Synthesis and Properties of a New Series of Bis(macrocyclic) Dicopper(II,II), Dinickel(II,II) and Dinickel(III,III) Complexes based on the 14-Membered Pentaaza Unit

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Template condensation of [M(danda)]$^{2+}$ (M = Ni or Cu; danda = 3,7-diazanonane-1,9-diamine) with formaldehyde and aliphatic diamines $H_2N(CH_2)_nNH_2$ (n = 2–5) results in new types of dinickel and dicopper bis(macrocyclic) complexes [M_2L^x]$^{4+}$ ($x = n$) in which two 1,4,6,8,11-pentaazacyclotetradecane subunits ([ML^1]$^{2+}$) are linked by polymethylene chains of various lengths through the unco-ordinated N^6 bridgehead atoms. The complexes synthesized were characterized by means of spectral (UV/VIS, IR and ESR) and electrochemical (cyclic voltammetry) techniques. The close similarity in properties of the bis(macrocyclic) dinickel(II), dicopper(II) and dinickel(III) complexes [M_2L^x]$^{m+}$ (m = 4 or 6) in comparison to their monocyclic analogues [ML^1]$^{m+}$ (m = 2 or 3) indicates the lack of interaction between the metal centres in the ditopic molecules. The only exception is [Cu_2L^2]$^{4+}$ having the shortest dimethylene connecting chain, for which effects caused by the electrostatic influence of the neighbouring metal ion were observed in the ESR spectrum and cyclic voltammograms. A study of equilibria between the low-spin square-planar and high-spin six-co-ordinated forms of the dinickel(II) complexes in neutral aqueous and acidic sulfate solutions revealed some peculiarities which may be related to the conformational properties of the ditopic compounds.

The creation of molecules containing several spatially separated reactive sites (in the simplest case ditopic compounds with two such centres) is one of the most promising and actively developing areas of chemistry today. Employment of principles of molecular design gives the possibility to adjust the electronic properties and relative position of these sites in the molecule which allows control of the selectivity of its interaction with different substrates depending on their structures.

Transition-metal ions in polyazamacrocyclic surroundings are very suitable for use as such reactive centres due to the high thermodynamic stability and kinetic inertness inherent in macrocyclic complexes and the ability to change easily the oxidation states of metal ions.[1,2] In addition, these compounds, at least in the case of tetradentate macrocycles, are co-ordinatively unsaturated and possess two positions in the co-ordination sphere of the metal ion accessible for binding of additional ligands (*i.e.* substrates).[2]

Synthetic approaches to the preparation of monomacrocyclic compounds have been thoroughly developed,[3] but relatively little work concerning the syntheses and characterization of bis(azamacrocyclic) complexes has been reported. Most of these studies deal with complexes containing two monomacrocyclic subunits connected by polymethylene or xylylene chains while the bridgehead nitrogen atoms are co-ordinated to the metal ions.[4,5] Another type of ditopic complexes are the macrocyclic compounds derived from bis(malonic acid esters) in which a direct C–C bond between the macrocycles is present.[6,7] Some other bis(macrocyclic) complexes were also described.[8]

The main problem in the preparation of most ditopic compounds is the necessity to carry out a multi-step synthesis with relatively small yields from some stages. In addition, the presence of tertiary bridgehead nitrogen atoms in the macrocycle leads to destabilization of high oxidation states of metal ions.[9] The complexes of malonic acid ester derived compounds do not possess this peculiarity, but the synthetic method available does not permit variation of the nature of the bridging chain between two macrocycles.

In the present paper a one-pot synthesis of new ditopic nickel and copper complexes and a detailed study of their spectral and electrochemical properties in comparison with monocyclic pentaaza and tetraaza analogues are reported. Preliminary results of our studies on dinickel[10a] and dicopper[10b] compounds have been communicated previously.

Results and Discussion

Synthesis and Identification of Ditopic Complexes.—Template condensation of co-ordinated primary polyamines, particularly en,† with formaldehyde and ammonia is widely used in the chemistry of macrocyclic compounds. Depending on the nature of the metal ions, the structure of the reagents, and their ratios, such reactions result in macrobicyclic (sepulchrate),[11] mono-macrocyclic[12] or non-macrocyclic[12a,13] condensation products. However, the replacement of ammonia by primary alkylamines (*e.g.* methylamine) leads to the formation of monomacrocyclic complexes 1 as the only product irrespective of whether nickel(II) or copper(II) ions act as template.[14]

The latter reaction, in our opinion, pointed the way to the elaboration of a simple and convenient method for preparation

1   2   3
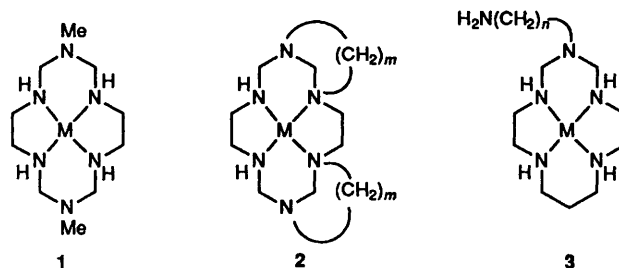
† Abbreviations used: en = ethane-1,2-diamine; daoda = 3,6-diaza-octane-1,8-diamine; danda = 3,7-diazanonane-1,9-diamine; dadda = 4,7-diazadecane-1,10-diamine; cyclam = 1,4,8,11-tetraazacyclotetra-decane; L^1 = 6-methyl-1,4,6,8,11-pentaazacyclotetradecane; L^x = 1,n-bis(1,4,6,8,11-pentaazacyclotetradecan-6-yl)-ethane (n = 2, L^2), -propane (n = 3, L^3), -butane (n = 4, L^4) and -pentane (n = 5, L^5).

