Inorganica Chimica Acta, *90* (1984) 169–178

Complexes of a Macrocyclic Ligand Having Both Mono- and Binucleating Capability: Binuclear Mn(II), Fe(II), Co(II), Ni(II), Zn(II) Complexes

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Received January 25, 1984

Bi-nuclear complexes of 28- atom membered macrocycles derived from 2,6-diacetyl pyridine and the amines 3,3′-diamino dipropylamine or 3,3′-diamino-N-methyl dipropylamine have been prepared by template synthesis on Ag^+ or Pb^{2+}. Template synthesis can also be accomplished, in the case of 3,3′-diamino dipropylamine, but not its N-methyl derivative, on Gp(II) metal ions, with accompanying rearrangement of the macrocycle. All the complexes produced by template synthesis can be transmetallated with the first transition series metal ions M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) to give binuclear and in some cases, mononuclear, derivatives. The binuclear complexes show no evidence of magnetic exchange interaction from magnetic susceptibility measurements in the range 93–300 K. The cyclovoltammetric behaviour of mono- and bi-nuclear Fe(II) complexes is compared.

Introduction

In a macrocyclic complex, the coordination requirements of the metal ion may dictate ligand conformation or alternatively, the steric properties of the ligand may enforce unusual coordination geometries upon the metal ion. Complexes of the series of ligands L^3–L^6, studied previously [1], nicely illustrate the balance between these effects. The ligands L^1 and L^2, described in the present study, being large and flexible, form complexes which fall in the first category. The ligand in these cases is able, from a variety of possible conformations, to select the one most appropriate to the metal ions requirements. Both macrocycles are capable of accommodating either one or two metal ions (in favourable cases) according to the conditions of preparation used.

In a great many bimetallic complexes, the metal ions share a bridging donor, which controls the distance between the metal centres. The absence of a bridging donor in these systems means that this distance is not so controlled, but can be varied, by ligand design, within the limits 3–8 Å. Thus, it should be possible, by preparing bimetallic complexes of a series of ligands of this type, to vary the degree of interaction between the metal centres, which are coordinated independently of each other in separate compartments. The present system represents a limiting case, the distance between the metal centres being too large for any but the weakest interaction.

Although not achieved in the present study, dual function mono/bi nucleating ligands offer the possibility of inserting a second different cation into the macrocyclic cavity, thus affording a route to heterobinuclear complexes.

Experimental

Template Syntheses

$[SrL^{1'}][BPh_4]_2$ and $[CaL^{1'}][BPh_4]_2$

0.01 mol $M(ClO_4)_2 \cdot H_2O$ (M = Ca, Sr) was dissolved in ~100 cm^3 Mg-dry MeOH. 6 cm^3 (0.04 mol) 3,3′-diamino di-propylamine was added to the warm solution and also 0.02 mol (3.26 g) DAP. The solution turned bright yellow. 0.02 mol $NaBPh_4$ dissolved in the minimum quantity of dry MeOH was filtered into the warm yellow solution. A precipitate of $[ML^1][BPh_4]_2$ started to form within ~½ hour and was filtered by suction.

$[Ag_2L^2][BPh_4]_2$

$AgNO_3$ (0.006 mol) was refluxed in 600 cm^3 MeOH; amine (0.005 mol) was added and DAP (0.005 mol). The yellow solution was refluxed overnight, cooled and sodium tetraphenylborate

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(0.006 mol) added. The beige ppt was filtered off, and recrystallized from acetonitrile.

$Pb_2L^1(NCS)_4$ and $Pb_2L^2(NCS)_4$

0.01 mol finely ground $Pb(NCS)_2$ was suspended in 400–500 cm^3 MeOH, DAP (0.012 mol) and the appropriate amine (0.012 mol) were added and the suspension stirred at 60 °C for 3–4 hours till all $Pb(NCS)_2$ (heavy pale solid) disappeared. The solution was filtered and evaporated to yield yellow crystals.

Transmetallation – (mononuclear complexes)

$[FeL^1][BPh_4]_2$

To Sr L^1 $[BPh_4]_2$ (0.0005 mol) in 10–150 cm^3 dry acetonitrile under N_2 was added $Fe(ClO_4)_2$ (0.0005 mol) and $NaBPh_4$ (0.001 mol). Around 15 cm^3 dry deoxygenated EtOH was added gradually and dark blue-purple crystals appeared on slight evaporation.

$[ML^2][BPh_4]_2 \cdot 2MeCN$ (M = Fe, Co, Ni)

$[Ag_2L^2][BPh_4]_2$ (0.001 mol) was dissolved in 200 cm^3 MeCN at about 50–60 °C, and 0.001 mol $M(ClO_4)_2 \cdot 6H_2O$ and 0.002 mol sodium tetraphenylborate added. The precipitate of $AgBPh_4$ was filtered, and the solution evaporated down to 10–20 cm^3. The product was recrystallised from MeCN/EtOH.

Transmetallation – (binuclear complexes)

$[M_2L^1(NCS)_4] \cdot xH_2O$ (M = Mn, Co, Ni, Zn)

To 0.001 mol $M(NCS)_2$ in dry EtOH was added 0.0005 mol $[SrL^{1'}][BPh_4]_2$ in 20–30 ml dry MeCN. The solution was left overnight to crystallise.

$[Fe_2L^1(H_2O)_4][ClO_4]_4$

Solid $Fe(ClO_4)_2 \cdot 6H_2O$ (0.0015 mol) was added to 0.0005 mol $[SrL^{1'}][BPh_4]_2$ in 15 cm^3 dry deoxygenated MeCN. 20 cm^3 EtOH was added and N_2 bubbled ~2 hours, after which time dark crystals were filtered off, which contained BPh_4^- impurity. Recrystallisation from MeCN/EtOH under N_2 yielded pure $[Fe_2L^1(H_2O)_4][ClO_4]_4$ in the second crop. *N.B. This solid explodes readily under slight friction.*

$[M_2L^1(MeCN)_2][ClO_4]_4 \cdot H_2O$ (M = Co, Ni)

$[SrL^{1'}][BPh_4]_2$ (0.001 mol) was dissolved in the minimum quantity of dry MeCN, and to this was added $M(ClO_4)_2 \cdot 6H_2O$ (0.002 mol) and 0.5 g $NaClO_4$. Around 15 cm^3 EtOH was added, and the solution left in a fridge to crystallise.

