheless, $[\text{Cu}_2\text{L}][\text{BF}_4]_2$ is stable in dichloromethane with respect to oxidation. Dismutation was not observed, either, and crystals of the dinuclear species were obtained as the only

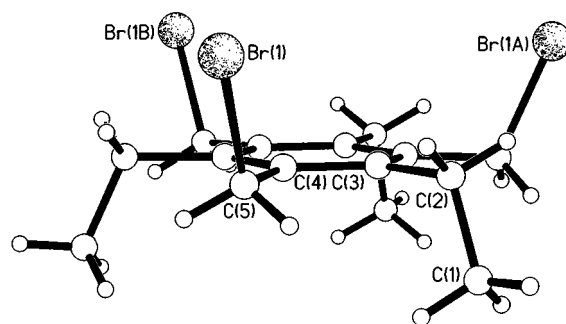


Fig. 7 Crystal structure of TriBr. Selected interatomic distances (Å): Br(1)–C(5) 1.987(3), C(5)–C(4) 1.497(4), C(4)–C(3) 1.409(4), C(3)–C(4a) 1.399(4), C(3)–C(2) 1.521(4) and C(2)–C(1) 1.508(6).

isolated product. The mirror symmetry and low conformational flexibility of $[\text{Cu}_2\text{L}][\text{BF}_4]_2$ is reflected by its NMR spectrum that shows very sharp signals, but is somewhat complicated by coupling between the high number of chemically inequivalent geminal protons.

Concluding remarks

The overall conformation of the new multidentate ligand L is dominated by the *ababab* conformation induced by its 1,3,5-trimethylenyl-2,4,6-triethylbenzene backbone that constrains the flexibility of the side chains and keeps all donor groups on the same side of the plane of the central benzene ring. Without exception this feature is conserved in the crystal structures of all the multinuclear metal complexes reported in this work and thereby causes a comparably close and well defined arrangement of the co-ordinated metal centres. Unfortunately, the chemistry of L with copper(I) species that carry weak terminal ligands is limited by their liability to be oxidised by dichloromethane because of the narrow bite of the bis(pyridin-2-yl)amino groups, that stabilises higher oxidation and co-ordination numbers. Notwithstanding, L provides a prototype of predisposed trinucleating ligands that can be derived by attaching suitable donor sets to the 1,3,5-trimethylenyl-2,4,6-triethylbenzene backbone. The structures presented in this work demonstrate the scope and limitation of conformational control that can be achieved with such ligands. Further work with related ligands and other metals is currently underway in this laboratory.

Note on the crystal structure of 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene (TriBr)

As a starting material 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene (TriBr) is of central importance to the study of L and similar ligands. Recently, we have shown that 1,3,5-tris(cyanomethyl)-2,4,6-triethylbenzene that is also derived from TriBr adopts an unexpected conformation in the crystal state with all substituents but one cyanomethyl group pointing to the same side of the benzene ring.¹⁷ This made us curious about the crystal structure of TriBr itself.

Crystals of TriBr were grown by layering *n*-hexane onto a solution of the compound in dichloromethane. Crystal data are given in Table 1. The compound crystallised on a special position in the trigonal space group $R\bar{3}$ (Fig. 7). As expected the ethyl and bromomethyl groups are arranged in an alternating pattern with all the ethyl groups pointing to one side and all the bromomethyl groups pointing to the opposite side of the benzene plane. The constitution of TriBr is half-way between hexaethylbenzene¹⁸ and hexakis(bromomethyl)benzene¹⁹ and topologically similar to hexakis(sulfanylmethyl)benzene²⁰ and hexaethylborazine.²¹ In the crystal state all of them adopt the corresponding conformation with the substituents alternately orientated to opposite directions. A different conformation is

found with decakis(bromomethyl)biphenyl that has been thoroughly discussed elsewhere.²²

Experimental

General

All experiments involving copper(I) species were carried out under an atmosphere of dinitrogen using standard box techniques. Dichloromethane was dried over CaH_2 , dmf over CaCO_3 and thf and ether over LiAlH_4 . The solvents were distilled from the drying agent under an atmosphere of dinitrogen (exception: dmf under reduced pressure) and degassed prior to use. Tetrakis(acetonitrile)copper(I) hexafluorophosphate was from Aldrich. The derivatives with perchlorate and tetrafluoroborate as anion were synthesized analogous to a literature procedure from Cu_2O and the corresponding acid in acetonitrile.²³

CAUTION: organic perchlorates are potential explosives and should not be handled on a large scale. 1,3,5-Tris(bromomethyl)-2,4,6-triethylbenzene⁵ and bis(pyridin-2-ylmethyl)-amine²⁴ were prepared by literature methods.

