

Macrocyclic complexes of the platinum metals

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Abstract — The synthesis and redox properties of a range of platinum metal complexes incorporating poly-aza and poly-thia macrocyclic ligands are described. The insertion of palladium(II), rhodium(III), iridium(III) and ruthenium(II) into tetra-aza macrocycles (L) has been achieved, and the structures of octahedral complexes incorporating mutually *cis* chloro-hydride ($[\text{IrCl}(\text{H})(\text{L})]^+$) and chloro-carbonyl ($[\text{RuCl}(\text{CO})(\text{L})]^+$) moieties are discussed in relation to the conformational characteristics of the coordinated macrocyclic ligand. Square planar complexes of palladium(II), $[\text{Pd}(\text{L})]^{2+}$, can be reduced electrochemically to afford highly reactive palladium(I) species. The potential of the palladium(II)/(I) redox couple is found to be dependent upon the degree of N-alkylation of the macrocycle. The synthesis, structures and redox properties of the homoleptic hexa-thia complexes $[\text{M}(\text{L})_2]^{x+}$ (L = 1,4,7-trithiacyclononane; M = Pd, Pt, Rh, Ir, Ru, Os; x = 2 or 3) are described. The stereochemical and electronic properties of these products are related to the ability of these poly-thia crown ligands to stabilise mononuclear platinum(III), palladium(III) and rhodium(II) species. These results are compared to the structural and redox chemistry of the homoleptic complexes of 1,4,8,11-tetrathiacyclotetradecane and 1,4,7,10,13,16-hexathiacyclooctadecane. A range of mixed sandwich carbocyclic-macrocyclic complexes $[\text{M}(\text{C}_5\text{Me}_5)(\text{L})]^{2+}$ (M = Rh, Ir) and $[\text{M}(\text{arene})(\text{L})]^{2+}$ (M = Ru, Os) (L = 1,4,7-triazacyclononane, N,N',N''-trimethyl-1,4,7-triazacyclononane, 1,4,7-trithiacyclononane) have been synthesised, and the redox properties of these organometallic derivatives assessed. With larger tetra- and hexa-thia macrocycles binuclear platinum metal complexes can be prepared.

INTRODUCTION

The protection and blocking of certain coordination sites at a metal centre with the simultaneous incorporation of specific, coordinatively labile positions is crucial in the design of catalytically active metal complexes. This is usually linked to the use of protecting ligands which can be stereochemically, electronically and/or chirally tuned to the requirements of the metal centre and the catalytic process.

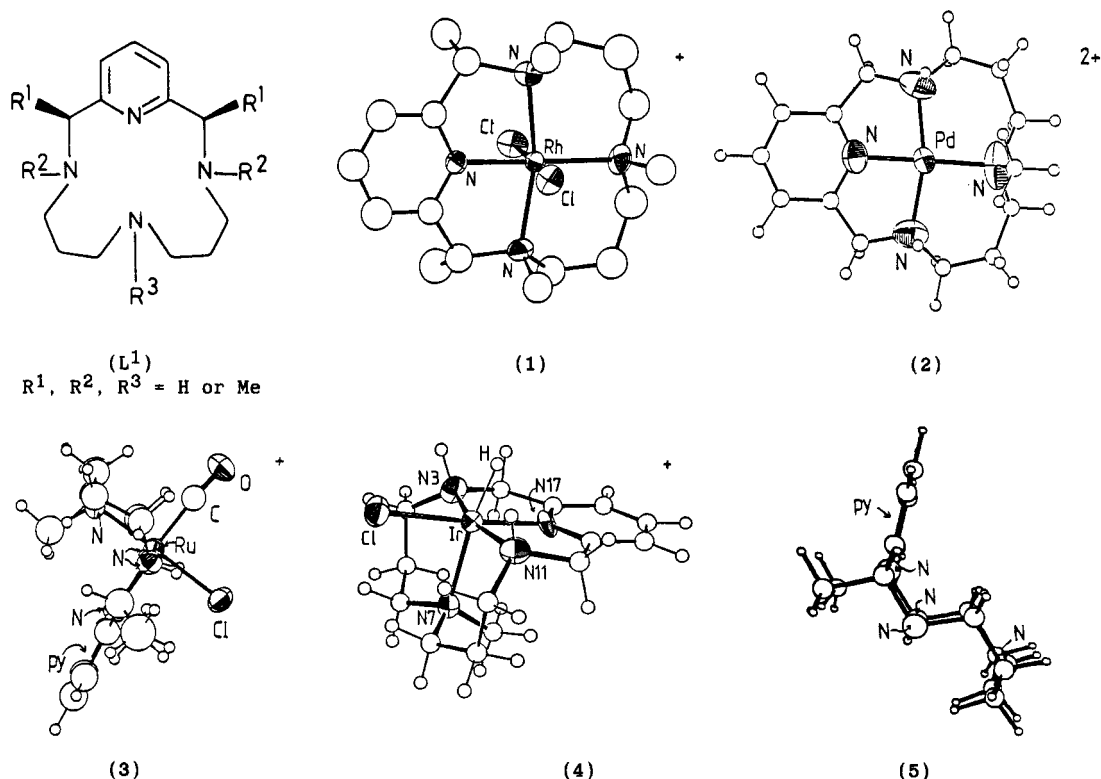
Macrocyclic ligands are well-known to form thermodynamically stable and kinetically inert complexes and may therefore be regarded as protecting groups for metal ion centres. This parallels the role of cyclopentadienyl and aryl ligands in traditional organometallic chemistry. The vast majority of transition metal macrocyclic complexes are of the first row series reflecting the many versatile routes to their synthesis and their importance in biomimetic and catalytic chemistry. The general paucity of non-porphyrinoid second and third row analogues and the potential for such products to show multi-redox and catalytic behaviour, has led us to initiate a programme on the synthesis and chemistry of macrocyclic complexes of the platinum group metals.