$[Co_2L^2NCS][BPh_4]_3 \cdot 3H_2O \cdot MeCN$

To a suspension of 0.0004 mol $Pb_2L^2(NCS)_4$ in 100 cm^3 MeCN, $Co(ClO_4)_2 \cdot 6H_2O$ (0.0008 mol) was added, and refluxed ~20 minutes until red brown solution forms. $Pb(NCS)_2$ was filtered off. 0.003 mol $Na(BPh_4)$ was added to filtrate, which was evaporated to low volume, and red brown crystals filtered off.

$[M_2L^2Cl_2][ClO_4]_2$ (M = Ni, Fe)

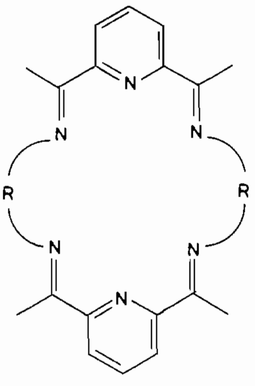
To 0.001 mol $Ag_2L^2(ClO_4)_2$ in 100 cm^3 dry MeOH was added 0.005 mol of the appropriate metal halide, and the mixture was refluxed for 1 hour. The precipitate of AgCl was filtered off, and volume reduced to ~20 cm^3 when crystals of the desired product were obtained.

N.B. $[Fe_2L^2Cl_2][ClO_4]_2$ *explodes readily under slight friction.*

Measurements

E.p.r. spectra of the mononuclear cobalt(II) complex were obtained as undiluted powders or as a glass in DMSO/MeOH, using a Varian E 9 instrument.

Electrochemical measurements were performed with a PAR model 174 polarographic analyser, a PAR model 175 universal programmer, and a Houston Omnigraph 2000 XY recorder A three-electrode system was used, with vitreous carbon as working electrode, a Pt spiral as auxiliary electrode, and S.C.E. reference. Solutions were 10^{-3} *M* in complex and 0.1 *M* in tetraethylammonium perchlorate, were degassed with O_2-free nitrogen and kept under a nitrogen blanket at 25 °C. Other physical measurements were made as described in earlier papers.

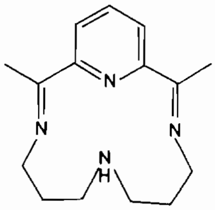


Structure 1

L^1 R = $(CH_2)_3$–NH–$(CH_2)_3$
L^2 R = $(CH_2)_3$–NMe–$(CH_2)_3$
L^3 R = $(CH_2)_3$
L^4 R = $(CH_2)_2$–S–$(CH_2)_2$
L^5 R = $(CH_2)_2$–NH–$(CH_2)_2$
L^6 R = $(CH_2)_2$–O–$(CH_2)_2$–O–$(CH_2)_2$

Results and Discussion

Template condensation of the amines 3,3′-diaminodipropylamine and its N-Me derivative, 3,3′-diamino-N-methyldipropylamine, with 2,6-diacetylpyridine, (DAP), on first transition series metal ions is well known [2] to result in (1 + 1) condensation yielding the 14-membered N_4 macrocycle L^7.



L^7

When the condensation of 3,3′-diaminodipropylamine and DAP is carried out on Ag^+, the product is the di-Ag(I) complex of the 28-membered N_8 macrocycle L^1, as described earlier [3]. We find, by mass spectral observation of the molecular ion peak at m/e 544, that the N-methylated amine, 3,3′-diamino-N-methyldipropylamine, also templates on Ag^+ by (2 + 2) condensation to give the 28-membered N_8 macrocycle L^2.

Use of $Pb(NCS)_2$ as template gives the 28-membered N_8 macrocycle with both the >NH and >NMe amine. This was shown by borohydride reduction of the condensation product to give the hydrogenated (polyaza) ligands (L^1 + 4H) and (L^2 + 4H) whose molecular ion peaks were observed at m/e 524 and 552 respectively.

Condensation of 3,3′-diaminodipropylamine with DAP on Ca(II) or Sr(II) takes place rapidly in dry alcohol at 50 °C, where addition of $NaBPh_4$ precipitates out complexes of stoichiometry $ML^1(BPh_4)_2$. Significantly, when the N-methylated amine is used the Gp(II) ions are ineffective as templates. This suggests that, on Gp(II) ions, ligand L^1 may adopt a ring-contracted form analogous to that observed in the Ba^{2+}-assisted template condensation of diethylenetriamine with DAP [4] (Fig. 1). Such contraction may be achieved by intramolecular attack on the C=N group by the secondary NH function, which in the present system is accompanied by extrusion from the macrocycle of a tetrahydropyrimidine ring. This attack may involve one or both secondary amine functions, reducing the size of the macrocyclic inner ring from 28- to 24- or 20-member atoms. This smaller size presumably allows more efficient coordination of the remaining N-donors by the single Sr^{2+} or Ca^{2+} ion.

Products of Template Condensation

An nmr study was undertaken in order to compare ligand geometry in the products of template condensation on the different metal ions. Both di-Ag(I) complexes exhibit an easily interpretable ^1H nmr spectrum (Table IIa), as expected for a normal (fully extended) 28-membered macrocycle.

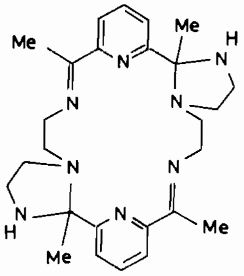


Fig. 1. Ring-contracted form of L^5.

