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Novel redox-active ruthenium cluster crown compounds capable of host–guest chemistry

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The new redox-active cluster compounds [$Ru_6C(CO)_{14}(\eta^6$-$C_6H_4C_8H_{16}O_5)$] and [$Ru_6C(CO)_{14}(\eta^6$-$C_6H_4C_{10}H_{20}O_6)$] have been synthesised by direct reaction of the aryl crown ether with the hexaruthenium carbido cluster [$Ru_6C(CO)_{17}$] and display host–guest type behaviour with cations Na^+ and NH_4^+ both spectroscopically and electrochemically.

In continuation of our development of the chemistry of the ruthenium arene clusters based on the Ru_6C unit,[1] we have examined ways of incorporating these redox active units[2] into supramolecular assemblies. Given the wealth of host–guest chemistry involving crown compounds[3] we elected to concentrate our initial investigations into this area with a view to examining the molecular sensor behaviour of the new materials. Furthermore, incorporation of such recognition characteristics (*e.g.* for RNH_3^+) in the cluster unit, may lead to several applications wherein these metal-rich domains may be directed on surfaces or large biomolecules with appropriate functionality on the nanoscale. Herein we would like to report: (i) the synthesis and characterisation of two new crown ether cluster compounds [$Ru_6C(CO)_{14}(\eta^6$-$C_6H_4C_8H_{16}O_5)$] **2** and [$Ru_6C(CO)_{14}$-(η^6-$C_6H_4C_{10}H_{20}O_6$)] **3** containing an electronic link between the redox-active cluster core and the receptor site; (ii) the structural characterisation of the model host–guest complex [$Ru_6C(CO)_{14}$-(η^6-$C_6H_4C_{10}H_{20}O_6$)]·NH_4PF_6 **3**·NH_4^+ in the solid state, thus establishing the host capabilities of **3**; (iii) the pronounced redox activity of **3** alone and in the presence of guests Na^+ and NH_4^+.

Our synthetic approach to the target compounds is novel for arene cluster chemistry in that it involves the direct thermolytic reaction of the *fully aromatised arene* with the preformed cluster [$Ru_6C(CO)_{17}$] **1** (*cf.* ref. 1 for previous synthetic routes). Thermolysis of **1** in the presence of excess benzo-15-crown-5 or benzo-18-crown-6 in di-*n*-butyl ether for 4.5 h gave a dark red-brown solution together with a small amount of dark precipitate. After cooling, the reaction mixture was initially passed through a short silica column using dichloromethane as eluent and the resulting brown-red solution reduced to dryness *in vacuo*. After separation by TLC the fully developed plates showed three distinct bands corresponding to unreacted **1**, the brown compounds **2** or **3** and unstable red materials **2a** or **3a**.

Preliminary characterisation ‡ of **2** and **3** was achieved on the basis of their solution infrared spectra in dichloromethane, which showed absorptions in the ν_{CO} region typical of an η^6-co-ordinated arene together with absorptions in the ν_{ether} region. Positive-ion fast atom bombardment mass spectra revealed parent ions (Found: $m/z = 1280$. Calc. for **2**: $m/z = 1279$. Found: $m/z = 1324$. Calc. for **3**: m/z 1323) and ions corresponding to the sequential loss of up to 14 carbonyl fragments. An additional peak was found at $m/z = 1302$ for **2** and is attributable to a Na^+ adduct.§ The fractions **2a** and **3a** were isolated in low yields and in each case appeared to consist of several isomers (shown by broad bands on the TLC plate and complex IR spectra). These materials are unstable and readily disproportionate in dry degassed solvents at ambient temperature to starting materials and product. Bearing in mind the possible co-ordinative diversity and relative instability of the Ru^0–OR_2 bond, it is tempting to suggest that **2a** and **3a** are intermediates wherein the cluster is co-ordinated to the ligand *via* the ether oxygens. Compounds of a similar nature have been isolated in well established reactions of Group 6 metal carbonyls with triglyme [CH_3-($OCH_2CH_2)_3OCH_3$].

The solid-state molecular structure of **3**·NH_4^+ is shown in Fig. 1 along with some key structural parameters as determined by single-crystal X-ray diffraction.¶ The asymmetric unit of the host–guest complex **3**·NH_4^+ contains one molecule. The arene ring is co-ordinated η^6 to a single ruthenium atom, and the interstitial carbon is displaced slightly from the centre of the ruthenium octahedron towards the arene ring. There is one bridging carbonyl ligand, spanning two ruthenium atoms adjacent to the arene ring. The oxygen atoms in the macrocyclic ring remain approximately planar (mean deviation 0.186 Å). This plane lies at an angle of 27.2° to the arene ring which bonds the macrocycle to the cluster. The catecholic oxygen conformational characteristics tend to suggest that the lone pairs on the oxygens interact with some arene carbons, thereby, producing an electronic link[4] between the receptor site and the redox-active cluster core.

