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A three-ring, linked cyclam derivative and its interaction with selected transition and post-transition metal ions

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Contents

Abstract

The interaction of a linearly linked tris-cyclam derivative incorporating *p*-xylyl linkages between nitrogen donor atoms on adjacent rings with nickel(II), copper(II), zinc(II), cadmium(II), and palladium(II) is reported. All five metals yield solid complexes in which the metal–ligand stoichiometry is 3:1. In the case of Cu(II), a spectrophotometric titration confirmed the formation of a complex of this stoichiometry in acetonitrile. Where appropriate, visible spectral, electrochemical, magnetic moment, ESR, and NMR studies have been performed to probe the nature of the respective complexes in both the solid state and in solution. Cyclic voltamograms of both the Ni(II) (low spin) and Cu(II) complexes both yield evidence for M(II)/M(III) as well as M(I)/M(II) couples in acetonitrile.

Keywords: Macrocycle; Transition metal; Post-transition metal; Electrochemistry; Trinuclear

1. Introduction

While there are many examples of systems that incorporate two singly-linked [1,2] or cofacially-linked macrocyclic rings [3], systems incorporating three or more such rings have received much less attention [4]. Our recent studies have focussed on this latter area and, for example, we have reported the efficient syntheses of symmetrical tri-linked species incorporating 16-membered, N_2S_2-donor macrocycles together with their interaction with metal ions such as silver(I) [5], palladium(II) [6] and platinum(II) [6]. As an extension of these studies a related system incorporating nine linked N_2S_2-macrocycles has been synthesized and its binding of nine Pd(II) ions demonstrated [7].

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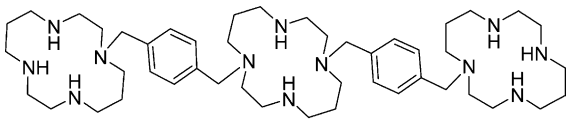
The success of the above studies has rested upon the application of the *N*-protecting groups, Boc and Troc, to the step-wise synthesis of the linked-ligand species [8]. Such methods, pioneered by Guilard et al. for aza macrocycles [9], have been extended by us to the preparation of new linked 1,4,8,11-tetraazacyclotetradecane (cyclam) derivatives such as the linearly-linked, tris(cyclam) ligand **1** [10].

The cyclam ring continues to be of special interest, despite its rich transition and post-transition metal chemistry having been well documented over many years, because of its ability to promote unusual metal complex properties such as high kinetic and thermodynamic stabilities and/or to aid access to particular less-common metal oxidation states [11]. Two cyclam units have been joined through a variety of bridges that include links between the respective ring donor nitrogens and links between carbon atoms in the framework of each tetraaza ring; various aspects of the metal ion chemistry of these species have been reported [2]. For example, such bis-cyclam derivatives have been employed to demonstrate the distance dependence of electrostatic and magnetic interactions in binuclear complexes since the inter-metal ion distances can be controlled to some degree by varying the size of the bridging group.

As an extension of this prior work we now report the first results of an investigation of the complexation behaviour of the tris(cyclam) linked species **1** with nickel(II), copper(II), zinc(II), cadmium(II) and palladium(II). In this context it is noted that aspects of the metal coordination chemistry of the related two-ring ligand **2** [12] and its analogue in which a *p*-xylyl bridge links two cyclams through the 6-position carbons of each ring [13] have been reported.



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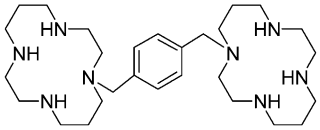

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2. Experimental

2.1. General

The synthesis of **1** has been reported recently by us [11]. Where available, all commercial reagents and solvents were of analytical (or HPLC) grade. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker Avance DPX300 spectrometer. The EPR spectrum of $[Cu_3(\mathbf{1})](ClO_4)_6{\cdot}3H_2O$ was obtained as a DMF glass at 77 K using a Bruker EMX EPR spectrometer at 9.464 GHz (X-band). Solid state UV–vis spectra were measured on a CARY 1E UV–vis spectrophotometer (samples spread on filter paper); solution UV–vis spectra were measured on a CARY 5E UV–vis-nir spectrophotometer.