Scheme 1

Scheme 2 $n = 2-5, x = n, M = Ni^{2+}$ or Cu^{2+}
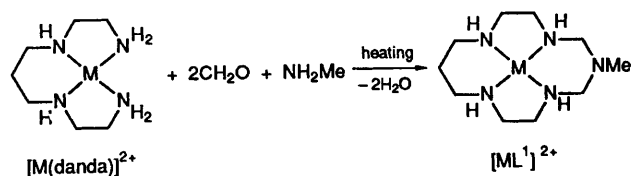
of bis(macrocyclic) structures. Two main problems needed to be solved in this connection. First, to prevent the formation of undesirable products, complexes containing only two reactive primary amino groups, namely $[M(danda)]^{2+}$ instead of $[M(en)_2]^{2+}$, must be used as a starting template. Preliminary study showed that the interaction of these complexes with formaldehyde and methylamine results in $[ML^1]^{2+}$ both for nickel(II) and copper(II) compounds (Scheme 1).[10,15] Secondly, it seemed very attractive to use in this reaction reagents which would exhibit a double function, simultaneously participating both in cyclization and formation of a bridge between macrocyclic subunits.

On this reasoning we supposed that interaction of stoichiometric quantities of $[M(danda)]^{2+}$, CH_2O and aliphatic α,ω-diamines could proceed according to Scheme 2 to give the desired ditopic products. Indeed, such reactions in water–methanol solutions have led to the formation of yellow (nickel) or purple (copper) compounds the analytical data (Table 1) and spectral characteristics (see below) of which are in accordance with a bis(macrocyclic) structure.

Surprisingly, it was recently reported that the employment of both nickel(II) and copper(II) complexes with daoda or dadda in the reaction with en and CH_2O at the same ratio of reagents as used by us results in the hexaaza monomacrocyclic compounds 2 ($m = 2$ or 3),[12c] not in bis(macrocyclic) complexes of type $[M_2L^2]^{4+}$. The reason for this, in our opinion, lies in the different co-ordination modes of the tetraamines used. Thus danda occupies the equatorial plane in the co-ordination sphere of metal ions, two *trans*-axial positions being vacant. Such co-ordination prevents bidentate binding of the diamine added and leads to a process in which each amino group of the diamine undergoes condensation in the co-ordination sphere of *different* metal ions. The ligands daoda and dadda are inclined to formation of polynuclear compounds or mononuclear ones with two vacant *cis* positions in the co-ordination polyhedron.[2] In this case the *intramolecular* cyclization reaction prevails, resulting in type 2 compounds. It is also possible that co-ordination of the diamine to the metal ion prior to the condensation reaction, even in a monodentate manner, is not necessary. This assumption follows from our data indicating that the reactions in Schemes 1 and 2 proceed successfully for square-planar nickel and copper complexes with various open-chain diamidodiamines which have a very weak tendency to axial co-ordination.[16]

The bis(macrocyclic) complexes $[M_2L^x][ClO_4]_4$ are moderately soluble (*ca.* 10^{-3} mol dm^{-3}) in water, acetonitrile, dimethyl sulfoxide (dmso), dimethylformamide (dmf), and, to a lesser extent, nitromethane. The conductivity of their *ca.* 10^{-3} mol dm^{-3} aqueous solutions (Λ_M *ca.* 400 Ω^{-1} cm^2 mol^{-1}) is typical for 1:4 electrolytes. In contrast to the starting $[M(danda)]^{2+}$ the dissociation of which in mild acidic solutions is very fast, the complexes under consideration are much more stable. This fact confirms their macrocyclic structure since such behaviour is characteristic of tetraazamacrocyclic complexes.[17] In strong acids, however, a slow destruction of the bis(macrocyclic) complexes is observed (the half-life $t_{\frac{1}{2}}$ in 0.1 mol dm^{-3} HClO$_4$ is *ca.* 30 h). This seems to be caused by acid hydrolysis of NCH$_2$N bonds in the macrocyclic backbone. Similar effects have been observed for the type 1 complexes.[14]

