interaction between Cu(II) ions is characterized by $J = -6$ cm^{-1}, which is quite a small value, in particular when compared to the interaction in copper(II) acetate, where four acetato groups bridge in a syn–syn fashion. It is also worth noting that the comparison between MnCu(obp)(H$_2$O)$_3$·H$_2$O and 1 confirms, if it was still necessary, that the magnitude of the interaction is not directly related to the separation between the magnetic centers. As a matter of fact, due to the anti–syn configuration, the Mn···Cu distance across the carboxylato bridge is much shorter in 1 than in MnCu(obp)(H$_2$O)$_3$·H$_2$O (5.3670 (4) Å and 6.066 (2) Å, respectively).

In the discussion, we have implicitly assumed, so far, that the Mn^{II}–Mn^{II} and Cu^{II}–Cu^{II} intrachain interactions between next nearest neighbor metal ions were negligible. This assumption could not be rigorously valid. Perhaps the observed magnetic behavior results from a subtle balance between a weak Mn(II)–Cu(II) antiferromagnetic interaction through the carboxylato bridge favoring the one-dimensional ferrimagnetism and weak Mn(II)–Mn(II) and/or Cu(II)–Cu(II) antiferromagnetic interactions

involving next nearest neighbors and favoring one-dimensional antiferromagnetism. The Mn(II)–Mn(II) dipolar interactions between high local spins could also play a role.

As already mentioned, our goal in this field of the bimetallic chains is both to obtain the one-dimensional ferrimagnetic behavior and to design molecular compounds exhibiting a spontaneous magnetization. To date, three compounds have already been investigated. One behaves as a one-dimensional ferrimagnet, with a three-dimensional ordering at very low temperature, another one exhibits a spontaneous magnetization below 14 K, and the third one behaves magnetically as isolated Mn^{II}Cu^{II} pairs with oxamido bridges. The EPR spectra, however, show that the pairs are not perfectly isolated but weakly interact through the carboxylato bridges, in agreement with the crystal structure.

Supplementary Material Available: Tables SV–SVIII, listing anisotropic thermal parameters for non-hydrogen atoms, hydrogen atomic parameters, bond distances and angles involving hydrogen atoms, and hydrogen bonds for MnCu(obzp)(H$_2$O)$_3$·H$_2$O (1), and Figure S6, giving the $\chi_M T$ versus T plot for MnCu(ophp)·5H$_2$O (2) (5 pages); a table of structure factors for MnCu(obzp)(H$_2$O)$_3$·H$_2$O (1) (17 pages). Ordering information is given on any current masthead page.

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Nickel(II) Complexes of [3k]aneN$_k$ Polyazacycloalkanes (k = 7–12). Solution and Solid-State Studies

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A potentiometric study of the equilibria between nickel(II) and the large polyazacycloalkanes of the series [3k]aneN$_k$ (k = 7–12) has been carried out at 25 °C in 0.15 mol dm^{-3} NaClO$_4$–water solution as ionic medium. The ligand [21]aneN$_7$ forms only mononuclear complexes, while [24]aneN$_8$ forms both mononuclear and binuclear complexes. Only binuclear complexes are formed when k = 9–12. The stability of the mononuclear complexes is compared with that previously reported for complexes formed by smaller macrocycles (k = 3–6). The equilibrium constants of mononuclear complexes increase on going from [9]aneN$_3$ to the hexadentate [18]aneN$_6$ and then decrease for [21]aneN$_7$ (log K = 16.563 (5)) and [24]aneN$_8$ (log K = 13.94 (5)). The stability of binuclear complexes increases with the dimension of the ligands and the number of donor atoms: [24]aneN$_8$ (log K = 23.30 (1)); [27]aneN$_9$ (log K = 26.24 (1)); [30]aneN$_{10}$ (log K = 30.02 (3)); [33]aneN$_{11}$ (log K = 31.07 (1)); [36]aneN$_{12}$ (log K = 32.09 (3)). Many protonated species are formed, and their equilibrium constants have been measured. Also hydroxodinickel(II) complexes have been detected. Magnetic properties of solid complexes and electronic spectra of these compounds, both in the solid state and in solution, are indicative of high-spin octahedral nickel(II) complexes. Only in the case of [24]aneN$_8$ has a dinickel(II) diamagnetic square complex ([Ni$_2$([24]aneN$_8$)](ClO$_4$)$_4$) been isolated. This compound dissolves in water to produce, over a period of some hours, octahedral species. The molecular structure of the dinickel(II) complex [Ni$_2$([30]-aneN$_{10}$)(H$_2$O)$_2$](NO$_3$)$_4$ ([30]aneN$_{10}$ = 1,4,7,10,13,16,19,22,25,28-decaazacyclotriacontane) has been determined by single-crystal X-ray analysis. This compound crystallizes in the $P2_1/a$ space group with a = 13.894 (2) Å, b = 9.386 (6) Å, c = 14.100 (2) Å, β = 113.13 (2)°, and Z = 2. Refinement of the atomic parameters by least squares gave a final R factor of 0.065 (R_w = 0.056) for 2140 unique reflections having $I \geq 3\sigma(I)$. The structure consists of centrosymmetric [Ni$_2$([30]aneN$_{10}$)(H$_2$O)$_2$]$^{4+}$ cations and uncoordinated nitrate anions. The nickel(II) ion of the complex cation is coordinated by five nitrogen atoms of the macrocyclic ligand and one water molecule in a distorted octahedral environment. Also, the crystalline compound [Ni([21]aneN$_7$)](ClO$_4$)$_2$ has been analyzed by X-ray diffraction. Crystals of this compound are orthorhombic, space group $P22_12_1$, with a = 9.692 (4) Å, b = 14.872 (1) Å, c = 32.366 (3) Å, and Z = 8. Only the two independent nickel(II) ions of two different molecules, the non-hydrogen atoms of a [Ni([21]aneN$_7$)]$^{2+}$ cation, and the four perchlorate anions were localized. Any attempt to localize the atoms of the macrocycle of the second complex cation was unsuccessful because of the disorder of this molecule; refinement of atomic parameters by least squares was interrupted (R factor about 20% for the 2395 reflections having $I \geq 3\sigma(I)$). The nickel(II) ion in the [Ni([21]aneN$_7$)]$^{2+}$ cation is coordinated by six nitrogen atoms of the ligand, one nitrogen remaining uncoordinated in an eight-membered chelate ring.

