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Extended multidecker sandwich architecture of Cs^+–18-crown-6 complexes stabilized in the environment of novel large iodocuprate(I) clusters obtained from zerovalent copper

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The interaction of zerovalent copper with a proton-donating agent (NH_4I) in acetonitrile solutions of CsX (X = Cl or I) and 18-crown-6 (18c6), in air, resulted in the formation of the novel mixed-metal complexes $[Cs(18c6)_2][Cu_5I_6(MeCN)_2]$ **1**, $[Cs_2(18c6)_3][Cu_8I_{10}(MeCN)_2]$ **2** and $[\{Cs(18c6)\}_6Cu_4I_7][Cs_3(18c6)_3][Cu_7I_{10}][Cu_{13}I_{14}]I_2$ **3**. The main structural feature of the compounds is the multidecker sandwich Cs^+–18c6 cations and finite iodocuprate(I) anions combined to form ionic lattices. It is proposed that the Cu^+ oxidation state is stabilized in the presence of the Cs^+–18c6 moieties in acetonitrile, and the overall formation of the solid phase is a template process of mutual stabilization of Cs^+ as bulky $[Cs_n(18c6)_m]^{n+}$ cations and Cu^+ as iodocuprate anions.

Introduction

Employing zerovalent metals in the synthesis of co-ordination compounds has proven to be a fascinating and versatile route to various metal complexes and there is still great scope for novel chemical and structural investigations of such systems.[1] In studying the interaction of metal powders, in particular copper and nickel, with non-aqueous solutions of ammonium salts we showed that metal oxidation and complex formation were conditioned by the presence of a proton-donating agent and dioxygen from the air *via* reaction (1) in which copper oxidation

$$M + 2NH_4^+ + \tfrac{1}{2}O_2 \longrightarrow M^{2+} + H_2O + 2NH_3 \quad (1)$$

occurred in the two-step process $Cu \longrightarrow Cu^+ \longrightarrow Cu^{2+}$.[2] The concept of necessity of a proton-donating agent in syntheses of co-ordination compounds from zerovalent metals in air was further developed into a methodology for the preparation of mixed-metal complexes. The strategy consisted of treating copper powder with a salt of another metal in a non-aqueous solution of an aminoalcohol that acts as a proton-containing agent. We believed that co-ordinatively unsaturated copper aminoalkoxide generated *in situ* could easily interact with other metal ions present in solution to afford formation of a mixed-metal compound due to the established ability of aminoalcohols to form polynuclear metal complexes.[3] This approach yielded various Cu/M complexes, including Cu/Pb,[4a] and those containing Ni, Co, Zn, Mn as the second metal.[4b]

In view of these facts, it was of interest to consider whether aggregation of metal ions with distinct co-ordination and donor atom requirements in the presence of cation selective ligands can be accomplished starting from zerovalent metal. The interaction of copper powder with ammonium iodide in the presence of CsX (X = Cl or I) and 18-crown-6 (18c6) resulted in the formation of novel mixed-metal complexes possessing unusual structures. Herein we report the synthesis and crystal structures of $[Cs(18c6)_2][Cu_5I_6(MeCN)_2]$ **1**, $[Cs_2(18c6)_3][Cu_8I_{10}(MeCN)_2]$ **2** and $[\{Cs(18c6)\}_6Cu_4I_7][Cs_3(18c6)_3][Cu_7I_{10}][Cu_{13}I_{14}]I_2$ **3**.

Experimental

All chemicals were of reagent grade and used as received, and all experiments were carried out in air. Elemental analyses were performed by standard titrimetric methods (for Cu and I) and with a Carlo Erba Strumentazion Analyzer (for C, H and N) by the Institute of Organic Chemistry, National Academy of Sciences of Ukraine microanalytical service. Infrared spectra were recorded as KBr discs on a UR-10 spectrophotometer in the 4000–400 cm^{-1} region using conventional techniques.

Syntheses

$[Cs(18c6)_2][Cu_5I_6(MeCN)_2]$ 1 and $[Cs_2(18c6)_3][Cu_8I_{10}(MeCN)_2]$ 2. Copper powder (0.064 g, 1 mmol), NH_4I (0.145 g, 1 mmol), CsCl (0.17 g, 1 mmol), 18c6 (0.26 g, 1 mmol) and MeCN (20 cm^3) were heated to 60 °C, and refluxed with stirring for 4–5 h. Then the mixture was allowed to stand at room temperature for 12 h, after which it was heated, refluxed and stirred again until total dissolution of Cu was observed (1 h). After cooling pale yellow crystals precipitated from the clear dark orange solution. Those were filtered off, washed with Pr^iOH and dried at room temperature to give an inseparable mixture of complexes **1** and **2** in ≈70% yield (per copper) (Found: C, 17.5; H, 2.1; Cu, 17.7; I, 42.1; N, 0.9. $C_{28}H_{54}CsCu_5I_6N_2O_{12}$ requires C, 18.4; H, 3.0; Cu, 17.4; I, 41.8; N, 1.5. $C_{20}H_{21}CsCu_4I_5NO_9$ requires C, 16.5; H, 1.4; Cu, 17.4; I, 43.5; N, 1.0%). The IR spectrum shows the typical absorptions corresponding to the 18-crown-6 ligand and the acetonitrile with the characteristic ν(C≡N) at 2265 cm^{-1}. The substance is insoluble in water and soluble in acetonitrile.

