Complexes of a New Mononucleating Cage Ligand; Livelier than Sepulchrates?

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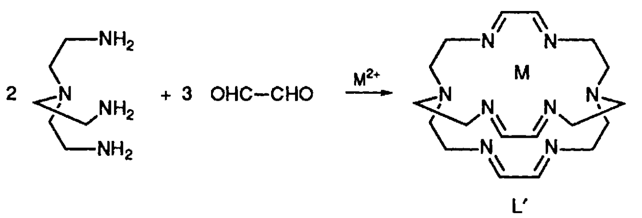
the new polyaza cryptand L^1, easily made by Schiff's base condensation using Group 2 ions, may be transmetallated with first transition series ions to give cryptates which electrochemical investigations show to have relatively stable +1 oxidation states; a preliminary *X*-ray crystallographic study of the Co^{II} cryptate is reported.

The elegant and comprehensive work of Sargeson *et al.*[1] on mononucleating cage ligands of the sep- and sar-type is subject to one significant limitation; {sep (sepulchrate) = 1,3,6,8,10,13,16,19-octa-azabicyclo[6.6.6]icosane, sar (sarcophagine) = 3,6,10,13,16,19-hexa-azabicyclo[6.6.6]icosane}. Because the synthesis uses a kinetically inert metal ion as template, subsequent removal of this metal ion presents difficulty. We have developed[2] a synthetic approach to cryptand ligands, involving the use of kinetically labile template ions, which avoids this difficulty. The [2 + 3] condensation of the tripod amine tris(2-ethylamino)amine with glyoxal using Group 2 metal ion templates (Scheme 1)

Table 1. Spectroscopic, magnetic, and electrochemical[c,d] properties of the cryptates.

	Π-Π* or charge-transfer bands[g]			μ/μ_B		E/mV					
Compound	$\lambda_{max.}$ /cm^{-1}	ε/dm^3 mol^{-1} cm^{-1}	d–d band[g] λ_{max}/cm^{-1}(ε)	293 K	93 K	$E^{I}_{\frac{1}{2}}$	(ΔE)	$E^{II}_{\frac{1}{2}}$	(ΔE)	$E^{III}_{\frac{1}{2}}$	(ΔE)
$[\mathrm{CaL^1}](\mathrm{BPh_4})_2$[h] (**1**)	35 710	1800	—	—	—	a		a		a	
$[\mathrm{MnL^1}](\mathrm{BPh_4})_2$[i] (**2**)	29 400	930	—	5.99	5.98	+1350[b]	Irr.	−987	76	−1276	76
$[\mathrm{FeL^1}](\mathrm{BPh_4})_2$[i] (**3**)	23 100	2300	—	0.95	0.40	+714[b]	Irr.	−962	61	−1332	77
	17 400	5600									
$[\mathrm{FeL^1}](\mathrm{ClO_4})_2$[j] (**4**)	23 100	1500	—	Dia.	Dia.	+810	127	−983	61	−1349	61
	17 460	3800									
$[\mathrm{CoL^1}](\mathrm{BPh_4})_2$[i] (**5**)	26 200	1900	11 430 (19)	4.30	4.20	+227	207	−847	87	−1402	87
$[\mathrm{CoL^1}](\mathrm{ClO_4})_2$[j] (**6**)	26 430	1600	11 100 (5)	4.43	3.95	+740[e]	Irr.	−815	61	−1371	77
						+131[f]					
$[\mathrm{NiL^1}](\mathrm{BPh_4})_2$[i] (**7**)	33 200	1600	12 500 (18)	3.04	3.01	+1166	Irr.	−1105	61	−1838	91
	25 900	1400									
$[\mathrm{CuL^1}](\mathrm{ClO_4})_2\cdot4\mathrm{H_2O}$[j] (**8**)	35 600	2700	15 500 (120)	1.86	1.61	+1216	Irr.	+282	77	−1197	96
	24 300	2150									