Introduction

It is a general idea in the synthesis of macrocyclic ligands to produce molecules in which one or more metal ions could be readily coordinated. Anyhow, in some cases, metal ions have to be forced

to enter into the macrocyclic cavity. A classic example is offered by nickel(II) with some tetraazacycloalkanes, for which the reaction of complexation in water is fast only at high temperatures.[2–4] The resulting complexes are characterized by a surprising ther-

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modynamic and kinetic stability,[3] which allows one to study their properties under severe conditions. Notwithstanding that, the inertness of these complexes represents the hardest hindrance to get insight into their thermodynamics of formation.[5,6]

In this paper we present the results of a study on the interaction between nickel(II) and the large polyazacycloalkanes [3k]aneN$_k$ (k = 7–12).
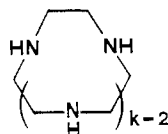
In recent studies[7–14] these ligands have shown a rather eclectic nature in their coordination to metal ions, because, owing to their dimension, to the number of donor atoms, and to their flexibility, they do not impose any preformed coordination site but adapt themselves to the steric requirements of the bound metal ions. We have observed that the reactions of complexation of nickel(II) by these ligands are fast enough to allow the determination of stability constants by the common potentiometric techniques. As a result of this study, it has been observed that the dinucleating tendency of these large polyazacycloalkanes, already shown with copper-(II),[7–11] zinc(II),[12,13] and cadmium(II)[14] ions, is maintained also with nickel(II), and dinickel(II) complexes are formed as main species in solution. To our best knowledge, this is the first series of dinickel(II) complexes of polyazacycloalkanes that have been reported and discussed in terms of thermodynamics of formation. Other macrocyclic ligands containing both nitrogen and oxygen donor atoms have been tested for coordination to nickel(II) ion in water solution. The hexaaza–dioxa macrocycle bisdien[15] forms dimetallic complexes with copper(II), cobalt(II) and zinc(II) ions but fails to form dinickel(II) species.[16] On the other hand, the macrobicycle bistren[15] containing eight nitrogens and two oxygens achieves formation of a dinickel(II) cryptate complex, although the stability of this complex is rather low with respect to that of the mononuclear one.[17]

Experimental Section

Materials. The polyazacycloalkanes and their hydrochloride salts employed in this work were obtained following previously reported procedures.[7–11] Satisfactory elemental analyses were obtained for all the compounds. All the potentiometric measurements were carried out in 0.15 mol dm^{-3} NaClO$_4$. NaClO$_4$ used as supporting electrolyte was purified according to the procedure already described.[18] Stock solutions of nickel(II) were prepared by dissolving NiCl$_2$·6H$_2$O in doubly distilled water and their concentrations determined by standard gravimetric methods. CO$_2$-free NaOH and HCl solutions were prepared following the procedure reported in ref 19.

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Table I. Experimental Details of the Emf Measurements in the Ni^{2+}/[3k]aneN$_k$ (k = 7–12) Systems

k	init quantities, mmol			pH range		no. of data points
	Ni^{2+}	[3k]aneN$_k$	H^{+a}	investigated	computed	
7	0.0672	0.0781	0.5464	3.0–11.2	4.2–7.8	40
	0.0579	0.0691	0.4835	3.4–10.2	4.2–7.2	27
	0.0706	0.0706	−0.0295	2.9–10.8	4.1–6.3	53
8	0.0880	0.0585	0.1148	3.0–9.0	3.0–4.6	53
	0.0880	0.0585	0.5042	3.0–11.1	3.1–11.0	63
	0.0915	0.0612	0.4892	3.3–9.8	3.8–7.7	31
9	0.0900	0.0602	0.5834	2.2–10.7	2.9–5.5	50
	0.0900	0.0602	−0.0256	3.0–11.0	3.4–5.9	61
10	0.0932	0.0583	−0.0514	3.2–10.6	3.9–5.4	27
	0.0903	0.0579	−0.0829	3.2–10.9	4.1–5.2	30
	0.1087	0.0635	0.6342	3.1–11.1	3.2–6.4	50
11	0.0809	0.0505	−0.0561	3.0–10.9	3.5–6.0	64
	0.0850	0.0499	0.5500	3.1–9.8	3.7–5.9	37
12	0.0588	0.0359	−0.0743	3.0–10.1	3.6–6.5	83
	0.0580	0.0358	−0.0658	2.2–10.7	3.6–6.4	64

^{a}Negative values refer to millimole excess of OH$^-$.

Synthesis of Complexes. All reagents (reagent grade) were used without further purification.

[Ni([21]aneN$_7$)](ClO$_4$)$_2$. A solution of Ni(ClO$_4$)$_2$·6H$_2$O (0.1 mmol) in 2 cm^3 of water was added to a boiling solution of [21]aneN$_7$ (0.1 mmol) in 3 cm^3 of water. The resulting blue solution was cooled at room temperature, and solid NaClO$_4$·H$_2$O was added in small portions up to incipient crystallization of the complex. The product formed was redissolved by heating and the solution kept at room temperature. Over a period of a few days blue prismatic crystals of the complex grew. The crystals were filtered out, washed with methanol, and dried in vacuo (yield 79%). (*Caution!* Perchlorate salts of metal complexes can be explosive and must be handled with care. Compounds should not be heated when in the solid state.) Anal. Calcd for C$_{14}$H$_{35}$Cl$_2$N$_7$NiO$_8$: C, 30.08; H, 6.31; N, 17.54. Found: C, 30.1; H, 6.3; N, 17.4. Selected crystals of this sample were used for X-ray analysis.