[{Cs(18c6)}$_6$Cu$_4$I$_7$][Cs$_3$(18c6)$_3$][Cu$_7$I$_{10}$][Cu$_{13}$I$_{14}$]I$_2$ 3. Copper powder (0.064 g, 1 mmol), NH$_4$I (0.145 g, 1 mmol), CsI (0.26 g, 1 mmol), 18c6 (0.26 g, 1 mmol) and MeCN (15 cm^3) were heated to 60 °C, refluxed and stirred for 4–5 h. Then the mixture was allowed to stand at room temperature for 12 h, after which it was heated, refluxed and stirred again until total dissolution of Cu was observed (1 h). Pale yellow crystals of the product precipitated from the clear dark orange solution over 1–2 d. The crystals were filtered off, washed with Pr^{i}OH and dried at room temperature. Mass collected 0.30 g, yield ≈80% (per copper) (Found: C, 14.2; H, 2.1; Cu, 16.2; I, 45.5. $C_{36}H_{72}Cs_3Cu_8I_{11}O_{18}$ requires C, 14.0; H, 2.3; Cu, 16.4; I, 45.1%). The IR spectrum shows the typical absorptions corresponding to the 18-crown-6 ligand. The compound is insoluble in water and soluble in acetonitrile.

Crystallography

Details of the data collection and processing, structure analysis and refinement are summarized in Table 1. Diffraction experiments were performed on a Rigaku AFC6S diffractometer (complex **1**), a STOE four-circle diffractometer using an Oxford Cryostream low temperature attachment (**2**) and a Siemens SMART area-detector diffractometer (ω rotation scans with narrow frames) (**3**) equipped with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Data sets were corrected for Lorentz-polarization effects and for the effects of absorption. The structures were solved by direct methods using the SHELXS 86[5] computer program, and refined by full-matrix least-squares methods on F^2 using SHELXL 93.[6]

In general all non-hydrogen atoms were refined anisotropically, hydrogen atoms were fixed in idealized positions and allowed to ride on the atom to which they were attached. Each hydrogen atom was assigned an isotropic thermal parameter of 1.2 or 1.5 times that of the attached C atom for CH$_2$ and CH$_3$ groups, respectively (**2**) or fixed U_{iso} = 0.08 Å^2 (**1**, **3**). Compound **1** exhibited disorder of three copper atoms which was modelled successfully in terms of two sets of positions, common occupancy refined to 40 and 60%.

In the case of complex **3** a range of copper and iodide atoms as well as the atom Cs(3) and two unique crown ethers of the [Cs$_3$(18c6)$_3$]$^{3+}$ moiety were disordered. Disorder of copper and iodide atoms of the [Cu$_4$I$_7$]$^{3-}$ cubic core was modelled in terms of two sets of positions so that the cluster may adopt any of the two equivalent orientations about the center of inversion which lies between Cu(7) and its symmetry equivalent, common occupancy of Cu(6), Cu(7), I(8), I(9) and I(10) refined to 50%. Disorder of the Cu(4), Cu(5), I(5) and I(6) atoms of the [Cu$_{13}$I$_{14}$]$^-$ cluster was modelled in terms of two sets of positions and is described in detail below; common occupancy of the copper and iodide atoms refined to 50% with copper atoms left isotropic. Unreasonably short Cu–Cu distances (2.35(4) and 2.43(4) Å) in the [Cu$_4$I$_7$]$^{3-}$ and [Cu$_{13}$I$_{14}$]$^-$ cores were consequences of disorder. Modelling two different conformations for the crown molecules was not successful and one of them was refined isotropically only, with C–O and C–C bond lengths being constrained to 1.43(2) and 1.48(2) Å, respectively.[7] Large thermal parameters of the two iodide anions, I(7) and its symmetry equivalent, co-ordinated to the Cs(3) atom were consequences of the disorder of these atoms between six crystallographic positions. A subsequent data set collected at low temperature on a CCD diffractometer gave worse results.

CCDC reference number 186/1565.

See http://www.rsc.org/suppdata/dt/1999/3087/ for crystallographic files in .cif format.

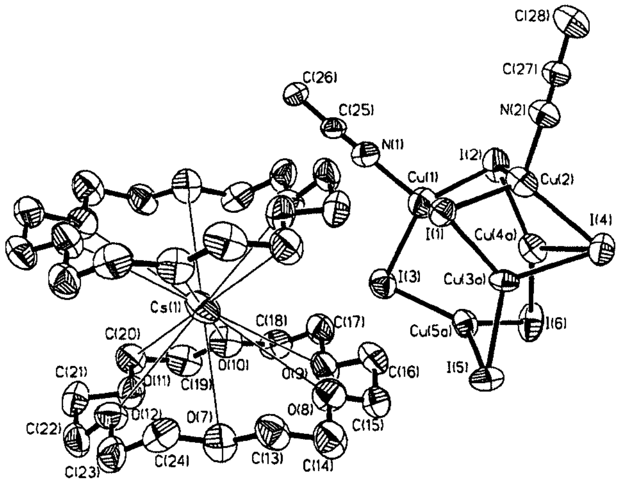


Fig. 1 Molecular structures of the [Cs(18c6)$_2$]$^+$ and [Cu$_5$I$_6$(MeCN)$_2$]$^-$ constituting complex **1** (H atoms omitted for clarity). Only one of the two possible sets of the Cu(3), Cu(4) and Cu(5) atoms is shown.

