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(II) and ruthenium(I) into tetra-aza macrocycles (L) has been achieved, and the structures of octahedral complexes incorporating mutually cis chloro-hydride ([IrCl(N)(L)]^+) and chloro-carbonyl ([RuCl(CO)(L)]^+) moieties are discussed in relation to the conformational characteristics of the coordinated macrocyclic ligand. Square planar complexes of palladium(II), [Pd(L)]^2+, can be reduced electrochemically to afford highly reactive palladium(0) 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 [M(L)2X^+ (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 [M(CpMe2)(L)]^2+ (M = Rh, Ir) and [M(arene)(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 stereocmehemically 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 N₄ macrocycles of general type (L¹; R¹, R², R³ = H or Me). Thus, reaction of RhCl₃ or Pd(OAc)₂ with (L¹) in CH₂OH or CH₂Cl₂ respectively affords the complex cations trans-[RhCl₂(L¹)]⁺, (1; R¹ = R² = R³ = Me), and [Pd(L¹)]³⁺, (2; R¹ = R² = H, R³ = 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)(L¹)]⁺, (3; R¹ = R³ = Me, R² = H), ([IrCl(H)(L¹)]⁺, (4; R¹ = R² = H, R³ = Me), ([Ir-Cl = 2.393, Ir-H = 1.57Å]) 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; R¹ = R² = R³ = 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 N₄ 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 (L¹) 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 (L², tmc) and related N₄ donor saturated ligands show a reversible reduction by cyclic voltammetry in CH₂CN. 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(II) and Cu(II) by tetra-aza macrocycles (ref. 5). Cyclic voltammetry of [Pd(L²)](PF₆)₂ (L² = tmc; (6), Pd-N = 2.051, 2.066Å) in CH₂CN at platinum electrodes shows a fully reversible reduction at E₁/₂ = -1.53V. vs Fe/Fe⁺, ΔEₚ = 85mV, Iₚ/Iₚ' = 1.0, at a scan rate of 100mV sec⁻¹. Controlled potential electrolysis of [Pd(L²)]⁺¹ at a platinum gauze in CH₂CN at -1.65V. under a stream of Ar at 20°C affords a highly air-sensitive, reactive species which can be assigned by e.s.r. spectroscopy to a d⁹ Pd(1) species [Pd(L²)]⁺ (measured at 77K in a frozen glass; gₚ = 2.302, g₁ = 2.076 with hyperfine coupling to lo⁵Pd, I₉ = 22.2%, A₀ = 50.8, A₁ = 400) (ref. 6). This is one of the first examples of stabilisation of a genuine mononuclear Pd(1) species (ref. 7). The complex [Pd(L²)](PF₆)₂, (7), likewise shows a reversible reduction but at a more positive potential, E₁/₂ = -1.27V. vs Fe/Fe⁺ in CH₂CN. The corresponding Pd(1) species can be generated and identified by e.s.r. 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.

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(\text{L}^2) \quad R = \text{Me} \\
(\text{L}^3) \quad R = \text{CH}_2\text{Ph}
\]

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 \(E_\text{q} = -0.99\text{V} \) 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.

**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 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 [M(L$^4$)]$^{2+}$ (M = Pd, 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 (Pd-S = 2.309, Pt-S = 2.296Å) with the two remaining sulphur donors of (L$^4$) being essentially non-bonded; Pd-S' = 3.273, Pt-S' = 3.380Å; <S'PdS = 75.1°, 104.9°, <S'Pts = 74.2°, 104.8°, (ref. 11). The tetra-thia crown (L$^5$) binds Pd(II) and Pt(II) equatorially to give square planar complexes with these metal ions; this has been confirmed by the single crystal X-ray structure of [Pd(L$^5$)]$^{2+}$ (10); Pd-S = 2.23-2.35Å.

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 [M(L$^6$)]$^{2+}$ (M = Co(II), Ni(II), Cu(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 [M(L$^6$)]$^{2+}$. The single crystal X-ray structure of [Pt(L$^6$)]$^{2+}$, (11), shows the orange complex to have an unusual square-based pyramidal stereochemistry (refs. 13, 14). The Pt(II) ion is coordinated by four thia donors in a square plane, Pt-S$_{equ}$ = 2.25-2.30Å, with one of the remaining sulphur ligands bound apically Pt-SAX = 2.88Å, <SPts = 84.0-97.2°. The sixth thia donor is not coordinated to the metal centre, Pt...S'' = 4.04Å. In contrast, the Pd(II) analogue [Pd(L$^6$)]$^{2+}$ (12) is green, and is not isostructural with the Pt(II) complex (11). The single crystal X-ray structure of (12) shows the centrosymmetric cation to have an unexpected distorted octahedral stereochemistry around Pd(II) with Pd-S$_{equ}$ = 2.332, 2.311 and Pd-S$_{AX}$ = 2.952Å (refs. 15, 16).