[Ni$_2$([24]aneN$_8$)](ClO$_4$)$_4$. A solution of Ni(ClO$_4$)$_2$ (0.2 mmol) in 5 cm^3 of dry methanol was added to a boiling solution of [24]aneN$_8$ (0.1 mmol) in 15 cm^3 of dry methanol, under nitrogen atmosphere. The solution became light blue as 0.1 mmol of Ni(ClO$_4$)$_2$ was added and then turned brownish red by addition of a further 0.1 mmol. The complex immediately separated, in quantitative yield, as a brownish red microcrystalline powder. This product was filtered out, washed with absolute methanol, and dried in vacuo at 50 °C. Anal. Calcd for C$_{16}$H$_{40}$Cl$_4$N$_8$Ni$_2$O$_{16}$: C, 22.35; H, 4.69; N, 13.03. Found: C, 22.2; H, 4.7; N, 12.9.

[Ni$_2$([27]aneN$_9$)](ClO$_4$)$_4$·3H$_2$O. A water solution of [27]aneN$_9$·9HCl (0.1 mmol) and Ni(ClO$_4$)$_2$·6H$_2$O (0.2 mmol) was neutralized, while boiling, by addition of a NaOH solution. Then 8 g of NaClO$_4$·H$_2$O was added to the pale blue solution (30 cm^3) and the volume reduced at 15 cm^3. On cooling of the solution, pale blue crystals of the complex formed. The product was filtered out, washed rapidly with water/methanol (50/50) mixture and then with methanol, and dried in vacuo (yield 57%). Anal. Calcd for C$_{18}$H$_{51}$Cl$_4$N$_9$Ni$_2$O$_{19}$: C, 22.56; H, 5.37; N, 13.17. Found: C, 22.7; H, 5.4; N, 13.1.

[Ni$_2$([30]aneN$_{10}$)](ClO$_4$)$_4$·2H$_2$O. A water solution of [30]aneN$_{10}$·10HCl (0.1 mmol) and Ni(ClO$_4$)$_2$·6H$_2$O (0.2 mmol) was neutralized, while boiling, by addition of a NaOH solution. To the resulting pale blue solution (20 cm^3) was added 10 g of NaClO$_4$·H$_2$O in small portions, maintaining the heating. On standing of the solution over a period of some hours, pale blue crystals of the complex separated. The product was filtered out, washed with methanol, and dried in vacuo (yield 83%). Anal. Calcd for C$_{20}$H$_{54}$Cl$_4$N$_{10}$Ni$_2$O$_{18}$: C, 24.46; H, 5.54; N, 14.26. Found: C, 24.6; H, 5.5; N, 14.3.

[Ni$_2$([30]aneN$_{10}$)](NO$_3$)$_4$·2H$_2$O. Crystals of this compound suitable for X-ray analysis were obtained by recrystallizing [Ni$_2$([30]aneN$_{10}$)]-(ClO$_4$)$_4$·2H$_2$O from a water solution of NaNO$_3$ in 2 mol dm^{-3} concentration. These pale blue crystals, formed over a period of few days, were filtered out, washed with a water/methanol (50/50) mixture and then with methanol, and dried in vacuo. Anal. Calcd for C$_{20}$H$_{54}$N$_{14}$Ni$_2$O$_{14}$: C, 28.87; H, 6.54; N, 23.57. Found: C, 29.0; H, 6.5; N, 23.6.

[Ni$_2$([33]aneN$_{11}$)](ClO$_4$)$_4$·H$_2$O. A water solution of [33]aneN$_{11}$·11HCl (0.1 mmol) and Ni(ClO$_4$)$_2$·6H$_2$O (0.2 mmol) was neutralized, while boiling, by addition of a NaOH solution. On cooling, the complex separated as a microcrystalline pale blue powder. The product was filtered

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Table II. Crystallographic Data for $[Ni_2([30]aneN_{10})(H_2O)_2](NO_3)_4$

formula	$C_{20}H_{54}N_{14}Ni_2O_{14}$	space gp	$P2_1/a$
mol wt	864.17	D_c, g cm^{-3}	1.63
a, Å	13.894 (2)	radiation	graphite-monochromated
b, Å	9.386 (6)	$(\lambda, Å)$	Mo Kα (0.7107)
c, Å	14.100 (2)	temp, °C	25
β, deg	113.13 (2)	μ, cm^{-1}	11.4
V, Å^3	1690.9 (8)	R^a	0.065
Z	2	$R_w{}^b$	0.056

$^a R = \sum\|F_o\| - F_c\|/\sum|F_o|.$ $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}.$

out, washed with methanol, and dried in vacuo (yield 52%). Anal. Calcd for $C_{22}H_{57}Cl_4N_{11}Ni_2O_{17}$: C, 26.24; H, 5.71; N, 15.30. Found: C, 26.1; H, 5.7; N, 15.3.

$[Ni_2([36]aneN_{12})](ClO_4)_4$. A solution (20 cm^3) of [36]aneN$_{12}$ (0.1 mmol) was heated under reflux, and then 10 cm^3 of aqueous solution of Ni(ClO$_4$)$_2$·6H$_2$O (0.2 mmol) was added in a few portions. NaClO$_4$·H$_2$O (2 g) was added to the pale blue solution and the volume reduced by heating up the solution to cause crystallization of the complex. The product, which separated out on cooling, was filtered out, washed with methanol, and dried in vacuo (yield 61%). Anal. Calcd for $C_{24}H_{60}Cl_4N_{12}Ni_2O_{16}$: C, 27.93; H, 5.86; N, 16.29. Found: C, 27.7; H, 5.9; N, 16.3.

