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Expanded-cap sepulchrates: a new series of mononuclear transition-metal ion cryptates

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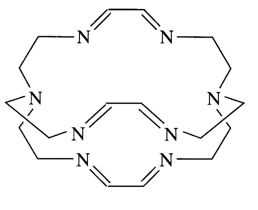
A series of transition-metal ion cryptates of a tris(2-aminoethyl)amine-capped ligand showed enhanced stability of the +2 oxidation state compared with the tighter-capped sepulchrate ligand; crystal-structure determination showed that the manganese(II) cryptate was unprotonated while cryptates of the smaller, more highly Lewis acidic, cations could be obtained in a protonated form.

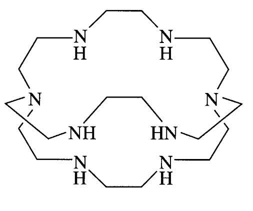
The mononucleating cage ligands synthesised by the Sargeson group have been elegantly exploited[1] for the purpose of encapsulating a wide range of transition-metal cation guests, with numerous consequent applications in redox, and more recently, surfactant and water purification chemistry.[2] Much of the current chemistry concentrates on carbon-bridgehead systems of the N_6-donor sarcophagine (sar = 3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane) type, because of the extreme difficulty[3] of removing the kinetically inert template ion from ligands of the sepulchrate (sep = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]icosane) (N_8) series and their likely instability, as *gem*-diamines, once isolated. The tren-based [tren = tris(2-aminoethyl)amine] nitrogen-bridgehead hexaimine cage L^1 (imBT) which we reported half a dozen years ago[4] avoids both problems, as the cryptand host may be synthesised either on a kinetically labile template ion or by a convenient metal-free route.[5] These hexa(Schiff base) cryptates do show high kinetic stability in respect of decomplexation of cationic guests, although their stability in respect of ligand hydrolysis has been called into question.[6] Tetrahydroborate reduction of the hexaimine cage generates, in good yield, a more chemically robust octaamine derivative L^2 (amBT) which has been used for sequestration of toxic heavy-metal cations.[7,8] The earliest synthesis of this octaamino cage, however, was not *via* the Schiff base condensation method but directly *via* a tripod capping route; in this study the basic host, in hexaprotonated form, was used for co-ordination not of cationic but of anionic guests.[9] Although the dicopper cryptates of both imBT and amBT have attracted a good deal of attention[6,10–13] on account of their unique average-valence $Cu_2(1.5)$ redox state, no study of complexation of other first transition series ions by amBT has been reported. We are now able to repair this omission by describing the synthesis and preliminary characterisation of a series of mononuclear amBT cryptates of transition series cations.

The cryptates were made by treatment of the free cryptand with the metal-ion salt.† Table 1 lists FAB mass spectrometry, conductivity, d–d spectra and magnetic susceptibility data for the series M = Mn^{II}–Zn^{II} with the exception of M = Cu^{II}. No data are reported for copper because, unlike the copper–L^1 system where use of 1 : 1 stoichiometry under appropriate solvent conditions generates the clean monocopper cryptate,[4,13] the product of reaction of amBT with $Cu(ClO_4)_2 \cdot 6H_2O$ in 1 : 1 ratio is a mixture, principally the well characterised average-valence cryptate[6,11,12] $[Cu_2L^2][ClO_4]_3$. This is shown by examination of the ESR spectrum of the solid product from the 1 : 1 Cu : L^2 reaction, where the characteristic seven-line pattern is dominant.[14] Electronic spectral monitoring of the intense far-red absorption confirms that in methanol solution under pH-neutral conditions, the dinuclear average-valence species dominates at 1 : 1 (and lower) Cu : L^2 stoichiometry. Given the evidence for copper–copper bonding[10–13] in these average-valence cryptates, such predominance of the 2 : 1 form is unsurprising. However, we have succeeded in crystallising out the monocopper(II) cryptate of amBT from the reaction mixture as the tetraphenylborate salt, which will be described elsewhere.[14] This monocopper cryptate shows a four-line ESR pattern, $g_{\parallel} \approx 2.19$, $g_{\perp} \approx 2.05$ and $A_{\parallel} \approx 110$ G.

The relatively high basicity of the aminocryptands[15] may be expected to favour protonation of any unco-ordinated secondary or primary amino-N donor, as frequently seen in diamsar (diamsar = 1,8-diaminosarcophagine, 1,8-diamino-3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane) cryptates,[16] even in the absence of deliberately added acid. The higher conductivity of complex **4** demonstrates that this is the case for the nickel product. Cryptates **1**–**3** however behave as 2 : 1 electrolytes in MeCN and analyse satisfactorily as $[ML^2]^{2+}$ salts.

