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COMMUNICATION

A new supramolecular macrocyclic host incorporated with ruthenocene ionosphere-synthesis and X-ray crystal structure of *N,N′,N″*-tris(ruthenocenylmethyl)-1,4,7-triazacyclononane perchlorate

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Abstract—The supramolecular host molecule *N,N′,N″*-tris(ruthenocenylmethyl)-1,4,7-triazacyclononane perchlorate [LH] ClO_4 was prepared and its molecular structure was determined by single crystal X-ray analysis. The guest proton was localized on one of the aza atoms of the macrocycle (N—H : 0.71 Å). Cyclic voltammetric measurement displays an irreversible oxidation wave at 0.84 V and is attributable to the oxidation of Ru^{II} to Ru^{III} of the appended metallocenes. © 1997 Elsevier Science Ltd

Keywords: ruthenocene; tacn; protonation; molecular structure; supramolecular host.

Design of supramolecular host–guest macrocyclic receptor molecules that comprise redox active ionophores in the confines of a molecular cavity is an area of intensive interest especially in mimicking bioinorganic recognition processes, producing molecular sensors for certain ions (including DNA) and redox catalysts [1]. Polyaza [2], polythio [3], polyoxo [4], polyazapolyoxo [5] macrocycles incorporated with one or more ferrocene moieties have been employed for such purposes. Little is known, however, about the corresponding role played by ruthenocene as redox-active centre [6]. In this communication we report the synthesis, characterisation and molecular structure of a new polyazamacrocyclic receptor incorporating three redox-active ruthenocenes.

Refluxing of equal molar of 1,4,7-triazacyclononane (tacn) with *N,N′,N″*-trimethyl,*N*-ruthenocenylammonium iodide [7] in degassed water for six hours produced a brown precipitate (Scheme 1). Filtration and recrystallisation of this brown precipitate from acetonitrile/methanol mixture in the presence of sodium perchlorate afforded the title complex [LH]ClO_4 based on spectroscopic and elemental analysis.†

The infrared spectrum of the complex recorded a strong absorption at 3095 cm^{-1}. In addition, an intense peak at 862 a.m.u. [corresponds to $\{LH\}^+$] appeared in the ESI mass spectrum of the complex. Both findings suggest that the complex was isolated in the protonated form with the guest proton coordinated to one of the aza atoms of the macrocycle and this is ascribed to the high stability of the $[tcanH]^+$ cation [8]. Existence of the guest is confirmed by a structural analysis of the complex (*vide infra*). Noticeably, the ^1H NMR signal corresponding to the α-H

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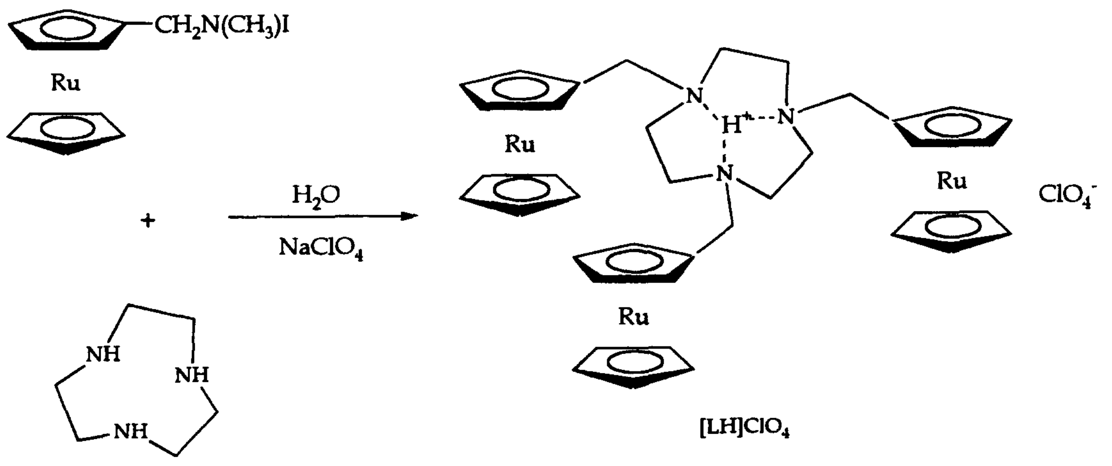
† Spectroscopic data: IR (KBr disk) 3095, 2925, 1540, 1457, 1087, 807 and 624 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.65 (t, 6H), 4.57 (m, 21H), 3.43 (s, 6H), 2.70 (s, 12H); ESI mass spectroscopy 863.5 (M—ClO_4), 618.7 (M—ClO_4—$RcCH_2$) Elemental analysis Found: C 48.2, H 4.7, N 4.1. Calc. for $C_{39}H_{46}ClN_3O_4Ru_3$: C 48.7, H 4.8, N 4.4%.