Emf Measurements. The potentiometric titrations were carried out by using equipment (potentiometer, cell, buret, stirrer, microcomputer, etc.) that has been fully described.[20] The reference electrode was Ag/AgCl in saturated KCl solution. The glass electrode (Orion Model 91-01) was calibrated, as a hydrogen concentration probe, by titration of well-known amounts of HCl acid with NaOH solution, determining the equivalent point by the Gran method,[21] which provides the standard potential of the cell ($E°$) and the ionic product of water (pK_w = 13.73 ± 0.01 at 25 °C in 0.15 mol dm^{-3} of NaClO$_4$). The protonation constants of the ligands here studied were already reported.[9–13] In Table I the initial concentrations of the reagents and the pH range explored for each titration are reported. The computer program SUPERQUAD[22] was used to calculate the stability constants. Only the experimental points related to the pH range in which complex formation occurs (Table I) were processed in the last refinements. In order to reach the equilibrium, several minutes were waited between each emf reading. Moreover, several measurements were made both in formation and in dissociation (from acid to alkaline solutions and vice versa) in order to test for reversibility of the reactions. The titration curves for each system were treated either as a single set or as separate curves without significant variation in the values of the stability constants. Furthermore, the sets of data were merged and treated simultaneously to give the final stability constants. The species models proposed and accepted in the computer treatment of the potentiometric data were those that could be justified on the basis of established principles of coordination equilibria in solution. Tentative species introduced to test the consistency of other models, following the procedure we have previously reported in ref 11, footnote 18, were rejected. In the case of [27]aneN$_9$, [30]aneN$_{10}$, [33]aneN$_{11}$, and [36]aneN$_{12}$, very slow reactions of formation of the complexes were observed in alkaline solutions. Attempts to follow these reactions by increasing the temperature were not successful. Under these conditions the attainment of equilibrium was doubtful and, consequently, statistical analysis of the relevant potentiometric data could provide erroneous interpretations. For this reason, restriction to the pH range in which the attainment of equilibrium was proved was adopted in calculation, although the formation of hydroxodinickel(II) complexes was observed.

Spectrophotometric Measurements. The electronic spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer equipped with 1-cm cells thermostated at 25 °C. Diffuse-reflectance spectra were also recorded with the same apparatus on Nujol mull samples supported on filter paper.

Magnetic Measurements. Magnetic susceptibility measurements were carried out at room temperature by using a pendulum-type apparatus.[23]

Collection and Reduction of X-ray Intensity Data. **[Ni$_2$([30]-aneN$_{10}$)(H$_2$O)$_2$](NO$_3$)$_4$.** A light blue crystal of this compound, of approximate dimensions 0.2 × 0.3 × 0.4 mm, was epoxied to a glass fiber and mounted on an Enraf-Nonius CAD-4 X-ray diffractometer. A summary of crystallographic data is reported in Table II. Unit cell

Table III. Positional Parameters (×10^4) and Thermal Parameters (×10^3) for $[Ni_2([30]aneN_{10})(H_2O)_2](NO_3)_4{}^a$

atom	x/a	y/b	z/c	U_{eq}/U_{iso}, Å^2
Ni	8927 (1)	4531 (1)	2743 (1)	27 (1)
O1	10457 (4)	4956 (5)	2753 (4)	39 (4)
C1	9911 (6)	7390 (8)	3988 (6)	37 (6)
N1	8922 (4)	6570 (6)	3512 (5)	32 (4)
C2	8196 (6)	7481 (9)	2706 (6)	36 (5)
C3	8367 (7)	7279 (9)	1720 (6)	41 (6)
N2	8280 (5)	5769 (6)	1418 (5)	33 (4)
C4	7200 (6)	5265 (10)	807 (6)	45 (6)
C5	6648 (6)	4802 (9)	1507 (6)	46 (6)
N3	7347 (5)	3996 (7)	2420 (5)	31 (4)
C6	7255 (6)	2423 (9)	2239 (6)	37 (6)
C7	7888 (6)	1915 (9)	1607 (6)	40 (6)
N4	8919 (5)	2595 (7)	1974 (5)	33 (4)
C8	9739 (6)	1679 (9)	2718 (6)	37 (5)
C9	9695 (6)	1702 (8)	3760 (6)	37 (5)
N5	9663 (5)	3209 (6)	4073 (4)	26 (4)
C10	9305 (6)	3346 (8)	4935 (6)	32 (5)
N6	2668 (5)	4566 (8)	5002 (5)	41 (2)
O11^b	3186 (8)	4776 (14)	5916 (7)	51 (3)
O21^b	2799 (12)	5296 (13)	4339 (9)	66 (4)
O31^b	1945 (7)	3644 (10)	4736 (11)	44 (3)
O12^c	13164 (34)	5152 (34)	4541 (27)	38 (12)
O22^c	11882 (25)	3806 (38)	4395 (40)	45 (12)
O32^c	13016 (33)	4459 (54)	5959 (29)	48 (14)
N7	9416 (6)	3478 (9)	−463 (7)	53 (2)
O41^d	8801 (10)	4434 (17)	−428 (11)	74 (5)
O51^d	9710 (10)	2650 (15)	305 (10)	63 (5)
O61^d	9580 (10)	3282 (14)	−1238 (10)	60 (5)
O42^e	9132 (12)	3593 (16)	231 (12)	73 (5)
O52^e	8953 (11)	4183 (16)	−1311 (12)	74 (6)
O62^e	10169 (12)	2790 (16)	−459 (13)	86 (6)

^{a} Estimated standard deviations in the last significant figures are in parentheses. $^{b–e}$ Population parameters for the indicated atoms are as follows: (b) 0.72%; (c) 0.28%; (d) 0.51%; (e) 0.49%.

parameters were determined by least-squares refinement of diffractometer setting angles of 25 carefully centered reflections. Intensities were corrected for Lorentz, polarization, and absorption effects. During data collection, three reflections were monitored periodically to check for the stability of the diffractometer and of the crystal. The structure was solved by the heavy-atom technique, which showed the position of the nickel atom. Subsequent Fourier maps showed all non-hydrogen atoms. Refinement was performed by means of the full-matrix least-squares method. The function minimized was $\sum w(|F_o|-|F_c|)^2$, with $w = a/\sigma^2(F)$, where a is an adjustable parameter. Hydrogen atoms, except those of the water molecules, were included in calculated positions with an overall temperature factor U of 0.05. Anisotropic temperature factors were used for non-hydrogen atoms of the complexed cation, whereas the hydrogen atoms and the atoms of nitrate ions were refined isotropically. Two different models were found for each independent nitrate ion. Population parameters were refined for the oxygen atoms of these anions. All calculations were performed on an IBM 85 80 computer with the SHELX-76[24] set of programs that use the analytical approximation for the atomic scattering factors and anomalous dispersion corrections for all the atoms from ref 25. The molecular plot was produced by the program ORTEP.[26] The final atomic coordinates for non-hydrogen atoms are listed in Table III.