Electronic absorption spectra for the protonated Ni^{II} cryptate **4** suggest a co-ordination geometry in solution not far from regular octahedral, which agrees with the magnetic moment. Two forms of the cobalt cryptate can be obtained. A sugar-pink finely crystalline Co^{II} cryptate **3** precipitates from alcohol, which on recrystallisation from MeCN–EtOH is obtained as the monoprotonated green cryptate **3a**. The two forms can be reversibly interchanged on alteration of pH. Magnetic susceptibility measurements confirm that both cobalt products are in the +2 oxidation state. Both have moments which suggest


L^1 (imBT)


L^2 (amBT)

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† Cryptate synthesis. Cryptand L^1 (0.1 mmol dm^{-3}) EtOH (3–5 cm^3) was stirred at 50 °C for 30 min with the metal perchlorate (0.1 mmol dm^{-3}). The cryptate was filtered off and recrystallised from MeCN–EtOH. Found (calculated) C, H, N, respectively: **1** 33.6 (32.9), 6.8 (7.0), 16.8 (17.0); **2** 32.0 (31.8), 6.6 (7.2), 15.6 (16.4); **3** 32.8 (32.7), 6.6 (7.0), 16.6 (16.9); **3a** 28.4 (27.7), 6.2 (6.1), 14.1 (13.8); **4** 30.4 (29.8), 6.2 (6.0), 15.6 (15.4); **5** 28.4 (28.1), 6.2 (6.0), 14.3 (14.5%).

Table 1 FAB mass and electronic absorption spectra and room temperature moments of L^2 cryptates

Cryptate	Colour	*m/z*	Electronic d–d spectra[a]	Λ/S cm^{-1} [b]	μ/μ_B [c]
1 $[MnL^2][ClO_4]_2\cdot 2H_2O$	White	524 (931[d], 1031[d])	*e*	246	6.03
2 $[FeL^2][ClO_4]_2\cdot 3H_2O$	Cream	525, 425	*e*	272	5.06
3 $[CoL^2][ClO_4]_2\cdot 2H_2O$	Pink	528, 428 (464w)	21.0 (70), 15.4 (sh)	306	4.65
3a $[CoHL^2][ClO_4]_3\cdot 3H_2O$	Green	528, 428 (628vw)	26.3 (sh), 21.7 (60), 16.4 (sh), 15.1 (24), 12.7 (br)(sh)	356	4.97
4 $[NiHL^2][ClO_4]_3$	Lavender	527, 427	26.9 (30), 17.3 (17), 10.0 (22)	404	3.46
5 $[ZnHL^2][ClO_4]_3\cdot 2H_2O$	White	533	—	316	—

[a] 10^{-3} mol dm^{-3} in MeCN; $\lambda/10^{-3}$ cm^{-1} (ε/dm^3 mol^{-1} cm^{-1}). [b] 10^{-3} mol dm^{-3} in MeCN. [c] $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}, 293 K. [d] Protonated MH_nL species, apparently formed under FAB conditions. [e] Not observable at concentrations attainable.

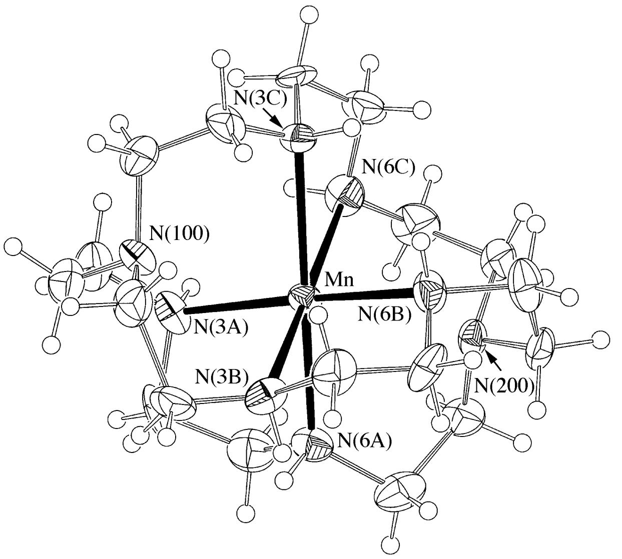

Fig. 1 Structure of the $[MnL^2]^{2+}$ cation. Selected distances (Å): Mn−N 2.36(2)–2.53(2), Mn−N (bridgehead) 2.80(2)

symmetry less than octahedral; d–d spectra indicate co-ordination number six for the pink, and five for the green, protonated form.