Preparations

1,3,5-Tris[bis(pyridin-2-ylmethyl)aminomethyl]-2,4,6-triethylbenzene (L). 1,3,5-Tris(bromomethyl)-2,4,6-triethylbenzene (2.500 g; 5.670 mmol) and a mixture of bis(pyridin-2-ylmethyl)amine (3.387 g; 17.01 mmol) and triethylamine (5.2 g; 51 mmol) were dissolved in 50 ml of thf each. After the two solutions had been chilled in ice they were combined and stirred for 5 h in an ice-bath and then at ambient temperature for 4 d. During this time the mixture turned dark green and a precipitate formed. It was evaporated under reduced pressure and the remainder treated with aqueous KOH and extracted with three portions of dichloromethane. The combined organic solutions were evaporated and the remainder was treated with ether to afford a solid that was washed with ether. (Though L is insoluble in ether, precipitation at this stage is sometimes incomplete and the ether solution should be kept and eventually evaporated to prevent potential loss of product.) The solid was extracted with 50 ml of warm toluene and the clear, dark red solution evaporated to afford an oil that was again solidified by treating with ether. This solid was recrystallised from acetonitrile to yield yellow-red crystals (1.110 g; 1.395 mmol; 25%), mp 185–190 °C (Found: C, 77.0; H, 7.3; N, 15.9. Calc. for $\text{C}_{17}\text{H}_{19}\text{N}_3$: C, 76.9; H, 7.2; N, 15.8%). $\delta_{\text{H}}(\text{CDCl}_3, 300 \text{ MHz})$ 0.66 (9 H, t, CH_3), 2.86 (6 H, q, ethyl CH_2), 3.63 (6 H, s, 1,3,5- CH_2), 3.69 (12 H, s, $\text{NC}_5\text{H}_4\text{CH}_2$), 6.70 (6 H, t), 7.14 (6 H, d), 7.41 (6 H, t) and 8.41 (6 H, d); $\delta_{\text{C}}(\text{CDCl}_3, 75 \text{ MHz})$ 15.89, 22.38, 51.24, 60.39, 122.16, 123.73, 132.23, 136.56, 145.49, 148.86 and 160.17.

$[(\text{CuI})_3\text{L}]$. Copper(I) iodide (143 mg; 0.751 mmol) and L (200 mg; 0.251 mmol) were heated in 10 ml of dmf until a clear solution was obtained. After the clear solution had cooled to r.t. ether was allowed to diffuse into the solution through the gas phase. Within a couple of days a microcrystalline yellow solid had precipitated that was filtered off and washed with ether. This solid was recrystallised from dichloromethane–ether to afford yellow crystals (195 mg; 0.143 mmol; 57%) (Found: C, 44.32; H, 4.22; N, 9.03. Calc. for $\text{C}_{51}\text{H}_{57}\text{Cu}_3\text{I}_3\text{N}_9$: C, 44.80; H, 4.20; N, 9.22%); $\delta_{\text{H}}(\text{CDCl}_3, 300 \text{ MHz})$ 0.61 (9 H, t, CH_3), 3.31 (6 H, br, ethyl CH_2), 3.64 (6 H, s, 1,3,5- CH_2), 3.83 (12 H, br s, $\text{NC}_5\text{H}_4\text{CH}_2$), 7.14 (6 H, br), 7.59 (12 H, br) and 8.81 (6 H, br).