The ammonium ion can be clearly seen to act as a guest within the macrocyclic cavity. The nitrogen atom lies 0.805(16) Å above the average plane of the oxygen atoms, with three of the hydrogen atoms (refined riding on the N atom which was

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‡ Spectroscopic data for **2**. IR (CH_2Cl_2/cm^{-1}): ν(CO) 2074m, 2030w (sh), 2022vs, 1979w (br), 1808w (br); ν(COC) 1269s, 1257s. ^{1}H NMR ($CDCl_3$): δ 5.66 (m, 2 H), 5.02 (m, 2 H), 3.5–4.2 (m br, 16 H) (Found: $Ru_6C(CO)_{14}C_6H_4C_{18}H_{16}O_5·CH_2Cl_2$: C, 28.05; H, 1.66. Calc. for **2**·CH_2Cl_2: C, 28.04; H, 1.71%).

Spectroscopic data for **3**. IR (CH_2Cl_2/cm^{-1}): ν(CO) 2073m, 2045w (sh), 2031w (sh), 2022vs, 1982w (br), 1811w (br); ν(COC) 1272s, 1258s. ^{1}H NMR ($CDCl_3$): δ 5.65 (m, 2 H), 5.02 (m, 2 H), 3.5–4.2 (m br, 20 H) (Found: $Ru_6C(CO)_{14}C_6H_4C_{10}H_{20}O_6·CH_2Cl_2$: C, 27.3; H, 1.86. Calc. for **3**·CH_2Cl_2: C, 27.5; H, 1.87%).

§ This would require scavenging of the alkali metal from some part of the work up. The silica plates used for the separation, for instance, have an appreciable sodium content (up to 200 ppm according to the suppliers Merck). In a further experiment solutions of **2** and **3** were treated with several alkali metal (Na^+, K^+ or Cs^+) and ammonium salts (NH_4^+ or $Bu^tNH_3^+$), after separation FAB$^+$ mass spectra were taken, which revealed peaks in each case corresponding to host–guest pairing

¶ Crystal data for **3**·NH_4^+: $C_{34.5}H_{32}F_6NO_{20}Ru_6$, $M = 1532.00$, monoclinic, space group $P2_1/c$, $a = 9.608(2)$, $b = 17.071(2)$, $c = 28.633(4)$ Å, $\beta = 95.806(14)°$, $U = 4672.2(12)$ Å^3, $Z = 4$, $\mu = 2.024$ mm^{-1}, $T = 220(2)$ K. $R1$ [$= F > 4\sigma(F)$] (5460 data) and $wR2$ (all data) are equal to 0.0545 and 0.1223, respectively. The H atoms were placed in calculated positions and allowed to refine riding on their respective atoms. The lattice contains a disordered toluene solvate molecule (one half per asymmetric unit in two orientations with equal occupancy). CCDC reference number 186/1031.