An X-ray crystallographic structure determination of **1** (Fig. 1)‡ illustrates a cation symmetrically placed within a slightly elliptical cryptand having an overall *lel* conformation.[1] There is a relatively wide range of Mn−N distances, no doubt because of steric strain in the complex. Distances from the central metal atom to the nitrogen atoms are N(6A) 2.36(2), N(6C) 2.403(13), N(6B) 2.423(13), N(3B) 2.475(13), N(3A) 2.489(12), N(3C) 2.53(2) Å. The shortest and longest bonds are *trans* to each other. The distances between the metal and the bridgehead carbon atoms are 2.801(15) and 2.798(16) Å for N(100) and N(200) respectively. These distances are of the order of those seen[8] in the cryptate of the larger Cd^{2+} cation with amBT. It appears, then, that even Mn^{II}, the largest cation of the series studied, is loosely held within this cage, in contrast to smaller more rigid cages such as sep, sar and imBT, where transition-metal ions exert their normal M−N co-ordination distances.[16] The poor match of cation dimension with cavity size in this conformation presumably explains the tendency of cryptates of the smaller transition series cations to adopt an alternative co-ordination mode which leaves some secondary amine donors unco-ordinated and available for protonation.

Despite the decreasing cation dimensions for Fe^{II} and Co^{II} *versus* Mn^{II}, powder X-ray diffraction patterns show that unprotonated cryptates **2** and **3** are isomorphous with **1**, while the protonated cryptates **3a** and **5** are isomorphous with each other, but not with the anhydrous Ni^{II} analogue **4**.

In comparison with the sep and sar complexes, where the +3 redox state is the norm for cobalt, and unusually high states such as Ni^{III} are easily accessed, the larger cavity presented by amBT may be expected to favour stabilisation of lower oxidation states[20] of encapsulated cations, *i.e.* of Co^{II} over Co^{III} and Fe^{II} against Fe^{III}. Qualitative experiments with aqueous oxidising agents, Ag^+ and Ce^{4+}, both of which are capable of oxidising the analogous sep or sar complexes show that Ce^{4+} is required for oxidation of the $[CoL^2]^{2+}$ cryptate, while Ag^+ is capable of oxidising both Fe^{II} and Mn^{II} analogues. In preliminary voltammetric experiments (Pt or glassy carbon electrodes; 100 mV s^{-1}, MeCN or H_2O solvents) disappointingly irreversible electrochemistry was observed for all the redox-active systems. The ligand itself shows electroactivity: an irreversible oxidation centred between 1.4 and 1.5 V *vs.* Ag–AgCl in aqueous solution is associated with an irreversible reduction close to 0 V, and a second broad reduction event around −0.7 V derives from a broad irreversible oxidation close to 0.9 V. This ligand activity complicates interpretation of the broad irreversible features seen in the redox-active transition-metal ion cryptates, but we believe that activity around 0.05 V may correspond to Fe^{II} oxidation, and around 1.1 V to Mn^{II} oxidation. It is not easy to identify with certainty any feature corresponding to Co^{II} oxidation, although there are candidates in the 1.4 V region where ligand redox occurs.

Complexes of amBT are expected to show enhanced flexibility relative to other small cryptates which have been studied, because (*cf.* sar) of the presence of the bridgehead nitrogen which is capable of inversion; or (*cf.* sep) of the longer methylene chain in the ligand cap; or (*cf.* imBT) because of the absence of sterically restricting imine bonds. The combination of the longer methylene chain and nitrogen bridgehead in the cryptand cap is responsible for the existence of dicopper complexes, which are not conformationally possible within the tighter sep or sar cages.[21] The conformational mobility allows cations to select a donor set which leaves secondary amines unco-ordinated and, in turn, facilitates a kinetic lability absent

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‡ Crystal data. $[MnL^2]\cdot[ClO_4]_2$, $C_{18}H_{42}Cl_2MnN_8O_8$ **1**, $M = 624.44$, monoclinic, space group $P2_1/n$, Mo-Kα radiation ($\lambda = 0.710\,73$ Å), $a = 9.602(9)$, $b = 16.607(13)$, $c = 17.029(14)$ Å, $\beta = 90.03(1)°$, $U = 2716(4)$ Å^3, $Z = 4$, $D_c = 1.527$ mg m^{-3}, $F(000) = 136$, crystal size 0.20 × 0.15 × 0.35 mm, $\mu = 0.740$ mm^{-1}, 3440 reflections were collected of which 2230 were independent [R(int) 0.0455]. Data were collected with Mo-Kα radiation using the MARresearch Image Plate system. The crystal was positioned at 75 mm from the image plate. 95 Frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program.[17] The structure was solved by heavy-atom methods using SHELXS 86.[18] The crystal suffered from 50% merohedral twinning but was refined successfully using the TWIN facility in SHELXL 93.[19] The perchlorates were also disordered and two sets of tetrahedra were refined around each chlorine with occupation factors adding up to 1.00. Apart from these disordered atoms all other non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. The structure was then finally refined on F^2 using SHELXL 93.[19] Final R indices [$I > 2\sigma(I)$] were $R1 = 0.0673$, $wR2 = 0.1916$. All calculations were carried out on a Silicon Graphics Workstation at the University of Reading. Atomic coordintes, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/440.

in sar or sep cages or in the hexaimine cryptand imBT. Preliminary experiments with aqueous KCN suggest that the coordinated Co^{II} cation can be removed from the L^2 host as $[Co(CN)_4]^{2-}$, indicating kinetic stability inferior to that of imBT cryptates.[4] However, the ability of the **3**–**3a** system to act as acid–base indicator in aqueous solution over a period of days testifies to the stability of the cryptates in water over a reasonable pH range (at least pH 3–11), as does the absence of precipitation on treatment with aqueous hydroxide solution.

