In memory of S. M. Nelson

Bicyclam [6,6′-Bi(1,4,8,11-tetra-azacyclotetradecane)]: a Ditopic Receptor for Homo- and Hetero-bimetallic Complexes†

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Bicyclam [6,6′-bi(1,4,8,11-tetra-azacyclotetradecane)] (L^2) was prepared by reducing 6,6′-bi(1,4,8,11-tetra-azacyclotetradecan-5,7-dione) (L^1) with B_2H_6 in bis(2-methoxyethyl) ether. Ligand L^2 forms homo- and hetero-binuclear complexes with Cu^{2+} and Ni^{2+}, the spectral properties and the electrochemistry of which have been studied. Whereas the visible spectra are very similar to those of the mononuclear complexes with cyclam (1,4,8,11-tetra-azacyclotetradecane), the electrochemistry indicates a weak interaction between the metal ions co-ordinated by bicyclam, as shown by a shift of the second oxidation potential $M^{2+} \longrightarrow M^{3+}$ to more positive values.

The interest in binucleating ligands able to co-ordinate two metal ions and keep them at a fixed distance has produced a large number of new chelating agents.[1] Several strategies have been employed and thus open chain,[2] monocyclic,[3] functionalized monocyclic,[4] and bicyclic[5] ligands have been described.

Binuclear Cu^{2+} complexes have been proposed as models for metalloproteins and used to study metal–metal interactions either through the ligands or through space, to determine the binding of ligands which can act as bridges between the metal ions, and to investigate multi-electron processes.[1] Each system has its own peculiar properties. However, macrocycles have proved to be excellent compounds in many aspects since their thermodynamic and kinetic properties are such that they permit the study of binuclear systems with a minimum of side reactions. In the past few years a novel class of binucleating ligand has been introduced,[6–12] in which the two sub-units consist of polyazamacrocycles connected to each other by a carbon chain. Bimetallic complexes of such bimacrocycles generally have properties which can be understood by weak metal–metal interactions through space, since each metal ion is encircled by one of the macrocycles and therefore relatively isolated from the other. Several macrocycles have been used as sub-units to build such derivatives. The first examples were a bimacrocycle consisting of two cyclam (1,4,8,11-tetra-azacyclotetradecane) units connected by a carbon–carbon bond,[6] and one built from two tetra-azamacrocycles containing a pyridine ring which were bridged by carbon chains of different length.[7]

Further examples of bimacrocycles with two 12-membered tetra-aza rings,[8] two 1,4,7-triazacyclononane units,[9] and two isocyclam units[10] as well as several bidioxomacrocycles[11] have been described in the literature. We report here a novel compound of this type, which comprises two cyclam units linked together by a C–C bond (L^2). This does not alter the co-ordination properties of the macrocycle itself and thus all the advantages of cyclam remain intact. Although this bicyclam [6,6′-bi(1,4,8,11-tetra-azacyclotetradecane)] is a symmetric ditopic ligand and therefore prone to give homobinuclear complexes, we were also able to prepare a heterobinuclear copper(II)–nickel(II) species, the electrochemistry of which has been described previously.[12]

Experimental

6,6′-Bi(1,4,8,11-tetra-azacyclotetradecan-5,7-dione) (L^1) was prepared as described.[11]