[Ni([21]aneN$_7$)](ClO$_4$)$_2$. Cell parameters were determined from the setting angles of 25 reflections, measured on a Enraf-Nonius CAD4 automatic diffractometer, Mo Kα radiation, by using a prismatic blue crystal of the compound having approximate dimensions 0.2 × 0.2 × 0.3 mm. The crystals are orthorhombic, space group $P22_12_1$, with a = 9.692 (4) Å, b = 14.872 (1) Å, c = 32.366 (3) Å, V = 4665.1 (3) Å^3, Z = 8, D_c = 1.57 g cm^{-3}, and λ(Mo Kα) = 0.710 69 Å. The intensities were collected, on the same diffractometer, in the range 5 ≤ 2θ ≤ 50° by using graphite-monochromated Mo Kα radiation and the ω–2θ scan technique. Variable scan widths of (0.70 + 0.35 tan ω)° were used with a scan speed of 0.06 deg s^{-1}. Three standard reflections were measured periodically

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Table IV. Selected Bond Distances (Å) and Angles (deg) for $[Ni_2([30]aneN_{10})(H_2O)_2](NO_3)_4$

		Distances		
Ni–N1	2.202 (6)[a]	Ni–N2	2.081 (6)
Ni–N3	2.120 (7)	Ni–N4	2.114 (7)
Ni–N5	2.143 (6)	Ni–O1	2.158 (6)

		Angles		
N1–Ni–N2	82.7 (2)	N1–Ni–N3	96.2 (3)
N1–Ni–N4	178.8 (2)	N1–Ni–N5	99.5 (2)
N2–Ni–N3	83.9 (3)	N2–Ni–N4	96.1 (3)
N2–Ni–N5	176.5 (3)	N3–Ni–N4	83.7 (3)
N3–Ni–N5	98.6 (2)	N4–Ni–N5	81.7 (2)
O1–Ni–N1	91.7 (2)	O1–Ni–N2	88.8 (2)
O1–Ni–N3	168.5 (2)	O1–Ni–N4	88.2 (2)
O1–Ni–N5	88.3 (2)		

[a] Estimated standard deviations in the last significant figures are in parentheses.
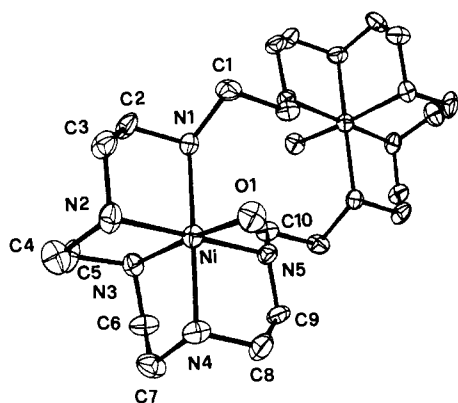
Figure 1. Perspective view of the centrosymmetric cation $[Ni_2([30]-aneN_{10})(H_2O)_2]^{4+}$. Only symmetry-independent atoms are labeled.

to check for the stability of the crystal and of the diffractometer. The 2395 reflections having $I \geq 3\sigma(I)$ (from a total of 4721 reflections) were considered observed and used in the structure analysis. The intensities were corrected for absorption and for Lorentz effects. Atomic scattering factors were taken from ref 25. The structure was solved by the heavy-atoms method, which gave the positions of the two independent nickel atoms of two different molecules. Successive F_o Fourier synthesis gave the positions of the atoms of the four perchlorate anions and of the non-hydrogen atoms of one $[Ni([21]aneN_7)]^{2+}$ cation. Any attempt to localize the atoms of the macrocycle in the second complex cation was unsuccessful, on account of the very high degree of disorder of this molecule. For this reason, after F_o and ΔF Fourier synthesis, the structure analysis was interrupted (R factor about 20%).

Results and Discussion

$[Ni_2([30]aneN_{10})(H_2O)_2](NO_3)_4$. The structure of the compound consists of centrosymmetric binuclear $[Ni_2([30]aneN_{10})(H_2O)_2]^{4+}$ units and disordered ' uncoordinated nitrate ions. In the binuclear unit each nickel atom is coordinated by five nitrogen atoms of the macrocycle and one water molecule, forming a distorted octahedron (Figure 1). Table IV lists selected interatomic distances and angles. The angles around the nickel(II) ion are somewhat distorted from the ideal octahedral angles with N1–Ni–N5 expanded to 99.5 (2)°, N1 and N5 being the bridgehead atoms between a complexed subunit and its symmetry related counterpart, and N3–Ni–O1 reduced to 168.5 (3)°. The Ni–O distance of 2.158 (6) Å appears to be normal. The Ni–N distances are in the range 2.08–2.20 Å, the two Ni–N bridgehead distances being significantly the longest. The Ni–N and Ni–O bond distances agree with those previously observed for the *cis*-[Ni(cyclam)(H_2O)_2]^{2+} complexed cation[27] (average Ni–N = 2.100 (9) Å; Ni–O = 2.140 (1), 2.130 (2) Å). The N–C and C–C bond distances (average N–C = 1.48 (1) Å; average C–C = 1.52 (3) Å) are essentially equal to those found for other high-spin nickel(II) complexes of tetraazacycloalkanes[27,28] and for the analogous
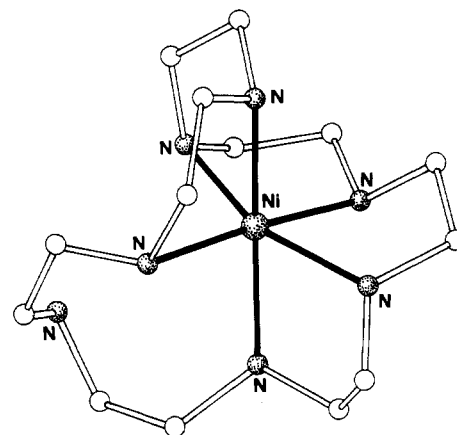
Figure 2. Schematic representation of the cation $[Ni([21]aneN_7)]^{2+}$.
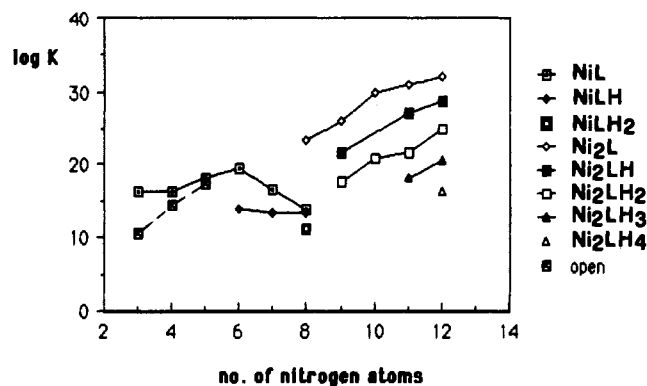
Figure 3. Logarithms of the formation constants relative to the general reaction $pNi^{2+} + H_qL^{q+} = (Ni_pH_qL)^{(q+2p)+}$ for L = $[3k]aneN_k$ (k = 3–12) polyazacycloalkanes versus the number of nitrogen donor atoms. As a comparison, the formation constants of nickel(II) complexes with some open-chain polyamines have been reported (dashed line). Charges have been omitted for clarity.