[a] No electrochemical activity in this range. [b] Poorly defined oxidation wave, partly obscured by counterion or solvent process. [c] Scan rate 50 mV s^{-1}; $E_{\frac{1}{2}}$ ferrocenium/ferrocene +362 mV, ΔE 92 mV *vs.* AgCl. [d] 10^{-3} M in dmf, 0.1 M $\mathrm{Et_4NClO_4}$. [e] Anodic component. [f] Cathodic component. [g] MeCN solution. [h] Made by template synthesis at 40—50 °C in EtOH. [i] Made by transmetallation of (**1**) or its Sr analogue with M^{2+} (M = Mn, Fe, Co, Ni, or Cu) in MeCN–EtOH. [j] Made by anion exchange of (**1**) with $\mathrm{AgClO_4}$ followed by transmetallation with $\mathrm{M(ClO_4)_2}$.



Scheme 1

results in formation of the hexaimino macrobicylic ligand L^1 in good yield.

The template ion may then be easily removed by transmetallation with *e.g.* first transition series ions to give mononuclear complexes (Table 1).

Crystals of $\mathrm{CoL^1(ClO_4)_2}$ have been studied by *X*-ray diffraction. The crystals show intimate twinning which precluded accurate determinations of bond lengths and angles; nevertheless the main features of the structure are clear.† The structure of the cation is shown in Figure 1, the cobalt atom and the two bridgehead nitrogen atoms lie on a crystallographic 3-fold axis. The metal is co-ordinated to all six imino donors (only two of which are crystallographically independent) and has D_3 symmetry. The Co–N (imine) distances are similar to those in the analogous $[\mathrm{Co(sep)}]^{2+}$ cryptate.[3] The unco-ordinated bridgehead amino N lies ≈3 Å from the metal ion within a near planar arrangement of adjacent methylene carbons, suggesting near sp^2 hybridization of tertiary amine nitrogens, as observed[4] in $[\mathrm{Ni(sep)}]^{2+}$. The methylene caps are staggered, with a twist angle ϕ of ≈55°.

The observed disorder–twinning chiefly affects the di-imino links and therefore only tentative conclusions are possible. It appears that these links are oblique rather than parallel. The perchlorate anions lie with one Cl–O bond along a 3-fold axis and they do not show any interactions with the cations.

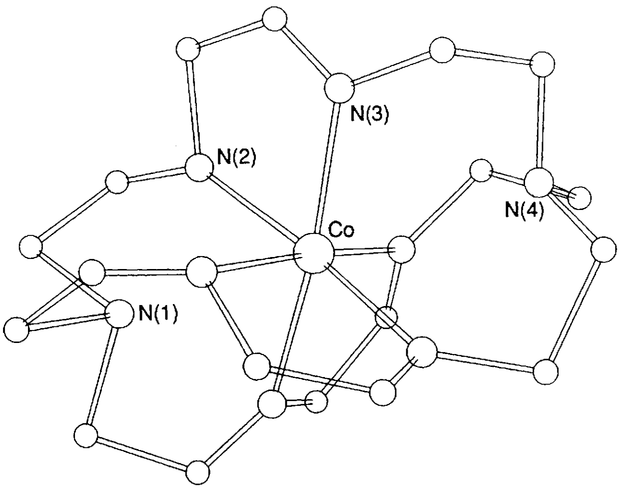


Figure 1. Preliminary crystal structure of $[\mathrm{CoL^1}]^{2+}$.

Although the tail of the broad and intense ligand-to-metal charge transfer (LMCT) absorption dominates the visible region of the electronic spectrum, low intensity bands around 11 000 and 12 000 cm^{-1} are, in the case of (**5**)/(**6**) and (**7**), seen and attributed to the lowest energy transition allowed in approximate O_h symmetry for Co^{II} and Ni^{II} respectively. Isomorphous powder patterns for (**5**) and (**7**) corroborate the spectral evidence. However (**2**) and (**3**) are not isostructural with (**5**)/(**7**) nor with each other reflecting presumably the varying influence of ligand field stabilising energy (LFSE) effects in favouring trigonal antiprismatic over the less strained trigonal pyramidal geometry in the order $\mathrm{Fe^{2+}} > \mathrm{Co^{2+}} > \mathrm{Mn^{2+}}$.

