Mononuclear Iron, Cobalt, and Nickel Complexes of a 30-Membered Macrocyclic Ligand

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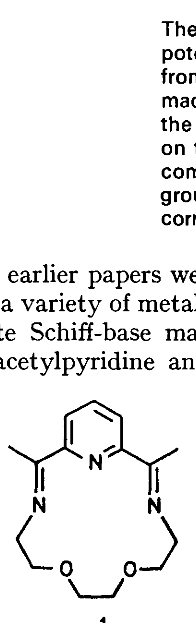
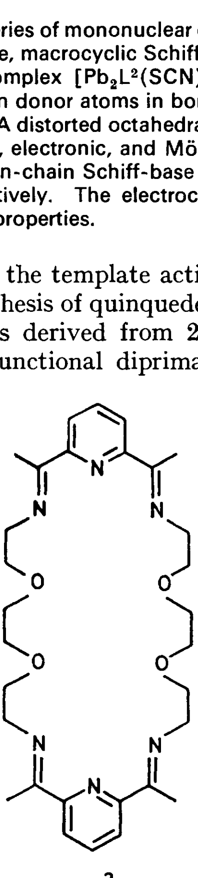
The preparation of a series of mononuclear complexes $[ML^2]X_n$ $\{M = Fe^{II}, Co^{III}, Co^{II}, \text{or } Ni^{II}$; L^2 = a 30-membered, potentially decadentate, macrocyclic Schiff base ligand; $X = [ClO_4]^-$, $[BPh_4]^-$, or $[Co(NCS)_4]^{2-}$, $n = 1, 2, \text{or } 3\}$ from the binuclear complex $[Pb_2L^2(SCN)_4]$ is described. Unlike the reactant lead(II) complex, in which the macrocycle uses all ten donor atoms in bonding to the metal ions, only the six nitrogen atoms are co-ordinated in the new complexes. A distorted octahedral (approximate D_{2d} symmetry) structure is assigned to all the complexes on the evidence of i.r., electronic, and Mössbauer spectra, magnetic data, and of the properties of corresponding complexes of two open-chain Schiff-base ligands. The d^6 and d^7 complexes have spin-singlet and spin-doublet ground states, respectively. The electrochemical behaviour of the iron and cobalt complexes is reported and correlated with other properties.

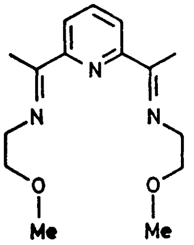
IN earlier papers we have described the template action of a variety of metal ions in the synthesis of quinquedentate Schiff-base macrocyclic ligands derived from 2,6-diacetylpyridine and several tetrafunctional diprimary amines. For example, the 15-membered macrocycle L^1 may be isolated in good yield (as the metal complex) when 2,6-diacetylpyridine and 3,6-dioxaoctane-1,8-diamine react in the presence of salts of Mg^{II}, Mn^{II}, Fe^{III}, Fe^{II}, or Co^{II}.[1] More recently, we have observed an interesting variant of this reaction when $Pb[SCN]_2$ is employed as the template salt.[2] Here, a '2 + 2' cyclic condensation of diketone and diprimary amine occurs to yield the binuclear complex $[Pb_2L^2(SCN)_4]$ of the 30-membered ring L^2, in high yield. We were interested to prepare other metal derivatives of this novel large cyclic ligand. Application of metal-exchange (transmetallation) reactions used successfully [3] in several of the smaller ring systems has proved effective in this case also. This paper describes the synthesis, properties, and structures of some mononuclear iron(II), cobalt(II), cobalt(III), and nickel(II) complexes of L^2. As an aid to the structural assignments it was found helpful to examine the properties of the corresponding complexes of the new open-chain ligands L^3 and L^4 and a brief description of these is included.