dinuclear complexes of $[30]aneN_{10}$ with copper(II),[10] zinc(II),[13] and cadmium(II)[14] ions. The 10-dentate ligand, in the dinuclear $[Ni_2([30]aneN_{10})(H_2O)_2]^{4+}$ unit, involves all its nitrogen atoms in coordination to the nickel(II) ions, which lie 6.536 (4) Å apart from each other, forming five-membered chelate rings in the gauche configuration. Also, the ethylenic chains, bridging the two complexed subunits, are in the gauche configuration with respect to the bridgehead nitrogens. Analysis of the interatomic bond angles (Table IV) shows that no particular strain in the macrocyclic framework is brought about by coordination to the nickel(II) ions and by formation of several hydrogen bonds between the secondary nitrogens of the ligand and the oxygens of the nitrate ions.

$[Ni([21]aneN_7)](ClO_4)_2$. The structure consists of two independent $[Ni([21]aneN_7)]^{2+}$ cations and of uncoordinated perchlorate anions. The positions of the atoms of one complex cation were determined, whereas for the second cation only the position of the nickel atom was determined (see Experimental Section). In the resolved complex cation, the nickel(II) ion appears to be 6-coordinated by six nitrogen atoms of the 7-dentate macrocycle, one nitrogen remaining uncoordinated in an eight-membered chelate ring (Figure 2). No more results are reported on account of the incompletely determined structure.

Solution Equilibria of Nickel(II) Complexes. The stability constants related to the formation in aqueous solution of nickel(II) complexes with large polyazacycloalkanes of the series $[3k]aneN_k$ (k = 7–12) have been reported in Table V. In Figure 3 the logarithms of the stability constants, relative to the general reaction $pNi^{2+} + H_qL^{q+} = Ni_pH_qL^{(q+2p)+}$ (L = $[3k]aneN_k$ for k = 7–12), are plotted versus the number of nitrogen donor atoms present

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Table V. Logarithms of the Formation Constants of Nickel(II) Complexes of Macrocycles [3k]aneNk (k = 7–12) in 0.15 mol dm⁻³ NaClO₄ Aqueous Solution at 25 °C

reacn[a]	[21]aneN7	[24]aneN8	[27]aneN9	[30]aneN10	[33]aneN11	[36]aneN12
				log k		
Ni + L = NiL	16.563 (5)[b]	13.94 (5)				
Ni + L + H = NiLH	23.172 (3)	23.03 (4)				
Ni + L + 2H = NiLH₂		30.26 (1)				
2Ni + L = Ni₂L		23.30 (1)	26.24 (1)	30.02 (3)	31.07 (1)	32.09 (3)
2Ni + L + H = Ni₂LH			31.46 (1)		36.98 (1)	38.62 (2)
2Ni + L + 2H = Ni₂LH₂			36.73 (1)	40.17 (2)	40.98 (6)	44.46 (1)
2Ni + L + 3H = Ni₂LH₃					46.44 (1)	48.95 (2)
2Ni + L + 4H = Ni₂LH₄						53.42 (2)
2Ni + L + H₂O = Ni₂L(OH) + H		13.19 (3)	c	c	c	c
NiL + H = NiLH	6.61	9.09				
NiLH + H = NiLH₂		7.59				
Ni₂L + H = Ni₂LH			5.22		5.91	6.53
Ni₂LH + H = Ni₂LH₂			5.27		4.00	5.84
Ni₂LH₂ + H = Ni₂LH₃					5.46	3.99
Ni₂LH₃ + H = Ni₂LH₄						4.47

[a] Charges omitted for clarity. [b] Values in parentheses are standard deviations in the last significant figure. [c] Hydroxodinickel(II) complexes have been detected in alkaline solution for this ligand.

in each macrocycle. In the same figure we have also reported the logarithms of the stability constants previously determined for the formation of the nickel(II) complexes of [9]aneN₃,[29] [12]-aneN₄,[30] [15]aneN₅,[31] and [18]aneN₆.[31] Although these stability constants have been determined in different experimental conditions and by different techniques, there is a clear trend showing increasing stability from the mononuclear nickel(II) complex of the smallest [9]aneN₃ to that of 6-dentate [18]aneN₆. With the 7-dentate [21]aneN₇ the stability of the nickel(II) complex falls down and further decreases with [24]aneN₈. As 6-coordination has been reached by the [18]aneN₆ ligand,[31–33] the decrease in stability showed by [21]aneN₇ could be due either to the involvement of only five donor atoms of the 7-dentate macrocyclic ligand in the coordination to the nickel(II) ion or to the formation of an eight-membered chelate ring, which lowers the overall complex stability. The X-ray study on the [Ni([21]aneN₇)]-(ClO₄)₂ crystalline compound shows that the nickel(II) cation is coordinated by six nitrogen atoms of [21]aneN₇ (see Figure 2), supporting the second hypothesis. Furthermore, the observation that only a monoprotonated form of [Ni([21]aneN₇)]²⁺ is present in solution (Table V) supports the same hypothesis.

Six-coordination of [24]aneN₈ in the mononuclear complex of nickel(II) should give rise to the formation of two 8-membered chelate rings or an 11-membered one, in which two nitrogen atoms of the ligand remain uncoordinated. Both these possibilties can account for the lower stability of this complex with respect to that found for [21]aneN₇, but as previously observed for the cadmium(II) complex,[14] the similarity of the stepwise protonation constants of [Ni([24]aneN₈)]²⁺ to form [Ni(H[24]aneN₈)]³⁺ and [Ni(H₂[24]aneN₈)]⁴⁺ gives strength to the formation of two eight-membered chelate rings each disposed far from the other.

We can observe that the trend of increasing stability of mononuclear nickel(II) complexes with the small macrocycles of this series is also followed by noncyclic polyamines. In Figure 3 have been reported (dashed line) the logarithms of the stability constants relative to the nickel(II) complex formation with the ligands den, trien, and tetren, taken from ref 29, which can be considered the noncyclic counterparts of the cyclic [9]aneN₃, [12]aneN₄, and [15]aneN₅, respectively. The stability constants for the noncyclic ligands are lower than those for their cyclic counterparts, the differences in stability becoming narrower as the number of nitrogen donors increases. As previously observed for cadmium(II),[14]
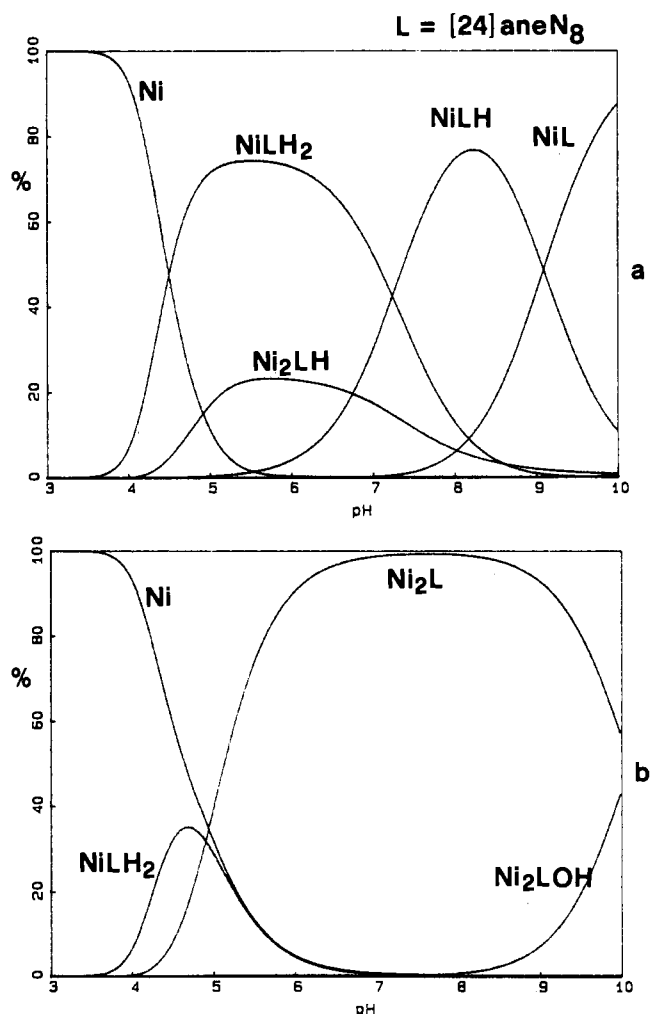
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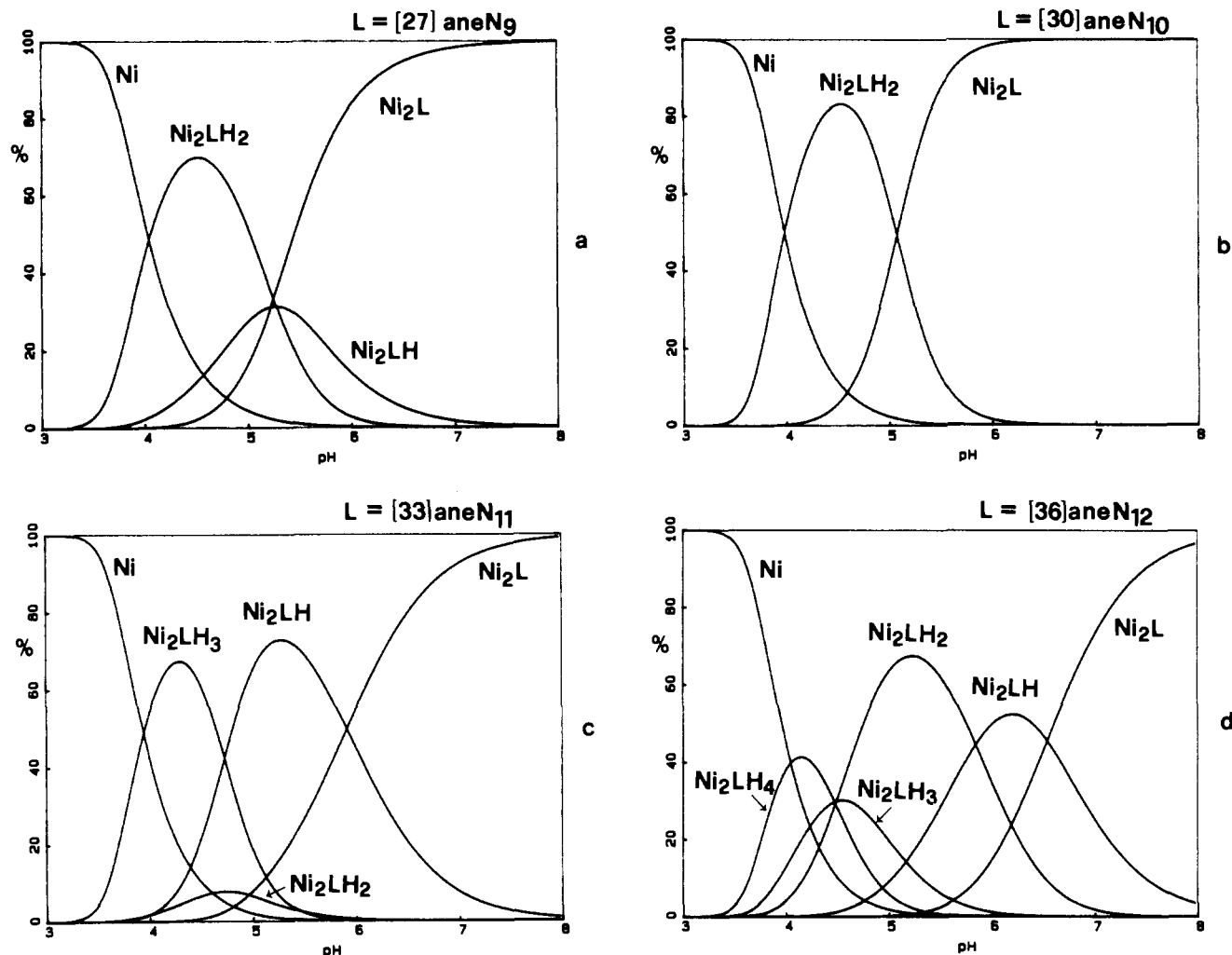