6,6′-Bi(1,4,8,11-tetra-azacyclotetradecane) (L^2).—A solution of L^1 (2.0 g, 4.4 mmol) in bis(2-methoxyethyl) ether (200 cm^3) (puriss.) was treated with B_2H_6 [120 cm^3, 1 mol dm^{-3} in tetrahydrofuran (thf)] and then heated to 100—110 °C. After *ca.* 1 h the insoluble starting compound had nearly dissolved, and after *ca.* 5 h the product began to precipitate. After 6 h additional B_2H_6 (100 cm^3, 1 mol dm^{-3} in thf) was added and the reaction mixture heated overnight. Then the excess of B_2H_6 was removed by careful addition of MeOH. The solution was rotatory evaporated and the residue hydrolysed over 1 h with concentrated HCl (16 cm^3), H_2O (32 cm^3), and MeOH (80 cm^3). Thereafter the solution was again rotatory evaporated, the residue taken up with 7 mol dm^{-3} KOH (25 cm^3) and extracted with $CHCl_3$ (7 × 50 cm^3). After drying and evaporating the organic phase the free base was converted into the hydrochloride by addition of MeOH (140 cm^3) and concentrated HCl (3 cm^3). Yield 2.4 g (79%). To obtain the analytically pure product the hydrochloride was recrystallised from MeOH (20 cm^3), concentrated HCl (0.5 cm^3), and a little water. Cooling to 4 °C gave 1.2 g (38%) of the colourless octahydrochloride. M.p. (decomp.) 248—250 °C. ^1H N.m.r. (D_2O): 2.0—2.5 (6 H, m, $C{-}CH_2{-}C$ and C–CH–C) and 3.1—3.3 (32 H, m, $-CH_2{-}N$) (Found: C, 33.10; H, 8.00; Cl, 38.80; N, 15.15. Calc. for $C_{20}H_{54}Cl_8N_8{\cdot}2H_2O$: C, 33.05; H, 8.05; Cl, 39.05; N, 15.40%).

Homobinuclear complexes were prepared by treating L^2 (50 mg, 0.125 mmol) dissolved in hot EtOH (2.5 cm^3) with the corresponding metal perchlorate (0.314 mmol) dissolved in hot EtOH (5 cm^3). The binuclear metal complexes precipitated as perchlorates. (**CAUTION**: Perchlorates can be explosive.)

$[Cu_2(L^2)][ClO_4]_4{\cdot}3H_2O$. Yield 83%, violet crystals (Found: C, 24.75; H, 5.25; Cu, 12.6; N, 11.40. Calc. for $C_{20}H_{46}Cl_4Cu_2N_8O_{16}{\cdot}3H_2O$: C, 24.55; H, 5.30; Cu, 13.00; N, 11.45%).

$[Ni_2(L^2)][ClO_4]_4{\cdot}3H_2O$. Yield 64%, yellow crystals (Found: C, 24.70; H, 5.40; N, 11.40; Ni, 11.9. Calc. for $C_{20}H_{46}Cl_4N_8Ni_2O_{16}{\cdot}3H_2O$: C, 24.80; H, 5.40; N, 11.55; Ni, 12.15%).

Heterobinuclear Complex, $[CuNi(L^2)][ClO_4]_4$.—The ligand L^2 (0.5 mmol) was dissolved in water (5 cm^3) and the pH adjusted to 7 with NaOH. To this solution $Ni(NO_3)_2{\cdot}6H_2O$

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† *Non-S.I. units employed:* B.M. = 9.27 × 10^{-24} J T^{-1}, cal = 4.184 J.

(0.5 mmol) dissolved in water (3 cm^3) was added and the mixture kept at 40—50 °C for *ca.* 3 h, with occasional readjustment of the pH to 7, whereby the solution turned yellow. Thereafter, $Cu(NO_3)_2 \cdot 3H_2O$ in water (3 cm^3) was added and the pH kept constant at 5 with occasional additions of NaOH for 1 h. The final solution is a mixture of $[Cu_2(L^2)]^{4+}$, $[Ni_2(L^2)]^{4+}$, and $[CuNi(L^2)]^{4+}$. To separate the three species the solution was applied to an SP-Sephadex C 25 (Pharmacia, Upsala) ion-exchange column from which three fractions were eluted with 0.4 mol dm^{-3} NaCl. First, a violet band, $[Cu_2(L^2)]^{4+}$, then a salmon pink band, $[CuNi(L^2)]^{4+}$, and finally a yellow band, $[Ni_2(L^2)]^{4+}$, were collected. The chromatographic separation was monitored through the absorptivities at 510 nm (corresponding to the Cu^{II} chromophore) and 460 nm (corresponding to the Ni^{II} chromophore). In Figure 1 the ratio $R = A_{510}/A_{460}$ is plotted against the fraction number. The middle fractions with constant ratio $R = 1.25$ were combined, evaporated to dryness, and treated several times with absolute EtOH (10 cm^3) in order to remove NaCl. After the final evaporation of EtOH the residue was taken up in water (2 cm^3). On addition of a saturated $NaClO_4$ solution a microcrystalline, salmon pink precipitate was obtained (yield 33%). This was recrystallized from water with addition of $NaClO_4$ (Found: C, 26.35; H, 5.10; Cu, 6.85; N, 12.20; Ni, 6.40. Calc. for $C_{20}H_{46}Cl_4CuN_8NiO_{16}$: C, 26.15; H, 5.05; Cu, 6.90; N, 12.20; Ni, 6.40%).

Physical Measurements.—Visible spectra were measured on a Cary 2300 spectrometer in 1-cm cells at 25 °C. Solutions were 2×10^{-3} mol dm^{-3} in pure water, or aqueous $CaCl_2$ of different concentrations to study the effect of ionic strength on the molar absorptivity. In some experiments the temperature was varied.

Magnetic moments were measured by the Evans method[13] in D_2O using t-butyl alcohol as indicator on a 90-MHz n.m.r. instrument. The solutions were 0.5 mol dm^{-3} in the binuclear complex nitrate.

Electrochemical measurements were made on an AMEL 472 polarograph with a platinum microsphere as the working electrode, and a silver wire as pseudo-reference electrode, which was calibrated *vs.* the Fe^{2+}–Fe^{3+} redox couple[14] used as internal standard in 70% $HClO_4$, and *vs.* $[Fe(\eta\text{-}C_5H_5)_2]^+$–$[Fe(\eta\text{-}C_5H_5)_2]$ in acetonitrile. Concentrated $HClO_4$ (Fluka, puriss.) was used as obtained, whereas acetonitrile was purified through distillation over CaH_2 and stored over molecular sieves under nitrogen. As supporting electrolyte in MeCN 0.1 mol dm^{-3} $[NEt_4][BF_4]$ (Erba) was used. The differential pulse polarography was run with 2 mV s^{-1} rates and pulses of 10 mV.

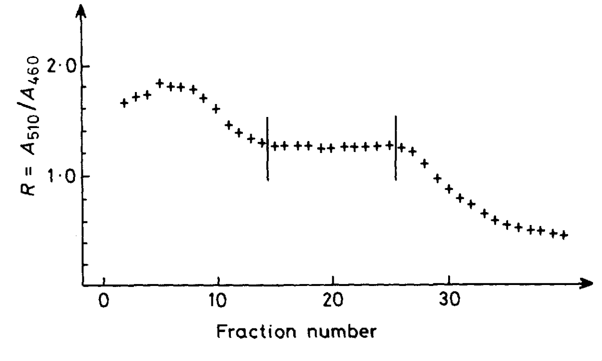


Figure 1. Ratio, *R*, of the absorptivities at 510 and 460 nm as a function of the fraction number. The counting of the fractions was started with elution of the first band

The e.s.r. spectra of the Cu^{2+} complexes were run on a Varian E-9 spectrometer using 10^{-3} mol dm^{-3} solutions in water–dimethylformamide (dmf) (2:1) at −120 °C. As external standard diphenylpicrylhydrazyl radical (g = 2.002 60) was used.

Results and Discussion

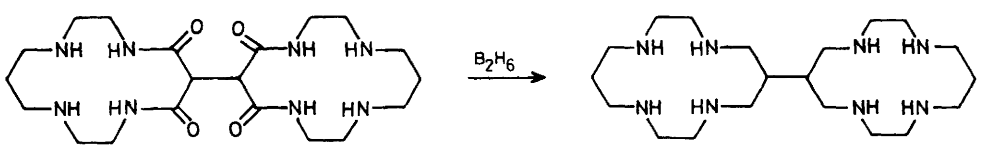
The ligand L^2 was prepared by reduction of L^1 with B_2H_6 (Scheme). In pure thf the reaction does not take place since L^1 is practically insoluble in this solvent, but addition of bis(2-methoxyethyl) ether in which L^1 is partially soluble helps to bring the reaction to completion. Bicyclam (L^2) is an ideal ditopic ligand since it has all the properties of cyclam, *i.e.* the thermodynamic[15] and kinetic[16] stability of its complexes and the easy access to the trivalent state of the co-ordinated metal ions.[17] The C–C bridging between the two macrocyclic subunits does not reduce the co-ordination tendencies of the macrocycle, in contrast to bridging of amine nitrogens.[8,10] The ligand L^2 easily gives homobinuclear complexes when treated with a two-fold excess of metal ion. Thus the binuclear complexes $[Cu_2(L^2)]^{4+}$ and $[Ni_2(L^2)]^{4+}$ can be prepared in aqueous solution or crystallized as perchlorates from EtOH. In addition we were also able to prepare a heterobinuclear $[CuNi(L^2)]^{4+}$ complex by stepwise addition of one equivalent of Ni^{2+} and one equivalent of Cu^{2+}. Assuming that the two rings behave independently in the complexation process, a statistical distribution of 25% $[Cu_2(L^2)]^{4+}$, 25% $[Ni_2(L^2)]^{4+}$, and 50% $[CuNi(L^2)]^{4+}$ results. This mixture can be separated by ion-exchange chromatography and the yield of 33% compares well with the theoretical one. The compound is a true binuclear species and not a mixture of equal amounts of $[Cu_2(L^2)]^{4+}$ and $[Ni_2(L^2)]^{4+}$, as shown by its chromatographic behaviour.

The absorption spectra of these compounds together with those of the mononuclear complexes with cyclam are given in Table 1. The $\lambda_{max.}$ values for $[Cu_2(L^2)]^{4+}$ and $[Ni_2(L^2)]^{4+}$ are

Table 1. Absorption maxima and molar absorptivities of the binuclear L^2 and the mononuclear cyclam complexes

Complex	$\lambda_{max.}$/nm	ε/dm^3 mol^{-1} cm^{-1}
$[Cu(cyclam)]^{2+}$	506	81
$[Cu_2(L^2)]^{4+}$	514	182*
$[Ni(cyclam)]^{2+}$	451	45
$[Ni_2(L^2)]^{4+}$	450	44*
$[CuNi(L^2)]^{4+}$	492	78*
$[Cu(cyclam)]^{2+}$ + $[Ni(cyclam)]^{2+}$	488	[illegible]

*ε Value for the complex, *i.e.* for two metal ions.



L^1 L^2 (1)

Scheme.

Table 2. Thermodynamic parameters for the equilibrium between the yellow and blue forms of $[\mathrm{Ni(cyclam)}]^{2+}$ and $[\mathrm{Ni_2(L^2)}]^{4+}$

	$\varepsilon_{\mathrm{yellow}}$/ dm^3 mol^{-1} cm^{-1}	K_e*	Form/%		ΔG°/ kcal mol^{-1}	ΔH°/ kcal mol^{-1}	ΔS°/ cal K^{-1} mol^{-1}
			Yellow	Blue			
$[\mathrm{Ni(cyclam)}]^{2+}$	63	2.3	70	30	−0.49	4.6	17
$[\mathrm{Ni_2(L^2)}]^{4+}$	61	4.0	80	20	−0.82	8.0	30

* At 25 °C and I = 0.2 mol dm^{-3}.

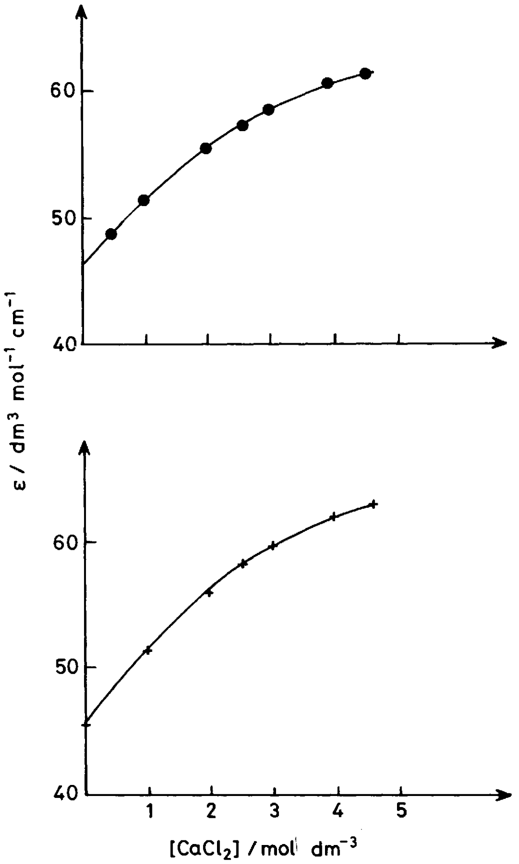


Figure 2. Molar absorptivity of the yellow form ($\varepsilon_{\mathrm{yellow}}$) of $[\mathrm{Ni(cyclam)}]^{2+}$ (●) and $[\mathrm{Ni_2(L^2)}]^{4+}$ (+) as a function of the ionic strength, controlled by $\mathrm{CaCl_2}$

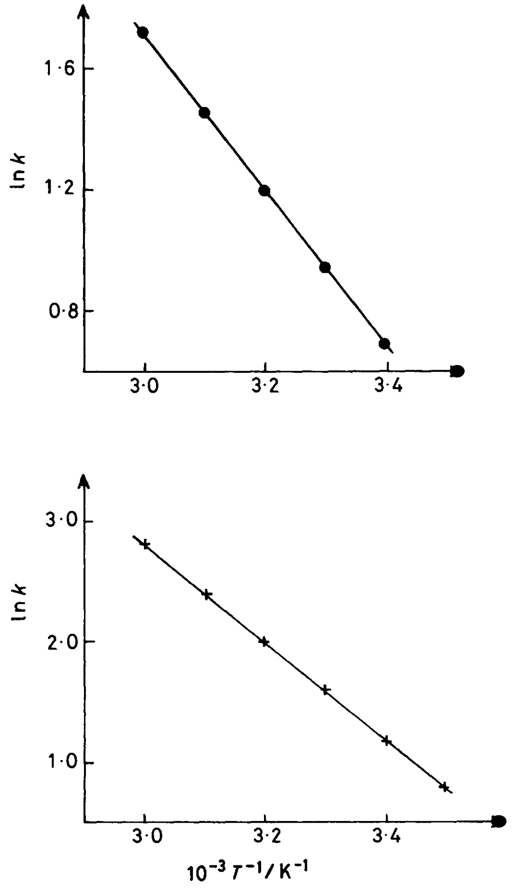


Figure 3. Temperature dependence of the equilibrium constant K_e between the blue and yellow forms of $[\mathrm{Ni(cyclam)}]^{2+}$ (●) and $[\mathrm{Ni_2(L^2)}]^{4+}$ (+)

closely similar to those of the corresponding complexes with cyclam. The spectrum of $[\mathrm{CuNi(L^2)}]^{4+}$ is practically equal to the sum of the spectra of $[\mathrm{Cu(cyclam)}]^{2+}$ and $[\mathrm{Ni(cyclam)}]^{2+}$ indicating that the two chromophores behave independently. Except for $[\mathrm{Ni_2(L^2)}]^{4+}$ the molar absorptivities are the sum of those of the mononuclear species.