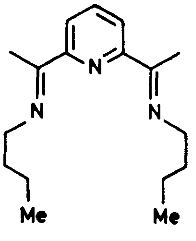
L^1



L^2



L^3



L^4

RESULTS AND DISCUSSION

The highly crystalline complexes (see Table 1) of the 30-membered 'N_6O_4' macrocycle L^2 with Fe^{II}, Co^{II}, and Ni^{II} were prepared in 65—90% yield by reaction of $[Pb_2L^2(SCN)_4]$ with an excess of the appropriate metal perchlorate (or thiocyanate) in methanol (see Experimental section for details). Replacement of the Pb^{2+} ions from the macrocycle was effected readily as judged by an almost instantaneous colour change on mixing of the reactants. The cobalt(III) complex was prepared by displacement of Ag^I from $[Ag_2L^2][ClO_4]_2$ by Co^{II} in which case a redox reaction occurred, the cobalt(II) ion being oxidized to Co^{III} with accompanying precipitation of Ag metal. Alternatively, the cobalt(III) complex may be prepared by oxidation of $[CoL^2]^{2+}$ with Ag^I. In general, the complexes appear indefinitely stable in the solid state. All are soluble to varying degrees in water and polar organic solvents. All appear stable to hydrolysis.

On the basis of the combined evidence of the physical properties and of preliminary *X*-ray data (see below) it is concluded that all the complexes are salts of the six-co-ordinate (approximately octahedral) $[ML^2]^{n+}$ cations in which the donor atoms are the six nitrogens of the macrocycle, the oxygen atoms being unco-ordinated [structure (I)]. Additional support for this structural formulation is provided by the very close correspondence in properties of the $[ML^2]^{n+}$ complexes with those of the $[ML^3{}_2]^{n+}$ and $[ML^4{}_2]^{n+}$ complexes. L^3 is an open-chain

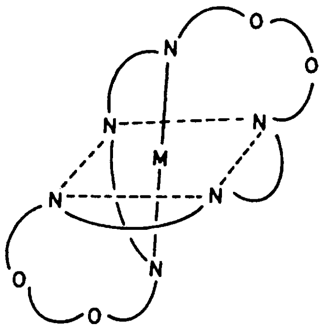
TABLE 1

Analytical, magnetic, and electrical conductance data for the complexes

Complex	Colour	Analysis (%)								$\mu_{eff.}$[a]	Λ[b]
		Found				Calc.					
		C	H	N	Metal	C	H	N	Metal	B.M.	S cm² mol⁻¹
$[FeL^2][ClO_4]_2\cdot H_2O$	Dark purple	43.7	5.3	10.3	6.8	43.8	5.4	10.2	6.8	0.80	337
$[FeL^2][BPh_4]_2$	Dark purple	74.9	6.8	6.7		75.3	6.6	6.8			
$[FeL^2][Co(NCS)_4]$	Dark lilac	45.0	4.8	15.7		45.5	4.7	15.6			
$[Co^{II}L^2][ClO_4]_2\cdot H_2O$	Dark red	43.3	5.3	10.3	7.1	43.6	5.4	10.2	7.1	1.98	344
$[Co^{II}L^2][Co(NCS)_4]$	Dark purple	44.3	4.7	15.7		45.3	4.7	15.6		3.51[c]	
$[Co^{III}L^2][ClO_4]_3\cdot H_2O$	Yellow-orange	38.6	4.6	8.8	6.3	38.9	4.6	9.1	6.4	0.90	423
$[NiL^2][ClO_4]_2\cdot H_2O$	Brown	43.3	5.3	10.4		43.6	5.4	10.2		3.12	344
$[FeL^3{}_2][ClO_4]_2$	Dark purple	44.4	5.8	10.1		44.5	5.7	10.4		0.95	338
$[Co^{II}L^3{}_2][ClO_4]_2$	Dark red	44.6	5.7	10.5		44.3	5.7	10.3		2.07	332
$[Co^{III}L^3{}_2][ClO_4]_3$	Yellow-orange	38.6	5.1	8.8		38.7	5.2	9.0		0.64	410
$[NiL^3{}_2][ClO_4]_2$	Brown	43.7	5.7	10.4		44.4	5.7	10.4		3.06	338
$[FeL^4{}_2][ClO_4]_2$	Dark purple	50.9	6.7	10.3		50.9	6.8	10.4		0.45	338
$[Co^{II}L^4{}_2][ClO_4]_2$	Dark red	50.8	6.8	10.4		50.8	6.8	10.4		2.27	329
$[Co^{II}L^4{}_2][Co(NCS)_4]$	Dark purple	51.0	6.1	15.6		50.9	6.1	15.6		3.44[c]	
$[Co^{III}L^4{}_2][ClO_4]_3$	Yellow-orange	45.2	6.1	9.4		45.2	6.0	9.3		0.59	391
$[NiL^4{}_2][ClO_4]_2$	Brown	50.7	6.7	10.5		50.8	6.8	10.4		3.18	342

[a] At 293 K; corrected for diamagnetism of ligands. [b] For 10^{-3} mol dm⁻³ MeCN solutions at 25 °C. [c] Average moment per metal atom.

analogue of one half of the 30-membered ring L². While it is potentially quinquedentate it is clear from the properties to be described below that in the bis complexes under discussion L³ is functioning as an ' N_3 ' terdentate ligand in exactly the same manner as L⁴ which, of course, has a maximum denticity of three. Analogous complexes of a number of terdentate ligands closely related to L³ and L⁴, for example pyridine-2,6-bis(*N*-methylcarbaldimine) and several 2,6-diacetylpyridine bis(hydrazones) have been described previously.[4] One of these bis[2,6-bis(1-hydrazonoethyl)pyridine]cobalt(II) iodide, has been structurally characterized by *X*-ray analysis [5] which confirms the six-co-ordinate nature of the cation, the planes of the two trimethine units intersecting at an angle of 83°.



(I)

Infrared Spectra.—The i.r. spectra of the L² complexes provide strong evidence that the L² macrocycle has remained intact during the metal-exchange process. Although there are many differences in detail there is an overall similarity with the spectrum of $[Pb_2L^2(SCN)_4]$. Importantly, no absorption at 3 200—3 400 cm⁻¹ or at *ca.* 1 700 cm⁻¹ was detected, indicating that no hydrolysis to precursor primary amine and carbonyl compound had occurred. However, significant differences in the spectra in the 1 500—1 700 cm⁻¹ region were apparent.

TABLE 2

Infrared (cm⁻¹) and electronic (10³ cm⁻¹) spectral data for the complexes

Complex	ν(C=N), py [a]	NCS [b]		$[ClO_4]^-$	Electronic spectra [c]
		ν_{asym}	δ		
$[FeL^2][ClO_4]_2\cdot H_2O$	1 630w, 1 600w 1 580w, 1 530w			1 110, 622	20.4 (19 000), 16.6 (26 300)
$[FeL^2][Co(NCS)_4]$	1 630w, 1 600w 1 560w, 1 530w	2 080	485		
$[Co^{II}L^2][ClO_4]_2\cdot H_2O$	1 628m, 1 588s			1 090, 622	24.0 (2 350), 20.7 (215), *ca.* 1 800 (sh)
$[Co^{II}L^2][Co(NCS)_4]$	1 625m, 1 588m	2 082	480		24.0 (2 600), 20.6 (2 350), 18.0 (1 800) 15.9 (1 100), 7.9 (50)
$[Co^{III}L^2][ClO_4]_3\cdot H_2O$	1 630w, 1 583s			1 090, 622	*ca.* 28.0 (sh), 22.2 (680), *ca.* 18.0 (sh)
$[NiL^2][ClO_4]_2\cdot H_2O$	1 632s, 1 590s			1 090, 622	*ca.* 18.0 (sh), 12.2 (48)
$[FeL^3{}_2][ClO_4]_2$	1 630w, 1 600w 1 560w, 1 530w			1 090, 624	20.0 (18 800), 16.6 (24 800)
$[Co^{II}L^3{}_2][ClO_4]_2$	1 632m, 1 595s			1 095, 624	23.6 (2 400), 20.4 (2 300), *ca.* 18.0 (sh)
$[Co^{III}L^2{}_2][ClO_4]_3$	1 625w, 1 590m			1 095, 620	*ca.* 28.0 (sh), 22.1 (700), *ca.* 18.0 (sh)
$[NiL^3{}_2][ClO_4]_2$	1 635s, 1 593s			1 090, 620	*ca.* 18.0 (sh), 12.2 (45)
$[FeL^4{}_2][ClO_4]_2$	1 630w, 1 600w 1 560w, 1 530w			1 090, 622	20.0 (18 000), 16.6 (26 500)
$[Co^{II}L^4{}_2][ClO_4]_2$	1 630m, 1 595s			1 090, 624	23.6 (2 400), 20.4 (2 200), *ca.* 18.0 (sh)
$[Co^{II}L^4{}_2][Co(NCS)_4]$	1 630m, 1 595s	2 078	485		24.1 (2 500), 20.6 (2 400), 17.6 (1 800), 16.0 (1 200), 7.9 (60)
$[Co^{III}L^4{}_2][ClO_4]_3$	1 625w, 1 588m			1 090, 622	*ca.* 28.0 (sh), 22.1 (660), *ca.* 18.0 (sh)
$[NiL^4{}_2][ClO_4]_2$	1 632s, 1 595s			1 090, 623	*ca.* 18.0 (sh), 12.2 (50)

[a] s = Strong, m = medium, w = weak. [b] In $[Co(NCS)_4]^{2-}$ counter ion. [c] In MeCN solution; ε/dm³ mol⁻¹ cm⁻¹ in parentheses.

In $[Pb_2L^2(SCN)_4]$ and in all previously investigated complexes of the ' single ' 15-membered macrocycle L^1, two strong bands, at 1 620—1 660 and at 1 580—1 600 cm^{-1}, occur in this region,[1,2] These are assigned to ν(C=N) and the highest-energy pyridine-ring vibration, respectively. For the present complexes, whether of L^2, L^3, or L^4, only the nickel(II) and cobalt(II) members display this pattern (Table 2), the intensities being somewhat reduced in the case of Co^{II}. In the case of the cobalt(III) complexes there is virtually no absorption at 1 620—1 660 cm^{-1} while for the iron(II) complexes the two strong bands are replaced by a set of four weak bands (Table 2). We associate the exceptional spectra of the cobalt(III) and iron(II) complexes with the fact that in both cases the metal ions are low spin (see below), the t_{2g}^6 configuration giving rise to strong metal–ligand interaction in the conjugated five-membered chelate rings. In such circumstances the simple group-frequency approach is inadequate and the characteristic C=N and pyridine-ring modes may be drastically altered in intensity and in position. Such effects have previously been observed in low-spin iron(II) complexes of α-di-imine ligands.[6]

Comparisons of the spectra of the perchlorate complexes with those of complexes containing other counter anions clearly show that the $[ClO_4]^-$ ν_3 and ν_4 modes at *ca.* 1 090 and at 620—625 cm^{-1}, respectively, are unsplit and characteristic of the unco-ordinated ion. In agreement, the electrical conductances in MeCN solution (Table 1) indicate that the compounds are salts of the $[ML^2]^{n+}$, $[ML^3{}_2]^{n+}$, and $[ML^4{}_2]^{n+}$ complex cations. In complexes containing the $[Co(NCS)_4]^{2-}$ counter anion the asymmetric $[NCS]^-$ stretch occurs as a strong band at *ca.* 2 080 cm^{-1} consistent with a terminal *N*-bonded mode.

Magnetic Measurements.—Magnetic moments at 293 K are in Table 1. The values for the iron(II) and cobalt(III) complexes are in all cases below 1.0 B.M.* consistent with fully spin-paired six-co-ordinate structures showing the usual small temperature-independent paramagnetism. The moments of the nickel(II) complexes are similarly consistent with an approximately octahedral constituent. The cobalt(II) complexes display room-temperature moments close to, or just a little above, the value appropriate to one unpaired electron and must therefore have spin-doublet ground states. Low-spin six-co-ordinate cobalt(II) complexes are relatively uncommon although several cobalt(II) complexes of α-di-imine and related ligands are known to exist in a thermally controlled high-spin $\rightleftharpoons$ low-spin equilibrium.[7] In order to see whether the present cobalt(II) complexes were fully in the low-spin form, magnetic susceptibility measurements were made over the temperature range 93—343 K. A small temperature dependence was observed for $[CoL^3{}_2][ClO_4]_2$ and $[CoL^4{}_2][ClO_4]_2$ suggesting that for these two complexes a small proportion of the metal ions is in the spin-quartet state. Thus, for the L^3 complex $\mu_{eff.}$ fell from 2.33 B.M. at 343 K to 1.89 B.M. at 93 K; the corresponding values for the L^4 complex are 2.52 and 1.85 B.M. No significant variation in $\mu_{eff.}$ was observed for $[CoL^2][ClO_4]_2 \cdot H_2O$ and it is concluded that this complex is virtually all in the low-spin state at these temperatures. It is one of the very few examples [8] for which this is the case.

Assuming $\mu_{eff.} = 4.4$ B.M. for Co^{II} in the tetrahedral anion, the calculated moments (293 K) of the cations in $[CoL^2][Co(NCS)_4]$ and $[CoL^4{}_2][Co(NCS)_4]$ are 2.1 and 2.3 B.M., respectively.

Mössbauer Spectra of the Iron(II) *Complexes.*—Measurements of isomer shift and quadrupole splitting were made at 293 and 77 K (Table 3). There is a very close similarity in the values of both parameters among the various complexes, in support of the view that all have a basically similar arrangement of donor atoms about the metal ion. The isomer shifts (0.1—0.2 mm s^{-1}, relative to natural iron) are in the range characteristic of low-spin six-co-ordinate iron(II).[9] The quadrupole splittings (*ca.* 0.9 mm s^{-1}) are large and presumably reflect splitting of the t_{2g} orbitals as a result of distortion from O_h symmetry (see below). The values are similar to, although somewhat smaller than, that (1.14 mm s^{-1} at 77 K) observed for the structurally related complex $[Fe(terpy)_2][ClO_4]_2$ (terpy = 2,2′:6′,2″-terpyridyl).[10]

TABLE 3

Mössbauer data (mm s^{-1}) for the iron(II) complexes

	Isomer shift [a,b] (δ)		Quadrupole splitting [b] (ΔE_Q)	
Complex	293	77 K	293	77 K
$[FeL^2][ClO_4]_2 \cdot H_2O$	0.12	0.20	0.94	0.91
$[FeL^2][BPh_4]_2$	0.14		0.97	
$[FeL^2][Co(NCS)_4]$	0.14	0.20	0.97	0.93
$[FeL^3{}_2][ClO_4]_2$	0.11	0.18	0.93	0.93
$[FeL^4{}_2][ClO_4]_2$	0.11	0.19	0.96	0.90

[a] Relative to natural ion. [b] Estimated error ±0.02 mm s^{-1}.

Electronic Spectra.—These were measured for both solids and solutions in MeCN in the range 5 000—30 000 cm^{-1}. Good agreement between the spectra for the two different phases was found and it is concluded that no decomposition or structural rearrangement occurs on dissolution. Data for solutions in MeCN are in Table 2. A significant observation is that the spectra of the complexes of a given metal ion are virtually identical, irrespective of the nature of the ligand.

The spectra of the iron(II) complexes consist of two intense bands at *ca.* 20 000 and *ca.* 16 600 cm^{-1}. The high intensities ($\varepsilon \sim 25\,000$ dm^3 mol^{-1} cm^{-1}) characterize the spectra as being charge transfer in origin and we therefore attribute them to transitions of the metal t_{2g} electrons to the $p_\pi{}^*$ antibonding orbitals of the tri-imine ligands. Krumholz [11] has attributed the occurrence of two well defined maxima in the charge-transfer spectra of related iron(II) complexes to splitting of the t_{2g} level. A preliminary single-crystal *X*-ray investigation [12] of $[Co^{II}L^2][ClO_4]_2 \cdot H_2O$, with which the iron(II) complex is isomorphous, has confirmed the six-co-ordinate bis(tri-

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* Throughout this paper: 1 B.M. ≈ 9.27 × 10^{-24} A m^2.

imine) structure proposed for these complexes. It further reveals that although the two pyridine nitrogens are exactly *trans* to each other the two distal imino-nitrogens of a given trimethine moiety are not, the N–Co–N bond angles being 156 and 161°. Thus the local symmetry about the metal ion is closer to D_{2d} than to O_h.† In this symmetry the triply degenerate t_{2g} set splits into e and b_2 levels; thus, both the electronic spectra and the large Mössbauer quadrupole splitting of the iron(II) complexes may be accounted for.

The electronic spectra of the cobalt(II) complexes comprise three bands in the range 18 000—24 000 cm^{-1}. Despite their high intensity (ε *ca.* 2 000 dm^3 mol^{-1} cm^{-1}) these bands seem likely to be *d–d* in origin, but in view of the lack of information on other low-spin six-co-ordinate complexes we defer making assignments. The relatively high intensities may be due to the absence of a centre of symmetry (D_{2d}).

Two spin-allowed transitions are expected for low-spin octahedral cobalt(III) complexes.[12] The present complexes display one well resolved band at 22 200 cm^{-1} but there is evidence for a second higher-energy band at *ca.* 28 000 cm^{-1} occurring as a shoulder on the tail of a much more intense band of the co-ordinated ligand. We assign these two bands to the transitions ${}^1A_{1g}\rightarrow{}^1T_{1g}$ and ${}^1A_{1g}\rightarrow{}^1T_{2g}$, respectively. A weak shoulder, on the low-energy side of the former transition, at *ca.* 18 000 cm^{-1} may be the spin-forbidden transition ${}^1A_{1g}\rightarrow{}^3T_{2g}$.

For the nickel(II) complexes the spectra all show a well resolved unsplit band at *ca.* 12 200 cm^{-1} which is assigned to ${}^3A_{2g}\rightarrow{}^3T_{2g}$ (in O_h symmetry). The greater than usual intensity (ε *ca.* 40 dm^3 mol^{-1} cm^{-1}) can once again be related to the absence of a centre of symmetry. The ${}^3A_{2g}\rightarrow{}^3T_{1g}$ transition is seen as a shoulder (at *ca.* 18 000 cm^{-1}) on the low-energy side of the co-ordinated-ligand absorption while the ${}^3A_{2g}\rightarrow{}^3T_{1g}(P)$ transition is completely obscured.

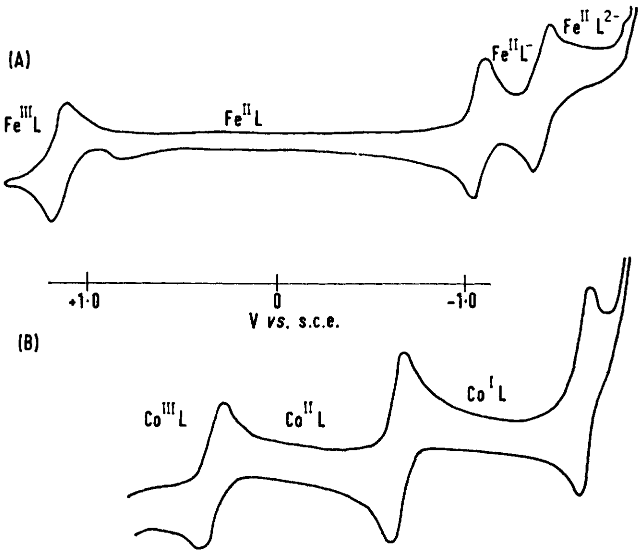
Complexes containing the $[Co(NCS)_4]^{2-}$ counter ion show, in addition, the expected bands at 15 900 and 7 900 cm^{-1} arising from the ${}^4A_2\rightarrow{}^4T_1(P)$ and ${}^4A_2\rightarrow{}^4T_1$ transitions.[13]

Electrochemical Measurements.—Cyclic voltammetry was carried out on dilute solutions (10^{-3} mol dm^{-3}) of the perchlorate salts of the iron(II) and cobalt(II) complexes in MeCN using 10^{-1} mol dm^{-3} $[NEt_4][ClO_4]$ as supporting electrolyte. As found for other properties investigated, the electrochemical results for a given metal are almost independent of the nature of the ligand, L^2, L^3, or L^4. Three redox waves were observed for the iron(II) complexes in the range +1.3 to −1.5 V (Figure). Values of $E_{Pc} - E_{Pa}$ were close to the theoretical value of 0.058 V for a reversible one-electron-transfer process in all cases (Table 4). The most positive wave ($E^{\ominus}$) in each case is ascribed to a redox process occurring at the metal, *viz.* Fe^{III} to Fe^{II}. The two redox processes ($E^{\ominus 2}$ and $E^{\ominus 3}$) occurring between −1.0 and −1.5 V are attributed to the formation of iron(II) complexes of, respectively, a radical anion $[L^2]^{-\cdot}$ and a diradical dianion $[L^2]^{2-\cdot}$ derived from L^2, or, in the case of L^3 and L^4, one and two radical anions, respectively. We prefer this assignment in which the added electrons are delocalized from the metal on to the ligand antibonding $p_\pi{}^*$ orbitals to the alternative interpretation in which the reduced species are iron(I) and iron(0) complexes of the neutral ligand. Support for this proposal is provided by the occurrence of the intense low-energy charge-transfer band in the visible spectrum. In fact, the function $F(E^{\ominus 1} - E^{\ominus 2})$, which on this model is the free energy associated with transfer of an electron from Fe^{II} to the co-ordinated ligand, has a value (212 kJ mol^{-1}) very close in magnitude to the mean energy (221 kJ mol) of the charge-transfer band system of the electronic spectrum. This numerical correspondence is remarkably close bearing in mind, as discussed earlier,[14] that the two energies refer to slightly different processes.

TABLE 4

Cyclic voltammetry data for the iron and cobalt complexes (10^{-3} mol dm^{-3}) in MeCN. The supporting electrolyte was 0.1 mol dm^{-3} $[NEt_4][ClO_4]$. Potentials in V *versus* the standard calomel electrode (s.c.e.). Sweep rate 0.05 V s^{-1}

Complex	$E^{\ominus 1}$	$E^{\ominus 2}$	$E^{\ominus 3}$
$[FeL^2][ClO_4]_2\cdot H_2O$	1.06	−1.14	−1.47
$[FeL^3{}_2][ClO_4]_2$	0.98	−1.13	−1.46
$[FeL^4{}_2][ClO_4]_2$	1.09	−1.15	−1.53
$[CoL^2][ClO_4]_2\cdot H_2O$	0.25	−0.76	−1.73
$[CoL^3{}_2][ClO_4]_2$	0.15	−0.72	−1.66
$[CoL^4{}_2][ClO_4]_2$	0.15	−0.70	−1.67



Cyclic voltammograms of $[FeL^2][ClO_4]_2\cdot H_2O$ (A), and $[CoL^2][ClO_4]_2\cdot H_2O$ (B) in MeCN. Potentials in V *versus* the s.c.e.; sweep rate 0.05 V s^{-1}

Three reversible redox waves were also observed for the cobalt(II) complexes (Figure). The most positive of these ($E^{\ominus 1}$) occurring at *ca.* +0.2 V is assigned to the Co^{III}–Co^{II} couple while that ($E^{\ominus 2}$) at *ca.* −0.75 V is assigned to the Co^{II}–Co^{I} couple. Thus, in this case we

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† In fact, the local symmetry about the metal is less than D_{2d} (actually C_2) because the planes of the two trimethine moieties intersect at an angle of 85 rather than 90°.

consider that on reduction of the cobalt(II) species the added electron is localized mainly on the metal rather than on the ligand as proposed for the iron system. This assignment is supported by the absence of charge-transfer absorption in the visible spectra of the cobalt(II) complexes and by the occurrence of $E^{\ominus 2}$ at a more positive potential for cobalt than for iron. The third redox wave occurs at a very negative potential of *ca.* −1.7 V. We have no means of determining whether the reduced species of this couple is better described as a cobalt(0) complex of the neutral ligand or as a cobalt(I) complex of the radical anion.

Conclusions.—The combined evidence of the physical properties detailed above leaves no doubt that all the complexes considered here are salts of the six-co-ordinate cations in which the six donors are the pyridine and azomethine nitrogen atoms. Thus, for the complexes of the macrocycle L^2 the four oxygen atoms of the ring are unco-ordinated. This behaviour contrasts with that found[2] for the complex $[Pb_2L^2(SCN)_4]$ where all ten donor atoms are used giving, with the thiocyanate groups, each metal atom a seven-co-ordinate environment. In the case of the iron(II), cobalt(III), and cobalt(II) complexes the large crystal-field stabilization energy (c.f.s.e.) accompanying the formation of spin-paired, approximately octahedral, structures is almost certainly the major driving force for the adoption by the macrocycle of this mode of co-ordination; spin pairing is not achieved in ' pentagonal ' complexes of these metal ions. No spin pairing occurs in the nickel(II) complexes, of course, although there is still a c.f.s.e. advantage in the octahedral as compared with pentagonal-bipyramidal symmetry. We have previously shown that Ni^{II} does not readily accommodate to a pentagonal arrangement of donor atoms.[3] Current work on the co-ordination chemistry of the 30-membered potentially decadentate macrocycle L^2 is directed towards the synthesis of bimetallic complexes capable, perhaps, of binding small molecules or ions between the two metal centres. Preliminary results show that in the case of Cu^{II} both mono- and bi-nuclear complexes may be prepared by appropriate control of reaction conditions.

EXPERIMENTAL

The complex $[Pb_2L^2(SCN)_4]$ was prepared as described previously.[2] The Schiff-base ligands L^3 and L^4 were prepared by condensation of 2,6-diacetylpyridine (0.03 mol) with, respectively, 2-methoxyethylamine (0.06 mol) and n-butylamine (0.06 mol) in benzene solution (48 h at room temperature) in the presence of molecular sieves.

All the L^2 complexes of the bivalent metal perchlorates were prepared by the same general method. The complex $[Pb_2L^2(SCN)_4]$ (0.001 mol) was dissolved in refluxing methanol (500 cm^3) and a 5 molar excess of the hydrated metal perchlorate was added. Refluxing was continued for 2 h at which time the solution was filtered and then concentrated on a rotary evaporator until crystallization began. Recrystallization was from methanol. Yields varied between 65 and 90%.

Tetraphenylborate salts were obtained by metathesis, as were the tetraisothiocyanatocobaltate(II) salts using a solution of $Co[NCS]_2$ and $Na[NCS]$ in methanol. The salt $[Co^{III}L^2][ClO_4]_2\cdot H_2O$ was obtained by addition of an excess of $Ag[ClO_4]$ to a hot methanol solution of the cobalt(II) complex. The precipitated Ag metal was removed and the product isolated in 88% yield from the filtrate.

The complexes of L^3 and L^4 were obtained by reaction of a 2.5 molar excess of the ligands with the appropriate metal salts in methanol.

Physical measurements were carried out as described in earlier papers.

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