We have initiated a series of studies on the chemistry of platinum metal complexes incorporating small to large ring poly-aza and poly-thia macrocyclic ligands thus generating a range of stereochemically and electronically controlled metal systems.

POLY-AZA COMPLEXES

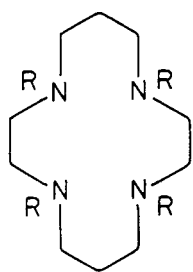
In general, the preparation of first row transition metal macrocyclic complexes can be readily achieved using template synthesis around a central metal ion(s), by direct metal insertion into a pre-formed ligand, or via transmetallation reactions (ref. 1). Template syntheses around more kinetically inert metal ions such as those of the second and third row transition series are generally unsuccessful due to the relative stability of the

intermediates formed in the template process. The synthesis of platinum metal macrocyclic complexes is therefore often restricted to the insertion of metal substrates into the pre-formed, metal-free ligands. Using this technique, we have synthesised (ref. 2) a series of Ru, Os, Rh, Ir, Pd and Pt complexes incorporating pyridyl N_4 macrocycles of general type (L^1 ; $R^1, R^2, R^3 = H$ or Me). Thus, reaction of $RhCl_3$ or $Pd(OAc)_2$ with (L^1) in CH_3OH or CH_2Cl_2 respectively affords the complex cations *trans*- $[RhCl_2(L^1)]^+$, (1; $R^1 = R^2 = R^3 = Me$), and $[Pd(L^1)]^{2+}$, (2; $R^1 = R^2 = H, R^3 = Me$). The single crystal X-ray structures of these products show equatorial coordination of the tetra-aza macrocycle to the metal centres. In contrast, the species *cis*- $[RuCl(CO)(L^1)]^{2+}$, (3; $R^1 = R^3 = Me, R^2 = H$), ($Ru-Cl = 2.422, Ru-C = 1.830\text{\AA}$) (ref. 2) and *cis*- $[IrCl(H)(L^1)]^+$, (4; $R^1 = R^2 = H, R^3 = Me$), ($Ir-Cl = 2.393, Ir-H = 1.57\text{\AA}$) show the macrocyclic ligand to adopt a folded conformation with the chloro-carbonyl and chloro-hydride moieties mutually *cis* to one another. The folded conformation of the coordinated tetra-aza ligand in (3) and (4) is similar to the conformation of the metal-free ligand (5; $R^1 = Me, R^2 = R^3 = H$) observed in the solid state, with the pyridyl ring in the free ligand making a dihedral angle of 65.6° to the least squares N_4 plane (see also ref. 3). Poon and co-workers have postulated the intermediacy of metal hydrido species in the synthesis of related complexes (ref. 4). The coordinative flexibility of (L^1) can therefore be utilised to generate mutually *trans* labile sites (as in (1)) or *cis* labile sites (as in (3) and (4)). These complexes represent an important new class of macrocyclic coordination compounds containing a pyridyl moiety.