The ^1H nmr spectra of $[CaL^{1'}][BPh_4]_2$ and $[SrL^{1'}][BPh_4]_2$, however, are far from simple and quite different from that of $[Ag_2L^1][BPh_4]_2$. The prominent feature is a multiplet lying between δ 2.65 and δ 2.45 which appears to contain three singlets underlain by other less intense complex absorption. There is a fourth singlet to high field of these three at δ 1.93 and numerous complex multiplets of low intensity covering the range δ 3.8 to δ 1.6. Using the aromatic signals as reference, the total integral over the 2.75 to 1.8 ppm range which includes these four singlets (which are of approximately equal intensity) is ~14 H. We believe that the four singlets correspond to four non-equivalent methyl groups, with the rest of the integral being accounted for by the underlying broad low-intensity absorption. The three singlets grouped around δ 2.6 presumably arise from (C)Me-groups in a similar chemical environment to that in $[Ag_2L^1][BPh_4]_2$ or $[Ag_2L^2][BPh_4]_2$, but in a situation of lower symmetry. The remaining high-field singlet at δ 1.93 must lie in a magnetic or chemical environment significantly different from the other three and from the (C)Me-groups in the disilver compounds. By comparison with the L^5 system [4], we tentatively assign the high field signal in $[SrL^{1'}][BPh_4]_2$ to the methyl group on the tetrahydropyrimidine ring.

The simplest interpretation of the ^1H nmr evidence would be to suggest formation of a 24-membered ring, contracted by expulsion of *one* tetrahydropyrimidine ring, containing three methyl groups on imine carbons and one on the fully substituted carbon of the tetrahydropyrimidine ring. The low symmetry of such an arrangement would result in none of the CH_3 or CH_2 groups being equivalent, explaining the complexity of the nmr spectrum of $L^{1'}$ complexes.

A ^{13}C nmr investigation of the more soluble complexes supports this idea. The mononuclear low–spin, $[FeL^1][BPh_4]_2$ and $[FeL^2][BPh_4]_2$ complexes, (described later) gave simple ^{13}C spectra (Table IIb) with just one peak for each of the chemically different carbon atoms in the molecule. $[SrL^{1'}][BPh_4]_2$ on the other hand, gave complex ^{13}C spectra with four times as many macrocyclic

TABLE I. Analytical, Infrared, and Conductance Data for Mono- and Bi-nuclear Complexes.

Complex	%N		%C		%H		Λ/S cm^2 mol^{-1} (MeCN)[a]	Infrared data		
	Calc.	Fd.	Calc.	Fd.	Calc.	Fd.		νNH or ν(N)CH$_3$	νC=N	νNCS$^-$ or νClO$_4^-$
$[SrL^{1'}][BPh_4]_2$	9.01	9.06	75.40	75.32	7.14	7.01	253	3268m	1625	–
$[CaL^{1'}][BPh_4]_2$	9.38	9.08	78.40	78.40	7.08	7.14	259	3260w	1627	–
$[Ag_2L^2][BPh_4]_2$	8.01	7.98	68.69	68.70	6.34	6.46	259	2790 2840	1630 1618	–
$PbL^1(NCS)_4$	14.44	14.29	35.10	35.37	3.81	3.79	insol	3240ms	1643, 1635sh	2080 2058 2030sh
$PbL^2(NCS)_4$	14.10	13.95	36.29	36.24	4.06	4.24	insol	2770 2790ms	1635	2090sh 2058s
$[FeL^2][BPh_4]_2\cdot 2MeCN\cdot H_2O$	10.5	10.8	75.3	75.2	7.4	7.1	263	2790 2835ms	–	
$[CoL^2][BPh_4]_2\cdot 2MeCN$	10.6	10.8	76.2	76.2	7.2	7.3	227	2790 2830ms	1618w	
$[NiL^2][BPh_4]_2\cdot 2MeCN$	10.6	10.7	76.2	76.5	7.2	7.2	232	2790 2830ms	1621ms	
$[FeL^1][BPh_4]_2$	9.3	9.4	77.4	77.6	7.0	7.1	261	3300b	–	
$[Mn_2L^1(NCS)_4]\cdot 4H_2O$	19.0	19.2	46.1	45.8	5.5	5.3	insol	3225	1620(m)	2070(sh) 2045(s)
$[Fe_2L^1(H_2O)_4][ClO_4]_4$	10.2	10.3	32.8	33.2	4.8	4.7	495	3170(b,m)	–	1090(vs b) 625(ms)
$[Co_2L^1(MeCN)_2][ClO_4]_4\cdot H_2O$	12.4	12.2	36.1	36.0	4.6	4.6	440	3240	1625(m)	1090(vs b) 625(s)
$[Co_2L^1(NCS)_4]\cdot 4H_2O$	17.9	17.3	43.5	43.5	5.6	4.9	insol	3215b	1623(m)	2075(b,s)
$[Ni_2L^1(NCS)_4]\cdot 2H_2O$	18.7	18.5	45.5	46.1	5.4	5.3	insol	3230	1618(m)	2090(sh) 2070 2040(s,b)
$[Ni_2L^1(MeCN)_4][ClO_4]_4\cdot 2H_2O$	13.2	13.0	35.9	35.6	4.4	4.4	421	3250	1620(m)	620 625 632ms
$[Zn_2L^1(NCS)_4]\cdot 2H_2O$	18.4	18.5	44.6	44.9	5.3	4.9	insol	3220b 3090	1640	2075(s) 2050(sh)
$[Co_2L^2(NCS)][BPh_4]_3\cdot MeCN\cdot 3H_2O$	7.5	7.9	72.4	72.6	6.3	6.6	306	2770, 2795	1625	2095(ms)
$[Fe_2L^2Cl_2(H_2O)_2][ClO_4]_2$	11.63	11.95	39.93	40.45	5.24	5.33	460	[b]	–	1090(vs,b) 625(ms)
$[Ni_2L^2Cl_2][ClO_4]_2\cdot 4H_2O$	11.15	11.12	38.27	38.90	5.62	5.26	380	[b]	1620(ms)	1090(vs,b) 625(ms)

[a] For 10^{-3} mol dm^{-3} solutions in MeCN. [b] Obscured by broad H-bonded absorption.