Scheme 1. The formation of $[LH]ClO_4$.

on the substituted ring (δ 4.65) is somewhat deshielded compared to that of the parent metallocene (δ 4.50). This can be rationalized by the electron-withdrawing character of the positively charged substituent $[tacnH]^+$.

Figure 1 shows a perspective view of the cation of

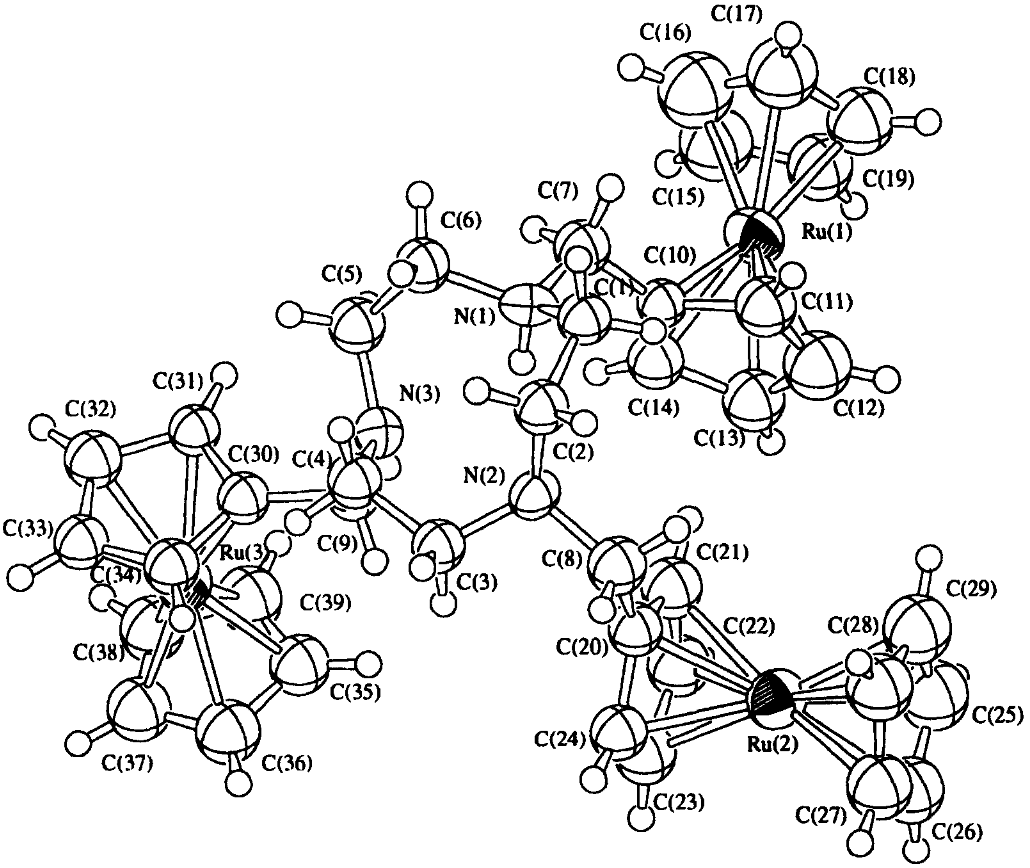


Fig. 1. A perspective drawing of $[LH]^+$, showing the numbering scheme for the atoms. Selected bond distances (Å) and angles (°): Ru(1)—Cp(1) 1.808, Ru(1)—Cp(2) 1.820, Ru(1)—$C_{Cp(1)}$ average 2.164(1), Ru(1)—$C_{Cp(2)}$ average 2.176(1), C(20)—C(21) 1.42(2), C(27)—C(28) 1.40(2), C(8)—C(20) 1.51(2), C(7)—C(10) 1.45(2), C(8)—N(2) 1.45(2), C(7)—N(1) 1.50(2), N(1)—C(6) 1.52(1), N(1)—C(1) 1.50(1), N(2)—C(2) 1.46(1), N(2)—C(3) 1.46(1), N(3)—C(4) 1.46(1), N(3)—C(5) 1.45(1), Cp(1)—Ru(1)—Cp(2) 174.96, N(2)—C(8)—C(20) 113(1), C(2)—N(2)—C(8) 113(1), C(3)—N(2)—C(8) 112(1). [The cyclopentadiene rings are labelled as Cp(1) (substituted ring) and Cp(2) (unsubstituted ring)]

$[HL]ClO_4$ which reveals the twist-boat-chair configuration of the tacn moiety.* The three ruthenocene units lie well below the plane defined by N(1)—N(2)—N(3) which is slightly twisted with respect to the plane defined by Ru(1), Ru(2) and Ru(3) (dihedral angle = 14.9°). The guest proton is located by the difference Fourier synthesis which is bonded to N(1) by 0.71 Å. This unique environment is also manifested in the elongated average C—N bond distance near N(1) [1.51(1) Å] as compared to those of N(2) [1.46(1) Å] and N(3) [1.45(2) Å] respectively. However, the ^1H NMR spectrum gives rise to a singlet for the ethylene protons of the tacn ligand, which implies that the guest proton may delocalize among the three aza nitrogen atoms in solution. The distances from Ru to the centroid of the unsubstituted Cp ring (1.814–1.821 Å) are slightly longer than those to be bonded to the [tacnH]-substituted counterparts (1.794–1.808 Å).