The complexes (11) and (12) each show, by cyclic voltammetry, a reversible one-electron oxidation at $E_M = +0.39$V, $\Delta E_p = 145$mV, and $E_M = +0.605$V, $\Delta E_p = 84$mV vs. Fe/Fe$^+$ respectively in CH$_3$CN at platinum electrodes. Controlled potential electrolysis of the complexes at +0.5V. and +0.7V. respectively at a platinum gauze affords the corresponding oxidation products [M(L$^6$)]$^{3+}$ which may be assigned by E.S.R spectroscopy as mononuclear Pd(III) and Pt(III) species respectively ($g_T$ = 1.987, $g_L$ = 2.044, $A_T$ = 85G, $A_L$ = 306G, 33.8%) for [Pt(L$^6$)]$^{3+}$; $g_T$ = 2.009, $g_L$ = 2.049, $A_T$ = 5G, $A_L$ = 208G, 22.2% for [Pd(L$^6$)]$^{3+}$. Interestingly, the Pd(II) and Pt(II) complexes of (L$^4$) and (L$^5$), (9) and (10), show no oxidative redox processes by cyclic voltammetry in CH$_3$CN. 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.
the relatively large Pd(II) and Pt(II) ions, while (L⁵) affords only square planar complexes with these metal ions. By contrast, coordination of two molecules of (L⁵) 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 (L⁵) in this system appears therefore to be crucial in stabilising the d⁷ metal centre with the positive charge in [M(L⁶)₂³⁺] being delocalised to some extent onto the thia ligands (refs. 13, 14, 15). Larger ring analogues of (L⁴) 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(L⁶)₂³⁺] (M = Pd, Pt) can be quantitatively generated from the parent 2⁺ cations electrochemically in CH₃CN or chemically in conc. aqueous HClO₄. These oxidations have been monitored by uv-vis spectroscopy and show identical isosbestic conversion of [Pt(L⁶)₂]²⁺ (λₘ𝑎ₓ = 432 nm (ε = 95M⁻¹cm⁻¹), 276 (7,000), 215 (12,850)) to [Pt(L⁶)₂]³⁺ (λₘₐₓ = 402 nm (ε = 3000M⁻¹cm⁻¹), 271 (10,000), 201 (6,600); λᵢₛₒ = 256nm), and [Pd(L⁶)₂]²⁺ (λₘₐₓ = 615nm (ε = 55M⁻¹cm⁻¹), 290 (15,000), 198 (9,900)) to [Pd(L⁶)₂]³⁺ (λₘₐₓ = 477nm (ε = 5,350M⁻¹cm⁻¹), 341 (16,100), 230 (8,100); λᵢₛₒ = 603nm, 316, 260, 216) respectively. Red paramagnetic crystals of [Pd(L⁶)₂]³⁺, (13), were obtained from aqueous HClO₄ 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-Sₑq = 2.3558, 2.3692Å and Pd-Sₐx = 2.5448Å and the <Pdₙₙₙ angles close to octahedral (ref. 17). On going from [Pd(L⁶)₂]²⁺ to [Pd(L⁶)₂]³⁺ therefore, the axial thia donors, Sₐₓ, move in towards the more electropositive metal ion to give a stereochemistry consistent with a Jahn-Teller distorted d⁷ configuration. A d⁶ 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(diamsar)]⁺ at low temperatures to afford the transient cation [Pt(diamsar)], the esr spectrum of which shows similar features to the spectrum observed for [Pt(L⁶)₂]³⁺. Slow oxidation of [Pt(L⁶)₂]³⁺ does, however, occur to afford a product which can be tentatively assigned to a Pt(IV) or ligand oxidised species (λₘₐₓ = 289nm (ε = 17,800M⁻¹cm⁻¹); λᵢₛₒ = 352nm, 273, 240, in aqueous HClO₄). 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 HClO₄ in these oxidations is unclear (see ref. 21 for a full discussion on HClO₄ oxidations).

The homoleptic d⁶ complexes [Rh(L⁶)₂]³⁺, (14), and [Ru(L⁶)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, 2.334Å; Ru-S = 2.327-2.336Å. An unexpected feature of the structure of [Ru(L⁶)₂](BPh₄)₂.2dms (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 (L⁶), O···H = 2.201, 2.419, 2.790, 3.291Å (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 CH₃CN and CH₃NO₂.
The complex \([\text{Ru}(L^6)_2]^2^+\), (15), is electrochemically inactive between -2.2 and +1.3 V. indicating particular stabilisation of \(d^6\) Ru(II) by hexa-thia coordination. The complex does show a quasi-reversible oxidation at \(E^\circ = +1.41\) V, vs Fe/Fe\(^+\) tentatively assigned to a Ru(II)/(III) couple (ref. 22). The complex \([\text{Rh}(L^6)_2]^3^+\), however, shows two reversible, one-electron reductions at \(E^\circ = -0.19\) V, \(\Delta E_p = 50\) mV. \(\Delta E_p = 71\) mV, assigned to Rh(III)/(II) and Rh(II)/(I) redox couples respectively. The Rh(II) species \([\text{Rh}(L^6)_2]^2^+\) can be generated electrochemically and shows an esr spectrum with \(g_1 = 2.007\) and \(g_2 = 2.088\) (measured at 77K as a CH\(_2\)CN glass) (ref. 17). Further reduction of this species affords an air sensitive diamagnetic product assumed to be the \(d^8\) Rh(I) species \([\text{Rh}(L^6)_2]^+\). 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 \([\text{Ir}(L^6)_2]^3^+\) has been prepared in low yield by extended reflux of \([\text{IrCl}_3(L^6)]\) 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 \(\text{cis-}[\text{MC}1_2(L^5)]^+\) (M = Rh, 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 \(\text{cis-}[\text{RhCl}_2(L^5)]^+\) (ref. 25).

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\text{ORGANOMETALLIC COMPLEXES}
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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 \([\text{MC}_5\text{Me}_5\text{Cl}_2]_2\) (M = Rh, Ir) and \([\text{MC}_5\text{Cl}_2(\text{arene})]_2\) (M = Ru, Os; arene = p-cymene, hexamethylbenzene, benzene) gave the mononuclear mixed sandwich species \([\text{MC}_5\text{Me}_5(L)]^{2+}\) (M = Rh, Ir) and \([\text{MC}_5\text{Cl}_2(\text{arene})]^{2+}\) (M = Ru, Os) \((L = L^6, L^7, L^8)\). The single crystal X-ray structures of \([\text{Ru}(p\text{-cymene})(L^7)]^{2+}\), (17), \((\text{Ru-N} = 2.13, \text{Ru-C} = 2.24\) Å), \([\text{Os}(p\text{-cymene})(L^6)]^{2+}\), (18), \((\text{Os-S} = 2.31, 2.35, \text{Os-C} = 2.24\) Å) and \([\text{Rh}(\text{C}_5\text{Me}_5)(L^8)]^{2+}\), (19), \((\text{Rh-N} = 2.195, 2.237, 2.155, \text{Rh-C} = 2.178-2.242\) Å) illustrate the stereochemical parallels between carbocyclic and macrocyclic ligands (ref. 26). The osmium arene complexes of the type \([\text{Os}(\text{arene})(L)]^{2+}\) are useful synthetic precursors for the formation of the complexes \([\text{Os}(L)]^{2+}\). Thus, reaction of \([\text{Os}(\text{arene})(L^6)]^{2+}\) with an excess of \((L^6)\) affords \([\text{Os}(L^6)]^{2+}\) (ref. 22).

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(16)
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(17)
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(17) \quad R = H
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(17) \quad R = \text{Me}
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The complex [Rh(C₅Me₅)(L⁶)]⁺²⁺ shows a quasi-reversible Rh(III)/(II) couple at -1.29V vs Fe/Fe⁺ by cyclic voltammetry. This is at a more negative potential than for the corresponding hexa-thia complex [Rh(L⁶)₂]⁺³⁺ suggesting that the C₅Me₅⁻ moiety is less efficient than (L⁶) in stabilising the d⁷ intermediate. This is confirmed by the relative instability of electrogenerated solutions of [Rh(C₅Me₅)(L⁶)]⁺ which decompose rapidly at room temperature probably via loss of C₅Me₅⁻.

Binuclear complexes

The ability of (L⁴) and (L⁵) 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 polymetallic centres. Thus, treatment of the carbocyclic dimers [M(C₅Me₅)Cl₂]₂ (M = Rh, Ir) and [MCl₂(arene)]₂ (M = Ru, Os; arene = p-cymene, hexamethylbenzene, benzene) with one equivalent of (L) affords the binuclear species [M₂(C₅Me₅)₂Cl₂(L)]²⁺ and [M₂Cl₂(arene)₂(L)]²⁺ (L = L⁴, L⁵) respectively. The single crystal X-ray structure of the di-rhodium(III) product [Rh₂(C₅Me₅)₂Cl₂(L⁴)]²⁺, (20), shows the metal ions bound to only two of the thia donors of (L⁴) with Rh-S = 2.377, 2.365, Rh-Cl = 2.387, Rh-C = 2.161-2.188Å [ref. 26]. The related products with (L⁵) have also been generated and in the case of [Rh₂(C₅Me₅)₂Cl₂(L⁵)]²⁺, (21), characterised crystallographically.

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REFERENCES