TABLE IIa. ^{1}H nmr Spectra of Disilver Complexes of L^1 and L^2 (δ in ppm vs. TMS, in CD_3CN).

$Ag_2L^1(ClO_4)_2$				$Ag_2L^2(BPh_4)_2$			
δ		Rel. Int.	Assignment	δ		Rel. Int.	Assignment
8.26	multiplet	3	pyridine protons	8.30–8.54	multiplet	3	pyridine protons
3.86	triplet	4	H_1	3.97	triplet	4	H_1
3.06	triplet	4	H_3	2.88	triplet	4	H_3
2.56	singlet	6	(C)Me	2.74	singlet	3	(N)Me
2.29	pentet	4	H_2	2.69	singlet	6	(C)Me
2.45[a]	broad singlet		(NH + H_2O)	2.40	pentet	4	H_2

[a] D_2O shake removes 2.45 signal, sharpens H_3.

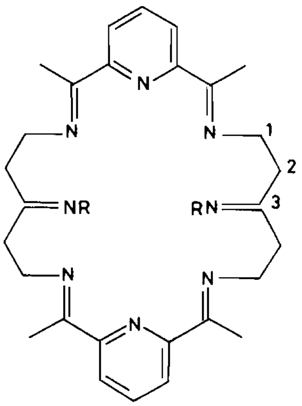


TABLE IIb. ^{13}C nmr Spectra for Soluble Diamagnetic Complexes of L^1 and L^2 (δ in ppm vs. TMS, in CD_3CN).

$FeL^1(BPh_4)_2$	$FeL^2(BPh_4)_2$	$SrL^{1'}(BPh_4)_2$				Assignment
17.3	17.9	11.3[a]	16.8[a]	16.2[a]	23.5[a]	CH_3
26.1	25.6	28.9	29.4	29.7	29.9	C_2
43.7	44.5	39.6	44.3	50.2	50.4[b]	C_3
50.0	50.8	50.6	51.8	52.0		C_1
	52.8					(N–)CH_3
121.7	122.4	122.6				$[BPh_4]^-$
125.5	126.5	126.2				$[BPh_4]^-$
135.7	136.5	136.8				$[BPh_4]^-$

[a] Off-resonance quartet. [b] Closely spaced doublet.

signals as were observed for the iron compounds. The inference is that each carbon atom in the L^1 macrocycle is giving rise to its own ^{13}C signal. The ^{13}C evidence suggesting low symmetry and four magnetically different methyl carbons favours the N_7 24-membered ring macrocycle. Independent evidence for this structure comes from the infrared intensity of the $\nu_{C=N}$ absorption. The intensity of this absorption in $[SrL^{1'}][BPh_4]_2$ is only about three-quarters that in $[Ag_2L^1][BPh_4]_2$ (using the pyridine ring absorptions as intensity reference). This suggests that only one of the four imine groups has been lost in the ring contracted form.

Complexes Obtained by Metal Exchange

Although template condensation on Sr^{2+} yields a ring-contracted form of the macrocycle L^1, treatment with transition metal ions easily converts this to the extended 28-membered ring form. A similar facile ring expansion was noticed with the analogous L^5 ring system.

TABLE III. Electronic Spectral, Mössbauer, and Magnetic Data.

Complex	Colour	μ_{eff}/BM[d]		Electronic Spectra[a]	Isomer Shifts mm s^{-1} *vs.* Fe foil	Quadrupole Splitting mm s^{-1}
		313 K	93 K			
$[Mn_2L^1(NCS)_4]\cdot 4H_2O$	apricot	5.78	5.80	26,200[b]	–	–
$[Fe_2L^1(H_2O)_4][ClO_4]_4$	dk. blue	1.30	0.98[c]	21,100(7000), 16,900(9400)	0.17	1.19
$[Co_2L^1(MeCN)_2][ClO_4]_4\cdot H_2O$	Mid brown	4.15	4.02	23,700(sh), 18,600(250), 15,000(85), 9.600(40)	–	–
$[Co_2L^1(NCS)_4]\cdot 4H_2O$	brown	4.80	–	24,600[b], 21,200sh[b], 18,000sh[b], 10,300[b]	–	–
$[Co_2L^2(NCS)](BPh_4)_3\cdot 3H_2O\cdot MeCN$	brown	4.10	3.92	23,530(700), 19,000(173), 15,000(22), 9,800		
$[Ni_2L^1(NCS)_4]\cdot 2H_2O$	lt. brown	3.18	3.02	19,800[b], 11,800[b]	–	–
$[Ni_2L^1(MeCN)_4][ClO_4]_4\cdot 2H_2O$	beige	3.13	3.15	22,800(180), 19,000(45), 11,600(160)	–	–
$[Zn_2L^1(NCS)_4]\cdot 2H_2O$	white	–	–	21,000[b]	–	–
$[Fe_2L^2Cl_2(H_2O)_2][ClO_4]_2$	dk. purple	0.20		20,830(6800), 18,010(sh), 17,390(sh), 16,950(9600)	0.15	1.11
$[Ni_2L^2Cl_2(H_2O)_2][ClO_4]_2\cdot 2H_2O$	beige	3.06		19,230(sh), 11,900(42)	–	–
$[FeL^1][BPh_4]_2$	dk. purple	0.60	–	20,760(10,700), 16,860(10,800)	0.14	1.10
$[FeL^2][BPh_4]_2\cdot 2MeCN\cdot H_2O$	dk. purple	1.20	1.61	20,280(14,400), 16,720(15,600)	0.13	1.10
$[CoL^2][BPh_4]_2\cdot 2MeCN$	dk. brown	3.25	2.32	20,530(2,100), 18,250(1450), 15,850(350)	–	–
$[NiL^2][BPh_4]_2\cdot 2MeCN$	pale brown	3.17	–	19,230(55), 12,050(53)	–	–

[a] Frequency in K, $\epsilon/dm^3\ mol^{-1}\ cm^{-1}$ in parenthesis. [b] Measured as nujol mull. [c] Measured at 110 K. [d] Moment per metal ion.

Binuclear derivatives of Ni(II) and Co(II) were obtained by refluxing di-Ag(I) or di-Pb(II) complexes of L^1 with methanolic solutions of the appropriate transition metal salt. An identical product could be obtained starting with an acetonitrile solution of $[SrL^{1'}][BPh_4]_2$, so in general, because of higher solubility, $[SrL^{1'}][BPh_4]_2$ was the preferred starting material for the synthesis of transition metal derivatives of L^1. Mononuclear derivatives were similarly obtained by refluxing $[Ag_2L^2][BPh_4]_2$, in methanol, with an equimolar solution of the transition metal salt. The only L^1 derivative which could be obtained pure as a mononuclear complex was $[FeL^1][BPh_4]_2$; attempts to prepare mononuclear Co(II) or Ni(II) derivatives of this macrocycle were unsuccessful.

Mononuclear complexes

These complexes had conductivities in MeCN at the lower end of the range [5] appropriate to 1:2 electrolytes, as is typical for tetraphenylborate salts. The infrared spectrum of the ligand moiety, outside the range 1700–1500 cm^{-1}, was largely unaltered on transmetallation; however, there were significant changes in the 1600 cm^{-1} region. The precursor compounds $Pb_2L^1(NCS)_4$ and $Pb_2L^2(NCS)_4$, *etc.*, all show at least two strong bands ~1630 cm^{-1} and ~1590 cm^{-1}, assigned to the $\nu_{C=N}$ and pyridine ring vibrations respectively. Of the mononuclear complexes, only $[NiL^2][BPh_4]_2\cdot 2MeCN$ displays this pattern. $[CoL^2][BPh_4]_2\cdot 2MeCN$ has a pair of weak absorptions at 1620 cm^{-1} and 1590 cm^{-1}, while no absorption is observed in the Fe(II) complexes at these frequencies. This indicates, as magnetic results confirm, that Co(II) and Fe(II) are in low-spin [6] octahedral coordination in these mononuclear complexes. A strong octahedral field can be achieved with these macrocycles if the ring is sufficiently flexible to allow the two trimethine entities to lie at right angles to each other. The –NH or –NMe groups are then 'squeezed out' and not coordinated to the metal ion.

Magnetic susceptibility data (Table III) for the iron compounds confirms the existence of spin-pairing in both $[FeL^1]^{2+}$ and $[FeL^2]^{2+}$ ions. Mössbauer spectra isomer shifts are in the range expected for low-spin octahedral Fe(II). The quadrupole splittings are large, comparable to the values obtained [7] in the $[FeL^6]^{2+}$ cation where the macrocycle has folded to allow 6-coordination of the Fe(II) by the two trimethine groups. These large quadrupole splittings presumably reflect splitting of the t_{2g} orbitals as a result of distortion from O_h symmetry. This distortion appears to be somewhat larger in L^1 and L^2 complexes than in the L^6 series, as judged by the values of ΔE_Q. This may arise because of steric constraints in the smaller L^1 and L^2 macrocycles.

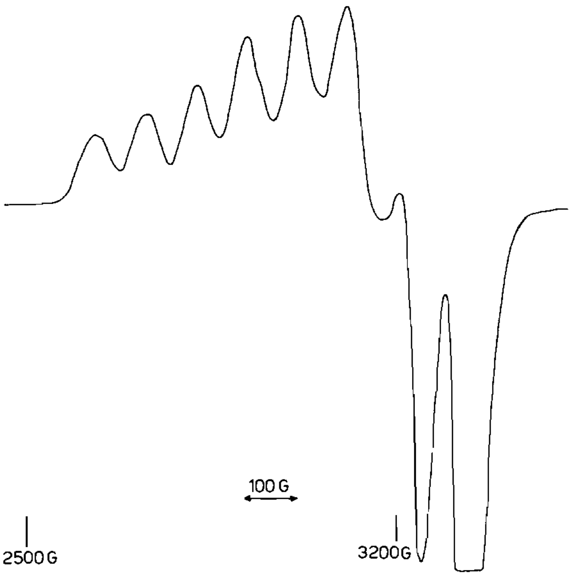


Fig. 2. E.S.R. spectrum of $[CoL^2][BPh_4]\cdot 2MeCN$ (polycrystalline sample at −160 °C).

A thermally controlled high-spin ⇌ low-spin equilibrium exists in the case of $[CoL^2][BPh_4]_2\cdot 2MeCN$, as shown by variable temperature magnetic susceptibility measurements. Such an equilibrium is fairly common in α-diimine complexes of Co(II) [8], and has also been observed [7] in mononuclear Co(II) complexes of L^6. In the present case, equilibrium lies well, but not completely, to the low–spin side at 93 K. The esr spectrum (Fig. 2) obtained at this temperature shows only peaks due to the low-spin form. The esr parameters of a polycrystalline sample at 93 K ($g_\perp$ 2.02, $g_\parallel$ 2.30, $A_\parallel$ 93 G) demonstrate that the octahedral arrangement around Co(II) is distorted by axial compression [9].

Examination of the electronic spectra of the complexes likewise provides evidence of distortion from regular O_h symmetry. Both $[FeL^1]^{2+}$ and $[FeL^2]^{2+}$ cations display a pair of equally intense charge-transfer absorptions close to 20,000 and 17,000 cm^{-1}. Such a splitting has been attributed [7] to separation of the t_{2g} level into e and b_2 levels as the symmetry diminishes from octahedral. No absorption attributable to d–d transitions was observed in the spectra of the Fe(II) complexes. The two strong bands in the $[CoL^2][BPh_4]_2\cdot 2MeCN$ electronic spectrum at 20,800 and 18,250 cm^{-1} are thought to be d–d rather than charge transfer in origin.