Cyclic voltammetry studies were performed using a conventional three-electrode configuration with *IR* compensation and a BAS Model 100B electrochemical system, operated by a computer using the BAS software. The working electrode employed was glassy carbon. The reference electrode was Ag/AgCl and was separated from the working and Pt wire auxiliary electrodes by a glass sleeve fitted with a Vycor frit. Solutions were prepared in HPLC-grade acetonitrile, 0.1 mol dm^{-3} in (n-Bu_4N)(ClO_4), and were purged with argon gas. Complex concentrations in the millimolar range were used throughout. Scans over the range 10–1000 mV s^{-1} were measured, with reported results being those recorded at 100 mV s^{-1}.

2.2. Metal complex syntheses

All complexes were dried over P_4O_{10} in a vacuum before microanalysis.

2.2.1. $[Ni_3(\mathbf{1})](ClO_4)_6{\cdot}3H_2O$

Ni(II) perchlorate hexahydrate (0.219 g, 0.600 mmol) in MeOH (5 cm^3) was added to **1** (0.161 g, 0.200 mmol) in MeOH (15 cm^3). The orange solution was stirred and heated for 0.5 h and then left to stand at room temperature overnight. The orange powder that formed was filtered off and recrystallized from water to yield the required compound as an orange powder (0.219 g, 67%). (Anal. Found: C, 33.73; H, 5.35; N, 10.24. Calc. for $C_{46}H_{90}Cl_6Ni_3N_{12}O_{27}$: C, 33.85; H, 5.56; N, 10.30%.)

2.2.2. $[Cu_3(\mathbf{1})](ClO_4)_6{\cdot}3H_2O$

Using a similar procedure to that described for $[Ni_3(\mathbf{1})](ClO_4)_6{\cdot}3H_2O$, Cu(II) perchlorate hexahydrate (0.222 g, 0.600 mmol) and **1** (0.161 g, 0.200 mmol) yielded the product as a red-purple powder (0.197 g, 60%) after recrystallization from water. (Anal. Found: C, 33.50; H, 5.32; N, 10.04. Calc. for $C_{46}H_{90}Cl_6Cu_3N_{12}O_{27}$: C, 33.55; H, 5.51; N, 10.21%.)

2.2.3. $[Zn_3(\mathbf{1})](NO_3)_6{\cdot}MeOH{\cdot}H_2O$

Zn(II) nitrate tetrahydrate (0.157 g, 0.600 mmol) in MeOH (10 cm^3) was added to a solution of **1** (0.161 g, 0.200 mmol) in MeOH (20 cm^3). The solution was stirred and heated for 0.5 h. Water was added drop-wise with stirring to the above suspension until a clear solution was obtained. This was left to stand in air overnight. The off-white powder that formed was filtered off and then recrystallized from MeOH/water to yield the product as a white powder (0.176 g, 62%). (Anal. Found: C, 39.92; H, 6.11; N, 17.50. Calc. for $C_{47}H_{90}N_{18}O_{20}Zn_3$: C, 39.66; H, 6.37; N, 17.71%.) ^{1}H-NMR (D_2O): δ 1.74–2.02 (m,

NCH_2CH_2, 8 H), 2.40–2.44 (m, NCH_2CH_2, 4 H), 2.58–3.57 (m, NCH_2, 48 H), 3.96–4.12 (m, $PhCH_2N$, 4 H), 4.29–4.34 (m, $PhCH_2N$, 4 H), 7.38–7.43 (m, ArH, 8 H). ^{13}C-NMR (D_2O, 350 K): δ 24.44, 24.55, 24.73, 28.29, 28.74, 45.55, 46.16, 46.75, 46.89, 47.62, 48.09, 49.37, 50.47, 50.99, 51.31, 51.70, 52.33, 52.43, 52.68, 52.85, 53.89, 54.09, 54.41, 54.74, 55.63, ~131.5–133.5 (overlapping signals).

2.2.4. $[Cd_3(\mathbf{1})](NO_3)_6\cdot MeOH\cdot 3H_2O$

Using a similar procedure to that described for $[Zn_3(\mathbf{1})](NO_3)_6\cdot MeOH\cdot H_2O$, Cd(II) nitrate tetrahydrate (0.185 g, 0.600 mmol) and **1** (0.161 g, 0.200 mmol) yielded the product as a white powder after recrystallization from MeOH/water (0.112 g, 35%). (Anal. Found: C, 35.36; H, 5.74; N, 15.51. Calc. for $C_{47}H_{94}Cd_3N_{18}O_{22}$: C, 35.27; H, 5.92; N, 15.75%.) ^{1}H-NMR (D_2O): δ 1.59–2.18 (m, NCH_2CH_2, 12 H), 2.42–3.43 (m, NCH_2, 48 H), 3.97–4.11 (m, $PhCH_2N$, 4 H), 4.27–4.47 (m, $PhCH_2N$, 4 H), 7.40–7.42 (m, ArH, 8 H). ^{13}C-NMR (D_2O): δ 27.13, 27.22, 27.37, 27.91, 30.80, 46.57, 47.56, 47.73, 48.26, 48.51, 48.87, 49.86, 51.00, 51.63, 52.05, 52.29, 52.44, 53.24, 53.90, 54.71, 55.44, 55.99, 57.35, 57.44, 58.87, 59.06, 59.53, 59.63, ~131–133 (overlapping signals).

2.2.5. $[Pd_3(\mathbf{1})](ClO_4)_6\cdot 1.5H_2O$

To Pd(II) diacetate (0.135 g, 0.600 mmol) in dichloromethane (10 cm^3) was added **1** (0.161 g, 0.200 mmol) in dichloromethane (5 cm^3). The solution was heated under reflux for 1 h. On cooling the solution, the solvent was removed under vacuum and the pale-brown residue was dissolved in MeOH (5 cm^3). Excess of saturated lithium perchlorate in MeOH was added to this solution and the powder that formed was filtered off. The required product was obtained as a yellow powder after recrystallization of the initial product from water (0.133 g, 38%). (Anal. Found: C, 31.74; H, 4.88; N, 9.45. Calc. for $C_{46}H_{87}Cl_6N_{12}O_{25.5}Pd_3$: C, 31.60; H, 5.02; N, 9.61%.) ^{1}H-NMR (DMSO-d_6): δ 2.07 (m, NCH_2CH_2, 12 H), 2.57–3.01 (m, NCH_2, 48 H), 4.13–4.17 (m, $PhCH_2N$, 4 H), 4.57–4.70 (m, $PhCH_2N$, 4 H), 5.60 (br s, NH, 3 H), 6.06 (br s, NH, 3 H), 7.58–7.61 (m, ArH, 8 H). ^{13}C-NMR (DMSO-d_6): δ 25.02, 25.27, 49–60 (overlapping signals), ~129–134 (overlapping signals).

CAUTION: perchlorate-containing complexes are potentially explosive and appropriate precautions should be in place for their preparation, handling and storage.

3. Results and discussion

3.1. Isolation of solid complexes

In an attempt to obtain crystalline products that might prove suitable for X-ray diffraction studies, the following solid complexes of **1** were successfully isolated: $[Ni_3(\mathbf{1})](ClO_4)_6\cdot 3H_2O$, $[Cu_3(\mathbf{1})](ClO_4)_6\cdot 3H_2O$, $[Zn_3(\mathbf{1})](NO_3)_6\cdot MeOH\cdot H_2O$, $[Cd_3(\mathbf{1})](NO_3)_6\cdot MeOH\cdot 3H_2O$ and $[Pd_3(\mathbf{1})](ClO_4)_6\cdot 1.5H_2O$. The syntheses of these products in reasonable yields proved straight forward by mixing hot solutions of the appropriate metal salt and ligand in MeOH or dichloromethane; in some cases saturated lithium perchlorate was added to the solution to induce crystallization as the perchlorate salt. While these studies served to confirm the 3:1 (metal–ligand) nature of each product in the solid state, unfortunately, no single crystals of X-ray diffraction quality were obtained.

3.2. Nickel(II) studies

The solid state UV–vis spectrum of the orange complex $[Ni_3(\mathbf{1})](ClO_4)_6\cdot 3H_2O$ shows a single band with maximum at 468 nm, consistent with the adoption by each Ni of a square planar (low spin) geometry. The absorption maximum of this complex in acetonitrile shows a major peak at 473 nm ($\varepsilon = 63\ M^{-1}\ cm^{-1}$), consistent with the solid state spectrum, while also showing 'additional' very weak peaks at ca. 728 and 944 nm that appear to reflect the presence of a small amount of 'yellow-to-blue' interconversion (see below) in this solvent.

The $[Ni(cyclam)]^{2+}$ cation [14] is well established to be square planar in both the solid state [15] and (in the absence of coordinating anions) also in aqueous solution; [16] in the latter solvent it gives a single absorption in the visible region at 450 nm ($\varepsilon = 45\ M^{-1}\ cm^{-1}$).

For comparison with the spectrum of $[Ni_3(\mathbf{1})](ClO_4)_6\cdot 3H_2O$, we have also determined the visible spectrum of $[Ni(cyclam)](ClO_4)_2$ in acetonitrile. In this solvent, the major absoption occurs at 461 nm ($\varepsilon = 13\ M^{-1}\ cm^{-1}$) but, in parallel with the above complex of **1**, there is also present very weak adsorbances at ca. 650 and 935 nm which may be assigned to the presence of a 'yellow-to-blue' equilibrium. Solution equilibrium between yellow (low spin, square planar) and blue (high spin, pseudo octahedral) complexes is well documented [17,18] for Ni(II) cyclam and its derivatives as well as for related open-chain ligand complexes under defined conditions; the position of such an equilibrium is solvent, anion, concentration as well as temperature dependent.

The electrochemical behaviour of $[Ni_3(\mathbf{1})](ClO_4)_6\cdot 3H_2O$ in acetonitrile has been investigated along with that of $[Ni(cyclam)](ClO_4)_2$ under similar conditions. In a prior study using other conditions, $[Ni(cyclam)]^{2+}$ has been reported to undergo reversible oxidation to the corresponding Ni(III) complex at moderate potentials [19]. In the present study, the $[Ni_3(\mathbf{1})]^{6+}$ cation was observed to display two partially overlapping reversible oxidation waves (Fig. 1) that are assigned to Ni(III)/(II) processes. The $E_{1/2}$ values of +1.259 V ($\Delta E = 60$ mV; the major wave) and +1.144 V ($\Delta E = 60$ mV) (vs. Ag/AgCl) are more positive than the values of +1.100 V ($\Delta E = 75$ mV) and +0.583 V ($\Delta E = 70$ mV) obtained for $[Ni(cyclam)]^{2+}$, indicating that the oxidation from Ni(II) to Ni(III) is more difficult in the former complex.

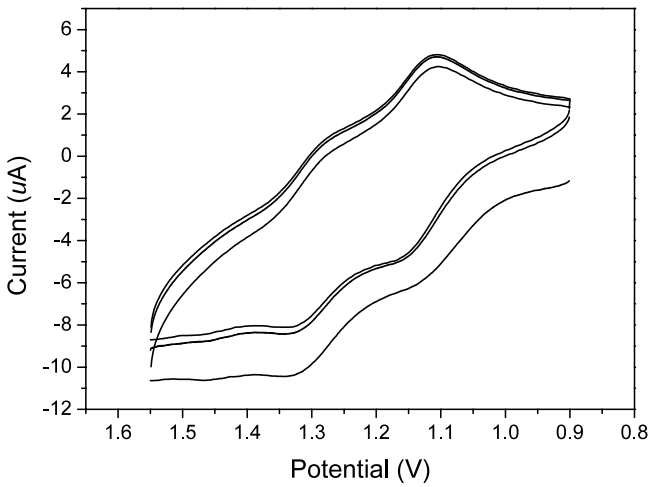

Fig. 1. Cyclic voltammogram for $[Ni_3(\mathbf{1})](ClO_4)_6{\cdot}3H_2O$ in the Ni(II)/Ni(III) region. Experimental conditions: glassy carbon working electrode, 100 mV s^{-1} scan rate, 0.3 mmol dm^{-3} solution in acetonitrile, 0.1 mol dm^{-3} $Bu_4N(ClO_4)$ electrolyte, potential vs. Ag/AgCl.

While the presence of two oxidation waves for $[Ni_3(\mathbf{1})]^{6+}$ could simply reflect the presence of two Ni environments in this species, the overall similarity of the cyclic voltammogram to that observed for [Ni(N-monobenzylated cyclam)]$^{2+}$ under the same conditions [20], for which two waves were also observed, suggests that the situation is more complicated than this. Although the overall situation may be clouded by the presence of a low spin/high spin equilibrium, it seems more likely that the observation of two waves in each cyclic voltammogram may instead largely reflect the presence of both free and adsorbed Ni complex species under the conditions employed for the measurements. In the case of the trinuclear species, even in the absence of electrostatic effects involving metal centres, it is noted that a small splitting due to statistical considerations is predicted—however, such splitting will be quite small and difficult to detect under the conditions used for the present measurements [21].

Two reduction processes were also observed for $[Ni_3(\mathbf{1})]^{6+}$ and assigned to Ni(II)/(I) couples; these occur at −1.052 V (reversibility limited or masked by adsorption phenomena) and −1.271 V ($\Delta E = 88$ mV). The corresponding value obtained for [Ni(cyclam)]$^{2+}$ is −1.447 V ($\Delta E = 225$ mV), in accordance with reduction from Ni(II) to Ni(I) being more facile in the case of $[Ni_3(\mathbf{1})]^{6+}$.

It is pertinent to compare the above electrochemical behaviour with that reported for the dinuclear Ni(II) complex of the corresponding bis(cyclam) system **2** [12] and for its isomeric analogue incorporating two linked *iso*-cyclam rings (for which metal complexation gives rise to 5,5,6,6 chelate ring sequences) [21]. In the former study [12], using differential pulse voltammetry in acetonitrile, it was concluded that the distance between the Ni(II) centres in the dinickel complex of **2** is too great to observe significant electrostatic interaction between the metal ion centres; a similar conclusion was drawn for the corresponding complex of the bis(*iso*-cyclam) system using conventional cyclic voltammetry and differential pulse voltammetry (also in acetonitrile) [21]. In parallel with the present system, the potentials for oxidation of the respective Ni(II) complexes are larger for both the above linked species than for the corresponding mono-ring reference complexes - this has been ascribed to the influence of decreased ligand fields in the linked-ligand species (arising from the presence of the *N*-xylyl-N substituents). It has been a general observation that a decrease in ligand field makes oxidation processes more difficult for d-metal-containing species [12].

3.3. Copper(II) studies

The room temperature magnetic moment (2.04 μ_B, per Cu atom) for the red-purple complex, $[Cu_3(\mathbf{1})](ClO_4)_6{\cdot}3H_2O$, falls in the normal range for a Cu(II) species with $S = {}^1/_2$. The EPR spectrum (X band) of a dimethylformamide glass of this complex yielded a single broad signal with an apparent *g* value at ca. 2.055; because of the poorly resolved parallel component(s) as well as the absence of hyperfine structure, no attempt was made to interpret this spectrum further.

Both the solid state and solution (acetonitrile) visible spectra of the above complex show a single broad band with maxima at 506 and 522 nm ($\varepsilon = 460$ M^{-1} cm^{-1}), respectively. Both are consistent with the presence of a Cu(II)-N_4 chromophore in a square planar arrangement [22,23]. The corresponding value for $[Cu(cyclam)](NO_3)_2$ in the solid state is 508 nm and in acetonitrile 511 nm ($\varepsilon = 58$ M^{-1} cm^{-1}).

A UV–vis spectrophotometric titration of Cu(II) nitrate with **1** was also carried out (Fig. 2). The plot of absorbance versus Cu:ligand ratio for **1** in dimethylsulfoxide shows a sharp 3:1 endpoint, confirming the expected stoichiometry for Cu binding in solution. The steady increment in the absorption at the wavelength employed (580 nm), suggests that both the high affinity and ligand field environment of the three binding sites for Cu(II) in the complex do not differ greatly in this system under the conditions employed.

The Cu(II) complex of **1** displays two quasi-reversible waves in its cyclic voltammogram that are assigned to Cu(III)/(II) and Cu(II)/(I) processes. As observed for the corresponding Ni(II) complex, the Cu(II) complex also yields $E_{1/2}$ values that are shifted to more positive (+1.720 V) [oxidation to Cu(III) more difficult] and less negative [$\Delta E = -0.609$ V and −0.771 ($\Delta E = 153$)] [reduction to Cu(I) easier] than the corresponding values observed for the reference complex [Cu(cyclam)]$^{2+}$ [+1.377 (irreversible) V and −0.853 ($\Delta E = 85$) V, respectively]. However, the peak position and shape were found to vary somewhat with the number of scans and with the state of the electrode, presumably reflecting the presence of severe adsorption phenomena [24]; the peak intensities also decreased with each successive cycle. In view of this an attempt at further intrepretation seemed inappropriate.

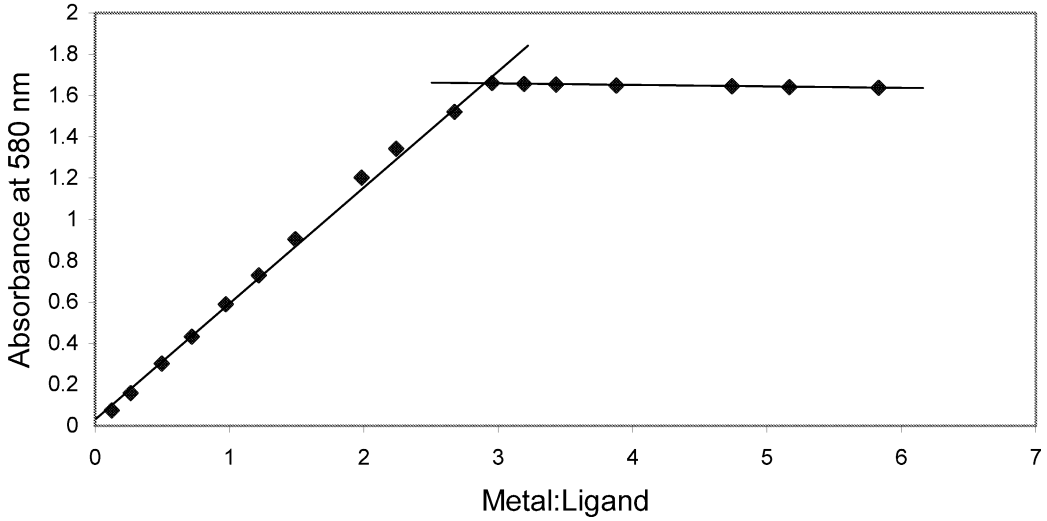

Fig. 2. Spectrophotometric titration curve for the addition of Cu(II) nitrate 2.5 hydrate to **1** (3.90×10^{-3} mol dm^{-3}) in dimethylsulfoxide (3 cm^3).

3.4. Other metal (NMR) studies

The ^{1}H- and ^{13}C-NMR spectra of the Zn(II), Cd(II) and Pd(II) complexes of **1** have been determined (see experimental for details). On complexation, the chemical shifts of the free ligand are shifted slightly downfield in the case of the ^{1}H-NMR spectra and upfield in the case of the ^{13}C-NMR spectra. For the methylene protons adjacent to the aromatic ring, the signals are split (from singlets for the free ligand) to multiplets in the case of each complex, indicating that loss of flexibility occurs on complexation; in most cases additional complexity elsewhere in the spectra also occurs.