Infrared spectra of all the ditopic compounds are very similar to each other and to the spectrum of $[NiL^1]^{2+}$. The lack of
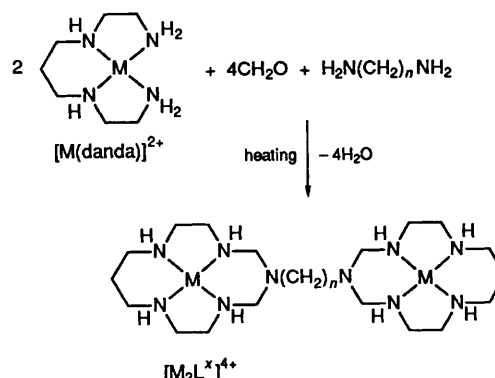
Table 1 Analytical and IR spectral data for the new complexes

Complex	Analysis[a] (%)			$\tilde{\nu}(NH)$[b]/cm^{-1}
	C	H	N	
$[Ni_2L^2][ClO_4]_4$[c]	25.6	5.0	14.9	3215m, 3160w
	(25.4)	(5.1)	(14.8)	
$[Ni_2L^3][ClO_4]_4$	26.3	5.1	14.4	3220w, 3175m
	(26.3)	(5.2)	(14.6)	
$[Ni_2L^4][ClO_4]_4$	27.3	5.2	14.2	3213m, 3170w
	(27.2)	(5.35)	(14.4)	
$[Ni_2L^5][ClO_4]_4$	27.8	5.5	13.8	3216w, 3155m
	(28.0)	(5.5)	(14.2)	
$[Cu_2L^2][ClO_4]_4$	24.4	5.2	14.5	3230w, 3187m
	(25.2)	(5.0)	(14.7)	
$[Cu_2L^3][ClO_4]_4$	26.3	5.4	14.3	3250w, 3200m
	(26.1)	(5.2)	(14.5)	
$[Cu_2L^4][ClO_4]_4$	27.1	5.3	13.8	3252w, 3195m
	(26.9)	(5.3)	(14.3)	
$[Cu_2L^5][ClO_4]_4$	28.0	5.5	13.7	3250w, 3193m
	(27.7)	(5.4)	(14.1)	

[a] Required values are given in parentheses. [b] In KBr discs. [c] Ni 12.2 (12.5)%.

bands typical of primary amino groups in $[M(danda)]^{2+}$ [$\nu_{asym}(NH_2)$ and $\nu_{sym}(NH_2)$ in the region 3400–3200 cm^{-1}, and $\delta(NH_2)$ at 1600 cm^{-1}] and the appearance in the spectra of bis(macrocyclic) compounds of bands attributable to stretching vibration of co-ordinated secondary amino groups (Table 1) is consistent with the structure suggested. It is interesting that for the nickel complexes an alternation of relative intensities of these bands is observed depending on the number of carbon atoms in the connecting bridge (odd or even). Among other changes caused by macrocyclization the appearance of one broad band at *ca.* 1290 cm^{-1} instead of two bands of moderate intensity at 1330 and 1300 cm^{-1} in the spectrum of $[NiL^1][ClO_4]_2$ and the presence of a specific doublet of bands in the region 930–900 cm^{-1} is to be mentioned.

The absence in the IR spectra of bands attributable to vibration of primary amino groups permits us to discard from consideration compounds of type 3. This conclusion is also confirmed by the unchanging visible spectra of nickel complexes at 2 < pH < 12 in perchlorate-containing solution, opposite to what would be expected if a pendant amino group is present in the macrocycle.[18]

Fast atom bombardment (FAB) mass spectroscopy has proven useful in establishing the ditopic formulation of the new compounds. Reasonable spectra were obtained despite the highly involatile nature of the tetrapositive cationic species. The spectra of $[Ni_2L^2][ClO_4]_4$ and $[Cu_2L^3][ClO_4]_4$ obtained in a matrix of neat glycerine with argon as a fast atom beam do not establish the presence of the molecular ions (M^+).

Table 2 Spectral data for the copper(II) complexes

	Absorption bands, $10^{-3}\tilde{v}/cm^{-1}$ ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$)[a]			ESR parameters[b]		
Complex	MeNO$_2$	MeCN	Water	$g_{\parallel}$	$g_{\perp}$	$10^4 A_{\parallel}^{Cu}/cm^{-1}$
[Cu(cyclam)]$^{2+}$	20.4 (80)	19.9 (79)	19.5 (70) 41.3 (6800)	2.194[c]	2.052[c]	206[c]
[CuL^1]$^{2+}$	20.4 (78)	20.4 (55)	19.8 (75) 40.1 (6800)	2.195	2.043	205
[Cu$_2$L^2]$^{4+}$	20.3 (76)	20.0 (70)	19.8 (79) 39.8 (8100)	2.185	2.048	108
[Cu$_2$L^3]$^{4+}$	20.5 (80)	20.0 (63)	19.8 (76) 39.7 (7000)	2.187	2.052	201
[Cu$_2$L^4]$^{4+}$	20.0 (82)	20.0 (66)	19.8 (69) 39.8 (7400)	2.195	2.046	200
[Cu$_2$L^5]$^{4+}$	20.4 (84)	19.8 (72)	19.8 (74) 40.0 (6500)	d		

[a] Values of ε for ditopic complexes were calculated per metal ion. [b] Frozen methanol–water (20:1 v/v) solution, 150 K, $g \pm 0.002$, $A_{\parallel}^{Cu} \pm 10 \times 10^{-4}$ cm^{-1}. [c] Frozen dmso solution. Data taken from ref. 20. [d] Not determined.