The electronic spectrum is the only physical measurement to offer information about coordination geometry in $[NiL^2][BPh_4]_2\cdot 2MeCN$. Of the three bands expected for octahedral Ni(II), two are observed at 19,000 and 12,000 cm^{-1}, ascribed, respectively, to the $^3A_{2g} \rightarrow {}^3T_{2g}$ and $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transitions. It seems clear from above results that, in mononuclear complexes, the ligands L^1 and L^2 have twisted as in Fig. 3, to adopt an N_6 octahedral conformation using only the trimethine entities as donors, and leaving the amine nitrogen uncoordinated. The local symmetry about the metal ion is less than octahedral.

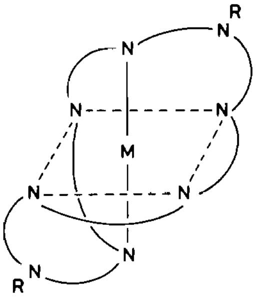


Fig. 3. Disposition of donors in octahedral coordination mode of L^1 and L^2.

Binuclear complexes

There has been much recent interest [10] in the synthesis of extendable macrocycles which can function as binucleating ligands. This work has been motivated by the hope that coordination of a substrate between a pair of metal ions might lead to a useful modification of its reactivity. In order to accommodate substrates of different sizes, it would be desirable to have available a selection of binucleating ligands providing a range of intermetallic distances. X-ray studies [3, 12] on disilver and dicopper derivatives of L^1 suggest that ligands L^1 and L^2 afford an intermetallic distance around 7 Å. A shorter intermetallic distance would be attainable were the ligands able to fold into a U-shape with cofacial trimethine entities; however models suggest that this arrangement would be highly strained. In the extended form of the macrocycle which X-ray analysis reveals for $[Ag_2L^1]^{2+}$ and $[Cu_2L^1]^{2+}$, a long (three- or four-atom) bridge might be achieved. Such binuclear complexes of L^1 and L^2 as have been prepared (with the exception of dicopper complexes, reported elsewhere) are described in Table I. Complexes of sufficient solubility have conductivity in MeCN typical of 1:4 electrolytes; the thiocyanate complexes are too insoluble for conductivity measurements, but their infrared spectra [11] suggest N-coordination.

Electronic spectral and magnetic data are assembled in Table III. Variable temperature magnetic susceptibility measurements in the temperature range 293–93 K do not indicate significant interaction between the metal centres, which accords with observations made on the di-Cu(II) complexes [12] where the existence of weak dipolar interaction between the metal centres can be inferred only from esr spectra.

TABLE IV. Cyclic Voltammetric Data for L^1 and L^2 Mono- and Bi-nuclear Complexes.

Complex	Scan Rate mV s^{-1}	(1) $E_{1/2}$/V	(1) ΔE_p/mV	(2) $E_{1/2}$/V	(2) ΔE_p/mV	(3) $E_{1/2}$/V	(3) E_p/mV
$[FeL^2][BPh_4]_2 \cdot 2MeCN$[a]	50	1.23	100	−1.26	60[d]	−1.47	60
$[FeL^1][BPh_4]_2$[a]	50	1.16	70	−1.31	60	−1.43	70
$[CoL^2][BPh_4]_2 \cdot 2MeCN$[a]	50	0.15	80	−0.82	60[d]	−1.78	90
$[NiL^2][BPh_4]_2 \cdot 2MeCN$[a]	50	b		−1.39	60	−1.75 −1.88	130 70
$[Fe_2L^1(H_2O)_4][ClO_4]_4$[c]	100	1.22br	180	−1.23 −1.37	80 30	−1.50	60
$[Co_2L^1(MeCN)_2][ClO_4]_4 \cdot H_2O$	100	0.17	irr	−0.74 −1.10br	70 70	−1.82	130

All potentials *vs.* S.C.E.; for irreversible waves, $E_{p,c}$ is quoted. [a] All BPh_4^- complexes show an irreversible anodic peak at 0.8 V due to BPh_4^- oxidation. [b] No cathodic wave assignable to Ni^{3+}/Ni^{2+} was observed. [c] Broad irreversible cathodic peak at −1.01 V. [d] Wave independent of scan rate (50–200 mV s^{-1}).

In Zn(II) and Mn(II) complexes, the ions are assumed to be 6-coordinate because ir spectra show –NCS to be coordinated in both cases.

The absence of infrared $\nu_{C=N}$ absorption in the 1600 cm^{-1} region suggests that both L^1 and L^2 complexes of Fe(II) are low spin, and this inference is confirmed by the Mössbauer parameters. Magnetic susceptibility measurements on these complexes were restricted by the fact that they are unpredictably explosive. The room temperature moment (measured on a 100 mg sample) of $[Fe_2L^2Cl_2(H_2O)_2][ClO_4]_2$ was low enough to rule out any residual paramagnetism, so no low temperature moments were measured. Both room temperature and 110 K moments were determined for $[Fe_2L^1(H_2O)_4]$-$[ClO_4]_4$. The values obtained clearly rule out a high spin ground state; the small paramagnetism observed at 293 K could be attributable either to a small amount of paramagnetic impurity or to the coexistence of a small amount of the high spin form in equilibrium with the low–spin form at this temperature. As the axial ligands (Cl^- or H_2O) in these complexes are weak, spin-pairing must arise from an unusually strong field in the N_4 plane. This arises, presumably, from particularly good fit of the Fe^{2+} ion in the macrocyclic cavity.

The infrared spectrum of $[Co_2L^1(NCS)_4] \cdot 4H_2O$ shows the NCS^- ion to be N-coordinated and the magnetic moment has the normal value associated with high-spin octahedral Co(II). The electronic spectrum of the mull shows the three absorptions at 24,000, 18,000 and 10,000 cm^{-1} corresponding to ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}$ transitions expected in octahedral symmetry.