All the mononuclear cryptates, as expected, show little temperature-dependence of magnetic moment with evidence of some deviation from regular octahedral geometry in the low values recorded for (**5**) and (**6**). The Fe^{II} cryptates (**3**) and (**4**)

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† Solved in the hexagonal space group $P6_3$, a = 9.164, c = 17.185 Å, current R = 0.11. Full details will be published elsewhere.

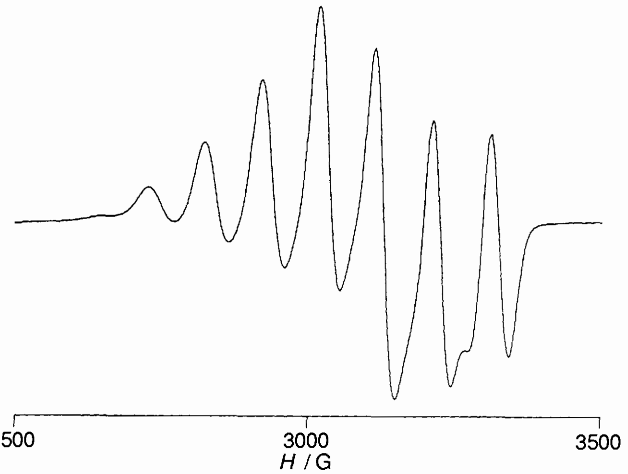

Figure 2. ESR spectrum of (**9**) as a dimethylformamide (dmf) glass at 113 K.

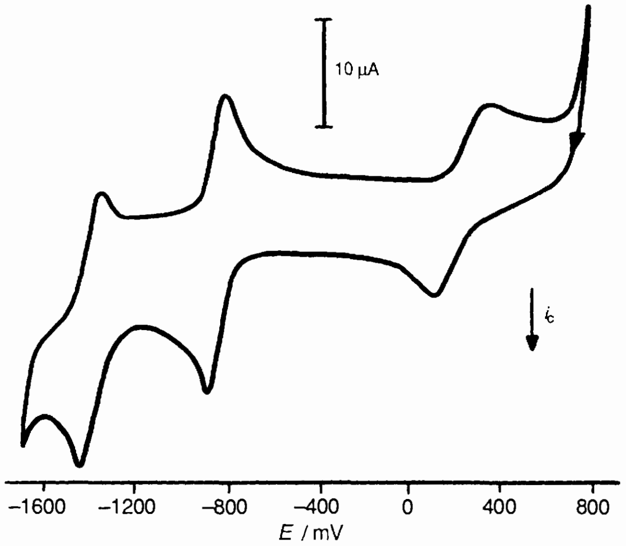

Figure 3. Cyclic voltammograms of (**5**) in dmf; scan rate 50 mV s^{-1}.

however, are in the ^1A_g low spin state at ambient temperature, suggesting that distortion from octahedral geometry, in the case of Fe^{II}, is not large.

The mononuclear Cu^{II} complex (**8**) exhibits the normal axial-type 4-line ESR signal with $g_{\parallel}$ ($\approx$2.28) > $g_{\perp}$ ($\approx$2.07) and $A_{\parallel}$ $\approx$143 G (1 G = 10^4 T), indicating extended tetragonal geometry for the co-ordination site.

An interesting observation arises from the isolation of a bi-nuclear copper cryptate $Cu_2L^1(ClO_4)_4$ (**9**) when the strontium template is refluxed in an alcohol–acetonitrile solvent with excess of Cu^{II} salt. Although elemental analysis suggests a dicopper^{II} formulation in the solid state, in solution an interesting 7-line ESR g = 2 signal (Figure 2) is seen, which persists as 7 lines down to 4 K in the DMF-glass spectrum.‡ The simple 7-line pattern strongly suggests that a mixed-valence Cu^{II}/Cu^{I} species has been formed *via* redox transformation, and its persistence to such low temperatures indicates an unusual degree of valence delocalization.

The template Group 2 cryptates are labile and in consequence easily transmetallated. Transition series ions, however, although easily encapsulated *via* the transmetallation process, appear to become kinetically inert once encapsulated; treatment of $[CoL^1]^{2+}$ with NaCN (aq.) fails to generate a $Co(CN)_2$ precipitate during several weeks. The aqueous stability of (**6**) is remarkable for a Schiff's base complex; water is indeed one of the best recrystallisation solvents for this complex.

The encapsulated transition series ions may thus be expected to function as sterically protected kinetically inert redox reagents of the 'innocent' kind. In contrast to Sargeson's hexamino cryptands,[5] our hexaimino donor set should favour to some degree the adoption of low oxidation states. The +3/+2 couples for cobalt complexes of sar and sep are seen at −200 and −220 mV respectively (*vs.* standard calomel electrode, SCE); *i.e.* some 400 mV less positive than the analogous quasi-reversible couple in (**5**) (Figure 3). The +2/+1 reduction for cobalt sar and sep complexes is irreversible and occurs at very negative (*ca.* −2000 mV) potential, whereas, as Figure 3 shows, reversible reductions at −830 and $\approx$ −1380 mV (*vs.* Ag/AgCl) are characteristic of $[CoL^1]^{2+}$. On the basis of related work with complexes of macrocyclic,[6,7] macrobicyclic,[8] chelating,[9] and catenand[10] sp^2-N donors, both these reduction processes may be assumed to be metal-centred. So it does appear that low oxidation states such as Co^{I} are stabilised by encapsulation within L^1.

A similar inference can be drawn from the appearance of an M^{II} reversible reduction wave around −1.0 V in the iron(II), nickel(II), and manganese(II) cryptates. The second reversible reduction process observed for (**2**), (**3**), (**4**), and (**7**) may originate either in $M^I \rightarrow M^0$ reduction or a metal ion-promoted $M^IL \rightarrow M^IL^-$ ligand reduction. ESR experiments are planned to distinguish between the various alternatives.

Oxidation waves are observed at +1350, 820, 1170, and 1220 mV (*vs.* Ag/AgCl) respectively for $[MnL^1]^{2+}$, $[FeL^1]^{2+}$, $[NiL^1]^{2+}$, and $[CuL^1]^{2+}$, but only in the case of $[FeL^1]^{2+}$ is there any hint of reversibility. The potentials recorded in Table 1 are not far removed[6,7] from those of other mononuclear complexes of sp^2-N$_6$ ligands. The major advantage of L^1 in comparison with these flexible macrocyclic ligands lies in the kinetic inertness of the encapsulated metal ion and the enhanced chemical stability towards *e.g.* hydrolysis of the cryptand ligand.

The positive potential recorded for the +2/+1 reduction in (**8**) is interesting. Such positive potentials of the order of those seen in blue copper proteins[11] are commonly associated with a co-ordination environment which favours tetrahedral geometry[10] and/or involves sulphur donors.[12] There are advantages to be gained from avoiding the use of S-donors where copper redox processes are involved because such ligands[13] are often found to be oxidisable at the sulphur site. The tetrahedral geometry enforced on the transition ion site, in Sauvage's innovative strategy, dispenses with the need for S-donors, but for some purposes may overenhance stability of the low oxidation state. We believe that the new copper cryptates described above, which show the borderline +2/+1 stability associated with efficient copper redox catalysis, may prove to be of value as chemically robust redox reagents for effecting mild redox transformations.

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‡ The lability of this species at ambient deters us from reporting its apparent solution properties at this stage.

spectrometer. We are grateful also to the SERC for fast-atom bombardment mass spectra recorded at the University of Wales, Swansea.

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