Three groups of peaks in each case were formulated as [M − 3ClO$_4$ − 2H]$^+$ (m/z of main peak in group 643), [M − 2ClO$_4$ − 2H]$^+$ (742), [M − ClO$_4$]$^+$ (843) for the dinickel and [M − 3ClO$_4$ − 2H]$^+$ (667), [M − 2ClO$_4$ − 2H]$^+$ (766), and [M − ClO$_4$]$^+$ (867) for the dicopper complexes, respectively. These fragments are consistent with the loss of perchlorate groups from the molecular ions, the remaining perchlorates being involved in intramolecular multiple hydrogen bonding, an interaction that might facilitate their vaporization. The same effect was indicated in the FAB mass spectra of [CuL^1][ClO$_4$]$_2$ ([M − 2ClO$_4$ − H]$^+$, m/z = 277; [M − 2ClO$_4$ − H + 2H$_2$O]$^+$, 313; [M − ClO$_4$]$^+$, 377; [M − ClO$_4$ − H + 2H$_2$O]$^+$, 412) and of a ditopic nickel complex containing tetraazamacrocyclic and crown ether fragments.[19]

Absorption and ESR Spectra of Bis(macrocyclic) Complexes of Nickel(II) and Copper(II).—Spectral characteristics of ditopic complexes of copper(II) and nickel(II) in comparison with their 14-membered monocyclic analogues are listed in Tables 2 and 3. The main peculiarity of the data presented is the similarity of the spectral parameters for mono- and bis-(macrocyclic) compounds. This fact unambiguously indicates the structural closeness of the co-ordination polyhedrons in all compounds with the macrocycles occupying the equatorial plane of the co-ordination spheres of the metal ions.[1,2]

In general, the spectra of the compounds studied are typical of tetragonal tetraamine nickel and copper complexes with a low-energy band attributable to d–d transition and a UV band caused by charge-transfer from co-ordinated nitrogen atoms to the metal ions.[2] The replacement of non-co-ordinating nitromethane by acetonitrile or water as solvent results in the conversion of the complexes from square-planar into square-(bi)pyramidal forms. For the copper compounds this process is manifested as a bathochromic shift of the d–d maximum. A similar effect was also found upon the addition of aliphatic amines to nitromethane solutions of [Cu$_2$L^x]$^{4+}$.[10b,21] For the nickel complexes, axial co-ordination of additional ligands, *i.e.* solvent molecules, is accompanied by a decrease in the effective molar absorption coefficient of the band near 22 000 cm^{-1} attributable to the square-planar species since the absorbance of the six-co-ordinated form in this region is an order of magnitude lower[1,2,22] [for example, in acetonitrile in which the content of the six-co-ordinated form is the greatest among the solvents studied, additional bands with low intensities ($\varepsilon < 10$ dm^3 mol^{-1} cm^{-1}) appear at 15 000 and <11 000 cm^{-1}].

The ESR spectra of the copper compounds (Table 2) confirm the tetragonal structure of the d^9 electron configuration with the unpaired electron occupying a d$_{x^2-y^2}$ orbital ($g_{\parallel} > g_{\perp}$),

Table 3 Absorption spectra for the nickel(II) complexes ($10^{-3}\tilde{v}/cm^{-1}$, $\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ in parentheses)[a]

Complex	MeNO$_2$	Water[b]		MeCN
[Ni(cyclam)]$^{2+}$	22.0 (62)	22.2 (48)	46.0 (12 000)	21.8 (18)
[NiL^1]$^{2+}$	22.1 (60)	22.3 (50)	48.0 (11 000)	21.7 (21)
[Ni$_2$L^2]$^{4+}$	22.2 (62)	22.3 (62)	48.2 (11 500)	21.6 (27)
[Ni$_2$L^3]$^{4+}$	22.1 (61)	22.3 (63)	46.0 (11 800)	21.7 (20)
[Ni$_2$L^4]$^{4+}$	22.1 (61)	22.4 (64)	47.0 (12 000)	21.6 (20)
[Ni$_2$L^5]$^{4+}$	22.0 (61)	22.3 (59)	46.0 (11 000)	21.8 (24)

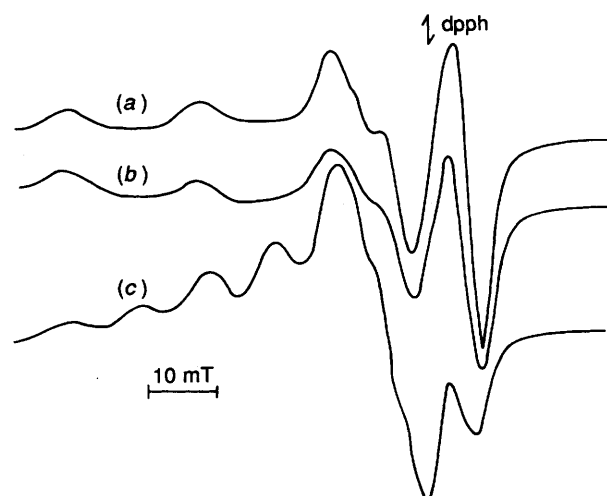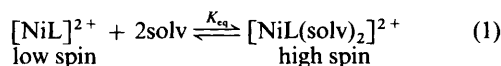[a] See footnote a of Table 2. [b] 0.1 mol dm^{-3} NaClO$_4$, pH $\approx$ 5, 298 K.

Fig. 1 The ESR spectra of frozen (150 K) methanol–water (20:1, v/v) solutions of the copper(II) complexes [CuL^1]$^{2+}$ (a), [Cu$_2$L^4]$^{4+}$ (b) and [Cu$_2$L^2]$^{4+}$ (c); dpph = diphenylpicrylhydrazyl

and show the absence of intramolecular interaction between the copper ions for all the complexes except [Cu$_2$L^2]$^{4+}$ which is characterized by the shortest bridge linking the macrocyclic subunits (Fig. 1). The hyperfine coupling constant $A_{\parallel}^{Cu}$ for this complex is about half that of other compounds indicating the presence of a metal–metal interaction. In such a case two septets shifted with respect to each other by the zero-field splitting parameter $2D_{\parallel}$ are expected. As it is difficult to observe all the possible lines, we have assumed that in the spectrum of [Cu$_2$L^2]$^{4+}$ the two septets are displaced by $A_{\parallel}^{Cu}$, so $D_{\parallel}$ is *ca.*

54×10^{-4} cm^{-1}. With this assumption the $g_{\parallel}$ values for all the complexes are very consistent, as expected from the similarity in their geometries. From the value of $D_{\parallel}$ one can calculate the mean distance between the paramagnetic centres using the equation $D_{\parallel} = 0.65g_{\parallel}^{2}R^{-3}$. This gives $R_{Cu-Cu} \approx 8.3$ Å, comparable to the metal–metal distances in other bis(macrocyclic) complexes with ethylene bridges.[4c,d] This would also indicate that the binuclear complexes in solution adopt a conformation in which the positively charged metal ions tend to be as far apart as possible.

The lack of coupling between the copper nuclei in $[Cu_2L^x]^{4+}$ $(x > 2)$ is not unexpected having regard to the large interionic distances in these compounds. However, it is noteworthy that the copper–copper interaction was manifested in the ESR spectra of ditopic compounds containing not only ethylene-[4a-c,23] but also longer tetramethylene-[4b,5a] and p-CH$_2$C$_6$H$_4$CH$_2$-[4c] bridged bis(macrocycles). If one accepts the superexchange mechanism through the CuN(CH$_2$)$_4$NCu chain proposed as the explanation of such interaction,[5a] its absence in our systems may be due to the fact that the bridgehead nitrogen atoms in this case are not co-ordinated to the metal ions.

Spin Equilibria in Bis(macrocyclic) Nickel(II) Complexes.—As mentioned above, low-spin square-planar tetraamine nickel(II) complexes are prone to transform in solutions into six-co-ordinated high-spin species with much lower absorption coefficients [equation (1), solv = solvent] and this phenomenon

$$[NiL]^{2+} + 2\text{solv} \underset{}{\overset{K_{eq}}{\rightleftharpoons}} [NiL(solv)_2]^{2+} \quad (1)$$
$$\text{low spin} \qquad\qquad\quad \text{high spin}$$

is well documented.[2,24] Assuming that the ε value of the band at *ca.* 22 000 cm^{-1} in non-co-ordinating nitromethane corresponds to 100% content of the low-spin form and is independent of the nature of the solvent,[4a,15] one can calculate the thermodynamic parameters of this process. Our data show that for all bis(macrocyclic) complexes the thermodynamic parameters for equilibrium (1) in aqueous solutions containing 0.1 mol dm^{-3} NaClO$_4$ or NaNO$_3$ are very close to each other (K_{eq} *ca.* 0.2 ± 0.1, ΔH *ca.* −20 ± 5 kJ mol^{-1}, ΔS *ca.* −80 ± 10 J K^{-1} mol^{-1} calculated per nickel ion*).

The enthalpic and entropic contributions to equilibrium (1) for the bis(macrocyclic) complexes are more closely related to those of $[Ni(cyclam)]^{2+}$ ($\Delta H = -23$ kJ mol^{-1}, $\Delta S = -84$ J K^{-1} mol^{-1})[24] than to those of their structural analogue $[NiL^1]^{2+}$ ($\Delta H = -39$ kJ mol^{-1}, $\Delta S = -144$ J K^{-1} mol^{-1}).[15] For the latter, as also for the type 1 nickel(II) complex,[14a] the shift of ΔH and ΔS to more negative values may be interpreted as being induced by the binding of three water molecules in the high-spin form instead of two in $[Ni(cyclam)(H_2O)_2]^{2+}$. The structure $[NiL^1(H_2O)_2 \cdot H_2O]^{2+}$ for such high-spin species has been proposed[15] in which the third solvent molecule is bound by hydrogen bonds to the axially co-ordinated water molecule and a lone electron pair of unco-ordinated nitrogen. It is interesting that the replacement of the N-methyl groups in 1 by N-ethyl substituents makes this compound resemble cyclam ($\Delta H = -19$ kJ mol^{-1}, $\Delta S = -75$ J K^{-1} mol^{-1}).[14a]

Another feature of our systems is the lack of a dependence of the K_{eq} values on the length of the connecting chain. For bis(macrocyclic) complexes linked through co-ordinated bridgehead nitrogen atoms this parameter was reported to decrease regularly from 3.4 (dimethylene) to 0.74 (pentamethylene bridge).[5c]

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* For the bis(macrocyclic) complexes equilibrium (1) should be written in the form $[NiNiL]^{4+} + 4H_2O \rightleftharpoons [NiNi(H_2O)_2L]^{4+} + 2H_2O \rightleftharpoons [Ni(H_2O)_2Ni(H_2O)_2L]^{4+}$. However, we have assumed that the conversion of each nickel ion from the low- into the high-spin form proceeds independently of the neighbouring ion, and the equilibrium constants were calculated as $K_{eq} = [\text{high-spin Ni}^{II}]_{total}/[\text{low-spin Ni}^{II}]_{total}$.

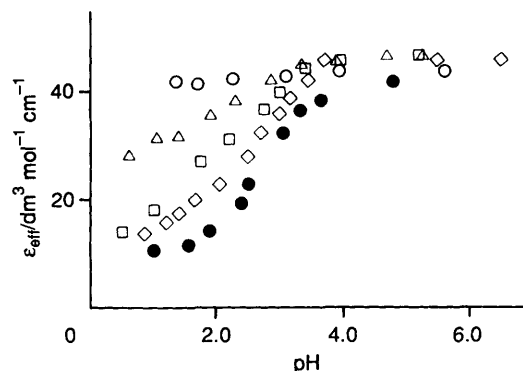**Fig. 2** Plot of ε_{eff} *versus* pH for the macrocyclic nickel(II) complexes in 0.2 mol dm^{-3} (H + Na)$_2$SO$_4$ ($I = 0.6$ mol dm^{-3}, $T = 295$ K): $[NiL^1]^{2+}$ (●), $[Ni_2L^2]^{4+}$ (○), $[Ni_2L^3]^{4+}$ (△), $[Ni_2L^4]^{4+}$ (□) and $[Ni_2L^5]^{4+}$ (◇)

We have shown earlier[15] that $[NiL^1]^{2+}$ transforms from a predominantly low- to a high-spin form at constant sulfate concentration upon changing the pH from *ca.* 3.5 to *ca.* 1.5. This effect was explained by a specific two-centre interaction of hydrogensulfate by co-ordination to nickel(II) and hydrogen bonding with an unco-ordinated nitrogen atom. For [Ni(cyclam)]$^{2+}$, as well as for other tetraazamacrocyclic complexes, such an effect has never been observed. From this point of view it was of interest to study the behaviour of the ditopic complexes in an acidic sulfate medium. For the bis(macrocyclic) compounds the conversion from the low- to the high-spin form and thus the effectiveness of the interaction with hydrogensulfate depends on the bridge length: the shorter the connecting chain, the greater is the content of the low-spin form of the complex in solution at the same pH, and the complex $[Ni_2L^2]^{4+}$ is practically insensitive to pH variations (Fig. 2).

An interpretation of the properties of the bis(macrocyclic) complexes in aqueous neutral and acidic sulfate solutions would require more detailed investigation. At this stage, reasons for the specific behaviour of the ditopic compounds as compared to their monomacrocyclic analogue $[NiL^1]^{2+}$ may be the differences in both their hydrophobicities and conformational characteristics. Possibly, the substitution of the methyl group at the unco-ordinated nitrogen atom in $[NiL^1]^{2+}$ by the polymethylene chain in $[Ni_2L^x]^{4+}$ changes or distorts the conformation of the six-membered chelate ring thus altering the spatial orientation of a lone electron pair of this atom, and also makes the ditopic molecules more hydrophobic on the whole. In addition, one can suppose that the presence in the bis(macrocyclic) structures of two positively charged ions in close proximity can alter the local properties of the medium, in particular the microscopic permittivity,[4d] thus affecting the solvation of the complexes and their interaction with anions.

Redox Behaviour of Ditopic Compounds and Spectral Properties of Dinickel(III) Complexes.—The study of metal(II)–metal(III) oxidation by means of cyclic voltammetry (CV) has shown that for the dicopper complexes these processes are irreversible in acetonitrile and water and such behaviour is in a good agreement with a low kinetic stability of the copper(III) ion in an equatorial tetraamine environment.[17,25] The voltammograms recorded show only one anodic peak whose potential (E_{pa}) for the bis(macrocyclic) systems is very close to that of the mononuclear complex. For $[Cu_2L^x]^{4+}$ $(x > 2)$ $E_{pa} = 1.51$ (acetonitrile, 0.02 mol dm^{-3} NBu$^n_4$ClO$_4$) and 1.07 V (water, 0.1 mol dm^{-3} NaClO$_4$), *cf.* 1.50 and 1.06 V for $[CuL^1]^{2+}$. The only exception is the ditopic complex $[Cu_2L^2]^{4+}$ which is characterized by two well defined anodic waves at 1.45 and 1.54 V in acetonitrile and at 1.00 and 1.07 V in aqueous solution. This difference, as in the case of the ESR spectra, seems to have an electrostatic basis.

Electrochemical oxidation of the nickel complexes has been

Table 4 Redox potentials $E_{\frac{1}{2}}/V$ vs. SCE for $Ni^{III}L$–$Ni^{II}L$ couples in macrocyclic complexes[a]

	Water		
Redox couple	0.5 mol dm^{-3} Na$_2$SO$_4$ (pH 3)	0.1 mol dm^{-3} NaClO$_4$ (pH 3)	MeCN
[Ni(cyclam)]$^{3+/2+}$	0.49 (70)	0.73 (70)	0.99 (75)
[NiL^1]$^{3+/2+}$	0.54 (70)	0.82 (80)	1.00 (60)
[Ni$_2$L^2]$^{6+/4+}$	0.51 (100)	0.80 (100)	1.01 (70)
[Ni$_2$L^3]$^{6+/4+}$	0.50 (100)	0.79 (100)	0.99 (65)
[Ni$_2$L^4]$^{6+/4+}$	0.51 (100)	b	0.99 (65)
[Ni$_2$L^5]$^{6+/4+}$	0.51 (130)^c	b	1.00 (65)

[a] Peak-to-peak separation ΔE/mV given in parentheses. [b] Complex is poorly soluble under these conditions. [c] 0.2 mol dm^{-3} Na$_2$SO$_4$.

found to be quasi-reversible with i_{pa}/i_{pc} ca. 1 and peak-to-peak separations (ΔE) depending on the solvent and, for aqueous solutions, on the pH and electrolyte added (Table 4). We did not observe separate oxidations of the metal centres in CV experiments. Similar observations were made earlier for other types of bis(macrocyclic) complexes, although the use of differential pulse voltammetry instead of CV revealed two redox transitions, at least for spiro-bis(macrocyclic) compounds[8a] and complexes with the shortest dimethylene bridge.[4c,d,5b]

As can be seen from Table 4, the presence of sulfate ions in aqueous solutions results in essential thermodynamic stabilization of the nickel(III) oxidation state. This is related to the co-ordination of sulfate to nickel(III) instead of water molecules or perchlorate anions in perchlorate-containing solutions.[26] The measure of this stabilization effect, $\delta E = E_{\frac{1}{2}}^{ClO_4} - E_{\frac{1}{2}}^{SO_4}$, reflects the stability constants of nickel(III)–sulfate complexes and it follows from the data obtained that the effectiveness of such interaction is practically the same for ditopic complexes and [NiL^1]$^{3+}$, but exceeds that of [Ni(cyclam)]$^{3+}$.

The relatively high kinetic stability of tetraazamacrocyclic nickel(III) compounds provides the possibility of preparing and characterizing authentic nickel(III) species both in the solid state and in solutions.[27] Nickel(III) bis(macrocyclic) complexes are readily produced in acidic aqueous or acetonitrile solutions by electrochemical or chemical ($S_2O_8^{2-}$, BrO_3^-, Ce^{IV}, H_2O_2 or $NOClO_4$) oxidation of the parent nickel(II) compounds. Their kinetic stability ($t_{\frac{1}{2}}$ for all the [Ni$_2$L^x]$^{6+}$ complexes in 0.1 mol dm^{-3} H_2SO_4 is ca. 130 h) resembles that of the cyclam complex which is one of the most stable nickel(III) macrocyclic compounds.[26,28] More positive values of the $Ni^{III}L$–$Ni^{II}L$ redox potentials in the absence of stabilizing sulfate anions are reflected in the lower kinetic stability of the ditopic nickel(III) compounds in perchloric acid solution (e.g. $t_{\frac{1}{2}} = 3.4$ h for [Ni$_2$L^2]$^{6+}$ and 1.2 h for [Ni$_2$L^3]$^{6+}$ in 0.1 mol dm^{-3} HClO$_4$).

Oxidation of the dinickel(II) complexes leads to six-co-ordinated low-spin nickel(III) compounds whose spectral characteristics in 0.1 mol dm^{-3} H_2SO_4 [$10^{-3}\tilde{v}$/cm^{-1} (ε/dm^3 mol^{-1} cm^{-1}): ca. 15.0 (sh) (100), ca. 28.0 (sh), 34.0 (11 500 $\pm$ 500)] and 0.1 mol dm^{-3} HClO$_4$ [18.0 (150), ca. 28.0 (sh), 33.0 (11 000 $\pm$ 500)] are very similar and to those of [Ni(cyclam)]$^{3+}$ (refs. 27 and 28) and [NiL^1]$^{3+}$.[15] Their ESR spectra in frozen aqueous solutions containing 0.1 mol dm^{-3} HClO$_4$ and 0.5 mol dm^{-3} NaClO$_4$ are nearly the same as those in sulfate solutions (0.15 mol dm^{-3} H_2SO_4 and 0.13 mol dm^{-3} Na$_2$SO$_4$) and, in general, the values of $g_{\parallel} = 2.028 \pm 0.001$ and $g_{\perp} = 2.231 \pm 0.002$ are typical of a low-spin d^7 electronic configuration in a tetragonal field with an unpaired electron localized on the d_{z^2} orbital ($g_{\parallel} < g_{\perp}$).[27] The similarity of the spectral parameters for bis- and mono-macrocyclic compounds both in sulfate and perchlorate solutions demonstrates the close relationship between the structures of the nickel(III) co-ordination polyhedrons (trans-N$_4$O$_2$) for all the complexes

studied. Noteworthy is the fact that we have observed no peculiarity which would indicate the presence of a nickel(III)–nickel(III) interaction in the ditopic compounds, neither in absorption spectra nor in ESR parameters.

Conclusion

The results obtained point the way to a convenient preparation of various di- and poly-topic transition-metal complexes. Our preliminary data show that these reactions should be limited neither by the structure of the aliphatic diamines used as bridging linkages nor the type of equatorially co-ordinated tetradentate diamine in the complexes acting as template. Apparently, such bis(macrocyclization) processes may be realized for complexes of other metal ions (e.g. Co^{3+} and Zn^{2+}). This makes possible the synthesis of molecules with variable spatial preorganization containing metal centres having different electronic structures. Such compounds represent ideal subjects for investigation of different aspects of substrate–receptor interaction. Thus, our data show that the geometric structure of ditopic compounds (in particular, the length of the polymethylene bridges between the macrocyclic subunits) substantially influences the thermodynamic parameters of interaction of diamines with copper complexes and the kinetic features of nickel(II) oxidation by two-electron oxidants (hydrogen peroxide or peroxodisulfate). These results as well as the synthesis and properties of heterobinuclear nickel–copper ditopic complexes will be published elsewhere.

Experimental

The general procedures and apparatus used were as in other recent publications from this laboratory.[15,28,29]

Cyclic voltammograms were obtained with a Gomel PI-50-1.1 potentiostat-galvanostat and N-307-X-Y recorder. A three-electrode system consisting of a platinum or glassy carbon working electrode, a commercial saturated calomel reference electrode (SCE), and platinum auxiliary electrode was used. All cyclic voltammograms were performed in acetonitrile containing 2×10^{-2} mol dm^{-3} NBu$^n_4$ClO$_4$ or in water (concentrations of supporting electrolytes are given in the text). The sweep rate was varied in the range 20–500 mV s^{-1}. The results obtained show little dependence on both the nature of the working electrode used and sweep rate applied. All potentials (vs. SCE) cited were obtained at a scan rate of 50 mV s^{-1}. Coulometric investigation of the oxidation of bis(macrocyclic) nickel(II) complexes was not performed but literature data[4d,5c] and the ratios i_p[bis(macrocyclic)]/i_p(monomacrocyclic) ca. 2 at equal concentrations of the compounds under study allow us to conclude that oxidation of the ditopic complexes proceeds via two one-electron steps at very close or identical potentials.

Preparation of Compounds.—**CAUTION**: Some of the compounds containing perchlorate anions must be regarded as potentially explosive and should be handled with care.

The nickel(II) and copper(II) complexes with danda, cyclam and L^1 were prepared according to the literature.[3,15]

General method for ditopic complexes. A sample of [M(danda)][ClO$_4$]$_2$ (M = Ni or Cu) (4.8 mmol) was dissolved by heating in a mixture of water (4 cm^3) and methanol (20 cm^3). To this solution the corresponding diamine (2.4 mmol) in methanol (3 cm^3) and formaldehyde (40%, 1 cm^3) in methanol (3 cm^3) were simultaneously added dropwise under reflux. The mixture was refluxed for 3 d, during which time a solid was gradually formed on the walls of the flask. After cooling in a refrigerator the precipitate which formed was filtered off, then recrystallized from hot water (15 cm^3) (undissolved impurity was filtered off). To the cooled filtrate, NaClO$_4$ (0.5 g) was added, the solution was acidified with HClO$_4$ to pH ca. 2 and left overnight in a refrigerator. The solid ditopic complex was

filtered off, recrystallized from hot water and dried in a vacuum desiccator over P_4O_{10}. The method of preparation was not optimized and the yields of products varied in the range 10–25% depending on the loading, but our observations show that deviation from the stoichiometric ratio of the reactants leads to a sharp decrease in yields.

Acknowledgements

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