Cyclic voltammetric measurement of the complex in acetonitrile with Bu_4NBF_4 as the supporting electrolyte shows an irreversible process. The anodic wave at 0.84 V is attributed to the oxidation of Ru^{II} to Ru^{III} and is more positive than that of ruthenocene (0.78–0.80 V) [9]. Changing the scan rate from 50 to 1000 mV s^{-1} results in an anodic shift of the potential from 0.75 to 0.89 V. Such irreversibility has also been observed in the electrochemical studies of some derivatives of ruthenocene [10]. Such unusual perturbation of the oxidation potential to scan rate may imply there is a time-dependent process, such as solvation since a coordinative solvent molecule can stabilise the oxidized product and make it less susceptible to reduction.

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*Crystal data: $Ru_3ClO_4N_3C_{39}H_{46}$ M = 959.47, monoclinic, space group $P2_1/n$ (No. 14), $a = 17.152(5)$, $b = 10.226(3)$, $c = 22.752(7)$ Å, $\beta = 111.24(6)°$; $V = 3719(2)$ Å^3, $Z = 4$, $D_c = 1.713$ g cm^{-3}, $F(000) = 1928$, $\lambda = 0.71073$ Å, $T = 298$ K, $\mu(\text{Mo-}K_\alpha) = 13.19$ cm^{-1}. Intensity data were collected on a Rigaku AFC7R diffractometer. Of a total of 5386 reflections collected, 5186 were unique and 2732 were considered as observed [$I > 3.00\sigma(I)$]. The structure was solved by a combination of direct methods and difference Fourier synthesis and refined by full-matrix least-squares procedures on F. Final $R = 0.055$, $R_w = 0.055$. Ru, Cl, O and N atoms were refined anisotropically. Hydrogen atoms were placed at their idealised position (C—H, 0.95 Å) except hydrogen attached to N(1) which is located by a difference Fourier technique. All calculations were performed on a Silicon-Graphics Computer with software package TEXSAN [11]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC).