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Potentiometric and spectroscopic study of copper(II) and nickel(II) complexes of *trans*-dioxopentaaza macrocycles in aqueous solution

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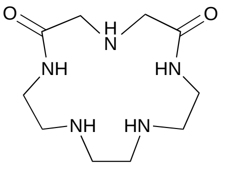
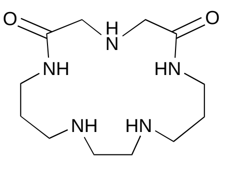
The *trans*-dioxopentaaza macrocycles 2,6-dioxo-1,4,7,10,13-pentaazacyclopentadecane (L^1) and 2,6-dioxo-1,4,7,11,14-pentaazacycloheptadecane (L^2) have been prepared. Their protonation and metal-binding properties with Cu^{2+} and Ni^{2+} have been investigated in 0.10 mol dm^{-3} KNO_3 (aq) at 25.0 °C by potentiometric pH-metry, calorimetry (in part), electronic absorption and IR spectroscopy. Metal-ion complexation promotes the deprotonation and the co-ordination of the amide nitrogens, resulting in neutral complexes with four nitrogen donors and a MLH_{-2} stoichiometry at pH 8. Additional complexes with stoichiometry MHL, ML and MLH_{-1} complete the complexation set. The overall stability constants of the complexes were calculated. The electronic spectra support a tetragonal co-ordination of Cu^{2+} and a square-planar co-ordination of Ni^{2+} in the MLH_{-2} complexes leaving one amino group unco-ordinated. It is suggested that the planar trigonal nature of the co-ordinated amido nitrogens in *trans* position to each other in the equatorial plane around Ni^{2+} or Cu^{2+} structurally prevents the fifth nitrogen donor from binding at an axial site. The NiL^2H_{-2} complex exhibits a yellow-to-blue conversion equilibrium.

The aqueous co-ordination chemistry of cyclic dioxopolyamines has been the subject of many investigations during the last fifteen years. In particular the dioxotetraaza macrocycles have attracted considerable chemical interest as these can co-ordinate Ni^{2+} and Cu^{2+} ions in a square-planar geometry with dissociation of two protons from the amido groups, thus forming neutral 1:1 complexes generally designated as MLH_{-2}.[1–4] More recently, the co-ordination chemistry of some dioxopentaaza macrocycles was investigated[5,6] and it was found that their nickel(II) complexes showed interesting adducts with molecular oxygen,[7–10] making them potential monooxygenase models.[9] In most of these studies the dioxopolyamine ligands have the two amido groups in neighbouring positions, thus occupying *cis* positions in the equatorial plane of their MLH_{-2} complexes. Only a few studies have been reported on the aqueous co-ordination chemistry of dioxopolyamine macrocycles with two amido groups in *trans* position in their MLH_{-2} complexes.[1,6,7,11] The most complete study concerned the complexation of Cu^{2+} and Ni^{2+} by 2,6-dioxo-1,4,7,10-tetraazacyclododecane. It forms square-planar MLH_{-2} complexes in which the macrocycle was thought to be slightly too small to encompass the metal ion, as indicated by a reduced ligand-field strength.[11] The $NiLH_{-2}$ complex of the *cis*-dioxopentaaza macrocycle 2,6-dioxo-1,4,7,10,14-pentaazacyclohexadecane[7] and the $CuLH_{-2}$ complex of 2,6-dioxo-1,4,7,10,13-pentaazacyclopentadecane[6] were previously reported without details.

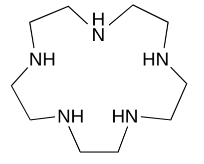
In view of this situation, it was considered worthwhile further to explore the aqueous co-ordination properties of *trans*-dioxopentaaza macrocycles. The compounds selected for this study are 2,6-dioxo-1,4,7,10,13-pentaazacyclopentadecane (L^1) and 2,6-dioxo-1,4,7,11,14-pentaazacycloheptadecane (L^2). The co-ordination chemistry with Ni^{2+} and Cu^{2+} is explored by potentiometric pH-metry and UV/VIS spectroscopy. As it was expected that several complexes could be formed over the range pH 2–11, IR spectroscopy in D_2O was used to establish the involvement of the amide oxygen or nitrogen donor in the course of the complexation process.



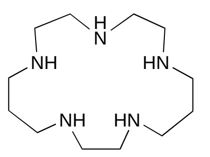
L^1



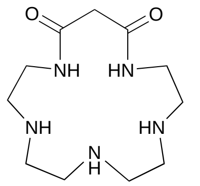
L^2



[15]aneN$_5$



[17]aneN$_5$



cis-dioxo-[16]aneN$_5$

Results and Discussion

Protonation

The ligands L^1 and L^2, each containing three secondary amino groups, were found to take up three protons in the range pH 2–11. The thermodynamic data for the successive protonations are given in Table 1. The values of the protonation constants ($K^H_n = [H_nL]/[H][H_{n-1}L]$; $n = 1–3$) for L^1 given by Kimura and co-workers[6] (log $K^H_1 = 8.35$, log $K^H_2 = 4.85$ and log $K^H_3 = ca.$ 2.6; 25 °C, ionic strength 0.2 mol dm^{-3}) differ quite considerably from ours. Compound L^2 is at each protonation step more basic than L^1, reflecting the greater positive inductive effect of

Table 1 Thermodynamic data for the successive protonation of L^1 and L^2 at 25 °C in aqueous KNO_3 (I = 0.100 mol dm^{-3})[a]

	n[b]	$\log K^H_n$[c]	$-\Delta H°_n$/kJ mol^{-1}	$T\Delta S°_n$/kJ mol^{-1}
L^1	1	8.94	37.4	12.5
	2	5.03	30.6	−2.3
	3	4.22	37.7	−13.7
L^2	1	9.41	44.1	9.6
	2	6.39	40.0	−3.5
	3	5.10	32.3	−3.2

[a] $\log K^H_n \pm 0.01$, $\Delta H° \pm 0.8$ kJ mol^{-1}, $T\Delta S° \pm 0.9$ kJ mol^{-1}. [b] nth Protonation step. [c] $K^H_n = [H_nL]/[H][H_{n-1}L]$; charges omitted.

Table 2 Stability constant data for the complexation of Cu^{2+} and Ni^{2+} by L^1 and L^2 at 25 °C in aqueous KNO_3 (I = 0.100 mol dm^{-3})

		$\log \beta_{pqr}$[a]	
Metal ion	pqr	L^1	L^2
Cu^{2+}	112	17.6(1)[b]	19.1(1)
	111	13.4(1)	14.7(2)
	110	8.5(3)	10.1(2)
	11-1	4.6(1)	3.3(3)
	11-2	−4.3(2)	−5.9(2)
Ni^{2+}	112	17.1(1)	19.3(3)
	111	13.2(1)	13.7(1)
	110	5.4(1)	6.4(1)
	11-1	−2.1(3)	−2.2(2)
	11-2	−10.2(3)	−10.8(2)

[a] $\beta_{pqr} = [M_pL_qH_r]/[M]^p[L]^q[H]^r$. [b] Standard deviation in parentheses.

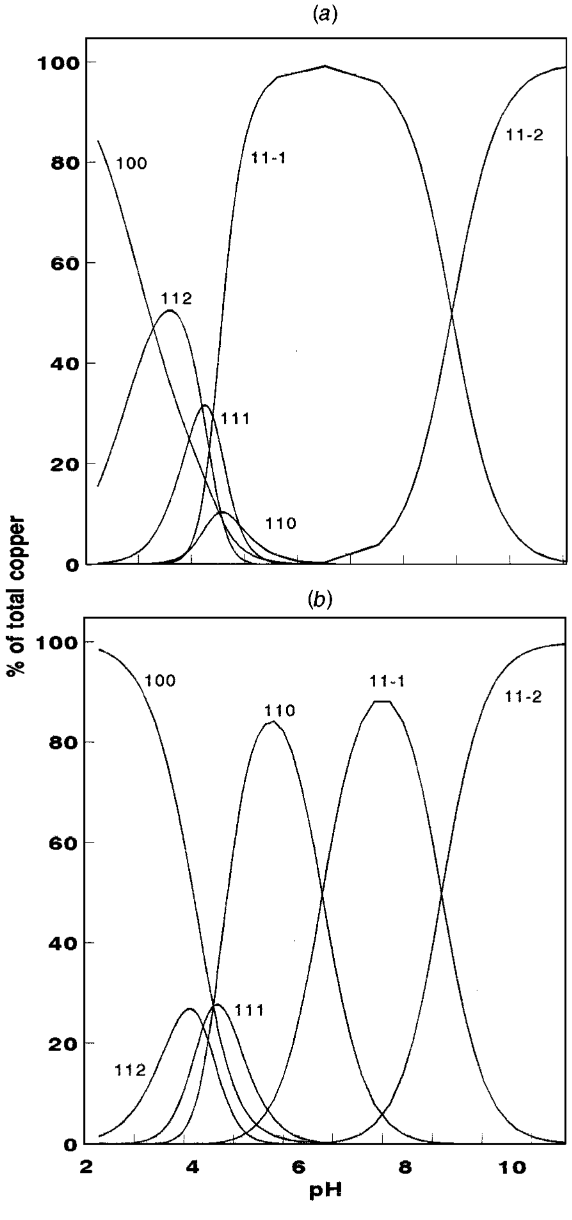


Fig. 1 Species distribution curves calculated for (*a*) the Cu^{2+}–L^1 system and (*b*) the Cu^{2+}–L^2 system, as a function of the pH (molar ratio 1 : 1; total ligand concentration 5.00 × 10^{-3} mol dm^{-3}). Only the copper-containing $Cu_pL_qH_r$ species are shown, indicated by their *pqr* notation

the larger number of carbon atoms and the lower electrostatic repulsion of charges upon protonation due to the larger ring size of L^2. There will be tautomeric forms for the proton binding to the three amino groups in HL^+ and H_2L^{2+}, but it can be expected that the third proton will be primarily added to the amino group situated between the two amido groups as their electron-withdrawing capacity will lower the basicity of this amino group the most. The protonation enthalpy changes for both ligands are in the range typical for secondary amino groups,[12] the values for L^2 being in average more exothermic than for L^1, in line with its greater basicity. The term $T\Delta S°_3$ for L^2 is less negative than for L^1 and may point to a lesser decrease in configurational entropy and less solvent electrorestriction[13] at the third protonation step due to its larger ring size.

Copper(II) complexes

All pH-metric titration curves were consistent with the formation of a $CuLH_{-1}$ and a $CuLH_{-2}$ as main complexes (charges omitted for simplicity): an inflection point at $a = 4$ and an endpoint at $a = 5$ (a is the number of moles of KOH titrant solution added per mol of macrocycle present). Optimization using the SUPERQUAD software[14] necessitated the introduction of CuH_2L, CuHL and CuL as additional complex species in the complexation set. The presence of these additional species is chemically acceptable in view of previous findings that the amido group is readily involved in the co-ordination of a metal ion through its carbonyl oxygen donor.[15,16] The calculated stability constants are given in Table 2. The species distribution curves are shown in Fig. 1. The values for the copper(II) complexes with L^1 reported casually by Kimura and co-workers[6] are again different from ours. They also proposed a much simpler complexation model.

The formation of CuL^1H_{-1} up to 100% at $a = 4$ (pH 6) is remarkable in view of the lower overall basicity of L^1 relative to L^2. As a consequence the formation of CuL^1 goes to a much lower extent compared to CuL^2. A second remarkable fact is that the pK_a value (= $\log \beta_{11\text{-}1} - \log \beta_{11\text{-}2}$) of $CuLH_{-1}$ (8.9 for L^1 and 9.2 for L^2) in the formation of the end-complex $CuLH_{-2}$ is equal within experimental error to the $\log K^H_1$ value of the corresponding free macrocycle ($\beta_{11-1} = [CuLH_{-1}]/[Cu][L][H]^{-1}$; $\beta_{11-2} = [CuLH_{-2}]/[Cu][L][H]^{-2}$; L = L^1 or L^2). This observation indicates that in the neutralization between $a = 4$ and 5 an ammonium group in $CuLH_{-1}$ is deprotonated, but remains unco-ordinated to the Cu^{2+} ion in the $CuLH_{-2}$ complex. For comparison it was proposed that in the $CuLH_{-2}$ complex with *cis*-dioxo-[16]aneN_5 all five nitrogen donor atoms were co-ordinated to the Cu^{2+} ion in a square-pyramidal geometry.[6] In agreement with this, it was later found that the pK_a value of the corresponding $CuLH_{-1}$ complex ($K_a = [CuLH_{-2}][H]/[CuLH_{-1}]$) was 2.65 log units lower than the first protonation constant of the free macrocycle,[10] thus supporting the co-ordination of this amino group in the formation of $CuLH_{-2}$.

In view of the literature data on the co-ordination of Cu^{2+} by dioxopentaaza macrocycles in aqueous solution[6,8,10] there is strong evidence from our pH-metric results that both amido groups in L^1 and L^2 are already deprotonated and co-ordinated

Table 3 Infrared spectral data (cm^{-1}) for the asymmetric amide carbonyl stretching vibration of the complexes of Cu^{II} and Ni^{II} with L^1 and L^2 at various extents of neutralization in D$_2$O solution at 25 °C

	Cu^{2+}		Ni^{2+}	
a[a]	L^1	L^2	L^1	L^2
0	1665, 1620	1659, 1626	1667	1661
2	1648, 1620	1648, 1624, 1578		
3	1613, 1578	1618, 1578		
4	1601, 1578	1601, 1578		
5	1601, 1578	1601, 1578	1603, 1569	1590[b]

[a] Number of mols KOH added per mol of ligand present. [b] Broad.

to Cu^{2+} in CuLH$_{-1}$ together with two amino groups, and that the fifth nitrogen donor is likely not involved in the co-ordination. This is also obvious from the IR spectra (see Table 3).

At $a = 0$ the band at 1665 cm^{-1} for L^1 and that at 1659 cm^{-1} for L^2 can be assigned to the asymmetric amide carbonyl stretching vibration in the H$_3$L form of both ligands. Along with a slight shift to lower frequency, the intensity of this band gradually decreases up to $a = 3$ where it has completely disappeared. This parallels the decreasing concentration of H$_3$L. The band at *ca.* 1620 cm^{-1} for L^1 and at *ca.* 1626 cm^{-1} for L^2 first increases in intensity between $a = 2$ and 3, but has completely disappeared at $a = 4$. These absorptions may be attributed to amide co-ordination to Cu^{2+} through the carbonyl oxygen[15,17] in the CuH$_2$L, CuHL and CuL species. At $a = 4$ a rather broad but strong absorption peak with maxima at 1601 and 1578 cm^{-1} is the only one left. This absorption may be assigned to an ionized amido group strongly co-ordinated to the Cu^{2+} ion through the negatively charged amide nitrogen,[18] as exemplified in many other studies.[15,17,19] The intensity of this absorption does not change between $a = 4$ and 5, demonstrating that both amido groups are already co-ordinated through the amide nitrogen to Cu^{2+} in the CuLH$_{-1}$ complex and that indeed an ammonium group is neutralized in going from CuLH$_{-1}$ to CuLH$_{-2}$. The IR data thus confirm that in CuLH$_{-1}$ two amide nitrogens and two amine nitrogens make up the equatorial co-ordination plane around the Cu^{2+} ion in a tetragonal environment. A broad d–d electronic absorption band with maximum at 17 240 cm^{-1} for CuL^{1}H$_{-1}$ and at 18 180 cm^{-1} for CuL^{2}H$_{-1}$ (see Table 4), and slightly asymmetric at the low-frequency side, is consistent with such a tetragonal co-ordination geometry at Cu^{2+}.[20,21] The position of these maxima is somewhat at the lower side for the tetragonal CuN$_4$ chromophore,[22] in particular since the deprotonated amide nitrogen is higher in the spectrochemical series and is a stronger σ donor than the amine nitrogen.[23] This may be explained by the destabilizing effect of the large eight- (for CuL^{1}H$_{-1}$) or nine-membered chelate ring (for CuL^{2}H$_{-1}$) bearing the ammonium group in these complexes.

The observation that the IR absorption at 1578 cm^{-1} is already present at $a = 3$ with L^1 and at $a = 2$ with L^2 indicates that the deprotonated amide nitrogen is involved in the co-ordination of Cu^{2+} at a very early stage. This can be explained by the fact that the least basic amino group in L^1 and L^2 is the one situated between the two amido groups. As this amino group is likely to co-ordinate to Cu^{2+} first, it immediately functions as an anchor[16] for ionization and co-ordination of one neighbouring amido group of which the carbonyl part will be in a favoured endocyclic position in the chelate five ring thus formed (see Fig. 2).

If the last amino group remains unco-ordinated to Cu^{2+} in CuLH$_{-2}$ as indicated by the acidity of CuLH$_{-1}$, one would expect not much of a change in the d–d spectrum of CuLH$_{-2}$ compared to that of CuLH$_{-1}$. This is more or less so for CuL^{1}H$_{-2}$ for which the ν_{d-d} maximum is shifted only by *ca.* 300 cm^{-1} to the blue along with a moderate decrease in molar absorptivity (see Table 4). This can be in line with a tetragonal co-ordination geometry around Cu^{2+}, but with less distortion in the complex, probably due to the neutralization of the last ammonium group. This tetragonal co-ordination geometry around Cu^{2+} in CuL^{1}H$_{-2}$ is then in contrast to the square-pyramidal co-ordination geometry in the CuL complex of [15]aneN$_5$, the fully saturated pentaaza macrocyclic analogue of L^1, as deduced from thermodynamic[24] and electronic spectral data[25–27] and confirmed by its crystal structure.[28] A key element in the assignment of a square-pyramidal structure to this complex on the basis of its d–d spectrum was the presence of a weaker second absorption band at *ca.* 12 120 cm^{-1},[27] in accordance with previous studies[29,30] and due to the $d_{z^2} \longrightarrow d_{x^2-y^2}$ electronic transition.[21] This weak absorption band might also be present in the d–d spectrum of CuL^{1}H$_{-2}$ since the absorption band is clearly asymmetric at the low-energy side, but a defined maximum can hardly be located.

Table 4 Electronic spectral data (cm^{-1}) for the complexes of Cu^{II} and Ni^{II} with L^1 and L^2 at various extents of neutralization in water solution at 25 °C

	Cu^{2+}		Ni^{2+}	
a[a]	L^1	L^2	L^1	L^2
3		17 100(99)[b]		
4	17 240(154)	18 180(112)		
5	17 540(127)	18 520(125)	23 260(102)	27 780(55)
		14 500(133)		20 410(79)
				16 000(sh)

[a] Number of mols of KOH added per mol of ligand present. [b] Molar absorptivity coefficient in dm^3 mol^{-1} cm^{-1} in parentheses.

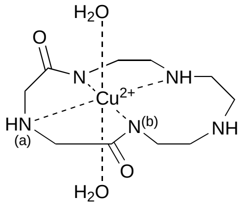


Fig. 2 Schematic representation of the co-ordination of L^1 in the CuL^{1}H$_{-2}$ complex with the amido groups in *trans* position. Indicated are: (a) the least basic amino group acting as anchor for amide co-ordination; (b) the sp^2-hybridized amide nitrogen preventing further axial co-ordination. This structure is also representative for CuL^{2}H$_{-2}$

The electronic spectrum of CuL^{2}H$_{-2}$ is totally different from that of CuL^{1}H$_{-2}$. The d–d absorption band for CuL^{2}H$_{-2}$ is broad, exhibiting two well defined maxima of about the same intensity resulting in twin peaks (see Table 4). The peak at lowest energy is the broadest of the two. The molar absorptivities of both peaks are nearly equal and have not changed much compared with that of the CuL^{2}H$_{-1}$ complex. To our knowledge this kind of d–d spectrum is quite unique compared to the spectra for pentaaza macrocyclic CuL complexes.[26] For instance, the d–d spectrum of the CuL complex with [17]aneN$_5$ exhibits a maximum at 16 950 cm^{-1} ($\varepsilon = 180$) and a weaker band at 11 900 cm^{-1} ($\varepsilon = 65$ dm^3 mol^{-1} cm^{-1}),[27] thus in the wavenumber ranges typical for a square-pyramidal configuration, as was confirmed by its crystal structure.[31] It was also suggested[6] that the CuLH$_{-2}$ complex of *cis*-dioxo-[16]aneN$_5$ would also be square pyramidal with two amine nitrogens and two deprotonated amide nitrogens lying at the basal positions and one amino group lying in an axial position, but no details on its d–d spectrum were given.

A precise explanation for the twin peak d–d spectrum of CuL^{2}H$_{-2}$ must await more structural information on this complex. However, in our opinion, the co-ordination geometry in both CuL^{1}H$_{-2}$ and CuL^{2}H$_{-2}$ is likely to be overall tetragonal with only weak axial interaction of the fifth nitrogen. A strong axial interaction by a nitrogen donor in $CuLH_{-2}$ would certainly shift its $\nu_{d\text{–}d}$ band to lower wavenumbers relative to $CuLH_{-1}$ resulting from a weakening of the in-plane ligand field by a synergic effect.[20] In fact, the opposite is observed. It may be that the folding of the ring and the axial binding of the fifth nitrogen donor is inhibited by the planar trigonal nature of the deprotonated sp^2-hybridized amide nitrogens bound in the equatorial plane (see Fig. 3).

The twin peak feature of the $\nu_{d\text{–}d}$ band of CuL^2H_{-2} is supposed to be the result of larger differences in energy of the electronic transitions to the $d_{x^2-y^2}$ orbital which normally occur under one absorption envelope for more formally tetragonal copper(II) complexes. This wider energy separation in CuL^2H_{-2} is probably related in some way to the presence of the six-membered chelate ring in the equatorial plane around the Cu^{2+} ion in combination with the two amide nitrogen donors in *trans* position. A definite conclusion on the co-ordination geometry in CuL^2H_{-2} must await further structural investigation.

Nickel(II) complexes

The potentiometric pH titration curves of Ni^{2+} with L^1 or L^2 in 1:1 molar ratio show a titration end-point at $a = 5$. This corresponds to the formation of a $NiLH_{-2}$ species. The complexation set was further completed with the species NiH_2L, NiHL, NiL and $NiLH_{-1}$, the latter being formed up to 83% with L^1 and up to 60% with L^2. The calculated stability constants are given in Table 2. The species distribution curves are shown in Fig. 3. The differences in stability for the corresponding nickel(II) complexes of L^1 and L^2 are rather small. The stability of the $NiLH_{-2}$ complex with L^1 or L^2 ($\beta_{11\text{-}2} = [NiLH_{-2}]/[Ni][L][H]^{-2}$; $L = L^1$ or L^2) is lower than the stability reported for the $NiLH_{-2}$ complex of *cis*-dioxo-[16]aneN_5 (log $\beta_{11\text{-}2} = -8.93$, ionic strength = 0.1 mol dm^{-3} KCl, 25 °C).[10] In the $NiLH_{-2}$ complex of L^1 and L^2 both amido groups are deprotonated and co-ordinated to the Ni^{2+} ion as evidenced by the IR spectra at $a = 5$ (see Table 3): absence of the carbonyl stretching band of the free macrocycle, respectively at 1667 cm^{-1} for L^1 and at 1661 cm^{-1} for L^2, and presence of new strong absorptions at lower wavenumbers.

The electronic absorption spectra of both $NiLH_{-2}$ complexes are typical for diamagnetic square-planar nickel(II) complexes with absorption maxima at 430 nm for NiL^1H_{-2} and at 490 nm for NiL^2H_{-2}. The corresponding d–d transition wavenumbers are given in Table 4. It must be concluded that in both $NiLH_{-2}$ complexes only four nitrogen donor atoms are co-ordinated. It is very likely that the two deprotonated amide nitrogens, the least basic amino group in between, and one of the two remaining amine nitrogens make up the square-planar co-ordination plane around the Ni^{2+} ion. This co-ordination geometry is in contrast with the overall pseudo-octahedral co-ordination of Ni^{2+} with the saturated pentaaza macrocycles [15]aneN_5 and [17]aneN_5[32,33] or with *cis*-dioxo-[16]aneN_5.[5,8,10] However, the electronic absorption spectrum of NiL^2H_{-2} also shows an additional weak band at 360 nm (27 780 cm^{-1}) and an ill defined shoulder at approximately 625 nm (16 000 cm^{-1}). These bands may be assigned to an octahedral form of the NiL^2H_{-2} complex in equilibrium with the square-planar form, since they disappear upon increasing the ionic strength of the solution [up to 7.0 mol dm^{-3} KNO_3 (aq)], while the yellow band at 490 nm increases in intensity.[20] The shoulder at about 16 000 cm^{-1} may correspond to the $^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$ transition in a formally high-spin octahedral nickel(II) complex. Its position at much lower energy than the second band in the electronic spectrum of the distorted octahedral nickel(II) complex of [17]aneN_5 (NiN_5O chromophore with second band maxima at 17 000 and 18 605 cm^{-1})[32] may indicate that in the octahedral form of NiL^2H_{-2} a NiN_4O_2 chromophore is present with water molecules in axial positions to complete the octahedral co-ordination. No high-spin octahedral form of NiL^1H_{-2} was detected. This is in agreement with the much stronger square-planar ligand field created by L^1 forming three linked five-membered chelate rings around the small low-spin Ni^{2+} ion. It is a general observation that the ligand-field strength in low-spin nickel(II) tetraaza complexes decreases as five-membered chelate rings are replaced by six-membered ones, thereby also increasing the ligand ring size in the case of macrocyclic tetraaza ligands.[4,34,35] The fact that the fifth nitrogen donor remains unco-ordinated in both $NiLH_{-2}$ complexes, as was also the case in the $CuLH_{-2}$ complexes, stresses the structural implication of the trigonal nature of the deprotonated sp^2-hybridized amide nitrogens when bound in *trans* positions in the equatorial plane of the metal ion: the folding of the macrocyclic ring allowing an additional donor to occupy an axial position in the co-ordination sphere of the metal ion is structurally prevented. Moreover, the joint ligand-field effects of the two amido and the amino groups are strong enough to overcome the destabilizing effect of the very large chelate ring present in the complex and to maintain a square-planar co-ordination geometry.

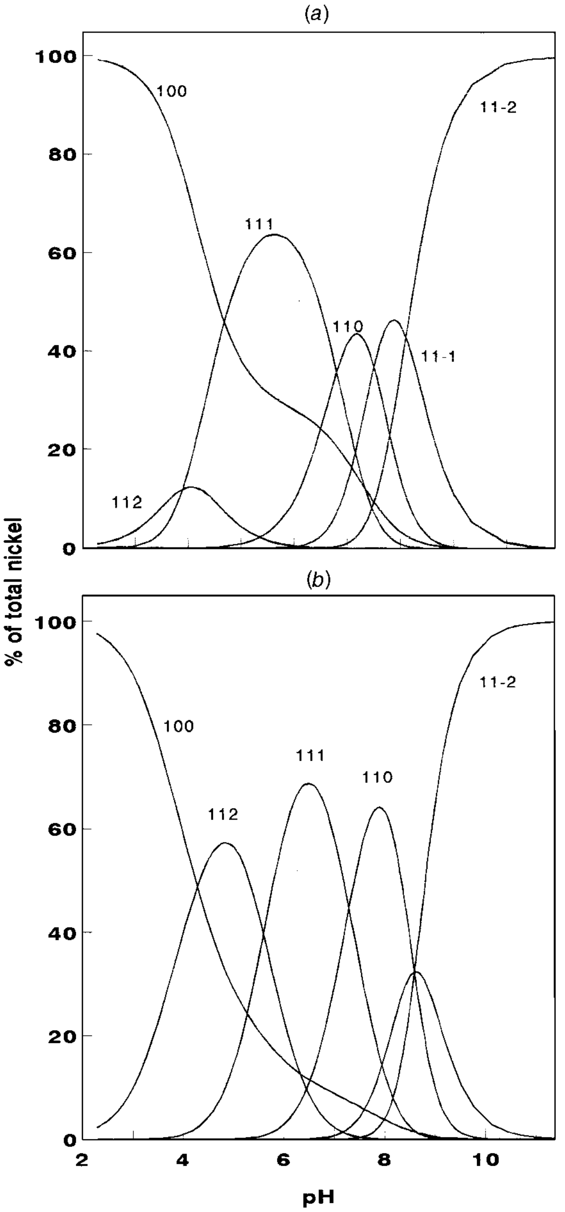


Fig. 3 Species distribution curves calculated for (*a*) the Ni^{2+}–L^1 system and (*b*) the Ni^{2+}–L^2 system, as a function of the pH (molar ratio 1:1; total ligand concentration 5.00 × 10^{-3} mol dm^{-3}). Only the nickel-containing $Ni_pL_qH_r$ species are shown, indicated by their *pqr* notation

Table 5 Summary of experimental parameters for the potentiometric stability constant measurements

System	L^1 or L^2 with H^+, Cu^{2+} or Ni^{2+} in water
Solution composition	[L] range/mol dm^{-3} 0.002–0.005, [M] range/mol dm^{-3} 0.002–0.005, ionic strength/mol dm^{-3} 0.100, electrolyte KNO_3
Experimental method	pH-Metric titration in the range pH 2–11, log $\beta_{00\text{-}1} = -13.78$; for instruments and calibration see refs. 37, 39
T/°C	25.0
$n_{tot}{}^{a}$	50–70
$n_{tit}{}^{b}$	4–6
Method of calculation	SUPERQUAD[14]

[a] Number of titration points per titration. [b] Number of titrations per metal–ligand system.

Experimental

Synthesis of the macrocycles

2,6-Dioxo-1,4,7,10,13-pentaazacyclopentadecane, L^1, was prepared by mixing the dimethyl ester of iminodiacetic acid hydrochloride (0.0847 mol, 16.76 g), a standardized NaOMe methanolic solution (0.0847 mol) and triethylenetetraamine (0.0847 mol, 12.39 g) in methanol (0.5 dm^3). This mixture was refluxed for 72 h after which the solvent was removed and the resulting residue dissolved in chloroform and chromatographed over silica gel (Merck $60F_{264}$) using methanol–chloroform (10 : 90 by volume) as eluent. The hydrochloric salt of the obtained product was prepared by adding HCl in methanol (2 mol dm^{-3}) until pH 1. The precipitate was filtered off, recrystallized from methanol and dried under reduced pressure until constant weight ($L^1 \cdot 3HCl \cdot H_2O$; 11.3 g, 55%); *m*/*z* 243.5 ($M + H^+$) [electrospray mass spectrometry, acetonitrile–water–formic acid (49 : 50 : 1)]; δ_H(360 MHz, solvent D_2O, pD 3.8, reference water) 4.10 (4 H, s, $NHCH_2CONH$), 3.69 (4 H, t, $CONHCH_2$-CH_2NH), 3.65 (4 H, s, $NHCH_2CH_2NH$) and 3.40 (4 H, t, $CONHCH_2CH_2NH$).

2,6-Dioxo-1,4,7,11,14-pentaazacycloheptadecane, L^2, was prepared in the same way, using *N*,*N'*-bis(3-aminopropyl)-ethane-1,2-diamine as tetraamine ($L^2 \cdot 3HCl \cdot H_2O$; 10.9 g, 48%); *m*/*z* 269 ($M + H^+$) [electrospray mass spectrometry, acetonitrile–water–formic acid (49 : 50 : 1)]; δ_H(360 MHz, solvent D_2O, pD 3.8, reference water) 4.08 (4 H, s, $NHCH_2$-CONH), 3.63 (4 H, s, $NHCH_2CH_2NH$), 3.35 (4 H, t, CONH-$CH_2CH_2CH_2NH$), 3.21 (4 H, t, $CONHCH_2CH_2CH_2NH$) and 1.88 (4 H, q, $CONHCH_2CH_2CH_2NH$).

Materials

All reagents were of reagent grade. Distilled and deionized water (Milli-Q quality, specific conductance < 0.05 μS cm^{-1}) was used throughout. Carbonate-free (< 0.5%) potassium hydroxide solutions (*ca.* 0.25 mol dm^{-3}) were prepared from Titrisol ampoules (Merck) and standardized by titration with stock solutions of hydrogen chloride. The stock solutions of hydrogen chloride were standardized by argentometry. Metal-ion stock solutions were prepared from metal nitrates (Merck) and standardized by complexometric titrations with the disodium salt of ethylenedinitrilotetraacetate using appropriate conditions.[36] All final solutions for the potentiometric, calorimetric and UV/VIS measurements were made up to an ionic strength of 0.100 mol dm^{-3} with potassium nitrate (Merck).

Potentiometric measurements

The potentiometric measurements were carried out at 25.0 ± 0.1 °C with the equipment and the general procedure previously described.[37] The glass electrode was calibrated for hydrogen-ion concentration measurements with correction made for non-linear behaviour below pH 2.5 and above pH 11.[37] A summary of the experimental parameters is given in Table 5. All equilibrium constants for ligand protonation and for metal-ion complexation were calculated with the program SUPERQUAD.[14] These equilibrium constants are concentration constants valid at 25 °C in 0.1 mol dm^{-3} aqueous ionic medium. Distribution curves were calculated with the program EQUIL.[38] Equilibrium was reached instantaneously for all systems.

Calorimetric measurements

The calorimetric measurements were carried out in duplicate with a Tronac model 1250 isoperibol calorimeter. The experimental procedure, the calibration of the calorimeter and the software used have been described.[39] For this study, the protonation heats were determined by titrating a solution (25.00 cm^3) containing the ligand in its basic form (*ca.* 0.05 mmol) with a standardized solution of HNO_3 (*ca.* 0.1 mol dm^{-3}). Dilution experiments were also done. The exact concentration of the components in each solution was determined by separate potentiometric titrations.

UV/VIS measurements

The electronic absorption spectra were recorded at 25 °C on a Hewlett-Packard 8451A diode-array spectrophotometer in the wavelength region between 300 and 820 nm. Aqueous solutions of Cu^{2+} or Ni^{2+} and the appropriate macrocycles were prepared with a $c_L : c_M$ ratio of *ca.* 1.05 to 1.00. A calculated volume of a standardized KOH solution was then added to obtain spectra at different extents of neutralization.

IR measurements

The spectra were recorded at 25 °C with a ATI Mason FTIR spectrometer in the wavenumber region between 1500 and 1700 cm^{-1}. Solutions in D_2O (Merck, +99%) were prepared at different extents of neutralization in the same way as for the electronic spectra.

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