4. Concluding remarks

It is worth noting that interest in linked dinucleating azamacrocyclic ligands has increased considerably by the finding that bis(cyclam) ligands (and selected metal-ion derivatives), incorporating either alkyl or aromatic linking groups between the rings, are effective in inhibiting several strains of human immunodeficiency virus type 1 (HIV-1) and type 2 (HIV-2) [25]. Such systems are structurally quite closely related to those investigated in the present study and hence the present systems may also prove to be of interest in this context.

Acknowledgements

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References

[1] L.F. Lindoy, Adv. Inorg. Chem. 45 (1998) 75.
[2] (a) L.F. Lindoy, Coord. Chem. Rev. 174 (1998) 327;
(b) A. McAuley, S. Subramanian, Coord. Chem. Rev. 200–202 (2000) 75;
(c) J.D. Chartres, L.F. Lindoy, G.V. Meehan, Coord. Chem. Rev. 216–217 (2001) 249.
[3] (a) M. Lachkar, B. Andrioletti, B. Boitrel, R. Guilard, A. Atmani, New J. Chem. 19 (1995) 777;
(b) F. Rabiet, F. Denat, R. Guilard, Synth. Commun. 27 (1997) 979;
(c) S. Brandes, F. Denat, S. Lacour, F. Rabiet, F. Barbette, P. Pullumbi, R. Guilard, Eur. J. Org. Chem. (1998) 2349;
(d) M. Lachkar, R. Guilard, A. Atmani, A. De Cian, J. Fischer, R. Weiss, Inorg. Chem. 37 (1998) 1575.
[4] (a) K. Wang, X. Han, R.W. Gross, G.W. Gokel, J. Chem. Soc. Chem. Commun. (1995) 641;
(b) L. Spiccia, B. Graham, M.T.W. Hearn, G. Lazarev, B. Moubaraki, K.S. Murray, E.R.T. Tiekink, J. Chem. Soc. Dalton Trans. (1997) 4089;
(c) E. Kimura, S. Aoki, T. Koike, M. Shiro, J. Am. Chem. Soc. 119 (1997) 3068;
(d) S. Sun, J. Saltmarsh, S. Mallik, K. Thomasson, Chem. Commun. (1998) 519;
(e) P.V. Bernhardt, E.J. Hayes, J. Chem. Soc. Dalton Trans. (1998) 3539;
(f) E. Kimura, M. Kikuchi, H. Kitamura, T. Koike, Chem. Eur. J. 5 (1999) 3113;
(g) I.M. Atkinson, D.M. Boghai, B. Ghanbari, L.F. Lindoy, G.V. Meehan, V. Saini, Aust. J. Chem. 52 (1999) 351;
(h) E. Abel, G.E.M. Maguire, O. Murillo, I. Suzuki, S.L. De Wall, G.W. Gokel, J. Am. Chem. Soc. 121 (1999) 9043;
(i) B. Graham, M.J. Grannas, M.T.W. Hearn, C.M. Kepert, L. Spiccia, B.W. Skelton, A.H. White, Inorg. Chem. 39 (2000) 1092.
[5] J.D. Chartres, A.M. Groth, L.F. Lindoy, G.V. Meehan, J. Chem. Soc. Dalton Trans. 3 (2002) 371.
[6] I.M. Atkinson, Jy D. Chartres, A.M. Groth, L.F. Lindoy, M.P. Lowe, G.V. Meehan, B.W. Skelton, A.H. White, J. Chem. Soc. Dalton Trans. (2001) 2801.
[7] I.M. Atkinson, J.D. Chartres, A.M. Groth, L.F. Lindoy, M.P. Lowe and G.V. Meehan, 2002, Chem. Commun., (2002) 2428.
[8] A.M. Groth, L.F. Lindoy, G.V. Meehan, J. Chem. Soc. Perkin Trans. 1 (1996) 1553.
[9] (a) B. Boitrel, B. Andrioletti, M. Lachkar, R. Guilard, Tetrahedron Lett. 36 (1995) 4995;
(b) S. Brandes, C. Gros, F. Denat, P. Pullumbi, R. Guilard, Bull. Soc. Chim. Fr. 133 (1996) 65.
[10] Y. Dong, L.F. Lindoy, Aust. J. Chem. 54 (2001) 291.
[11] (a) L.F. Lindoy, The Chemistry of Macrocyclic Ligand Complexes Cambridge University Press, Cambridge, UK, 1989, pp. 210–212;
(b) H. Elias, Coord. Chem. Rev. 187 (1999) 37.