Table 1 Crystal data for [Cs(18c6)$_2$][Cu$_5$I$_6$(MeCN)$_2$] **1**, [Cs$_2$(18c6)$_3$][Cu$_8$I$_{10}$(MeCN)$_2$] **2** and [{Cs(18c6)}$_6$Cu$_4$I$_7$][Cs$_3$(18c6)$_3$][Cu$_7$I$_{10}$][Cu$_{13}$I$_{14}$]I$_2$ **3**

	1	**2**	**3**
Formula	$C_{28}H_{54}CsCu_5I_6N_2O_{12}$	$C_{40}H_{42}Cs_2Cu_8I_{10}N_2O_{18}$	$C_{108}H_{216}Cs_9Cu_{24}I_{33}O_{54}$
M	1822.74	2914.16	9287.66
Crystal system	Triclinic	Triclinic	Cubic
Space group	$P\bar{1}$	$P\bar{1}$	$Pa\bar{3}$
a/Å	10.891(2)	10.501(5)	28.2558(1)
b/Å	10.959(2)	13.849(7)	28.2558(1)
c/Å	21.645(4)	14.153(7)	28.2558(1)
α/°	88.93(3)	64.28(3)	
β/°	89.58(3)	89.16(3)	
γ/°	82.31(3)	80.49(3)	
U/Å^3	2559.7(8)	1825(2)	22559.2(1)
Z	2	1	4
T/K	293	180	293
Total number of reflections	9530	6145	82209
Number of unique reflections (R_{int})	7794 (0.020)	4742 (0.028)	4624 (0.078)
Observed reflections [$I > \sigma(I)$]	5137	4170	3555
$R1$ (obs.)	0.037	0.029	0.096
$wR2$ (obs.)	0.102	0.074	0.197

Table 2 Geometry of the Cs^+–18-crown-6 systems

		Separations/Å			
Cation	Compound	Cs · · · Cs	Cs–O	Cs deviation from from the mean oxygen atoms plane	Ref.
$[Cs(18c6)_2]^+$	$[Cs(18c6)_2][Cu_5I_6(MeCN)_2]$[a]	—	3.194(6)–3.719(7)	2.051(3)	This work
			3.261(5)–3.700(6)	2.067(3)	
$[Cs_2(18c6)_3]^{2+}$	$[Cs_2(18c6)_3][Cu_8I_{10}(MeCN)_2]$	4.501(3)	3.204(5)–3.486(5)	1.850(2)	This work
			3.431(5)–3.795(5)	2.249(1)	
$[Cs(18c6)]^+$	$[\{Cs(18c6)\}_6Cu_4I_7][Cs_3(18c6)_3][Cu_7I_{10}][Cu_{13}I_{14}]I_2$	—	Cs(1): 3.06(2)–3.23(2)	1.401(9)	This work
$[Cs_3(18c6)_3]^{3+}$	$[\{Cs(18c6)\}_6Cu_4I_7][Cs_3(18c6)_3][Cu_7I_{10}][Cu_{13}I_{14}]I_2$	3.844(7)	Cs(2): 3.32(2)–3.64(4)	2.084	This work
		4.289(7)	3.40(3)–3.69(3)	2.14(1)	
			Cs(3): 3.12(4)–3.47(5)	1.760	
$[Cs_2(18c6)_3]^{2+}$	$[Cs_2(18c6)_3][HX_2]_2\cdot 2HX\cdot 2H_2O$[b]	4.335(1)	3.152(6)–3.413(8)	1.640(3)	11
			3.393(5)–3.636(5)	2.167(1)	
$[Cs(18c6)]_\infty^{\infty+}$	$[Cs(18c6)][TcNCl_4]$	4.275(4)	3.34(1)–3.68(1)	2.138(4)	12
$[Cs(18c6)]^+$ and $[Cs_2(18c6)_3]^{2+}$	$[Cs_9(18c6)_{14}]^{9+}[Rh_{22}(CO)_{35}H_x]^{5-}[Rh_{22}(CO)_{35}H_{x+1}]^{4-}$	4.658	3.29(8)–4.25(8)	2.35	13
			3.51(8)–3.67(8)	1.78	
			3.35(8)–3.96(8)	2.29	
			3.76(8)–4.32(8)	1.88	

[a] There are two unique Cs atoms in the unit cell. [b] X^- = α-Cyanobenzothiazole-α-carbaldehyde oximate.

Results and discussion

Synthesis

The compounds were prepared employing zerovalent copper, ammonium iodide, 18-crown-6 and caesium iodide/chloride as starting materials in acetonitrile. The interaction in such a system is complex and the composition of the products appeared to depend mainly on the initial Cu : I ratio, so that the larger amount of iodide in the initial mixture in the case of **3** afforded a more complicated composition and, as was revealed by X-ray studies, the bulkier structural moieties.

The pale yellow prismatic crystals of the product of the interaction of copper, NH_4I, CsCl and 18c6 gave no satisfactory elemental analyses and were considered to be a mixture of several caesium iodocuprate complexes with 18-crown-6. We were not able to separate this mixture either by recrystallization from acetonitrile or by manual separation due to the visual uniformity of the crystals. Examination of the lattice parameters for the separate single crystals showed the presence of at least two different species. Their composition was established from the X-ray investigations as $[Cs(18c6)_2][Cu_5I_6(MeCN)_2]$ **1** and $[Cs_2(18c6)_3][Cu_8I_{10}(MeCN)_2]$ **2**.

Crystal structure of complex 1

The compound consists of sandwich $[Cs(18c6)_2]^+$ cations and novel pentanuclear iodocuprate(I) $[Cu_5I_6(MeCN)_2]^-$ anions (Fig. 1). The Cs^+ cations are in typical "sunrise" co-ordination to 18c6, which has D_{3d} symmetry with characteristic C–O and C–C distances of 1.40(1)–1.44(1) and 1.47(1)–1.52(1) Å, respectively. The distances and angles in $[Cs(18c6)_2]^+$ (Table 2) are comparable to those found in related systems.[7] In the cluster anion $[Cu_5I_6(MeCN)_2]^-$ four copper atoms are arranged in a tetrahedron bridged on all edges by iodides and with one face capped by the fifth copper atom. Three of the copper atoms, Cu(3), Cu(4), Cu(5), are disordered over two positions each in such a way that Cu(1) caps the face of the tetrahedron built from Cu(2), Cu(3), Cu(4) and Cu(5), while for the tetrahedron built from Cu(1), Cu(3a), Cu(4a) and Cu(5a) the capping atom is Cu(2). The Cu · · · Cu distances vary from 2.565(3) to 2.860(2) and the Cu–I bond lengths from 2.484(2) to 2.719(4) Å (Table 3). Three of the five copper(I) ions, Cu(3), Cu(4), Cu(5), have a nearly planar trigonal co-ordination (the maximum shift of a copper atom from the plane of three iodides is 0.231(3) Å). The Cu(1) and Cu(2) atoms are tetrahedrally co-ordinated by iodide anions and nitrogen atoms, N(1) and N(2), from the acetonitrile molecules. The cluster is reminiscent of the copper(I) framework seen for the $[Cu_4I_6]^{2-}$ unit in $[K_7(12\text{-crown-}4)_6][Cu_4I_6][Cu_8I_{13}]$[8a] or in $[MePPh_3]_2[Cu_4I_6]$,[8b] that have the closest stoichiometric ratio to $[Cu_5I_6(MeCN)_2]^-$.

Table 3 Selected bond distances (Å) and angles (°) for the $[Cu_5I_6(MeCN)_2]^-$ anion of complex **1**[a]

Cu(1)–N(1)	2.000(8)	Cu(4a)–I(4)	2.700(2)
Cu(2)–N(2)	1.982(8)	Cu(5a)–I(3)	2.484(2)
Cu(1)–I(3)	2.655(2)	Cu(5a)–I(6)	2.565(2)
Cu(1)–I(1)	2.682(2)	Cu(5a)–I(5)	2.593(2)
Cu(1)–I(2)	2.709(2)	Cu(3b)–I(5)	2.531(3)
Cu(2)–I(2)	2.671(2)	Cu(3b)–I(1)	2.562(3)
Cu(2)–I(4)	2.683(2)	Cu(3b)–I(3)	2.668(3)
Cu(2)–I(1)	2.684(2)	Cu(4b)–I(6)	2.517(3)
Cu(3a)–I(5)	2.547(2)	Cu(4b)–I(2)	2.591(4)
Cu(3a)–I(1)	2.567(2)	Cu(4b)–I(3)	2.719(4)
Cu(3a)–I(4)	2.646(2)	Cu(5b)–I(4)	2.509(3)
Cu(4a)–I(6)	2.546(3)	Cu(5b)–I(5)	2.568(4)
Cu(4a)–I(2)	2.549(3)	Cu(5b)–I(6)	2.601(3)
I(3)–Cu(1)–I(1)	112.14(6)	I(3)–Cu(5a)–I(6)	122.40(9)
I(3)–Cu(1)–I(2)	114.64(6)	I(3)–Cu(5a)–I(5)	122.05(9)
I(1)–Cu(1)–I(2)	114.77(5)	I(6)–Cu(5a)–I(5)	115.40(9)
I(2)–Cu(2)–I(4)	110.55(6)	I(5)–Cu(3b)–I(1)	124.6(1)
I(2)–Cu(2)–I(1)	115.97(5)	I(5)–Cu(3b)–I(3)	117.3(1)
I(4)–Cu(2)–I(1)	110.32(6)	I(1)–Cu(3b)–I(3)	115.7(1)
I(5)–Cu(3a)–I(1)	123.72(9)	I(6)–Cu(4b)–I(2)	126.2(2)
I(5)–Cu(3a)–I(4)	117.86(8)	I(6)–Cu(4b)–I(3)	115.3(2)
I(1)–Cu(3a)–I(4)	115.33(8)	I(2)–Cu(4b)–I(3)	116.5(1)
I(6)–Cu(4a)–I(2)	126.79(9)	I(4)–Cu(5b)–I(5)	122.3(1)
I(6)–Cu(4a)–I(4)	117.4(1)	I(4)–Cu(5b)–I(6)	122.6(1)
I(2)–Cu(4a)–I(4)	113.90(9)	I(5)–Cu(5b)–I(6)	115.0(1)

[a] Atoms Cu(3), Cu(4) and Cu(5) are disordered on two positions 'a' and 'b' with population 0.6 and 0.4, respectively.

Crystal structure of complex 2

The compound is built up from cations $[Cs_2(18c6)_3]^{2+}$ and finite iodocuprate(I) anions $[Cu_8I_{10}(MeCN)_2]^{2-}$. Both these large moieties have comparable sizes (Fig. 2) and co-operate to form a simple ionic lattice. The structure of the anion is unprecedented and can be viewed as a S-shape chain of seven Cu_2I_2 rhombohedrons, that share opposite edges with two additional iodide atoms, I(1) and I(1a), bridging the copper atom of the "central" and "end" rhombohedrons. These bridges lead to the formation of two six membered Cu_3I_3 rings of chair conformation (Fig. 2), thus both characteristic motifs of the

Table 4 Selected bond distances (Å) and angles (°) for the $[Cu_8I_{10}(MeCN)_2]^{2-}$ anion of complex **2**[a]

Cu(1)–I(1)	2.568(2)	Cu(4)–N(1)	1.988(7)
Cu(1)–I(2a)	2.624(2)	Cu(4)–I(4)	2.590(2)
Cu(1)–I(5a)	2.701(2)	Cu(4)–I(5)	2.658(2)
Cu(1)–I(2)	2.739(2)	Cu(4)–I(3a)	2.802(2)
Cu(2)–I(2)	2.546(2)	I(2)–Cu(1a)	2.624(2)
Cu(2)–I(3)	2.564(2)	I(3)–Cu(3a)	2.629(2)
Cu(2)–I(5a)	2.568(2)	I(3)–Cu(4a)	2.802(2)
Cu(3)–I(1)	2.512(2)	I(5)–Cu(2a)	2.568(2)
Cu(3)–I(4)	2.530(2)	I(5)–Cu(1a)	2.701(2)
Cu(3)–I(3a)	2.629(2)		
I(1)–Cu(1)–I(2a)	119.52(5)	I(1)–Cu(3)–I(4)	126.70(5)
I(1)–Cu(1)–I(5a)	106.93(6)	I(1)–Cu(3)–I(3a)	117.68(5)
I(2a)–Cu(1)–I(5a)	107.81(5)	I(4)–Cu(3)–I(3a)	113.80(5)
I(1)–Cu(1)–I(2)	108.55(5)	N(1)–Cu(4)–I(4)	112.0(2)
I(2a)–Cu(1)–I(2)	106.02(5)	N(1)–Cu(4)–I(5)	102.4(2)
I(5a)–Cu(1)–I(2)	107.48(5)	I(4)–Cu(4)–I(5)	119.57(5)
I(2)–Cu(2)–I(3)	119.98(5)	N(1)–Cu(4)–I(3a)	106.9(2)
I(2)–Cu(2)–I(5a)	118.13(5)	I(4)–Cu(4)–I(3a)	106.52(5)
I(3)–Cu(2)–I(5a)	119.92(5)	I(5)–Cu(4)–I(3a)	108.90(5)

[a] Atoms designated a are related by the symmetry operation $1 - x, 2 - y, 1 - z$.

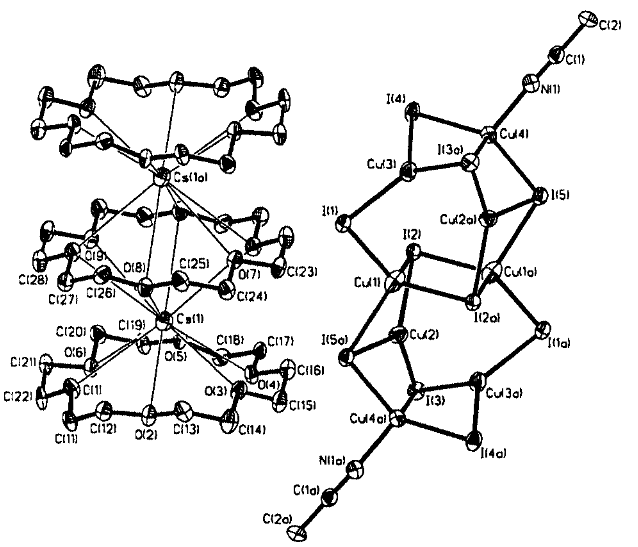


Fig. 2 Molecular structures of the $[Cs_2(18c6)_3]^{2+}$ and $[Cu_8I_{10}(MeCN)_2]^{2-}$ constituting complex **2** (H atoms omitted for clarity).

iodocuprate species (Cu_2I_2 and Cu_3I_3)[9] are present in the structure of the anion. The copper atoms Cu(2) and Cu(3) adopt triangular planar and Cu(1) and Cu(4) tetrahedral coordination (Cu–I 2.512(2)–2.802(2) Å) (Table 4). The tetrahedral environment of Cu(4) is completed by the nitrogen atom of the acetonitrile molecule (Cu(4)–N(1) 1.988(7) Å); this coordination apparently prevents polymerization of the $[Cu_8I_{10}]^{2-}$ units into the usual one dimensional infinite $[Cu_2I_3]^-{}_n$ or $[Cu_3I_4]^-{}_n$ chains.[8a,10]

The cation in complex **2** is a unique example of such a large multidecker 18c6 complex cation being free from disorder or extremely high anisotropy in the thermal motion of the atoms. The Cs···Cs separations of 4.501(3) Å as well as the deviation of the caesium atom from the mean plane of the "central" 18c6 molecule (2.249(1) Å) are greater than those observed for $[Cs_2(18c6)_3][HX_2]_2 \cdot 2HX \cdot 2H_2O$ (X = α-cyanobenzothiazole-α-carbaldehyde oximate)[11] or the "infinite sandwich" $[Cs(18c6)]_\infty^{\infty+}$ [12] (Table 2). Thus the interaction between the Cs ions and the crown ligands in the present structure is somewhat weaker (Cs–O 3.204(5)–3.795(5) Å), than the majority of those listed in Table 2. This may be attributed to the adaptability of the club sandwich structure to steric demands of the anionic counterpart. The geometry of the crown ligand is sensitive to such an elongation of the M–O contacts, the OCCO torsion angles (for the central 18c6 molecule ±59.9(8)–64.8(7)°, average ±61.8(8)°), corresponding to a *gauche* conformation, are less than the usual values of ±65–75°.[7] Both the independent macrocycles have a typical D_{3d} conformation with characteristic C–O and C–C distances of 1.407(9)–1.436(9) and 1.47(1)–1.50(1) Å, respectively.