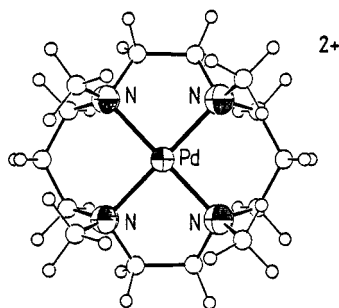


We have investigated the redox properties of these, and related, tetra-aza complexes using electrochemical techniques. The square planar Pd(II) complexes of tetramethylcyclam (L^2 , tmc) and related N_4 donor saturated ligands show a reversible reduction by cyclic voltammetry in CH_3CN . The degree of reversibility of these reductions is found to increase with increasing N-alkylation, with the redox potentials occurring at less negative potentials with increasing N-alkylation. Meyerstein and co-workers have reported similar observations on the stabilisation of Ni(I) and Cu(I) by tetra-aza macrocycles (ref. 5). Cyclic voltammetry of $[Pd(L^2)](PF_6)_2$ ($L^2 = tmc$; (6), Pd-N = 2.051, 2.066 \AA) in CH_3CN at platinum electrodes shows a fully reversible reduction at $E_{1/2} = -1.53V$. vs Fc/Fc^+ , $\Delta E_p = 65mV$, $I_{pa}/I_{pc} = 1.0$, at a scan rate of $100mV.sec^{-1}$. Controlled potential electrolysis of $[Pd(L^2)]^{2+}$ at a platinum gauze in CH_3CN at $-1.65V$. under a stream of Ar at $20^\circ C$ affords a highly air-sensitive, reactive species which can be assigned by esr spectroscopy to a d^9 Pd(I) species $[Pd(L^2)]^+$ (measured at 77K as a frozen glass; $g_{\parallel} = 2.302, g_{\perp} = 2.076$ with hyperfine coupling to $^{105}Pd, I = \frac{5}{2}, 22.2\%, A_{\parallel} = 53G, A_{\perp} = 40G$) (ref. 6). This is one of the first examples of stabilisation of a genuine mononuclear Pd(I) species (ref. 7). The complex $[Pd(L^3)](PF_6)_2$, (7), likewise shows a reversible reduction but at a more positive potential, $E_{1/2} = -1.27V$. vs Fc/Fc^+ in CH_3CN . The corresponding Pd(I) species can be generated and identified by esr spectroscopy. The single crystal X-ray structures of (6) and (7) show both these Pd(II) complexes to have square planar stereochemistries with the functionalised

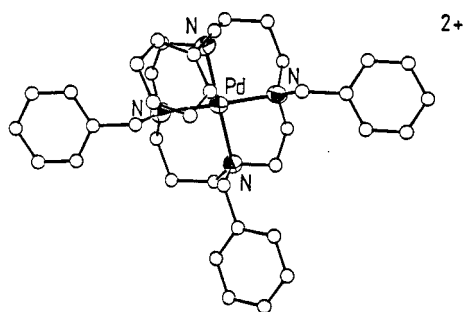
macrocyclic ring adopting an R.S.R.S. conformation in each case...that is, with the methyl or benzyl functions lying on the same side of the PdN₄ plane. Interestingly, the structure of (7) shows a tetrahedral distortion at the Pd(II) ion with one of the phenyl groups twisting around to sit above a five membered chelate ring of the coordinated macrocycle.



(L²) R = Me
(L³) R = CH₂Ph

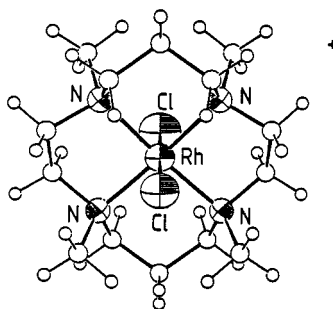


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(7)

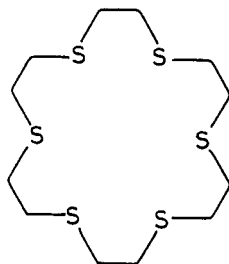
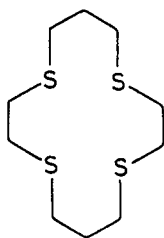
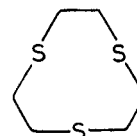
Reaction of RhCl₃ with (L²) in MeOH affords *trans*-[RhCl₂(L²)]⁺, (8), which shows an R.S.S.R. conformation with two methyl groups above and two methyl groups below the RhN₄ coordination plane. The complex shows a quasi-reversible Rh(III)/(II) couple in CH₃CN at E_{1/2} = -0.99V vs Fc/Fc⁺. Quantitative reduction of the Rh(III) species at -1.1V affords a reactive Rh(II) intermediate which loses Cl⁻ to yield a five coordinate or solvated species.



(8)

POLY-THIA COMPLEXES

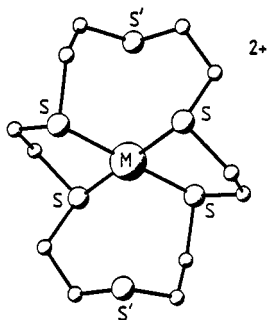
Parallel to the above studies on tetra-aza ligand binding, we have been investigating the complexation of the platinum group metals by the poly-thia crown ligands 1,4,7,10,13,16-hexathiacyclooctadecane (L⁴), 1,4,8,11-tetrathiacyclotetradecane (L⁵) and 1,4,7-trithiacyclononane (L⁶). It has been shown previously that the potentially hexadentate

(L⁴)(L⁵)(L⁶)

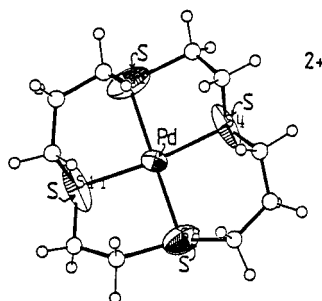
ligand (L⁴) (the thia analogue of 18-crown[6]) readily binds first row transition metal ions such as Ni(II), Co(II) and Cu(II) to give octahedral complexes (ref. 8); the structures of these complexes were subsequently confirmed by diffraction studies (ref. 9, 10). These ligands are attractive since they would be expected to bind very effectively to the relatively soft second and third row metal ions and lead to the formation of homoleptic thioether complexes. No work had been published previously on the coordination of (L⁴) and (L⁶) to platinum metal ions, and we reasoned that the effect of inserting large metal ions

into such ionophores would lead to products that might exhibit unusual stereochemical, electronic and redox properties.

Reaction of PdCl_2 or PtCl_2 with (L^4) gave 1:1 products $[\text{M}(\text{L}^4)]^{2+}$ ($\text{M} = \text{Pd}, \text{Pt}$), (9). The single crystal X-ray structures of these complexes confirm square planar coordination of four thia donors of (L^4) to the metal ions ($\text{Pd-S} = 2.309$, $\text{Pt-S} = 2.296\text{\AA}$) with the two remaining sulphur donors of (L^4) being essentially non-bonded; $\text{Pd-S}' = 3.273$, $\text{Pt-S}' = 3.380\text{\AA}$; $\langle \text{S}'\text{PdS} = 75.1^\circ, 104.9^\circ, \langle \text{S}'\text{PtS} = 74.2^\circ, 104.8^\circ$, (ref. 11). The tetra-thia crown (L^5) binds $\text{Pd}(\text{II})$ and $\text{Pt}(\text{II})$ equatorially to give square planar complexes with these metal ions; this has been confirmed by the single crystal X-ray structure of $[\text{Pd}(\text{L}^5)]^{2+}$ (10); $\text{Pd-S} = 2.23\text{--}2.33\text{\AA}$.



(9)

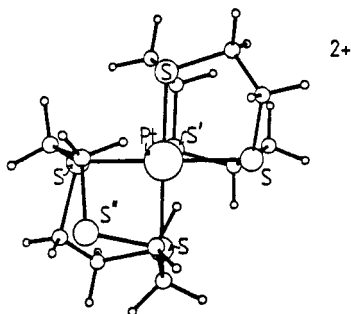


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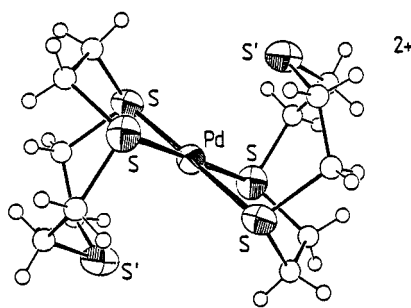
The small ring tri-thia ligand (L^6) has been shown previously to bind first row transition metal ions in a facial manner; thus, *bis*-macrocyclic species of type $[\text{M}(\text{L}^6)_2]^{2+}$ ($\text{M} = \text{Co}(\text{II}), \text{Ni}(\text{II}), \text{Cu}(\text{II})$) have been prepared and shown to have octahedral MS_6 stereochemistries (refs. 10, 12). We have extended these studies to the platinum metal series.

Reaction of (L^6) with PdCl_2 and PtCl_2 in a 2:1 molar ratio yielded complex cations of stoichiometry $[\text{M}(\text{L}^6)_2]^{2+}$. The single crystal X-ray structure of $[\text{Pt}(\text{L}^6)_2]^{2+}$, (11), shows the orange complex to have an unusual square-based pyramidal stereochemistry (refs. 13, 14). The $\text{Pt}(\text{II})$ ion is coordinated by four thia donors in a square plane, $\text{Pt-S}_{\text{equ}} = 2.25\text{--}2.30\text{\AA}$, with one of the remaining sulphur ligands bound apically $\text{Pt-S}'_{\text{ax}} = 2.88\text{\AA}$, $\langle \text{SPTs}' = 84.0\text{--}97.2^\circ$. The sixth thia donor is not coordinated to the metal centre, $\text{Pt}\cdots\text{S}' = 4.04\text{\AA}$. In contrast, the $\text{Pd}(\text{II})$ analogue $[\text{Pd}(\text{L}^6)_2]^{2+}$ (12) is green, and is *not* isostructural with the $\text{Pt}(\text{II})$ complex (11). The single crystal X-ray structure of (12) shows the centrosymmetric cation to have an unexpected distorted octahedral stereochemistry around $\text{Pd}(\text{II})$ with $\text{Pd-S}_{\text{equ}} = 2.332, 2.311$ and $\text{Pd-S}'_{\text{ax}} = 2.952\text{\AA}$ (refs. 15, 16)

The complexes (11) and (12) each show, by cyclic voltammetry, a reversible one-electron oxidation at $E_{\text{M}} = +0.39\text{V}$. $\Delta E_{\text{p}} = 145\text{mV}$. and $E_{\text{M}} = +0.605\text{V}$. $\Delta E_{\text{p}} = 84\text{mV}$. vs. Fc/Fc^+ respectively in CH_3CN at platinum electrodes. Controlled potential electrolysis of the complexes at $+0.5\text{V}$. and $+0.7\text{V}$. respectively at a platinum gauze affords the corresponding oxidation products $[\text{M}(\text{L}^6)_2]^{3+}$ which may be assigned by esr spectroscopy as mononuclear $\text{Pt}(\text{III})$ and $\text{Pd}(\text{III})$ species respectively ($g_{\parallel} = 1.987$, $g_{\perp} = 2.044$, $A_{\parallel} = 85\text{G}$, $A_{\perp} = 30\text{G}$ (^{195}Pt , $I = \frac{1}{2}$, 33.8%) for $[\text{Pt}(\text{L}^6)_2]^{3+}$; $g_{\parallel} = 2.009$, $g_{\perp} = 2.049$, $A_{\parallel} = 5\text{G}$, $A_{\perp} = 20\text{G}$ (^{105}Pd , $I = \frac{5}{2}$, 22.2%) for $[\text{Pd}(\text{L}^6)_2]^{3+}$). Interestingly, the $\text{Pd}(\text{II})$ and $\text{Pt}(\text{II})$ complexes of (L^4) and (L^5) , (9) and (10), show no oxidative redox processes by cyclic voltammetry in CH_3CN . The electrochemical inactivity of these latter species may be explained by the inability of the macrocycles (L^4) and (L^5) to form octahedral complexes with Pd and Pt centres. From the crystal structure of (9), the ligand (L^4) appears to have a cavity too small to fully encapsulate octahedrally



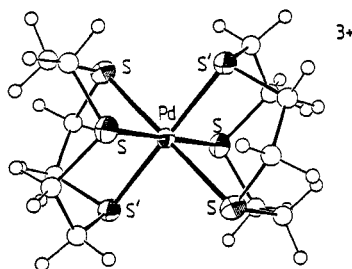
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(12)

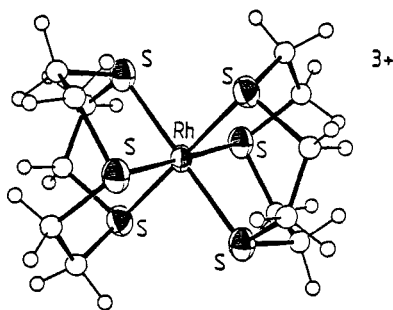
the relatively large Pd(II) and Pt(II) ions, while (L^5) affords only square planar complexes with these metal ions. By contrast, coordination of two molecules of (L^6) to Pd(II) and Pt(II) enables a preferred distorted octahedral stereochemistry to be achieved on oxidation to the metal(III) species. The coordinative flexibility of (L^6) in this system appears therefore to be crucial in stabilising the d^7 metal centre with the positive charge in $[M(L^6)_2]^{3+}$ being delocalised to some extent onto the thia ligands (refs. 13, 14, 15). Larger ring analogues of (L^4) with larger ring cavities should be capable sterically of full octahedral coordination to Pd and Pt centres, although the coordinative stability of such systems may be reduced.

The oxidised 3+ cations $[M(L^6)_2]^{3+}$ ($M = Pd, Pt$) can be quantitatively generated from the parent 2+ cations electrochemically in CH_3CN or chemically in conc. aqueous $HClO_4$. These oxidations have been monitored by uv-vis spectroscopy and show identical isosbestic conversion of $[Pt(L^6)_2]^{2+}$ ($\lambda_{max} = 432nm$ ($\epsilon = 95M^{-1}cm^{-1}$), 278 (7,000), 245 (12,850)) to $[Pt(L^6)_2]^{3+}$ ($\lambda_{max} = 402nm$ ($\epsilon = 3000M^{-1}cm^{-1}$), 271 (10,000), 201 (6,600); $\lambda_{iso} = 256nm$), and $[Pd(L^6)_2]^{2+}$ ($\lambda_{max} = 615nm$ ($\epsilon = 55M^{-1}cm^{-1}$), 296 (15,000), 198 (9,900)) to $[Pd(L^6)_2]^{3+}$ ($\lambda_{max} = 477nm$ ($\epsilon = 5,350M^{-1}cm^{-1}$), 341 (16,100), 230 (8,100); $\lambda_{iso} = 603nm$, 316, 260, 216) respectively. Red paramagnetic crystals of $[Pd(L^6)_2]^{3+}$, (13), were obtained from aqueous $HClO_4$ solution. The single crystal X-ray structure of (13) shows the cation to have a tetragonally distorted octahedral stereochemistry, the Pd atom lying on an inversion centre with $Pd-S_{equ} = 2.3558, 2.3692\text{\AA}$ and $Pd-S_{ax} = 2.5448\text{\AA}$ and the $\langle SPdS' \rangle$ angles close to octahedral (ref. 17). On going from $[Pd(L^6)_2]^{2+}$ to $[Pd(L^6)_2]^{3+}$ therefore, the axial thia donors, S_{ax} , move in towards the more electropositive metal ion to give a stereochemistry consistent with a Jahn-Teller distorted d^7 configuration. A d^6 Pd(IV) species would be expected to show a symmetrical octahedral geometry. Few examples of mononuclear Pt(III) or Pd(III) complexes have been reported in the literature (refs. 18, 19, 20). Sargeson and co-workers have described (ref. 19) the γ -radiolysis of $[Pt(\text{diamsar})]^{4+}$ at low temperatures to afford the transient cation $[Pt(\text{diamsar})]^{3+}$, the esr spectrum of which shows similar features to the spectrum observed for $[Pt(L^6)_2]^{3+}$. Slow oxidation of $[Pt(L^6)_2]^{3+}$ does, however, occur to afford a product which can be tentatively assigned to a Pt(IV) or ligand oxidised species ($\lambda_{max} = 289nm$ ($\epsilon = 17,800M^{-1}cm^{-1}$); $\lambda_{iso} = 352nm$, 273, 240, in aqueous $HClO_4$). Our work has concentrated up to now on the synthesis and characterisation of the oxidised complex cations; it should be stressed that the precise role of $HClO_4$ in these oxidations is unclear (see ref. 21 for a full discussion on $HClO_4$ oxidations).

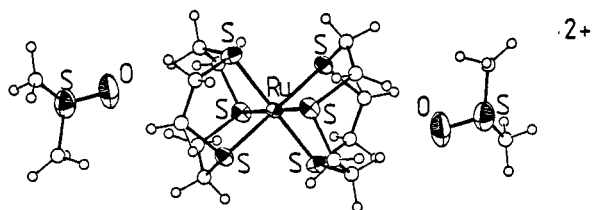


(13)

The homoleptic d^6 complexes $[Rh(L^6)_2]^{3+}$, (14), and $[Ru(L^6)_2]^{2+}$, (15), have also been synthesised. The single crystal X-ray structures of these products confirm their symmetric octahedral stereochemistries with $Rh-S = 2.332, 2.334\text{\AA}$; $Ru-S = 2.327-2.336\text{\AA}$. An unexpected feature of the structure of $[Ru(L^6)_2](BPh_4)_2 \cdot 2dmsO$ (15) is the approach of the dmsO solvate molecules towards the outer face of the coordinated tri-thia ligands. This occurs via H-bonding of the O-donor of the dmsO solvates with the protons of the methylene groups of (L^6), $O \cdots H = 2.201, 2.419, 2.790, 3.291\text{\AA}$ (ref. 22). This secondary interaction between the dmsO molecules with the rear cone/cavity of the coordinated tri-thia ligand may be regarded as a weak inclusion of solvent; this is supported by the observation that dmsO may be replaced by two molecules of other donor solvents such as CH_3CN and CH_3NO_2 .



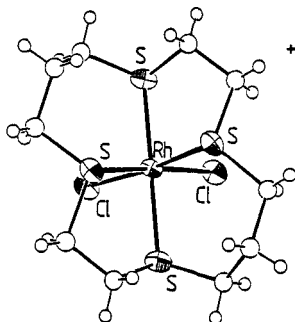
(14)



(15)

The complex $[\text{Ru}(\text{L}^6)_2]^{2+}$, (15), is electrochemically inactive between -2.2 and $+1.3\text{V}$, indicating particular stabilisation of d^6 Ru(II) by hexa-thia coordination. The complex does show a quasi-reversible oxidation at $E_M = +1.41\text{V}$, vs Fc/Fc+ tentatively assigned to a Ru(II)/(III) couple (ref. 22). The complex $[\text{Rh}(\text{L}^6)_2]^{3+}$, however, shows two reversible, one-electron reductions at $^1E_M = -0.71\text{V}$, $\Delta E_p = 71\text{mV}$, $^2E_M = -1.08\text{V}$, $\Delta E_p = 127\text{mV}$, assigned to Rh(III)/(II) and Rh(II)/(I) redox couples respectively. The Rh(II) species $[\text{Rh}(\text{L}^6)_2]^{2+}$ can be generated electrochemically and shows an esr spectrum with $g_{\parallel} = 2.007$ and $g_{\perp} = 2.088$ (measured at 77K as a CH_3CN glass) (ref. 17). Further reduction of this species affords an air sensitive diamagnetic product assumed to be the d^8 Rh(I) species $[\text{Rh}(\text{L}^6)_2]^+$. As in the generation of d^7 Pd(III) and Pt(III), the ability of the tri-thia macrocycles to conform to the stereochemical requirements of the Rh(II) ion is thought to be crucial. For other examples of mononuclear Rh(II) species see ref. 23. The corresponding *bis*-sandwich Ir(III) complex $[\text{Ir}(\text{L}^6)_2]^{3+}$ has been prepared in low yield by extended reflux of $[\text{IrCl}_3(\text{L}^6)]$ with (L^6) in ethylene glycol; an alternative synthesis of this cation based on the reaction of two equivalents of (L^6) with Ir(I) is being developed.

Reaction of RhCl_3 and IrCl_3 with (L^5) in refluxing MeOH affords the corresponding six coordinate complexes *cis*- $[\text{MCl}_2(\text{L}^5)]^+$ ($\text{M} = \text{Rh}$ (16), Ir) (ref. 24). We have confirmed the *cis* orientation of the chloride ligands in these products by crystallographic studies on both complexes. A similar *cis* stereochemistry has been observed for *cis*- $[\text{RuCl}_2(\text{L}^5)]^+$ (ref. 25).

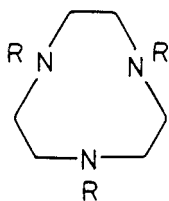


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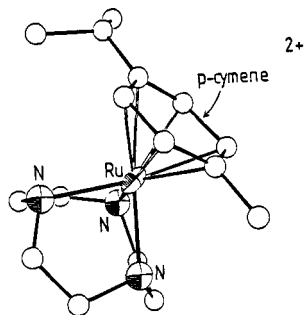
ORGANOMETALLIC COMPLEXES

Mononuclear complexes

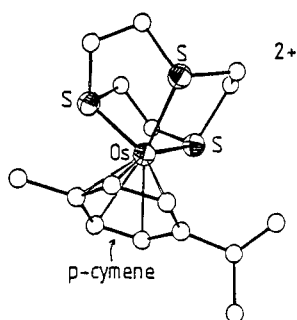
We wished to investigate the analogy between small ring tridentate macrocyclic ligands and their carbocyclic analogues, eg aryl, cyclopentadienyl species. We were therefore interested in the synthesis of mixed sandwich complexes incorporating these fragments. Reaction of the tri-thia macrocycle (L^6) and the tri-aza analogues (L^7) and (L^8) with the carbocyclic chloro-bridged dimers $[\text{M}(\text{C}_5\text{Me}_5)\text{Cl}_2]_2$ ($\text{M} = \text{Rh}, \text{Ir}$) and $[\text{MCl}_2(\text{arene})]_2$ ($\text{M} = \text{Ru}, \text{Os}$; arene = *p*-cymene, hexamethylbenzene, benzene) (ratio of $\text{M}:\text{L} = 1:1$) gave the mononuclear mixed sandwich species $[\text{M}(\text{C}_5\text{Me}_5)(\text{L})]^{2+}$ ($\text{M} = \text{Rh}, \text{Ir}$) and $[\text{M}(\text{arene})(\text{L})]^{2+}$ ($\text{M} = \text{Ru}, \text{Os}$) ($\text{L} = \text{L}^6, \text{L}^7, \text{L}^8$). The single crystal X-ray structures of $[\text{Ru}(\text{p-cymene})(\text{L}^7)]^{2+}$, (17), ($\text{Ru}-\text{N} = 2.13$, $\text{Ru}-\text{C} = 2.24\text{\AA}$), $[\text{Os}(\text{p-cymene})(\text{L}^6)]^{2+}$, (18), ($\text{Os}-\text{S} = 2.31, 2.35$, $\text{Os}-\text{C} = 2.24\text{\AA}$) and $[\text{Rh}(\text{C}_5\text{Me}_5)(\text{L}^8)]^{2+}$, (19), ($\text{Rh}-\text{N} = 2.195, 2.237, 2.155$, $\text{Rh}-\text{C} = 2.178-2.242\text{\AA}$) illustrate the stereochemical parallels between carbocyclic and macrocyclic ligands (ref. 26). The osmium arene complexes of the type $[\text{Os}(\text{arene})(\text{L})]^{2+}$ are useful synthetic precursors for the formation of the complexes $[\text{Os}(\text{L})_2]^{x+}$. Thus, reaction of $[\text{Os}(\text{arene})(\text{L}^6)]^{2+}$ with an excess of (L^6) affords $[\text{Os}(\text{L}^6)_2]^{2+}$ (ref. 22).