[12] M. Ciampolini, L. Fabbrizzi, A. Perotti, A. Poggi, B. Seghi, F. Zanobini, Inorg. Chem. 26 (1987) 3527.
[13] H. Kido, M. Takada, M. Suwabe, T. Yamaguchi, T. Ito, Inorg. Chim. Acta 228 (1995) 133.
[14] B. Bosnich, M.L. Tobe, G.A. Web, Inorg. Chem. 4 (1965) 1109.
[15] (a) K.R. Adam, M. Antolovich, L.G. Brigden, A.J. Leong, L.F. Lindoy, P.J. Baillie, D.K. Uppall, M. McPartlin, B. Shah, D. Proserpio, L. Fabbrizzi, P.A. Tasker, J. Chem. Soc. Dalton Trans. (1991) 2493;
(b) K.A. Adam, I.M. Atkinson, L.F. Lindoy, Inorg. Chem. 36 (1997) 480;
(c) M.A. Donnelly, M. Zimmer, Inorg. Chem. 38 (1999) 1650.
[16] (a) E.K. Barefield, F. Wagner, A.W. Herlinger, A.H. Dahl, Inorg. Synth. 16 (1976) 220;
(b) E. Zeigerson, G. Ginzburg, D. Meyerstein, L.J. Kirschenbaum, J. Chem. Soc. Dalton Trans. (1980) 1243.
[17] (a) C.K. Jøgensen, Acta Chem. Scand. 11 (1957) 399;
(b) A. Anichini, L. Fabbrizzi, P. Paoletti, R.M. Clay, Inorg. Chim. Acta 24 (1977) L21;
(c) L. Sabatini, L. Fabbrizzi, Inorg. Chem. 18 (1979) 438;
(d) L. Fabbrizzi, M. Micheloni, P. Paoletti, Inorg. Chem. 18 (1980) 535;
(e) M. Ciampolini, L. Fabbrizzi, M. Licchelli, A. Perotti, F. Pezzini, A. Poggi, Inorg. Chem. 25 (1986) 4131.
[18] R.W. Hay, B. Kinsman, C.I. Smith, Polyhedron 14 (1995) 1245.
[19] (a) F. Fabbrizzi, Comments Inorg. Chem. 4 (1985) 33;
(b) A. De Blas, G. De Santis, L. Fabbrizzi, M. Licchelli, P. Pallavicini, Pure Appl. Chem. 65 (1993) 455.
[20] L.F. Lindoy, G.A. Lawrance, Y. Dong, unpublished work.
[21] R. Schneider, A. Riesen, Th. Kaden, Helv. Chim. Acta 69 (1986) 53.
[22] (a) R. Buxtrof, T.A. Kaden, Helv. Chim. Acta 57 (1974) 1035;
(b) M. Hediger, T.A. Kaden, Helv. Chim. Acta 66 (1983) 861.
[23] L. Fabbrizzi, L. Montagna, A. Poggi, T.A. Kaden, L.C. Siegfried, J. Chem. Soc. Dalton Trans. (1987) 2631.
[24] S. Yamanaka, H. Okawa, K. Motoda, M. Yonemura, D.E. Fenton, M. Ebadi, A.B.P. Lever, Inorg. Chem. 38 (1999) 1825.
[25] G.J. Bridger, R.T. Skerlj, S. Padmanabhan, S.A. Martellucci, G.W. Henson, M.J. Abrams, H.C. Joao, M. Witvrouw, K.D. Vreese, R. Pauwels, E. De Clercq, J. Med. Chem. 39 (1996) 109.