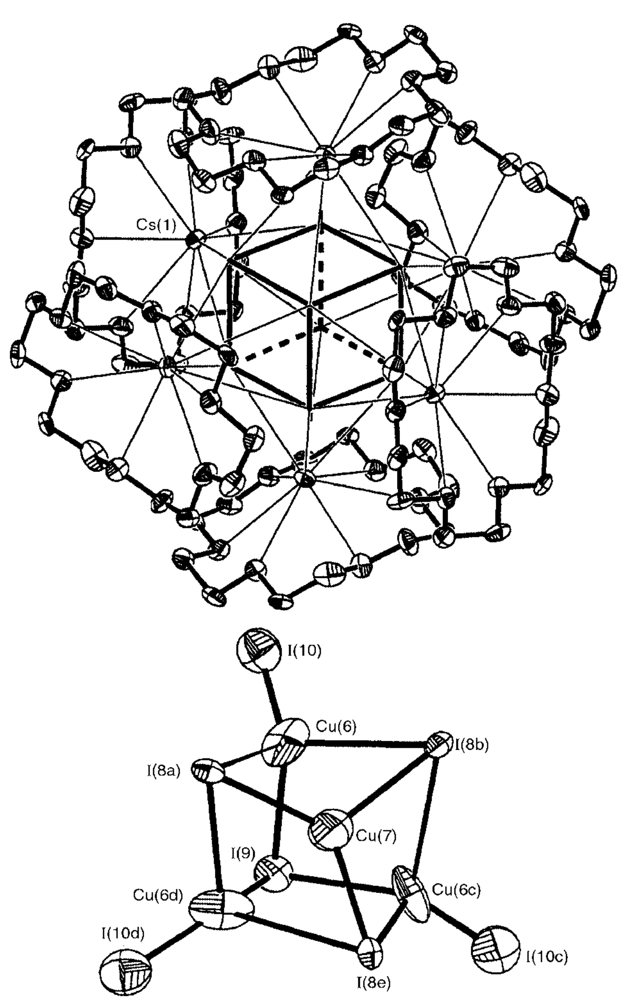


Fig. 3 View of the $[\{Cs(18c6)\}_6Cu_4I_7]^{3+}$ unit in complex **3** (H atoms omitted for clarity), showing the arrangement of six Cs(18c6) around the central iodocuprate(I) core. Also shown at the bottom is one of the two possible orientations of the cubic core.

Crystal structure of complex 3

The structure was modeled to include several different moieties: three iodocuprate(I) clusters $[Cu_4I_7]^{3-}$, $[Cu_7I_{10}]^{3-}$ and $[Cu_{13}I_{14}]^-$, additional iodide anions, novel 3:3 club sandwiches $[Cs_3(18c6)_3]^{3+}$ and the usual half-sandwich encapsulates $[Cs(18c6)]^+$ (Figs. 3 and 4).

The $[Cu_4I_7]^{3-}$ cluster is made up of a copper tetrahedron interlocked with an iodine tetrahedron, plus three iodine atoms bonded to the three metal atoms, and is closely related to the cubane $Cu_4I_4L_4$ archetype[14] (Fig. 3); selected bond parameters are listed in Table 5. All faces of the heterocubane core are remarkably non-planar, their edges are of different length and the least-squares rhombohedral planes of the faces are mutually non-orthogonal. Six caesium atoms, each bound in the sunrise geometry by the crown macrocycle, are positioned at the faces of this virtual cube (Cs–I 3.699(7) and 3.82(1) Å), forming the supramolecular cation $[\{Cs(18c6)\}_6Cu_4I_7]^{3+}$ (Fig. 3). Examples of self-assembled cations in which anions exhibit an unambiguous organizational role are quite rare in the literature, with only a few examples being reported: $[\{K(15\text{-crown-}5)\}_4Br]^{3+}$,[15a] $[\{A(\text{dibenzo-}18c6)\}_3AgX_3]^+$,[15b] and $[\{A(18c6)\}_4$-

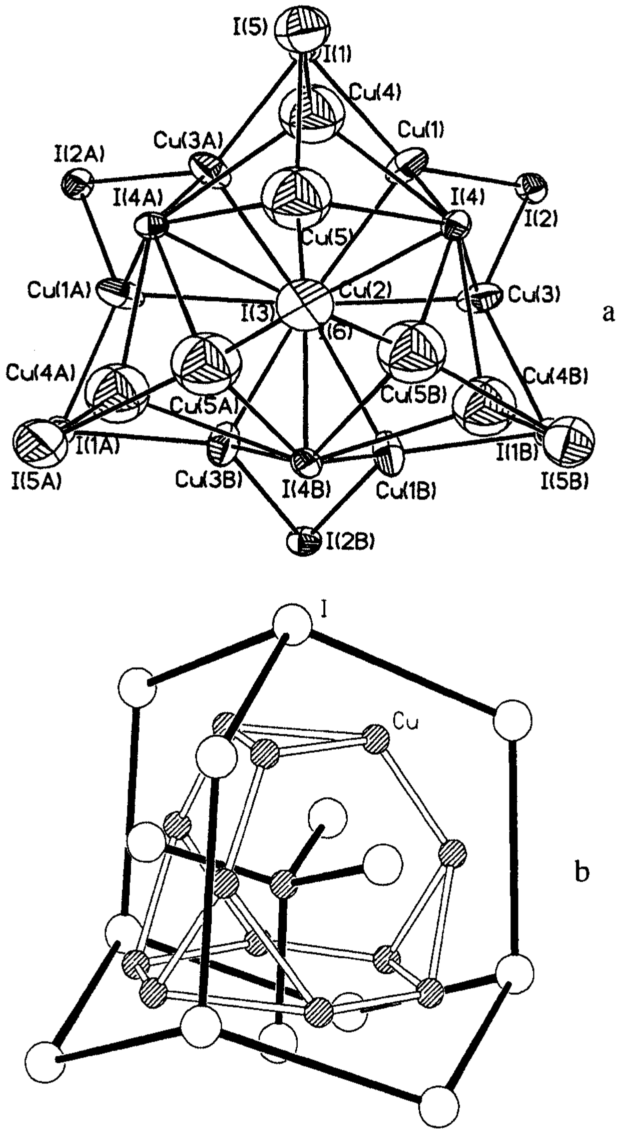


Fig. 4 The arrangement of Cu and I atoms in the $[Cu_{13}I_{14}]^-$ cluster of complex **3**. (a) View of the cluster down the I(6)–Cu(2)–I(3) axis. (b) Truncated tetrahedron of 12 Cu atoms centered around the thirteen copper atom in an "adamantane-like" disposition of 10 iodide atoms; 4 iodide atoms center hexangulated faces of the copper cluster. The lines connecting Cu–Cu and I–I atoms do not represent bonds.

Table 5 Selected bond distances (Å) and angles (°) for iodocuprate(I) clusters of complex **3**[a]

$[Cu_{13}I_{14}]^-$			
Cu(1)–I(1)	2.534(4)	I(4)–Cu(1)–I(3)	98.1(2)
Cu(1)–I(2)	2.602(5)	I(4^1)–Cu(2)–I(4)	112.1(2)
Cu(1)–I(4)	2.692(5)	I(4^1)–Cu(2)–I(4^2)	112.1(2)
Cu(1)–I(3)	3.099(6)	I(4)–Cu(2)–I(4^2)	112.1(2)
Cu(2)–I(4^1)	2.643(3)	I(4^1)–Cu(2)–I(3)	106.7(2)
Cu(2)–I(4)	2.643(3)	I(4)–Cu(2)–I(3)	106.7(2)
Cu(2)–I(4^2)	2.643(3)	I(4^2)–Cu(2)–I(3)	106.7(2)
Cu(2)–I(3)	2.82(1)	I(1^1)–Cu(3)–I(2)	122.1(2)
Cu(3)–I(1^1)	2.540(4)	I(1^1)–Cu(3)–I(4)	117.3(2)
Cu(3)–I(2)	2.636(5)	I(2)–Cu(3)–I(4)	103.8(2)
Cu(3)–I(4)	2.738(5)	I(1^1)–Cu(3)–I(3)	110.8(2)
Cu(3)–I(3)	2.953(6)	I(2)–Cu(3)–I(3)	98.8(2)
Cu(4)–I(5)	2.52(3)	I(4)–Cu(3)–I(3)	100.6(2)
Cu(4)–I(1)	2.57(3)	I(5)–Cu(4)–I(1)	125(1)
Cu(4)–I(4)	2.76(3)	I(5)–Cu(4)–I(4)	105(1)
Cu(4)–I(4^2)	2.93(3)	I(1)–Cu(4)–I(4)	114(1)
Cu(5)–I(5)	2.54(3)	I(5)–Cu(4)–I(4^2)	99.4(9)
Cu(5)–I(6)	2.58(3)	I(1)–Cu(4)–I(4^2)	109.8(9)
Cu(5)–I(4^2)	2.76(3)	I(4)–Cu(4)–I(4^2)	100.7(8)
Cu(5)–I(4)	2.90(3)	I(5)–Cu(5)–I(6)	121(1)
I(1)–Cu(1)–I(2)	125.8(2)	I(5)–Cu(5)–I(4^2)	103.6(9)
I(1)–Cu(1)–I(4)	118.1(2)	I(6)–Cu(5)–I(4^2)	116(1)
I(2)–Cu(1)–I(4)	106.0(2)	I(5)–Cu(5)–I(4)	100.1(9)
I(1)–Cu(1)–I(3)	106.6(2)	I(6)–Cu(5)–I(4)	111.6(9)
I(2)–Cu(1)–I(3)	95.9(2)	I(4^2)–Cu(5)–I(4)	101.6(8)
$[Cu_4I_7]^{3-}$			
Cu(6)–I(10)	2.21(4)	I(9)–Cu(6)–I(8^5)	105(1)
Cu(6)–I(9)	2.60(3)	I(10)–Cu(6)–I(8^4)	105(1)
Cu(6)–I(8^5)	2.92(4)	I(9)–Cu(6)–I(8^4)	102(1)
Cu(6)–I(8^4)	3.03(4)	I(8^5)–Cu(6)–I(8^4)	98(1)
Cu(7)–I(8^4)	2.646(9)	I(8^4)–Cu(7)–I(8^3)	115.6(4)
Cu(7)–I(8^3)	2.646(9)	I(8^4)–Cu(7)–I(8^5)	115.6(4)
Cu(7)–I(8^5)	2.647(9)	I(8^3)–Cu(7)–I(8^5)	115.6(4)
Cu(7)–I(9)	2.96(3)	I(8^4)–Cu(7)–I(9)	102.3(6)
I(10)–Cu(6)–I(9)	125(2)	I(8^3)–Cu(7)–I(9)	102.3(6)
I(10)–Cu(6)–I(8^5)	118(1)	I(8^5)–Cu(7)–I(9)	102.3(6)

[a] Symmetry transformations used to generate equivalent atoms (indicated by superscript): 1 $-y, z-0.5, -x+0.5$; 2 $-z+0.5, -x, y+0.5$; 3 $-x, -y, -z$; 4 $-y, -z, -x$; 5 $-z, -x, -y$.

$MX_4]^{2+}$ (A = monocation, M = 3d element).[15c] Thus in the formation of the $[\{Cs(18c6)\}_6Cu_4I_7]^{3+}$ moiety the $[Cu_4I_7]^{3-}$ anion may be recognized as a templating agent, that possesses the shape, charge and size suitable for the assembly of the bulky crown ether "supercomplex".

The triple decker 3:3 club sandwich $[Cs_3(18c6)_3]^{3+}$ is a novel structural unit; its main geometrical parameters are summarized in Table 2. The Cs(2)$\cdots$Cs(2) $\{-x, -y, 1-z\}$ separation of 4.289(7) Å agrees well with the data for Cs(μ-18c6)Cs systems, while the Cs(2)$\cdots$Cs(3) contact is considerably shorter (3.844(7) Å) and, in fact, is the shortest such separation observed so far in structures of this type.[7] A very short Cs$\cdots$Cs separation of the same nature (3.923(4) Å) was discussed in terms of a "short bond of order zero" for $[Cs_2(18c6)][SO_4(AlMe_3)_3]$.[16]

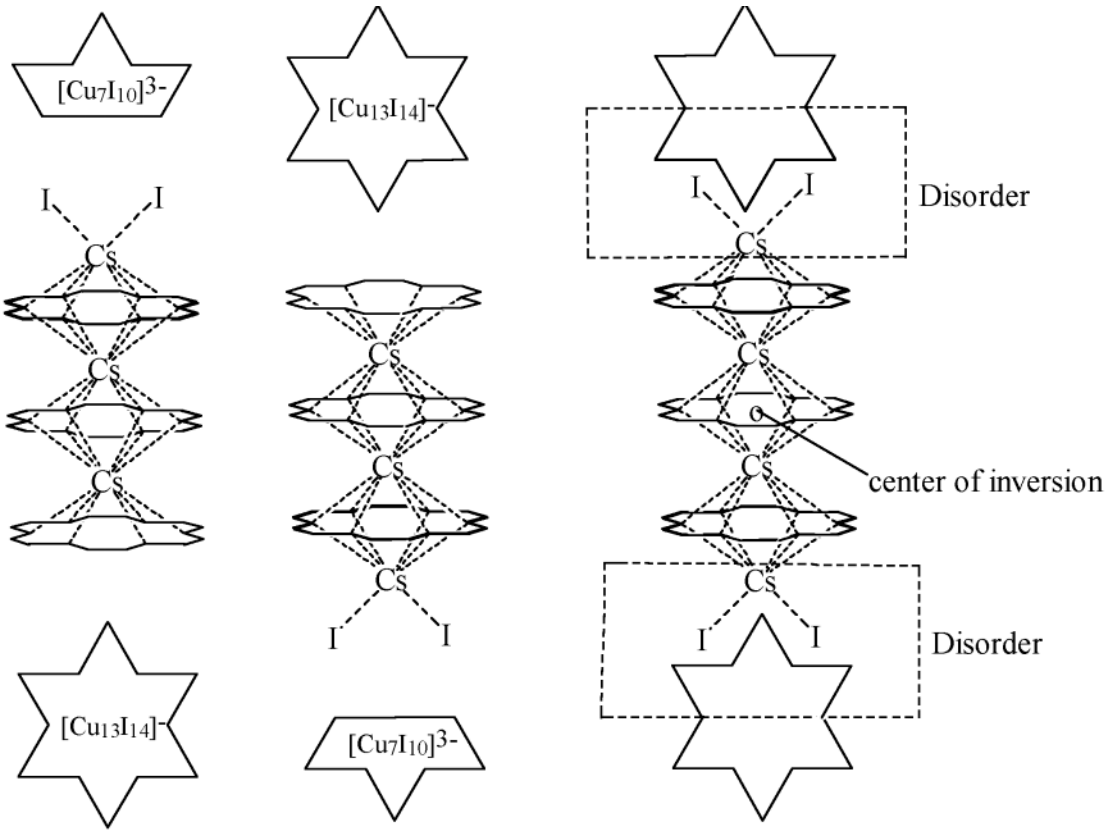
The $[Cs_3(18c6)_3]^{3+}$ cation contains metal atoms on a threefold axis and in the lattice has iodide and iodocuprate(I) anions at both ends along the threefold axis. The anions are related by the operation of an inversion centre, which is located in the centre of the central crown macrocycle. The Cu, I and Cs(3) atoms, that occupy partly populated positions, are disordered in such a way that the "crown" end of the triple decker sandwich is adjacent to the $[Cu_{13}I_{14}]^-$ cluster while the caesium atom at the other end of the cation co-ordinates two iodide anions and abuts with the $[Cu_7I_{10}]^{3-}$ moiety. Thus the smaller cluster $[Cu_7I_{10}]^{3-}$ is a symmetry equivalent of the larger anion $[Cu_{13}I_{14}]^-$. The disorder in the system is illustrated in Scheme 1.

The novel polynuclear iodocuprate(I) cluster $[Cu_{13}I_{14}]^-$ has a nearly perfect spherical structure, in which twelve copper atoms describe a truncated tetrahedron, centered by the thirteenth metal atom (Cu$\cdots$Cu 2.542(6)–3.032(7) Å) (Fig. 4). In the polyhedron all tri- and hex-angulated faces as well as six common edges of the latter ones are centered by iodides, so that ten of the iodide atoms exhibit an "adamantane-like" disposition. The copper atoms adopt tetrahedral co-ordination, six iodide atoms serve as μ_2 bridges (Cu–I 2.52(3)–2.636(5) Å), four as μ_3-bridges (Cu–I 2.534(4)–2.58(3) Å), and four are μ_7 bridges (Cu–I 2.643(3)–3.099(6) Å) (Table 5).

The highest condensed iodocuprate(I) ion observed so far is the $[Cu_{36}I_{56}]^{20-}$ polyanion in the compound $[(Hpy)]_2[Cu_3I_5]$ in which 24 Cu atoms occupy the corners of a cube with octahedral habit, *i.e.* the positions formed by cutting off the corners of a cube; the 12 remaining Cu atoms lie at the middle of the edges of this cube.[17]

Conclusion

This study has demonstrated that interaction of zerovalent copper with ammonium iodide in presence of Cs^+–18c6 cations leads to the formation of iodocuprate(I) species of different



Scheme 1

stoichiometry. This is unlike the Cu–NH$_4$I interaction in the presence of such ligands as pyridine, ethylenediamine, aminoalcohols that usually result in Cu^{2+} co-ordination compounds.[18] It may reasonably be proposed that the intermediate Cu$^+$ oxidation state is stabilized in presence of the Cs$^+$–18c6 moieties in acetonitrile, a solvent which is known to stabilize the Cu$^+$ by itself.[19] The intricate nature of the interaction apparently results in the equilibrium mixture of various iodocuprates(I) present in solution and the overall formation of the solid phase is a template process of mutual stabilization of Cs$^+$ as bulky [Cs$_n$(18c6)$_m$]$^{n+}$ cations and Cu$^+$ as iodocuprate anions.

Despite the complicated molecular architecture of the triple decker club sandwiches [Cs$_n$(18c6)$_3$]$^{n+}$ ($n = 2$ or 3), formation of such complexes, in the light of the present work and our previous publication,[11] should be considered as a general feature of 18-crown-6 co-ordination chemistry.

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