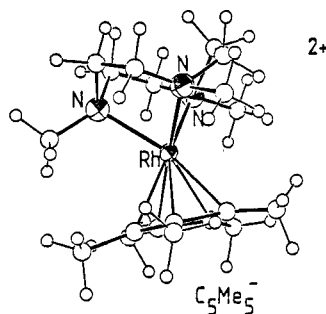
(L⁷) R = H
(L⁸) R = Me



(17)



(18)

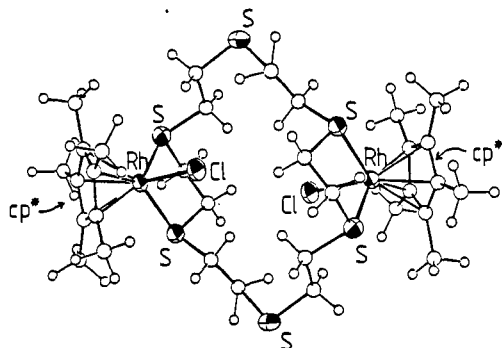


(19)

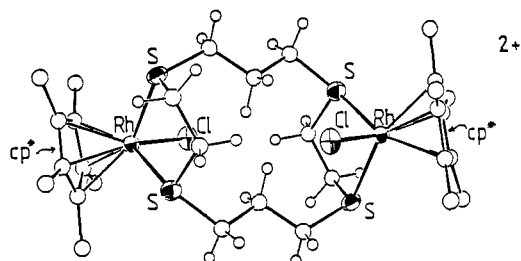
The complex $[\text{Rh}(\text{C}_5\text{Me}_5)(\text{L}^6)]^{2+}$ shows a quasi-reversible Rh(III)/(II) couple at -1.29V vs Fc/Fc^+ by cyclic voltammetry. This is at a more negative potential than for the corresponding hexa-thia complex $[\text{Rh}(\text{L}^6)_2]^{3+}$ suggesting that the C_5Me_5^- moiety is less efficient than (L^6) in stabilising the d^7 intermediate. This is confirmed by the relative instability of electrogenerated solutions of $[\text{Rh}(\text{C}_5\text{Me}_5)(\text{L}^6)]^+$ which decompose rapidly at room temperature probably via loss of C_5Me_5^- .

Binuclear complexes

The ability of (L^4) and (L^5) to act as binucleating ligands has been demonstrated previously (refs. 27, 28). We initiated a study on the reactivity of these large ring systems with organometallic metal substrates with a view to investigating their coordination to polymeric centres. Thus, treatment of the carbocyclic dimers $[\text{M}(\text{C}_5\text{Me}_5)_2\text{Cl}_2]_2$ ($\text{M} = \text{Rh}, \text{Ir}$) and $[\text{MCl}_2(\text{arene})_2]_2$ ($\text{M} = \text{Ru}, \text{Os}$; arene = *p*-cymene, hexamethylbenzene, benzene) with one equivalent of (L) affords the binuclear species $[\text{M}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_2(\text{L})]^{2+}$ and $[\text{M}_2\text{Cl}_2(\text{arene})_2(\text{L})]^{2+}$ ($\text{L} = \text{L}^4, \text{L}^5$) respectively. The single crystal X-ray structure of the di-rhodium(III) product $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_2(\text{L}^4)]^{2+}$, (20), shows the metal ions bound to only two of the thia donors of (L^4) with $\text{Rh-S} = 2.377, 2.365$, $\text{Rh-Cl} = 2.387$, $\text{Rh-C} = 2.161-2.188\text{\AA}$ (ref. 26). The related products with (L^5) have also been generated and in the case of $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_2(\text{L}^5)]^{2+}$, (21), characterised crystallographically.



(20)



(21)

Acknowledgements

I am most grateful to Michael N. Bell, Alan J. Holder, Timothy I. Hyde, Aidan J. Lavery and Gillian Reid who carried out the synthetic and electrochemical studies described herein, and to Alexander J. Blake and Robert O. Gould for their crystallographic work. Support from the Science and Engineering Research Council (UK), B.P. Chemicals Plc and Johnson Matthey Plc is gratefully acknowledged. Structural diagrams are reproduced with permission.

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