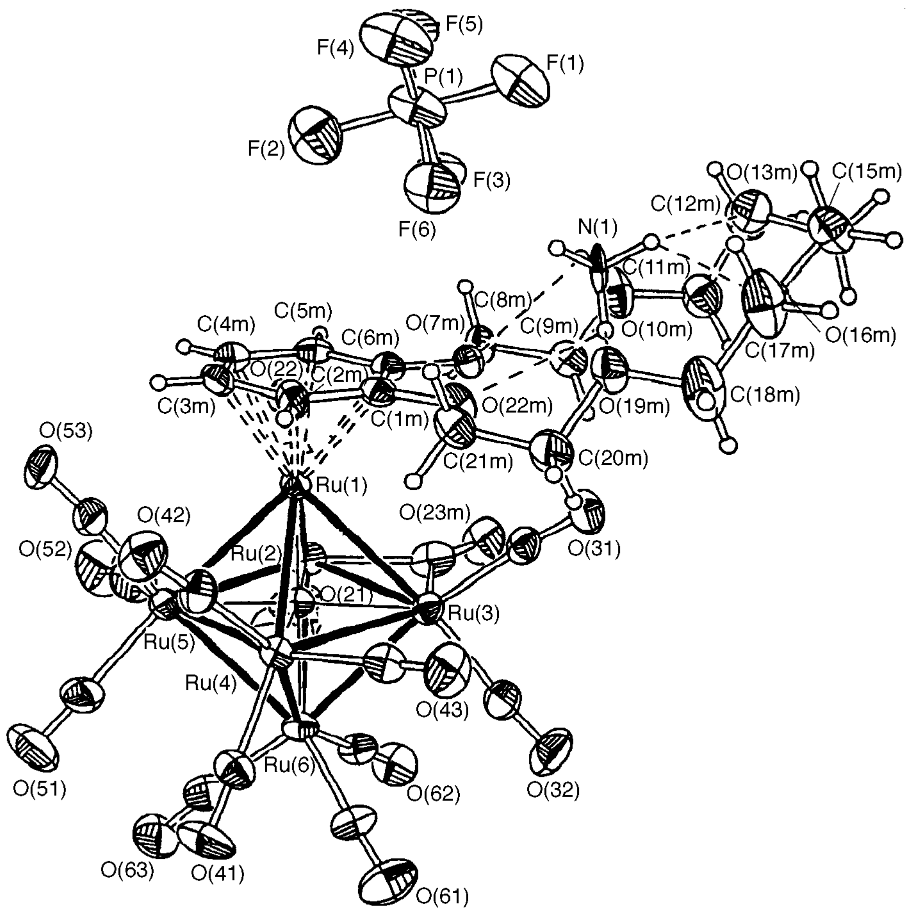

Fig. 1 The solid-state molecular structure of $3{\cdot}NH_4^+$ with important interatomic distances (Å): Ru(1)–C(1m) 2.288(9), O(7m)–N(1) 2.94(2), Ru(1)–C(2m) 2.246(9), O(10m)–N(1) 2.84(2), Ru(1)–C(3m) 2.216(10), O(13m)–N(1) 2.80(2), Ru(1)–C(4m) 2.203(10), O(16m)–N(1) 2.79(2), Ru(1)–C(5m) 2.255(9), O(19m)–N(1) 2.87(2), Ru(1)–C(6m) 2.291(9), O(22m)–N(1) 3.02(2), C(1m)–C(2m) 1.397(13), N(1)–F(1) 3.05(2), C(2m)–C(3m) 1.420(12), N(1)–F(3) 3.07(2), C(3m)–C(4m) 1.416(14), N(1)–F(6) 2.96(2), C(4m)–C(5m) 1.388(14), C(5m)–C(6m) 1.390(14), C(6m)–C(1m) 1.417(13)

allowed to rotate as a rigid body) interacting with two oxygen atoms each, and the remaining hydrogen directed towards the counter ion. The N atom is shifted significantly away from the slightly electron-deficient catecholic oxygens and toward the four remaining ether oxygens by *ca.* 0.15 Å, this is contrary to the observations of Truter and co-workers[5] who found roughly equal N···O distances in a comparable system wherein the arene ring was not co-ordinated. The aliphatic methylene groups of the crown in $3{\cdot}NH_4^+$ are orientated such that they encircle a carbonyl oxygen. This serves to support the normally conformationally mobile crown ether oxygens in an orientation resembling that observed in benzo-crown compounds bound to cationic guests. At the same time such an *intra*molecular interaction may enhance the selectivity of the host compound by inhibiting co-ordination with larger guests.[6]

An examination of the redox chemistry[||] of **3** [Fig. 2(a)] revealed an expected irreversible two-electron reductive wave at −0.91 V with a daughter peak on the oxidative sweep at −0.17 V. The peak shapes and relative intensities of both the two-electron reductive and daughter peaks are very similar to those observed for the parent cluster $[Ru_6C(CO)_{17}]$ and $[Ru_6C(CO)_{14}R]$ (R = arene) in which concomitant CO expulsion is observed with a reductive process.[2] The reduction product of **3** has also been synthesised by chemical reduction with sodium naphthalide and isolated as $[Ru_6C(CO)_{13}(\eta^6\text{-}C_6H_4C_{10}H_{20}O_6)]^{2-}$.[7] Precise addition of the salts NH_4BF_4 and $NaBF_4$ to the electrolyte solution containing a known amount of **3** produced a marked change in the position of the reduction wave, in particular the appearance of a new peak significantly anodically shifted in both cases. Cyclic voltammograms for these two experiments are shown in Figs. 2(b)–2(d). The cyclic voltammograms obtained during the addition of the Na^+ ion to the electrolyte show the gradual evolution of a second peak at −0.66 V which corresponds to a large anodic shift (*ca.* 250 mV) of the reduction potential of **3** [Fig. 2(b)]. This may be ascribed to the formation of a simple host–guest complex between the cluster's pendant crown ether and the alkali metal cation. The corresponding experiment wherein ammonium ions were added to the electrolyte also gave a new peak (−0.65 V) corresponding to a host–guest complex of the $3{\cdot}NH_4^+$ type when the ratio of the two components was unity or more [Fig. 2(c)]. However, when the total amount of ammonium ions was less than that of the host cluster **3** a second new peak was observed at −0.78 V [see Fig. 2(d)] which may correspond to a dimer in which two crown ether moieties complex a single ammonium ion.[**]