$[(\text{CuBr})_3\text{L}]$. Copper(I) bromide (198 mg; 1.38 mmol) and L (367 mg; 0.461 mmol) were heated in 10 ml of dmf until a clear solution was obtained. Vapour diffusion of ether into this solution afforded a yellow-orange powder. This was recrystallised from dichloromethane–ether to afford bushes of yellow needles. These needles apparently lost solvated solvent and gave a

yellow powder that contained only one molecule of solvated dichloromethane per formula unit (430 mg; 0.323 mmol; 71%) (Found: C, 47.77; H, 4.62; N, 9.58. Calc. for $\text{C}_{51}\text{H}_{57}\text{Br}_3\text{Cu}_3\text{N}_9\cdot\text{CH}_2\text{Cl}_2$: C, 47.63; H, 4.54; N, 9.61%); $\delta_{\text{H}}(\text{CDCl}_3, 300 \text{ MHz})$ 0.60 (9 H, t, CH_3), 3.26 (6 H, br, ethyl CH_2), 3.63 (6 H, s, 1,3,5- CH_2), 3.80 (12 H, br s, $\text{NC}_5\text{H}_4\text{CH}_2$), 7.11 (6 H, br), 7.59 (12 H, br) and 8.75 (6 H, br).

$[(\text{CuNCMe})_3\text{L}][\text{PF}_6]_3$. The complex $[\text{Cu}(\text{NCMe})_4]\text{PF}_6$ (170 mg, 0.465 mmol) was added to a solution of L (113 mg, 0.142 mmol) in 12 ml of CH_2Cl_2 . The mixture was stirred for 15 min and then filtered to remove the excess of $[\text{Cu}(\text{NCMe})_4]\text{PF}_6$. The filtrate was evaporated to reduce the volume to some 30%. Crystals suitable for crystallographic characterisation were obtained by storing the solution at -35°C . According to crystal structure analysis these contain 7 molecules of solvated dichloromethane per formula unit. Out of solution the crystals rapidly lost most of the solvent and gave a yellow powder, $[(\text{CuNCMe})_3\text{L}][\text{PF}_6]_3\cdot\text{CH}_2\text{Cl}_2$ (116 mg; 0.0212 mmol; 50%) (Found: C, 42.82; H, 4.47; N, 10.62. Calc. for $\text{C}_{57}\text{H}_{60}\text{N}_{12}\text{Cu}_3\text{F}_{18}\text{P}_3\text{F}_{18}\cdot\text{CH}_2\text{Cl}_2$: C, 42.75; H, 4.21; N, 10.31%); $\delta_{\text{H}}(\text{CD}_2\text{Cl}_2, 300 \text{ MHz})$ 0.72 (9 H, t, CH_3), 2.32 (12 H, s, CH_3CN), 3.09 (6 H, br, ethyl CH_2), 3.78 (18 H, br, $\text{NC}_5\text{H}_4\text{CH}_2$, $\text{C}_6\text{CH}_2\text{N}$), 7.25 (12 H, br), 7.58 (6 H, br) and 8.56 (6 H, br).

$[\text{Cu}_3\text{Cl}(\text{ClO}_4)_2\text{L}]\text{ClO}_4$. A mixture of 80 mg (0.10 mmol) of L and 120 mg (0.367 mmol) of $[\text{Cu}(\text{NCMe})_4]\text{ClO}_4$ in 10 ml of dichloromethane was stirred for 15 min. the clear yellow solution was filtered to remove the excess of $[\text{Cu}(\text{NCMe})_4]\text{ClO}_4$. Samples of the clear solution were placed into diffusion tubes and layered with ether. The layered solutions turned green within a day and amorphous solids precipitated. After a few days some tiny clusters of green crystals had grown among the amorphous solids. A single-crystalline fragment was cut from one such cluster and used for structure determination. No attempt to further characterise this compound was made.