The combination of kinetic and thermodynamic stability which applies determines the potential usage of any new cryptate system. Where kinetic lability is high, there is the possibility of using the cryptand in monitoring devices or as carriers in transport processes; should kinetic stability prove high, the possibility of application as imaging or detoxification agents is available. We need to carry out a complete study of electrochemical and other properties of these cryptates to discover their potential for application. Solution complexation studies currently in progress[22] will form an important element in these studies.

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References

1 A. M. Sargeson, *Pure Appl. Chem.*, 1986, **58**, 1511.
2 C. A. Behm, P. L. F. Boreham, I. I. Creaser, B. K. Korybutdaswkiewicz, D. J. Maddelena, A. M. Sargeson and G. M. Snowdon, *Aust. J. Chem.*, 1995, **48**, 1009; A. M. Sargeson, *Biocoordination chemistry: inorganic compounds with framework structures*, ESF conference, Karrebaeksminde, September 1996.
3 G. A. Bottomley, J. J. Clark, I. I. Creaser, L. M. Engelhardt, R. J. Geue, K. S. Hagen, J. M. Harrowfield, G. A. Lawrence, P. A. Lay, A. M. Sargeson, A. J. See, B. W. Skelton, A. H. White and F. R. Wilner, *Aust. J. Chem.*, 1994, **47**, 143.
4 J. Hunter, J. Nelson, C. J. Harding, M. McCann and V. McKee, *J. Chem. Soc., Chem. Commun.*, 1990, 1148.
5 P. H. Smith, M. E. Barr, J. R. Brainard, D. K. Ford, H. Frieser, S. Muralidharar, S. D. Reilly, R. R. Ryan, L. A. Selles and W. H. Yu, *J. Org. Chem.*, 1993, **58**, 7939.
6 M. E. Barr, P. H. Smith, W. E. Antholine and B. Spencer, *J. Chem. Soc., Chem. Commun.*, 1993, 1649.
7 N. Martin, V. McKee and J. Nelson, *Inorg. Chim. Acta*, 1994, **218**, 5.
8 J. A. Thompson, M. E. Barr, D. K. Ford, L. A. Silks, B. J. McCormick and P. H. Smith, *Inorg. Chem.*, 1996, **35**, 2025.
9 B. Dietrich, J. M. Lehn, J. Guilheim and C. Pascard, *Tetrahedron Lett.*, 1989, **30**, 4125.
10 C. J. Harding, V. McKee and J. Nelson, *J. Am. Chem. Soc.*, 1991, **113**, 9684.
11 C. J. Harding, J. Nelson, M. C. R. Symons and J. Wyatt, *J. Chem. Soc., Chem. Commun.*, 1994, 2499.
12 J. A. Farrar, V. McKee, A. H. R. Al-Obaidi, J. J. McGarvey, J. Nelson and A. J. Thomson, *Inorg. Chem.*, 1995, **34**, 1302.
13 J. Coyle, A. H. R. Al-Obaidi, P. Jayaswarra, V. McKee, J. J. McGarvey and J. Nelson, *Biocoordination chemistry; inorganic compounds with framework structures*, ESF conference, Karrebaeksminde, September 1996.
14 J. Coyle, C. J. Harding, V. McKee and J. Nelson, unpublished work.
15 S. D. Reilly, G. R. K. Khalsa, D. K. Ford, J. R. Brainard, B. P. Hay and P. H. Smith, *Inorg. Chem.*, 1995, **34**, 569.
16 I. I. Creaser, L. M. Engelhardt, J. M. Harrowfield, A. M. Sargeson, B. W. Skelton and A. H. White, *Aust. J. Chem.*, 1993, **46**, 465.
17 W. Kabasch, *J. Appl. Crystallogr.*, 1988, **21**, 916.
18 G. M. Sheldrick, SHELXS 86, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
19 G. M. Sheldrick, SHELXL, Program for crystal structure refinement, University of Göttingen, 1993.
20 R. J. Geue, A. Hohn, S. F. Ralph, A. M. Sargeson and A. C. Willis, *J. Chem. Soc., Chem. Commun.*, 1994, 1513.
21 G. Morgan, V. McKee and J. Nelson, *Prog. Inorg. Chem.*, in the press.
22 F. Arnaud-Neu and J. Nelson, unpublished work.

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