Since it is known that macrocyclic Ni^{2+} complexes exist in a blue and in a yellow form [18] [see equation (2)] it was interesting

$$\underset{\text{blue}}{[\mathrm{Ni}_n\mathrm{L}(\mathrm{H_2O})_m]^{2n+}} \overset{K_e}{\rightleftharpoons} \underset{\text{yellow}}{[\mathrm{Ni}_n\mathrm{L}]^{2n+}} + m\mathrm{H_2O} \qquad (2)$$

to study the binuclear species $[\mathrm{Ni_2(L^2)}]^{4+}$ in this regard. The limiting value of $\varepsilon_{\mathrm{yellow}}$ was determined by adding large amounts of $\mathrm{CaCl_2}$ to the solution (Figure 2). From this value the equilibrium constant K_e at 25 °C and I = 0.2 mol dm^{-3} can be calculated (Table 2). In addition the temperature dependence of the spectrum also allows the determination of K_e at different temperatures (Figure 3) and from these the thermodynamic parameters can be calculated (Table 2). A glance at these results shows that ΔH° and ΔS° of the binuclear complex are nearly twice those of $[\mathrm{Ni(cyclam)}]^{2+}$. So again the two units seem to behave independently. At room temperature and I = 0.2 mol dm^{-3} the aqueous solution of $[\mathrm{Ni_2(L^2)}]^{4+}$ contains *ca.* 80% of the yellow square-planar form and 20% of the blue pseudo-octahedral species. This is also reflected in the magnetic moment, which is 0.9 B.M. per nickel ion, whereas for a pure diamagnetic yellow species 0 B.M. would be expected.

We have also recorded the e.s.r. spectra of $[\mathrm{Cu(cyclam)}]^{2+}$ and $[\mathrm{CuNi(L^2)}]^{4+}$ in water–dmf glass at −120 °C. The spectra of $[\mathrm{Cu(cyclam)}]^{2+}$ and $[\mathrm{CuNi(L^2)}]^{4+}$ are practically identical (Figure 4) and typical of axial symmetry, with $g_{\parallel}$ split by the hyperfine coupling constant into a quartet. In both cases we expect that Cu^{2+} has a square-planar co-ordination geometry. In $[\mathrm{CuNi(L^2)}]^{4+}$ the Ni^{2+} also exhibits square-planar geometry and therefore does not interact with the Cu^{2+}.

Table 3. Oxidation potentials (mV) for Cu^{2+} and Ni^{2+} complexes with cyclam and bicyclam (L^2) in 70% $HClO_4$ (*vs.* standard hydrogen electrode) and in MeCN–0.1 mol dm^{-3} $[NEt_4][BF_4]$ {*vs.* $[Fe(\eta\text{-}C_5H_5)_2]^+$–$[Fe(\eta\text{-}C_5H_5)_2]$} at 25 °C

	70% $HClO_4$		MeCN–0.1 mol dm^{-3} $[NEt_4][BF_4]$	
	$E_{\frac{1}{2}}$ (1)	$E_{\frac{1}{2}}$ (2)	$E_{\frac{1}{2}}$ (1)	$E_{\frac{1}{2}}$ (2)
$[Ni(cyclam)]^{2+}$	1.042		0.600	
$[Ni_2(L^2)]^{4+}$	1.022[a]	1.088[a]	0.576[b]	0.651[b]
$[Cu(cyclam)]^{2+}$	1.162		0.968	
$[Cu_2(L^2)]^{4+}$	1.142[c]	1.238[c]	Not stable	
$[CuNi(L^2)]^{4+}$	1.047	1.222	0.600	0.998

[a] Calculated from the work function given by D. E. Richardson and H. Taube (*Inorg. Chem.*, 1981, **20**, 1278) and $\delta_{\frac{1}{2}} = 130$ mV. [b] Calculated with $\delta_{\frac{1}{2}} = 150$ mV. [c] Calculated with $\delta_{\frac{1}{2}} = 190$ mV.