The low, virtually temperature-independent value of μ_{eff} found for $[Co_2L^1(MeCN)_2] \cdot (ClO_4)_4 \cdot H_2O$ suggests a 5-coordinate geometry for the Co^{2+} ion, made up of four ligand donors in a square plane with an acetonitrile molecule coordinated in the apical position. Infrared spectra confirm CH_3CN coordination. The observed moment of 4.15 BM is presumably explained by the decreased orbital contribution expected for Co(II) in square pyramidal (or trigonal bipyramidal) fields. $[Co_2L^2(NCS)][BPh_4]_3 \cdot MeCN \cdot 3H_2O$ may also be assumed to be 5-coordinate. The electronic spectra of both these cobalt complexes are similar to those of Co(II) complexes known to be 5-coordinate [13]. The high ν_{NCS} infrared frequency indicates bridging thiocyanate, so we suggest a dimeric $[Co_4L_2{}^2(NCS)_2]^{6+}$ assembly where the two L^2 units are held together by two –NCS– bridges linking one metal ion in the first macrocycle with another in the second. An analogous dimeric assembly has recently been characterised [14] in the L^6 system.

$[Ni_2L^1(NCS)_4] \cdot 2H_2O$ clearly contains 6-coordinate nickel, as the infrared spectrum shows that –NCS is coordinated. The electronic spectrum is as expected for octahedral Ni(II), absorptions occurring at much the same frequency as in mononuclear $[NiL^2][BPh_4]_2$, showing that substitution of two –NCS and one amine NH ligands for the second trimethine unit has had little effect on the ligand field. In $[Ni_2L^2Cl_2(H_2O)_2]^{2+}$, the electronic absorptions are shifted slightly to lower energies as a consequence of substitution for NCS of weaker axial ligands. The Ni(II) complexes have moments in the range expected for octahedral Ni(II).

Electrochemical Measurements

Cyclic voltammetry was carried out on the mononuclear transition metal complexes and also, for comparison, on some of the binuclear complexes of L^1. Results are listed in Table IV.

Mononuclear iron complexes showed three reversible or quasi-reversible processes. The most anodic wave at $E_{1/2}$ = +1.23 V for $[FeL^2][BPh_4]_2$ and $E_{1/2}$ = +1.16 V for $[FeL^1][BPh_4]_2$, corresponds to a redox process occurring at the metal, *i.e.* Fe^{2+}/Fe^{3+} interconversion. This indicates a slight stabilisation of the +2 state over that in $[FeL^6]^{2+}$ where $E_{1/2}(Fe^{III}/Fe^{II})$ is found ~100–150 mV less positive [7]. The enhanced difficulty of oxidation in the case of L^1 and L^2 complexes may arise from a hole-size effect [15] in these more strained arrangements, producing a larger effective cavity than in the relatively strain-free L^6 complex. A larger hole size is expected to favour the larger Fe^{2+} ion [16].

Two reversible waves are seen at cathodic potentials corresponding to successive one-electron reductions of $[Fe(mac)]^{2+}$. Without esr investigations of the reduction products it is difficult to decide the extent to which these reductions are metal-centred. However the intense charge transfer absorption described earlier suggests that at least one of these processes involves the ligand. We believe that the least cathodic of the two reversible waves in L^2 and L^1 complexes should be assigned to the formation of an Fe(II) complex of the radical anion of the ligand. The second wave probably corresponds to further ligand reduction.

If the reduced species in process (2) is an Fe(II) complex of the ligand anion then it may be expected [17] that the energy of the charge transfer absorption would be comparable to the difference between the energies of the two most anodic processes, $F[E^{\ominus}(1) - E^{\ominus}(2)]$. This difference corresponds to an energy (ΔG ~238 kJ) within 10% of the average energy (~220 kJ) of the charge transfer band in the electronic spectrum. While this is a good correspondence, it must be remembered that the two energies refer [7] to slightly different processes. The complex $[Co(L^2)][BPh_4]_2 \cdot 2MeCN$ also shows three reversible or quasi-reversible processes; the most anodic a quasi-reversible wave at +0.15 V, the second, reversible, at –0.82 V, and a third *quasi*-reversible, at –1.78 V in MeCN. The first two are attributed to redox processes occurring at the metal; the Co^{III}/Co^{II} and Co^{II}/Co^{I} transformations, which are found at very similar potentials in the $[CoL^6]^{2+}$ system. Process (2) is thought to be mainly metal-centered in this case because it occurs at much more positive potential than for iron. The reduced species in the third (most cathodic) process may be either a cobalt(0) complex of the neutral ligand or, more probably, a cobalt(I) complex of the radical anion. Cyclovoltammograms of $[NiL^2][BPh_4]_2 \cdot 2MeCN$ show a reversible process at –1.39 V (in MeCN) which may correspond either to a metal-centered Ni^{II}/Ni^{I} or ligand-centered $Ni^{II}L/Ni^{II}L^-$ redox process where the added electron goes into a π^* ligand orbital. Esr experiments are planned which should clarify whether this and other reductions effect a change in metal oxidation state.

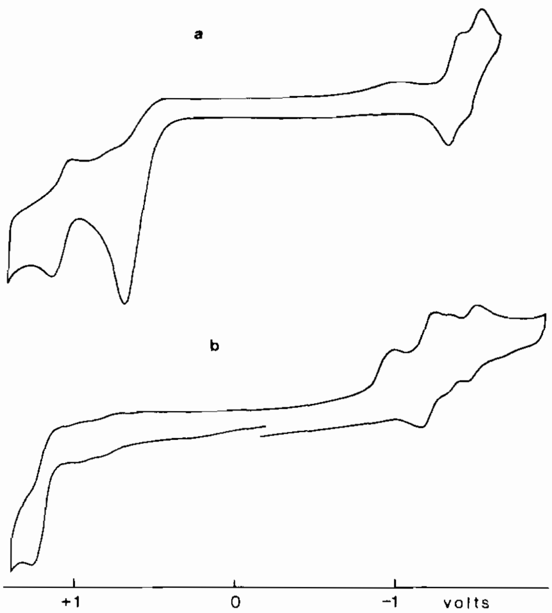


Fig. 4. Cyclic voltammograms for mono-nuclear and binuclear complexes: a) $[FeL^1][BPh_4]_2$; b) $[Fe_2L^1(H_2O)_4][ClO_4]_4$.

Preliminary measurements on the binuclear complexes, reported in Table IV, show that redox processes are more complex than for the mononuclear species. Figure 4 compares the cyclovoltammograms obtained with mononuclear and binuclear Fe(II) complexes. Because of differences in the coordination environment an exact correspondence of $E_{1/2}$ values in the mono- and the bi-nuclear case is not to be expected. However, there is considerable similarity between the voltammograms for mono- and bi-nuclear Fe(II) complexes, the major difference being the appearance, in the case of the binuclear complex of an irreversible reduction peak at –1.01 V, and of a pair of reversible waves in place of the –1.31 V wave seen in the mononuclear complex. One of these has a peak to peak separation of only 30 mV, which is suggestive of a two-electron process. The Fe^{3+}/Fe^{2+} interconversion takes place at virtually the same potential in mono- and binuclear complexes, although the wave is much broader in the di-Fe(II) case. The occurrence of the Fe^{3+}/Fe^{2+} couple at relatively positive potential in the di-Fe^{II} complex shows that Fe(II) is stabilised to the same extent in the binuclear as in the mononuclear complex, owing presumably to the unusually good fit of the ion in the N_4 macrocyclic plane. Given that $E_{1/2}(Fe^{3+}/Fe^{2+})$ has a very similar value in mono- and bi-nuclear complexes, formation of the ligand radical anion complex might also be expected to require similar potential in the two cases. The correspondence of $E_{1/2}(2)$ and $E_{1/2}(3)$ values (Table IV) in mono- and bi-nuclear cases supports the idea that the reversible waves which appear at cathodic potential are ligand centered (in so far as the term can apply to delocalised systems such as these) in both cases.

Further investigations on the electrochemistry of these and other binuclear complexes are needed before speculation about the origin of the waves can be confirmed.

Conclusions

These ligands are flexible enough to accommodate a range of geometries. Thus when stretched out, they can accommodate a pair of metal ions each coordinated to four macrocyclic donor sites. The metals can accept further anionic or solvent donors to achieve coordination number 5 or 6, as desired. This elongated arrangement is adopted in the binuclear complexes formed with Pb(II) or Ag(I) and transition metal ions M(II) (M = Mn–Zn).

In none of the L^1 complexes studied is there any evidence to suggest intramolecular bridging of the metal centres by NCS^-. The separation of the centres is probably not too different form the 7 Å reported [12] on the basis of X-ray crystallographic analysis for a dicopper complex of L^1, $[Cu_2L^1(NCS)_2][BPh_4]_2 \cdot 2MeCN$. This distance could accommodate a lengthwise thiocyanate bridge between metal centres were there no steric constraints in the macrocycle. In the present case, however, NCS is prevented from functioning as an 'equatorial' bridge by the presence of four macrocyclic N-donors arranged around each metal centre in approximately planar geometry. Thiocyanate appears to function only intermolecularly as an axial bridge, producing the dimeric tetranuclear assembly suggested for $[Co_4L_2^2(NCS)_2][BPh_4]_6$. When coordinating just one metal ion, the ligand can twist or contract to provide a 6- or 7-coordination site with donors in the appropriate geometry. For 6- coordination of transition metals the ligand twists to present to the metal two trimethine units at approximately right angles, providing a distorted octahedral site. Electrochemical results suggest that steric effects produce a somewhat larger cavity size than in the structurally related octahedral complexes of L^6. For Gp(II) metal ions Ca(II) and Sr(II), ring contraction takes place allowing the larger cation to coordinate 7 of the N-donors.

Acknowledgements

We thank the Open University for the award of a Higher Degrees studentship (to B.P.M.). The support of NATO Research Grant 01381 (to M.F.C.) is also acknowledged.

References

1 S. M. Nelson, *Pure Appl. Chem., 52,* 2461 (1980).
2 J. L. Karn and D. H. Busch, *Nature, 211,* 160 (1966).
R. L. Rich and G. I. Stucky, *Inorg. Nucl. Chem. Lett.* 85 (1965).
R. H. Price, D. A. Stotter and P. R. Wooley, *Inorg. Chim. Acta, 9,* 51 (1974).
3 M. G. Drew, S. G. McFall, S. M. Nelson and C. P. Waters, *J. Chem. Res.,* 16 (1979).
4 S. M. Nelson, J. Nelson and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.,* 1678 (1981).
5 W. J. Geary, *Coord. Chem. Rev., 1,* 81 (1971).
6 W. Stratton and D. H. Busch, *J. Am. Chem. Soc., 82,* 4834 (1960).
7 S. M. Nelson, M. McCann, C. Stevenson and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.,* 1477 (1979).
8 J. S. Judge and W. A. Baker, *Inorg. Chim. Acta,* 158 (1967).
9 Y. Nishida, K. Ida and S. Kida, *Inorg. Chim. Acta, 38,* 113 (1980).
10 U. Casellato, P. A. Vigato, D. E. Fenton and M. Vidali, *Chem. Soc. Rev., 8,* 199 (1979).
11 P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.,* 1912 (1960).
12 S. M. Nelson, J. Nelson, M. G. B. Drew and B. Murphy, to be published.
13 M. Crampolini and N. Nardi, *Inorg. Chem., 5,* 1150 (1966).
14 M. McCann, *Ph.D. thesis, Q.U.B.,* 1980.
15 D. H. Busch, D. C. Pillsbury, F. V. Lovechio, A. M. Tait, Y. Hung, S. Jackels, Mary C. Rakowski, W. P. Schannal and L. Y. Martin, 'Electrochemical Studies of Biological Systems', *Am. Chem. Soc. Symposium Series No. 38,* 1977.
16 D. D. Watkins, D. P. Piling, J. A. Stone and D. M. Birsch, *Inorg. Chem., 15,* 387 (1976).
17 J. Nelson, S. M. Nelson and W. D. Perry, *J. Chem. Soc., Dalton Trans.,* 1282 (1976).