In this work we have been able to show that hexaruthenium

[||] Electrochemical experiments were carried out using a DSL 286-D PC with General Purpose Electrochemical System (GPES) Version 3 software coupled to an Autolab system containing a PSTAT 10 potentiostat. A conventional three-electrode cell was employed with Pt counter and micro-working electrodes and Ag–AgCl reference electrode against which the Fc–Fc^+ couple was measured at +0.55 V. All electrochemical experiments were performed in 0.5 M tetrabutylammonium tetrafluoroborate solution in CH_2Cl_2 under an atmosphere of dry oxygen-free argon. All cyclic voltammograms were recorded at a scan rate of 200 mV s^{-1} save the experiment on **3** alone (50 mV s^{-1}).

[**] In a similar experiment to those detailed above using the cluster **1** no significant shift in the reduction potential was observed on addition of either alkali metal or ammonium cations. This serves to show that the observed electrochemical behaviour of **3** in the presence of NH_4^+/Na is a direct consequence of host–guest type complex formation in solution.

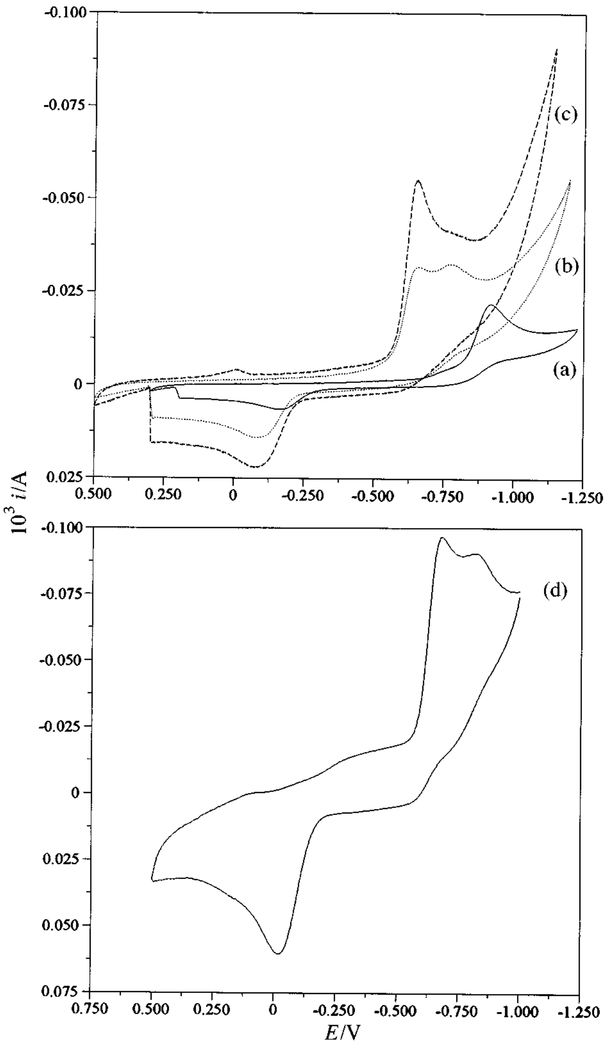

Fig. 2 Cyclic voltammogram of (a) **3**, (b) **3** in the presence of 0.6 equivalent NH_4BF_4, (c) **3** in the presence of 1.0 equivalent NH_4BF_4, and (d) **3** in the presence of 0.8 equivalent $NaBF_4$

clusters may be derivatised such that they may participate in host–guest chemistry. We are presently undertaking a range of related experiments to elucidate the nature of the host–guest interactions (including binding constants and selectivity) with these and other cluster derivatised compounds in solution and at surfaces with a view to constructing highly ordered nanostructures containing metal-rich domains.

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