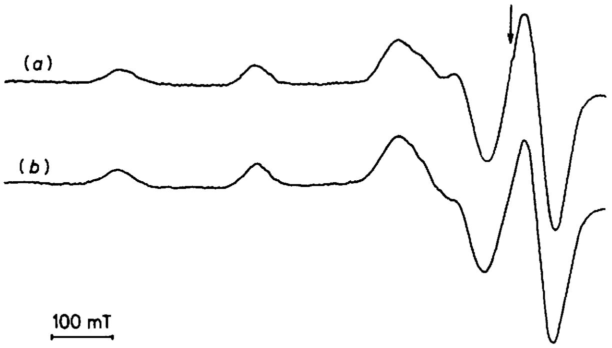


Figure 4. E.s.r. spectra of $[Cu(cyclam)]^{2+}$ (*a*) and $[CuNi(L^2)]^{4+}$ (*b*) in H_2O–dmf (2:1) at −120 °C. The arrow indicates the *g* value of the external reference (*g* = 2.002 60)

The electrochemistry of the homobimetallic complexes of L^2 with Ni^{2+} and Cu^{2+} displays a two-electron oxidation step, analogous to that observed in other complexes of bimacrocycles.[10,11] The two steps $E_{\frac{1}{2}}$ (1) and $E_{\frac{1}{2}}$ (2) for $[Ni_2(L^2)][ClO_4]_4$ and $[Cu_2(L^2)][ClO_4]_4$ are between 66 and 96 mV apart in MeCN and $HClO_4$ (Table 3). This indicates that a weak coulombic interaction between the two metal centres occurs, since after one metal ion has been oxidized, the other feels the higher charge and the following oxidation takes place at higher potential. The electrochemistry of the heterobinuclear species $[CuNi(L^2)]^{4+}$ was reported earlier[12] and shows two well separated peaks corresponding to the $Ni^{2+} \longrightarrow Ni^{3+}$ and $Cu^{2+} \longrightarrow Cu^{3+}$ oxidation steps. A comparison with a synthetic mixture of $[Cu(cyclam)]^{2+}$ and $[Ni(cyclam)]^{2+}$ shows that the $Ni^{2+} \longrightarrow Ni^{3+}$ oxidation occurs at the same potential for the mono- and bi-nuclear complexes whereas the $Cu^{2+} \longrightarrow Cu^{3+}$ step is displaced by 30 and 60 mV in MeCN and 70% $HClO_4$, respectively, to higher values than that of the monomeric $[Cu(cyclam)]^{2+}$, due to the same coulombic interaction as mentioned before.

In conclusion bicyclam (L^2) is an ideal ditopic ligand to bind metal ions in the two macrocyclic units and has the properties expected from the mononuclear species.