$[\text{Cu}_2\text{L}][\text{BF}_4]_2$. To a stirred solution of 100 mg (0.126 mmol) of L in 15 ml of dichloromethane was added 79 mg (0.251 mmol) of solid $[\text{Cu}(\text{NCMe})_4]\text{BF}_4$. After 10 min ether was allowed to diffuse into the clear solution through the gas phase. Within days yellow blocks had formed that were washed with ether and dried *in vacuo*. According to elemental and X-ray diffraction analysis these crystals contained one molecule of dichloromethane per formula unit that was not removed *in vacuo* (70 mg; 0.06 mmol; 48%) (Found: C, 53.16; H, 5.49; N, 10.66. Calc. for $\text{C}_{51}\text{H}_{57}\text{B}_2\text{Cu}_3\text{F}_8\text{N}_9\cdot\text{CH}_2\text{Cl}_2$: C, 52.85; H, 5.03; N, 10.66%); $\delta_{\text{H}}(\text{CD}_2\text{Cl}_2, 300 \text{ MHz})$ 0.24 (6 H, t, $^3J = 7$, CH_3), 1.19 (3 H, t, $^3J = 7$, CH_3), 1.76 (2 H, m), 2.70 (2 H, m), 2.82 (2 H, d, $^2J = 17$), 3.15 (2 H, q, $^3J = 7$), 3.41 (2 H, d, $^2J = 17$), 3.65–3.94 (12 H, overlapping signals), 4.02 (2 H, d, $^2J = 16$), 7.04 (2 H, “t”, $^3J = 6$), 7.27–7.56 (8 H, overlapping signals), 7.72 (2 H, dt, $^3J = 8$, $^4J = 1.5$), 7.84 (2 H, dt, $^3J = 8$, $^4J = 1.5$), 8.05 (2 H, dt, $^3J = 7$, $^4J = 1$), 8.15 (4 H, “t”, $^3J = 7$), 8.64 (2 H, d, $^3J = 5$) and 8.83 (2 H, d, $^3J = 5 \text{ Hz}$).

Crystallography

Crystals were obtained as described in the experimental procedures. Crystal data are given in Table 1. The crystals were attached with grease to glass fibres and mounted on a Siemens Smart diffractometer. With the exception of TriBr (5 cm) all data collections were performed with a detector distance of 6 cm. The raw data were processed with the program SAINT,²⁵ and a semiempirical absorption correction from ψ scans was applied with the program SADABS.²⁶ The structures were solved by direct methods and refined with the program package SHELXTL.²⁷

In the case of $[(\text{CuNCMe})_3\text{L}][\text{PF}_6]_3\cdot 7\text{CH}_2\text{Cl}_2$ refinement was hampered by probable disorder of CH_2Cl_2 solvate molecules

Table 1 Crystallographic data for L, its copper complexes and TriBr

	L	[(CuI) ₃ L]	[(CuNCMe) ₃ L][PF ₆] ₃ ·7CH ₂ Cl ₂	[Cu ₃ Cl(ClO ₄) ₂ L]ClO ₄ ·2CH ₂ Cl ₂	[Cu ₂ L][BF ₄] ₂ ·CH ₂ Cl ₂	TriBr
Formula	C ₅₁ H ₅₇ N ₉	C ₅₁ H ₅₇ Cu ₃ I ₃ N ₉	C ₆₄ H ₈₀ Cl ₁₄ Cu ₃ F ₁₈ P ₃	C ₅₃ H ₆₁ Cl ₈ Cu ₃ N ₉ O ₁₂	C ₅₂ H ₅₉ B ₂ Cl ₂ Cu ₂ F ₈ N ₉	C ₁₅ H ₂₁ Br ₃
<i>M</i>	796.06	1367.38	2139.23	1490.33	1181.68	441.05
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Trigonal
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>R</i> 3
<i>a</i> /Å	12.0751(3)	16.6703(4)	16.3631(2)	13.7370(3)	10.034(4)	16.565(1)
<i>b</i> /Å	12.4215(3)	14.0313(4)	17.4425(2)	14.5407(3)	27.69(3)	16.565(1)
<i>c</i> /Å	16.7708(1)	22.9276(5)	17.7148(1)	16.7511(3)	19.83(2)	5.3351(4)
α /°	85.288(2)		71.314(0)	65.871(1)		
β /°	81.273(1)	104.948(1)	77.771(1)	83.257(1)	92.45(5)	
γ /°	67.557(1)		68.974(1)	88.697(1)		
<i>U</i> /Å ³	2297.22(8)	5181.4(2)	4443.72(8)	3031.4(1)	5506(8)	1267.78(15)
<i>Z</i>	2	4	2	2	4	3
<i>T</i> /K	293(2)	293(2)	188(2)	188(2)	188(2)	296(2)
<i>D</i> /g cm ^{−3}	1.151	1.753	1.599	1.633	1.426	1.733
μ (Mo-K α)/mm ^{−1}	0.070	3.052	1.270	1.463	0.941	7.143
<i>F</i> (000)	852	2688	2160	1522	2432	648
Colour	Reddish	Yellow	Yellow	Green	Yellow	Colourless
Crystal shape	Plate	Block	Plate	Fragment	Block	Block
Crystal size/mm	0.4 × 0.4 × 0.3	0.2 × 0.1 × 0.15	0.5 × 0.4 × 0.4	0.15 × 0.15 × 0.25	0.05 × 0.03 × 0.03	0.2 × 0.2 × 0.5
No. reflections measured	9106	20652	18103	12319	21943	2671
No. independent reflections	6738	8181	13379	9110	8689	1341
<i>R</i> _{int}	0.0517	0.0420	0.0136	0.0220	0.0694	0.0528
Data collection range/°	1.77 < θ < 24.41	1.92 < θ < 24.32	1.91 < θ < 24.21	1.89 < θ < 24.18	1.79 < θ < 24.16	4.08 < θ < 28.34
No. variables	541	595	1068	794	704	57
<i>R</i> [<i>I</i> > 2 σ (<i>I</i>)], <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0748, 0.2058	0.0433, 0.0790	0.0662, 0.1819	0.0529, 0.1200	0.0783, 0.1368	0.0282, 0.0678
<i>R</i> (all data), <i>wR</i> ₂ (all data)	0.1510, 0.2783	0.0922, 0.0990	0.0749, 0.1936	0.0698, 0.1335	0.1300, 0.1602	0.0290, 0.0689
Goodness of fit	0.902	1.044	1.049	1.135	1.181	1.056
ρ_{\min} , ρ_{\max} /e Å ^{−3}	−0.308, 0.294	−0.623, 0.712	−1.167, 1.296	−0.762, 0.548	−0.660, 0.561	−0.350, 0.491

that could not be further resolved and caused somewhat high residual electron density after refinement had converged.

On the basis of the Flack parameter²⁸ as provided by the SHELXTL package in the course of final refinement the crystal of TriBr appeared to be inversion-twinned, and the structure was refined to relative twin contributions of 0.4 and 0.6.

CCDC reference number 186/1320.

See <http://www.rsc.org/suppdata/dt/1999/923/> for crystallographic files in .cif format.

Electrochemistry

The supporting electrolyte tetrabutylammonium perchlorate (Fluka) was recrystallised twice from ethyl acetate and dried *in vacuo*. The electrochemical instrumentation consisted of an EG & G Princeton Applied Research Model 273 potentiostat/galvanostat driven by a Model 270/250 software. All electrochemical experiments were carried out in a glove-box under an atmosphere of dinitrogen.

Cyclic voltammetry. A standard three-electrode cell was employed with a platinum disk working electrode, a platinum-wire auxiliary electrode and an Ag–Ag⁺ reference electrode (silver wire|0.01 M AgNO₃|0.1 M n-Bu₄NClO₄, in acetonitrile). The working electrode was cleaned by polishing with 1 µm diamond and 0.05 µm alumina paste. At the beginning of each experiment a voltammogram of the solution containing only the supporting electrolyte was measured. To this solution solid samples of the complexes were added to achieve a *ca.* 1 mM concentration. As a reference the potential of ferrocene was measured under the same conditions with $\Delta E_{1/2}(\text{Fc–Fc}^+)$ at 225 mV. All potentials in this article are reported *vs.* $\Delta E_{1/2}(\text{Fc–Fc}^+)$.

Controlled potential coulometry. The coulometric cell contained a platinum-gauze working electrode, a platinum-gauze counter electrode that was separated from the sample solution by a porous glass frit and an Ag–Ag⁺ reference electrode. The stirred solutions were oxidised at potentials (*vs.* Ag–Ag⁺) of 700, [(CuBr)₃L], and 900 mV, [(CuI)₃L], for 2–6 h before the solutions were reduced again. With [(CuBr)₃L] the solution changed from yellow to green and back to yellow; with [(CuI)₃L] the solution changed from yellow to rust-red and back to yellow.

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Paper 8/09179J