The Preparation and Co-ordination Chemistry of 2,2′:6′,2″-Terpyridine Macrocycles. Part 5.[1] Unsubstituted Fifteen-membered-ring Macrocycles containing 2,2′:6′,2″-Terpyridine†

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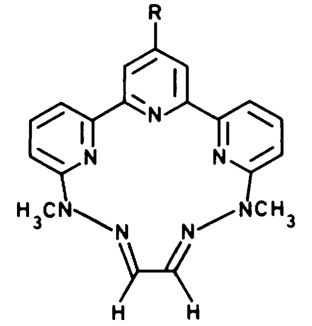
The preparation of a simple unsubstituted quinquedentate macrocycle incorporating a 2,2′:6′,2″-terpyridine moiety by a transient template reaction is described. The cobalt(II), nickel(II), copper(II), and zinc(II) complexes of the ligand are described, as is the oxidation–reduction chemistry of these compounds. E.s.r. studies indicate that pentagonal-bipyramidal complexes, with solvent molecules occupying the axial sites, are formed.

We recently reported the preparation of a phenyl-substituted macrocycle incorporating a 2,2′:6′,2″-terpyridine moiety[1–4] (L^1), and demonstrated the novel transient template behaviour of dimethyltin(IV) in the synthesis of the metal-free ligand. Our previous experiences with substituted 2,2′:6′,2″-terpyridine complexes[5] indicated that the unusual redox properties of the transition metal complexes of L^1 might be sensitive to the nature of the substituents. In this paper, we describe the synthesis and co-ordination chemistry of the parent macrocyclic ligand, L^3.

Results and Discussion

The functionalised 2,2′:6′,2″-terpyridines were prepared by a modification of the procedures we have previously used for the preparation of L^1. The central ring of the 2,2′:6′,2″-terpyridine ring system was generated by the condensation of derivatives of 2-acetyl-6-bromopyridine. The enone, 2-bromo-6-(3′-oxopropenyl)pyridine, could not be prepared by the condensation of 2-acetyl-6-bromopyridine with formaldehyde under a wide variety of conditions. However, the enone equivalent, the Mannich base, 2-bromo-6-(3′-dimethylammonio-1′-oxopropyl)pyridine chloride (**1**), was readily obtained by the reaction of 2-acetyl-6-bromopyridine with dimethylammonium chloride and paraformaldehyde. This compound reacted smoothly with the previously reported pyridinium salt (**2**)[1–4] in the presence of ammonium acetate to give 6,6″-dibromo-2,2′:6′,2″-terpyridine (**3**) in 45% yield. Nucleophilic displacement of bromide by methylhydrazine proceeded readily at elevated temperature to give 6,6″-bis(α-methylhydrazino)-2,2′:6′,2″-terpyridine (L^2) in 64% yield (Scheme).

The bis(α-methylhydrazino) ligand, L^2, reacted with chloroform solutions of $[SnMe_2Cl_2]$ to give a yellow precipitate of the adduct $[SnMe_2(L^2)]Cl_2$. This is a reaction exactly analogous to that by which the phenyl-substituted compound $[SnMe_2(L^1)]Cl_2$ is prepared.[4] We have previously demonstrated that the latter compound possesses a pentagonal-bipyramidal dication, with the tin-bonded methyl groups occupying the axial sites.[1] We consider that the unsubstituted complex, $[SnMe_2(L^2)]Cl_2$, possesses a similar geometry; support for this comes from the ^1H n.m.r. spectrum of solutions of the complex. The spectrum indicates that the molecule possesses the expected C_2 symmetry on the n.m.r. time-scale at observation frequencies of 400, 250, and 80 MHz. The NMe and SnMe groups appear as singlets at each frequency. The assignment of the spectrum was made on the basis of homonuclear decoupling experiments, and is reported in the Experimental section. The magnitude of the two-bond coupling between the tin-bonded methyl groups and the metal is also indicative of the proposed structure. The observed coupling constants, $^2J(^{119}SnH)$ 111.7 Hz, $^2J(^{117}SnH)$ 107.4 Hz (^{119}Sn, 8.58%, $I = \frac{1}{2}$; ^{117}Sn, 7.61%, $I = \frac{1}{2}$),[6] are characteristic of a *trans*-diaxial arrangement of the methyl groups, with a C–Sn–C angle close to 180°.[7]



L^1 R = Ph

L^3 R = H

The reaction of $[SnMe_2(L^2)]Cl_2$ with ethanedial (glyoxal) proceeded as expected, and the salt of the metal-free macrocycle, $[H_2L^3][PF_6]_2$, was obtained after filtration to remove tin oxides and the addition of ammonium hexafluorophosphate. There seems to be no reason to suspect that the hole size of the unsubstituted ligand L^3 should differ from that of L^1, which we have characterised by an *X*-ray single-crystal structural analysis.[4] We consider the transient template behaviour to arise from a mismatch in metal-ion size and ligand hole size, specifically from the contraction of the N_5 donor set on passing from the open-chain hydrazine ligand to the macrocyclic bis(hydrazone), resulting in the labilisation of the metal.

The identity of the product was confirmed by ^1H n.m.r. and mass spectroscopy. The mass spectrum of the salt $[H_2L^3][PF_6]_2$ exhibited a highest mass peak at *m/z* 343, corresponding to $[L^3]^+$. Decoupling experiments established the assignments for the aromatic resonances reported in the Experimental section. A number of interesting comparisons may be drawn between the ^1H n.m.r. spectra of compound (**3**), L^2, $[SnMe_2(L^2)]Cl_2$, $[H_2L^3][PF_6]_2$, and $[Zn(H_2O)L^3][PF_6]_2$ (see later). The crystal structure of (**3**) has been determined, and the compound shown to possess the expected *trans,trans* coplanar arrangement of pyridyl rings.[8] We assume that the bis(α-methylhydrazino) ligand L^2 adopts the same conformation, in the absence of any hydrogen-bonding interactions stabilising the *cis,cis* coplanar arrangement. A comparison of the spectra of L^2 and its adduct with dichlorodimethyltin(IV) reveals the expected downfield

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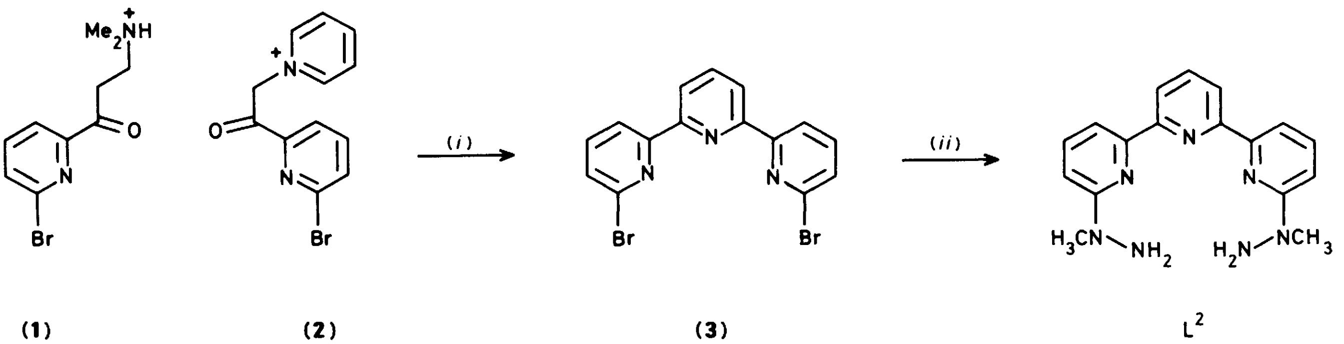
† *Non-S.I. unit employed:* G = 10^{-4} T.



Scheme. (*i*) NH_4O_2CMe; (*ii*) $MeNHNH_2$

Table. Analytical data * for the complexes $[M(H_2O)_2L^3][PF_6]_2$

M	Colour	Analysis (%) C	H	N
Co	Red	30.5	3.2	12.5
		(30.6)	(3.1)	(13.1)
Ni	Yellow	30.9	2.8	13.5
		(31.3)	(2.9)	(13.4)
Cu	Brown	30.8	2.7	13.3
		(31.1)	(2.9)	(13.3)
Zn	Yellow	31.1	2.7	13.2
		(31.0)	(2.9)	(13.3)

* Required values are given in parentheses.

shift associated with deshielding resulting from the build-up of positive charge on the ligand. The shifts of H^4 ($\Delta\delta$ 0.68) and $H^{4,4''}$ ($\Delta\delta$ 0.58) are larger than those of the remaining protons in the molecule. This is consistent with the transmission of the positive charge to the rear of the ring, and major build-up of positive charge at C^4 of the pyridines. The downfield shifts of these same protons in the spectra of $[H_2L^3][PF_6]_2$ and $[Zn(H_2O)_2L^3][PF_6]_2$ indicate that there is a considerable interaction between the co-ordinated ligand and the central ion in these cases as well. This is particularly interesting in view of our previously reported observation that the nickel atom in $[Ni(EtOH)_2L^1][PF_6]_2$ is displaced towards the nitrogen atom of the central pyridine ring; this was attributed to a π-type interaction between the metal atom and the pyridine ring.[4] The build-up of positive charge at this site will favour conjugation of the 4′-phenyl substituent with the ring, and hence increase the multiple-bond character of the nitrogen–nickel bonding.

Metal complexes of the macrocyclic ligand L^3 were readily prepared by the reaction of the metal acetate or metal chloride with $[H_2L^3][PF_6]_2$ in methanol. The complexes $[M(H_2O)_2L^3][PF_6]_2$, with M = cobalt(II), nickel(II), copper(II), or zinc(II), were prepared in good yield. In each case, analysis and i.r. spectroscopy established the presence of two co-ordinated water molecules. We thus propose pentagonal-bipyramidal geometries for all the complexes, with the water molecules occupying the axial sites. This is a similar geometry to that observed for the nickel(II) complex of L^1 which we have structurally characterised.[3]

The red complex cation $[Co(H_2O)_2L^3]^{2+}$ was converted into the acetonitrile complex cation $[Co(MeCN)_2L^3]^{2+}$ by treating an acetonitrile solution of the hexafluorophosphate salt with molecular sieves (4 Å). The cyclic voltammogram of $[Co(MeCN)_2L^3]^{2+}$ in acetonitrile exhibited a reversible oxidation wave at +1.102 V, and a quasi-reversible reduction at 1.340 V (scan rate 100 mV s^{-1}). The former undoubtedly corresponds to the formation of the cobalt(III) complex cation, $[Co(MeCN)_2L^3]^{3+}$; the corresponding oxidation of $[Co(MeCN)_2L^1]^{2+}$ occurs at +1.11 V. Treatment of the solution with either of the π-acceptor ligands, carbon monoxide or trimethyl phosphite, results in the disappearance of the oxidative wave, and the development of a fully reversible reduction wave at −1.250 V and an irreversible reduction wave at −1.8 V. This parallels the behaviour of the phenyl-substituted compound, which exhibits a reversible reduction at −1.36 V, which moves to −1.24 V upon the addition of π-acceptor ligands. The reduction of complexes incorporating ambivalent π-acceptor ligands, such as 2,2′-bipyridine or 2,2′:6′,2″-terpyridine, may be ligand- or metal-centred. The reduction products of $[M^{II}L]^{2+}$ may be depicted by the limiting formulae $[M^{II}(L^{\bullet -})]^+$ or $[M^{I}L]^+$. Simple electrochemical techniques cannot distinguish between these two cases; we have demonstrated that the combination of preparative electrochemistry with e.s.r. spectroscopy is a powerful technique for the investigation of reduction products of these types. In the cases of both $[Co(MeCN)_2L^3]^{2+}$ and $[Co(MeCN)_2L^1]^{2+}$, the reduction product, in the absence of added π-acceptor ligands, is the green ligand-centred radical, $[Co^{II}(MeCN)_2(L^{\bullet -})]^+$ resulting from a ligand-centred reduction. The solutions exhibit broad anisotropic signals due to the cobalt(II) centre, and a sharp isotropic signal at *g* 2.002 in their e.s.r. spectra; no hyperfine coupling is observed to the isotropic signal. In contrast, in the presence of π-acceptor ligands such as carbon monoxide or trimethyl phosphite, no e.s.r. signal is observed at 77 K, after preparative electro-reduction at the potential of the first reduction wave. This is the expected behaviour for a d^8 cobalt(I) complex. We have structurally characterised the trimethyl phosphite adduct of an electrogenerated cobalt(I) complex of a related quinquedentate macrocycle based on 1,10-phenanthroline.[9] Electrogeneration at the second reduction potential resulted in the formation of $[Co^{I}(MeCN)_2(L^{\bullet -})]^0$, again characterised by e.s.r. spectroscopy.

The nickel(II) complex of the macrocycle L^3 was isolated as its hexafluorophosphate salt, $[Ni(H_2O)_2L^3][PF_6]_2$. An exactly analogous method to that described for the cobalt(II) complex was used for the conversion of the diaqua complex into the bis(acetonitrile) species, $[Ni(MeCN)_2L^3]^{2+}$. The electrochemical behaviour of this complex differed in some interesting ways from that of $[Ni(MeCN)_2L^1]^{2+}$. Cyclic voltammetry of the acetonitrile solution revealed a quasi-reversible oxidation at +1.09 V, a quasi-reversible reduction at −1.5 V, and an irreversible reduction at −1.5 V (all at scan rate 100 mV s^{-1}). In contrast, the complex with L^1 exhibits fully reversible reductions at −1.07 and −1.49 V. These were shown to correspond to reduction to the nickel(I) complex $[Ni^{I}(MeCN)_2L^1]^+$ and the nickel(I) ligand-radical complex $[Ni^{I}(MeCN)_2(L^{1\bullet -})]^0$ respectively. This indicates that the phenyl-substituted ligand stabilises the nickel(I) centre more efficiently than the parent macrocycle L^3. Although changes in the positions of the reduction waves occurred upon the addition of trimethyl phosphite, no fully reversible reductions developed for the ligand L^3. Repeated attempts to electrogenerate a nickel(I) complex of L^3 under a wide variety of conditions failed, the only products being dark coloured materials which did not exhibit e.s.r. spectra.

We consider that the 4′-phenyl substituent plays a vital role in stabilising the low oxidation state of the metal. This has also been observed by Hughes *et al.*[10] in their studies of octahedral first-row transition-metal complexes with phenyl-substituted derivatives of 2,2′-bipyridine and 2,2′:6′,2″-terpyridine. The stabilisation probably has two origins. First, the presence of the bulky phenyl substituent in the 4′ position effectively prevents dimerisation through this site, and hence lengthens the lifetime of the radical species. The second function is to provide an effective electron sink for the excessive electron density on the nickel(I) site. This may be achieved by the overlap of filled *d* orbitals on the nickel with the lowest unoccupied molecular orbital (l.u.m.o.) of the polypyridine; extending the conjugation over the phenyl group will lower the energy of the l.u.m.o. The displacement of the nickel atom towards the central pyridine ring which bears the phenyl substituent in $[Ni(EtOH)_2L^1][PF_6]_2$ has already been mentioned; we now believe this to represent a significant bonding interaction. This same interaction is reflected in the low dihedral angle which the phenyl group makes with the central pyridine ring, which represents a compromise between the van der Waals interactions, favouring a perpendicular arrangement, and the overlap of π orbitals favouring coplanarity.

The copper(II) complex $[Cu(MeCN)_2L^3]^{2+}$ was prepared by dehydration of an acetonitrile solution of $[Cu(H_2O)_2L^3][PF_6]_2$. The complex exhibited a reversible reduction at -0.31 V, an irreversible reduction at -1.90 V, and a quasi-reversible oxidation at $+1.20$ V (scan rate 100 mV s^{-1}). This latter oxidation became fully reversible upon lowering the temperature of the solution to $-30°$ C, and probably corresponds to the formation of the copper(III) complex. We are currently investigating the nature of these highly coloured oxidation products. Controlled-potential electrolysis at -0.31 V resulted in the formation of a green-brown, diamagnetic solution containing $[Cu^I(MeCN)_nL^3]^+$. A low-intensity band at 471 nm (21 231 cm^{-1}) was observed in the electronic spectrum of the copper(II) complex; this band disappeared upon reduction to the copper(I) species, and may thus be assigned to the $^2E_g \longleftarrow {}^2T_{2g}$ transition of the d^9 copper(II) ion. The e.s.r. spectrum of $[Cu(MeCN)_2L^3]^{2+}$ exhibits a broad anisotropic resonance, $g_{\parallel}$ 2.45, $g_{\perp}$ 2.07, and $A_{\parallel}$ (av.) 65 G [Figure (*a*)]. These values are consistent with the copper ion being in an axially elongated pentagonal-bipyramidal environment.[11] The unpaired electron resides in a $d_{x^2-y^2}$ orbital, which leads to the predicted ordering of *g* values, $g_{\parallel} > g_{\perp} > 2$; the high value of $g_{\parallel}$, which is more commonly close to 2.2, suggests a relatively small energy gap between the $d_{x^2-y^2}$ and d_{xy} orbitals.

Upon the addition of imidazole to an acetonitrile solution of the copper(II) complex, an immediate colour change from orange-brown to yellow occurred. The potential for reduction to the copper(I) complex moved to markedly more negative potential at -0.48 V. This indicates that the reduction of the imidazole adduct, presumably $[Cu(Him)_2L^3]^{2+}$ (Him = imidazole), is more difficult than that of the acetonitrile adduct. This is fully in accord with the known strong π- and σ-donor properties of imidazole as a ligand. The e.s.r. spectrum of the imidazole adduct is shown in Figure (*b*). An intense $g_{\perp}$ signal is observed, which clearly exhibits hyperfine coupling to the copper nucleus ($I = \frac{3}{2}$), and a less intense $g_{\parallel}$ signal, again exhibiting coupling to copper. The ground state of the complex is inverted with respect to that of the acetonitrile adduct, with the electron residing in a $d_{x^2-y^2}$ orbital. The parameters derived from the spectrum ($g_{\parallel}$ 2.00, $g_{\perp}$ 2.25, $A_{\parallel}$ 97 G, and $A_{\perp}$ 86 G) are consistent with a pentagonal-bipyramidal environment, in which the axial field is very much stronger than that in the equatorial plane, as would be expected for a complex with axial imidazole ligands. Similar inversions of the ground state in imidazole adducts of other copper(II) complexes with quinquedentate ligands based on 2,2′-bipyridine or 1,10-phenanthroline have been observed.[12]

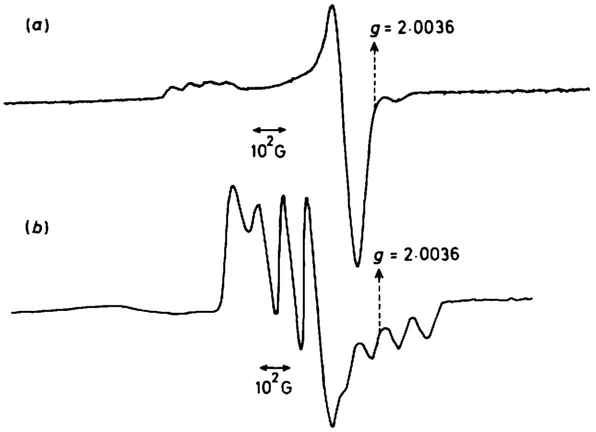


Figure. The e.s.r. spectrum of the complexes $[CuX_2L^3]^{2+}$; (*a*) X = MeCN; (*b*) X = Him

The zinc complex $[Zn(H_2O)_2L^3][PF_6]_2$ was similarly prepared as a slightly soluble (acetone, methanol, acetonitrile) yellow solid. The ^1H n.m.r. spectrum of this complex closely resembled that of the free ligand.

We have formulated the imidazole and acetonitrile adducts as the pentagonal-bipyramidal bis compounds by analogy with the related complexes with L^3, for which we have structural data for the imidazole adducts with each metal.[8]

Experimental

Infra-red spectra were recorded on a Perkin-Elmer 983 spectrophotometer as suspensions in Nujol or in compressed potassium bromide discs. N.m.r. spectra were recorded on Bruker WP 80, WM 250, or WH 400 spectrometers. Electrochemical measurements were made using a P.A.R. model 170 electrochemistry system or a Metrohm E506 Polarecord and Metrohm E612 va Scanner connected to a home-built OTTLE cell in a Pye Unicam PU 8800 spectrophotometer. E.s.r. spectra were measured on a Varian E 109 spectrometer (*X*-band).

2,6-Dibromopyridine, [2′-(6″-bromo-2″-pyridyl)-2′-oxoethyl]pyridinium iodide, and 2-acetyl-6-bromopyridine were prepared by the literature methods.[1,13,14] Dimethyltin(IV) dichloride was used as supplied (Strem).

All electrochemical potentials are quoted with reference to an external silver–silver(I)(acetonitrile) reference electrode.

Syntheses.—2-*Bromo*-6-(3′-*dimethylammonio*-1′-*oxopropyl*)-*pyridine chloride* (1). 2-Acetyl-6-bromopyridine (2.45 g, 12.25 mmol), dimethylammonium chloride (2.45 g, 30 mmol), and paraformaldehyde (1.8 g, 60 mmol CH_2O) were heated to reflux in ethanol (25 cm^3) with concentrated hydrochloric acid (0.05 cm^3) for 3 h with strict exclusion of moisture. On cooling, the required compound was precipitated as a pale purple solid (2.5 g, 70%), $\nu_{max.}$ 3 066m, 3 045s, 2 956m, 2 653s, 2 555s, 1 696s, 1 328s, and 781s cm^{-1} (KBr disc); *m/z* 257 and 259 (M^+).

6,6″-*Dibromo*-2,2′:6′,2″-*terpyridine* (3). Compound (1) (0.465

g, 1.58 mmol), [2′-(6″-bromo-2″-pyridyl)-2′-oxoethyl]pyridinium iodide (**2**) (0.620 g, 1.58 mmol), and ammonium acetate (2.0 g) were heated to reflux in methanol (15 cm^3) for 2 h. On cooling, 6,6″-dibromo-2,2′:6′,2″-terpyridine (**3**) was precipitated as a pale brown solid (0.28 g, 45%) (Found: C, 46.2; H, 2.6; Br, 41.0; N, 10.8; M^+ 389,391,393. $C_{15}H_9Br_2N_3$ requires C, 46.0; H, 2.3; Br, 41.0; N, 10.7%; M^+ 389, 391, 393); $\nu_{max.}$ 3 057w, 1 602m, 1 575m, and 1 542s cm^{-1} (Nujol); δ_H ($CDCl_3$) 7.51 (2 H, d, *J* 7.8, $H^{5,5''}$), 7.70 (2 H, t, *J* 7.8, $H^{4,4''}$), 7.95 (1 H, t, *J* 7.9, $H^{4'}$), 8.45 (2 H, d, *J* 7.9, $H^{3',5'}$), and 8.53 (2 H, d, *J* 7.8 Hz, $H^{3,3''}$); *m*/*z* 389, 391, and 393 (M^+), 310, 312 (M − Br).

6,6″-*Bis*(α-*methylhydrazino*)-2,2′:6′,2″-*terpyridine* (L^2). Compound (**3**) (0.5 g, 1.28 mmol) was heated to reflux (under a nitrogen atmosphere) with methylhydrazine (15 cm^3) for 15 h. On cooling, pale yellow plates of L^2 separated (0.24 g, 64%) (Found: C, 63. 3; H, 6.0; N, 30.7%; M^+ 321. $C_{17}H_{19}N_7$ requires C, 63.6; H, 5.9; N, 30.5%; M^+ 321); $\nu_{max.}$ 3 330w, 3 195w, 3 050w, 3 005w, 2 900w, 1 635s, and 1 565s cm^{-1} (Nujol); δ_H ($CDCl_3$) 3.36 (6 H, s, N–CH_3), 4.2 (4 H, br s, NH_2), 6.98 (2 H, t, *J* 7.9, $H^{3,3''}$), 7.65 (2 H, t, *J* 7.9, $H^{4,4''}$), 7.79 (1 H, t, *J* 7.8, $H^{4'}$), 8.38 (2 H, d, *J* 7.8, $H^{3',5'}$), and 7.99 (2 H, d, *J* 7.9 Hz, $H^{5,5''}$).

[6,6″-*Bis*(α-*methylhydrazino*)-2,2′:6′,2″-*terpyridine*]*dimethyltin*(IV) *chloride*. Dichlorodimethyltin(IV) (0.22 g, 1 mmol) and compound L^2 (0.321 g, 1 mmol) were heated to reflux in chloroform (25 cm^3) for 2 h. The yellow precipitate was collected and air-dried to yield $[SnMe_2L^2]Cl_2$ (0.51 g, 94%) (Found: C, 42.4; H, 4.3; N, 18.0. $C_{19}H_{25}Cl_2N_7Sn$ requires C, 42.1; H, 4.6; N, 18.1%); $\nu_{max.}$ 3 435m, 3 360w, 3 340w, 3 150s, 3 038s, 2 927m, 1 619s, 1 600s, and 1 555s cm^{-1} (Nujol); δ_H (CD_3SOCD_3) 0.93 [6 H, s, Sn–CH_3, *J*(^{119}SnH) 111.7, *J*(^{117}SnH) 107.4], 3.60 (6 H, s, N–CH_3), 7.36 (2 H, d, *J* 7.7, $H^{3,3''}$), 8.17 (2 H, d, *J* 7.7, $H^{5,5''}$), 8.23 (2 H, t, *J* 7.7, $H^{4,4''}$), 8.67 (1 H, t, *J* 7.8, $H^{4'}$), and 8.81 (2 H, d, *J* 7.8 Hz, $H^{3',5''}$).

$[H_2L^3][PF_6]_2$. The complex $[SnMe_2L^2]Cl_2$ (0.096 g, 1.77 mmol), ethanedial (40% w/w aqueous solution, 0.257 µl), and hydrochloric acid (0.1 cm^3) were heated to reflux in methanol (20 cm^3) for 2 h to give a turbid orange suspension. This was filtered hot through Celite, and the filtrate treated with ammonium hexafluorophosphate (0.2 g) to give an orange precipitate of $[H_2L^3][PF_6]_2$ (0.064 g, 57%) (Found: C, 33.2; H, 3.0; N, 14.9. $C_{19}H_{19}F_{12}N_7P_2$ requires C, 33.3; H, 3.0; N, 14.9%); $\nu_{max.}$ 3 221m, 3 127w, 1 635s, 1 611s, 1 567w, 1 526m, 840s, and 559s cm^{-1} (KBr disc); δ_H (CD_3SOCD_3) 3.83 (6 H, s, N–CH_3), 7.88 (2 H, d, *J* 7.7, $H^{3,3''}$), 8.00 (2 H, s, N=CH), 8.21 (2 H, d, *J* 7.7, $H^{5,5''}$), 8.54 (2 H, t, *J* 7.7, $H^{4,4''}$), 8.63 (2 H, d, *J* 7.8 $H^{3',5''}$), and 8.44 (1 H, t, *J* 7.8 Hz, $H^{4'}$); *m*/*z* 343 (M^+).

Metal complexes of L^3. The salt $[H_2L^3][PF_6]_2$ (0.10 g, 0.16 mmol) was heated in methanol (25 cm^3) with the appropriate metal acetate (0.16 mmol) for 2 h. The pale yellow solutions so obtained were treated with aqueous ammonium hexafluorophosphate solution to yield the metal complexes as yellow or red solids (90—100%). See the Table for analytical data.

Acknowledgements

We should like to thank the S.E.R.C. for the award of a Research Studentship (to J. M. H.) and a Post-Doctoral Studentship (to R. C. S. M.). We should also like to thank Mr. Paul Loveday for assistance in running e.s.r. spectra.

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Received 28*th October* 1985; *Paper* 5/1875