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References

1 For a review see 'Copper-co-ordination Chemistry: Biochemical and Inorganic Perspectives,' eds. K. D. Karlin and J. Zubieta, Adenine Press, New York, 1984.
2 A. Zuberbühler and Th. A. Kaden, *Helv. Chim. Acta*, 1968, **51**, 1805; A. Bencini, D. Gatteschi, C. Zanchini, J. G. Haasnoot, R. Prins, and J. Reedijk, *Inorg. Chem.*, 1985, **24**, 2812; Y. Journeaux, O. Khan, and J. Sletten, *ibid.*, p. 4055; M. T. Youinou, J. A. Osborn, J. P. Collins, and P. Lagrange, *ibid.*, 1986, **25**, 453; L. Casella, M. Gullotti, C. Pessina, and A. Pintar, *Gazz. Chim. Ital.*, 1986, **116**, 41; J. M. Berg and K. O. Hodgson, *Inorg. Chem.*, 1986, **25**, 1800; L. R. Gahan, K. E. Hart, C. H. L. Kennard, M. A. Kingston, G. Smith, and T. C. W. Mak, *Inorg. Chim. Acta*, 1986, **116**, 5.
3 P. K. Coughlin and S. J. Lippard, *J. Am. Chem. Soc.*, 1981, **103**, 3228; *Inorg. Chem.*, 1984, **23**, 1446; A. E. Martin and S. J. Lippard, *J. Am. Chem. Soc.*, 1984, **106**, 2579; R. Motekaitis, A. Martell, B. Dietrich, and J. M. Lehn, *Inorg. Chem.*, 1984, **23**, 1588; Y. Agnus, R. Louis, J. P. Gisselbrecht, and R. Weiss, *J. Am. Chem. Soc.*, 1984, **106**, 93; S. M. Nelson, *Pure Appl. Chem.*, 1980, **52**, 2461; P. K. Coughlin, A. E. Martin, J. Dewan, E. Watanabe, J. E. Bulkowski, J. M. Lehn, and S. J. Lippard, *Inorg. Chem.*, 1984, **23**, 1004; A. E. Martin and J. E. Bulkowski, *J. Org. Chem.*, 1982, **47**, 415; J. M. Lehn, *Pure Appl. Chem.*, 1980, **52**, 2441.
4 I. Murase, M. Mikuriya, H. Sonoda, Y. Fukuda, and S. Kida, *J. Chem. Soc., Dalton Trans.*, 1986, 953; N. W. Alcock, K. P. Balakrisnhnan, and P. P. Moore, *ibid.*, p. 1743; A. Riesen, M. Zehnder, and Th. A. Kaden, *Helv. Chim. Acta*, 1986, **69**, 2067; A. Riesen, M. Zehnder, and Th. A. Kaden, *ibid.*, p. 2074.
5 J. M. Lehn, *Pure Appl. Chem.*, 1980, **52**, 2441 and refs. therein; R. Motekaitis, A. Martell, B. Dietrich, and J. M. Lehn, *Inorg. Chem.*, 1984, **23**, 1588; A. Alberts, R. Annunziata, and J. M. Lehn, *J. Am. Chem. Soc.*, 1977, **99**, 8502.
6 E. K. Barefield, D. Chueng, and D. G. Van Derveer, *J. Chem. Soc., Chem. Commun.*, 1981, 302.
7 I. Murase, K. Hamada, and S. Kida, *Inorg. Chim. Acta*, 1981, **54**, L171.
8 M. Ciampolini, M. Micheloni, N. Nardi, F. Nizza, A. Buttafava, L. Fabbrizzi, and A. Perotti, *J. Chem. Soc., Chem. Commun.*, 1984, 998.
9 N. Tanaka, Y. Kobayasi, and S. Takamoto, *Chem. Lett.*, 1977, 107; K. Wieghardt, J. Tolksdorf, and W. Hermann, *Inorg. Chem.*, 1985, **24**, 1230.
10 R. Schneider, A. Riesen, and Th. A. Kaden, *Helv. Chim. Acta*, 1986, **69**, 53.
11 L. Fabbrizzi, F. Forlani, A. Perotti, and B. Seghi, *Inorg. Chem.*, 1984, **23**, 807.
12 L. Fabbrizzi, L. Montagna, A. Poggi, Th. A. Kaden, and L. Siegfried, *Inorg. Chem.*, 1986, **25**, 2671.
13 J. Löliger and R. Scheffold, *J. Chem. Educ.*, 1972, **49**, 646.
14 L. Ciavatta, *Ann. Chim. (Rome)*, 1980, 551.
15 D. K. Cabbiness and D. W. Margerum, *J. Am. Chem. Soc.*, 1969, **91**, 6540.
16 D. K. Cabbiness and D. W. Margerum, *J. Am. Chem. Soc.*, 1970, **92**, 2151.
17 A. Bencini, L. Fabbrizzi, and A. Poggi, *Inorg. Chem.*, 1981, **20**, 2544.
18 A. Sabatini and L. Fabbrizzi, *Inorg. Chem.*, 1979, **18**, 438; L. Fabbrizzi, *J. Chem. Soc., Dalton Trans.*, 1979, 1857.

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