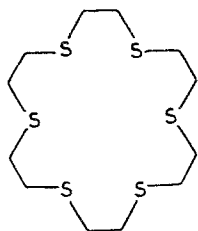


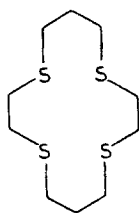
TRANSITION METAL COMPLEXES OF HOMOLEPTIC POLYTHIA CROWNS

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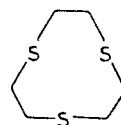
The binding of transition metal ions to polydentate macrocyclic ligands to give mono-, bi- and poly-nuclear complexes is well known. We have been investigating the complexation of transition metal ions, particularly those of the platinum group metals, by the homoleptic polythia crown ligands 1,4,7,10,13,16-hexathiacyclooctadecane (L^1), 1,4,8,11-tetrathiacyclotetradecane (L^2) and 1,4,7-trithiacyclononane (L^3). These ligands were attractive since they would be expected to bind effectively to the relatively soft second and third row metal ions and lead to the formation of complexes exhibiting unusual stereochemical, electronic and redox properties.



(L^1)



(L^2)

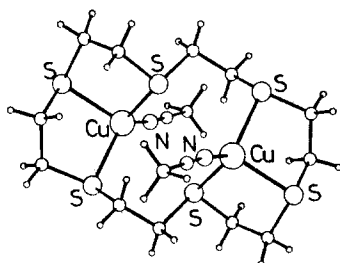


(L^3)

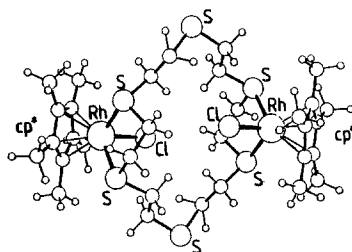
It was shown originally by Black and coworkers (*Tet. Lett.* 1969, 3961) that the potentially hexadentate ligand (L^1) (the thia analogue of 18-crown[6]) could readily encapsulate first row transition metal ions such as Ni^{2+} and Co^{2+} in an octahedral manner. The ability of (L^1) to act as a binucleating ligand had not however been demonstrated. We therefore initiated a study on the reactivity of (L^1) with a variety of metal substrates with a view to investigating its coordination to polymetallic centres.

Reaction of (L^1) with two molar equivalents of $[Cu(NCCH_3)_4]^+$ gave the di-copper(I) complex $[Cu_2(L^1)(NCCH_3)_2]^{2+}$ (1); the single crystal X-ray structure of (1) shows each tetrahedral copper(I) ion bound to three thia donors of (L^1) , $Cu-S = 2.32-2.34\text{\AA}$, and one molecule of CH_3CN , $Cu-N = 1.94\text{\AA}$, with a $Cu..Cu$ distance of 4.25\AA .

Treatment of the isoelectronic, carbocyclic dimers $[M(cp^*)Cl_2]_2$ ($M = Rh, Ir$) and $[MCl_2(arene)]_2$ ($M = Ru, Os$; arene = p-cymene, hexamethylbenzene, benzene) with (L^1) affords the binuclear species $[M_2(cp^*)_2Cl_2(L^1)]^{2+}$ and $[M_2Cl_2(arene)_2(L^1)]^{2+}$ respectively. The single crystal X-ray structure of the di-rhodium(III) product $[Rh_2(cp^*)_2Cl_2(L^1)]^{2+}$ (2) shows the metal ions bound to only two of the thia donors of (L^1) with $Rh-S = 2.377, 2.365$, $Rh-Cl = 2.387$, $Rh-C = 2.161-2.188\text{\AA}$.



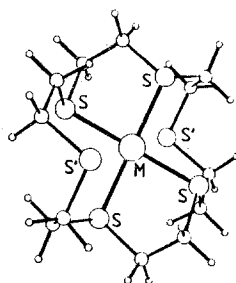
(1)



(2)

A series of mononuclear platinum metal complexes have also been prepared.

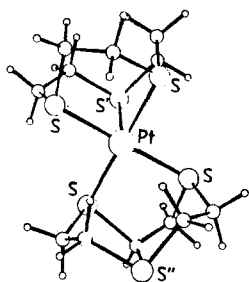
Reaction of $PdCl_2$ or $PtCl_2$ with (L^1) gave 1:1 complexes $[M(L^1)]^{2+}$ ($M = Pd, Pt$) (3). The crystal structure analyses of these complexes confirm square planar coordination of the metal ions to four thia donors of (L^1) ($Pd-S = 2.309$, $Pt-S = 2.296\text{\AA}$) with the two remaining sulphur donors of (L^1) being essentially non-bonded ($Pd-S' = 3.273$, $Pt-S' = 3.380\text{\AA}$; $\angle S'PdS = 75.1^\circ, 104.9^\circ$, $\angle S'PtS = 74.2^\circ, 104.8^\circ$). The dangling thia donors S' are therefore unable to complete octahedral coordination around $Pd(II)$ and $Pt(II)$ due to the relatively large radii of these metal ions.



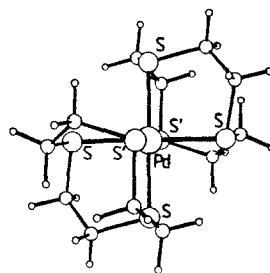
(3)

The small ring trithia macrocycle (L^3) has been shown to bind to first row transition metal ions in a facial manner. Thus bis-macrocyclic species of type $[M(L^3)_2]^{2+}$ ($M = Co(II), Ni(II), Cu(II)$) have been generated previously and shown to have octahedral MS_6 stereochemistries (Glass and coworkers, *Inorg. Chem.*, 1983, 22, 266). Reaction of (L^3) with $PdCl_2$ and $PtCl_2$ in a 2:1 molar ratio yielded complex cations of stoichiometry $[M(L^3)_2]^{2+}$; their structural and redox properties were assessed.

The single crystal X-ray structure of $[Pt(L^3)_2]^{2+}$ (4) shows the complex to have an unusual square-based pyramidal stereochemistry. The Pt(II) ion is coordinated by four thia donors in a square plane, $Pt-S = 2.25-2.30\text{\AA}$, with one of the remaining sulphur ligands bound apically $Pt-S' = 2.88\text{\AA}$, $\angle SPTs' = 84.0-97.2^\circ$. The sixth thia donor is not coordinated to the metal centre, $Pt\dots S'' = 4.04\text{\AA}$. In contrast to the yellow Pt(II) complex (4), the isoelectronic Pd(II) species $[Pd(L^3)_2]^{2+}$ (5) is green and not isostructural. The crystal structure of (5) shows the centrosymmetric cation to have an unexpected distorted octahedral stereochemistry around Pd(II) with $Pd-S_{equ} = 2.332, 2.311$ and $Pd-S'_{ax} = 2.952\text{\AA}$.



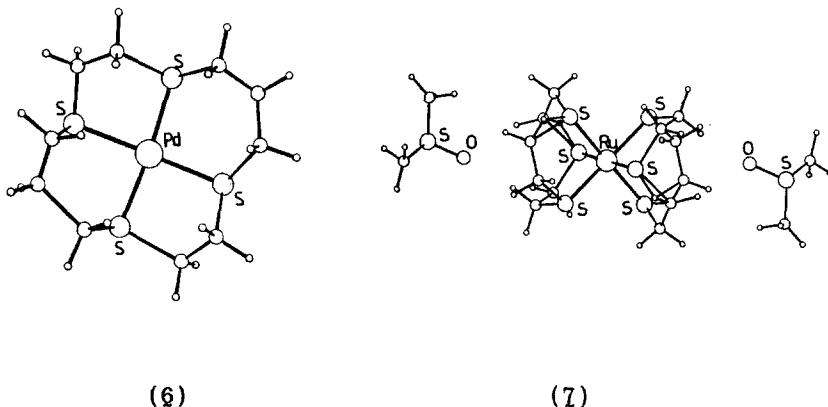
(4)



(5)

The complexes (4) and (5) each show, by cyclic voltammetry, one, one electron oxidation at $E_{1/2} = +0.39V$. $\Delta E_p = 145mV$. and $E_{1/2} = +0.605V$. $\Delta E_p = 84mV$. vs. Fc/Fc^+ respectively in CH_3CN 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 $[M(L^3)_2]^{3+}$ which have been identified by esr spectroscopy as formally metal(III) species; $g_{\parallel} = 1.987$, $g_{\perp} = 2.044$, $A_{\parallel} = 85G$, $A_{\perp} = 30G$ (^{195}Pt , $I = \frac{1}{2}$, 33.8%) for $[Pt(L^3)_2]^{3+}$, $g_{\parallel} = 2.009$, $g_{\perp} = 2.049$, $A_{\parallel} = 5G$, $A_{\perp} = 20G$ (^{105}Pd , $I = \frac{5}{2}$, 22.2%) for $[Pd(L^3)_2]^{3+}$. Interestingly, the Pd(II) and Pt(II) complexes of (L^1) and (L^2), ((3) and (6)), show no oxidative redox processes by cyclic voltammetry in CH_3CN . The electrochemical inactivity of these latter species may be rationalised by the inability of the macrocycles (L^1) and (L^2) to form octahedral complexes with Pd and Pt centres. The ligand (L^1) may be regarded as being too small to fully encapsulate octahedrally the relatively large Pd(II) and Pt(II) ions. (L^2) would

be expected to bind equatorially to give square planar complexes; this has been confirmed by the single crystal X-ray structure of $[\text{Pd}(\text{L}^2)]^{2+}$ (6); Pd-S = 2.23-2.33Å. By contrast, coordination of two molecules of (L^3) 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^3) in this system appears therefore to be crucial in stabilising the d^7 metal centre. In addition, the positive charge in $[\text{M}(\text{L}^3)_2]^{3+}$ would be expected to be stabilised further by delocalisation onto the thia ligands. The extent of positive charge on the thia donors is currently being assessed.



The homoleptic hexathia complexes $[\text{Rh}(\text{L}^3)_2]^{3+}$ and $[\text{Ru}(\text{L}^3)_2]^{2+}$ have also been synthesised. The single crystal X-ray structures of these products confirm their octahedral stereochemistries with Rh-S = 2.330, 2.332; Ru-S = 2.327-2.336Å. An unexpected feature of the structure of $[\text{Ru}(\text{L}^3)_2](\text{BPh}_4)_2 \cdot 2\text{dmsO}$ (7) is the approach of the dmsO solvate molecules towards the outer face of the coordinated trithia ligands. This occurs via H-bonding of the O-donor of the dmsO solvates with the protons of the methylene groups of (L^3), O...H = 2.201, 2.419, 2.790, 3.291Å. This secondary interaction between the dmsO molecules with the rear cone/cavity of the coordinated trithia 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 . The development of related systems incorporating larger and deeper cavities is under investigation.

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