Figure 4. Calculated distribution of the equilibrium species formed in the system Ni²⁺/[24]aneN₈ in 0.15 mol dm⁻³ NaClO₄–water solution at 25 °C: (a) Ni²⁺ and [24]aneN₈ (10⁻³ mol.dm⁻³) (b) Ni²⁺ (2 × 10⁻³ mol dm⁻³) and [24]aneN₈ (10⁻³ mol dm⁻³). The species [Ni₂([24]aneN₈)-OH]³⁺ (concentration <1%) and [Ni(H[24]aneN₈)]³⁺ (concentration <0.5%) are also formed in the systems a and b, respectively. Charges have been omitted for clarity.

the "macrocyclic effect" in mononuclear complexes vanishes as the number of donor atoms and the flexibility of the cyclic ligand increases.

[24]aneN₈ is able to bind a second nickel(II) ion, forming the binuclear complex [Ni₂([24]aneN₈)]⁴⁺. The tendency of this ligand to form both mononuclear and binuclear complexes has

Figure 5. Calculated distribution of the equilibrium species formed in the systems $Ni^{2+}/[27]aneN_9$ (a), $Ni^{2+}/[30]aneN_{10}$ (b), $Ni^{2+}/[33]aneN_{11}$ (c), and $Ni^{2+}/[36]aneN_{12}$ (d) in 0.15 mol dm^{-3} NaClO$_4$-water solution at 25 °C: $[Ni^{2+}] = 2 \times 10^{-3}$ mol dm^{-3}; [ligand] = 10^{-3} mol dm^{-3}. Charges have been omitted for clarity.

already been observed in the study of the solution equilibria with zinc(II)[13] and cadmium(II)[14] ions, while only binuclear complexes were observed with copper(II).[7] The logarithm of the stability constant related to the reaction of addition of a nickel(II) ion to the mononuclear $[Ni([24]aneN_8)]^{2+}$ species to form $[Ni_2([24]aneN_8)]^{4+}$ (log K = 9.36) clearly shows that the ability of $[24]aneN_8$ to form binuclear complexes is much more marked in the case of nickel(II) than with cadmium(II) (log K = 3.69).[14] In Figure 4a,b have been reported the distribution of the complexes formed as a function of pH, calculated by using the equilibrium data obtained for the system nickel(II)/$[24]aneN_8$, in 1:1 (Figure 4a) and 2:1 (Figure 4b) molar ratios. In 1:1 molar ratio solutions, $[Ni_2([24]aneN_8)]^{4+}$ is a minor species (Figure 4a), while it becomes of major importance when the molar ratio is 2:1, being the only species in solution over a wide pH range (Figure 4b). On the other hand, a different behavior was observed in the case of the cadmium(II) ion, for which the ability of $[24]aneN_8$ to form binuclear complexes is not so large as to prevent precipitation of cadmium(II) hydroxide in 2:1 molar ratio alkaline solutions.[14]

The dinucleating ability toward nickel(II) ion presented by the large macrocycles $[24]aneN_8$, $[27]aneN_9$, $[30]aneN_{10}$, $[33]aneN_{11}$, and $[36]aneN_{12}$ grows rapidly at such extent that the last four macrocycles form, under the experimental conditions employed, only binuclear complexes. The formation of these species occurs at low pH values where many protonated dinickel(II) complexes are formed (Figure 5a–d). As the pH increases, the unprotonated dinickel(II) complexes $[Ni_2(L)]^{4+}$ are rapidly formed, becoming unique in alkaline solutions (Figure 5a–d). At higher pH values hydroxo–dinuclear species have been detected, but the great slowness of the reaction of formation of these complexes did not

allow the determination of the stability constants (see Experimental Section).

All the values of the stability constants determined for the binuclear species increase with the number of the nitrogen atoms present in the macrocyclic framework, accordingly with an increasing number of donor atoms involved in the coordination to the two nickel(II) ions. It is noticeable that all these constants fall between those of the stability constants, observed under the same experimental conditions, for the corresponding species of zinc(II)[12,13] and cobalt(II)[34] (lower values) and those observed for copper(II)[7–11] (higher values), following an order that could be expected on the basis of an Irving–Williams series. The experimental results are in agreement with the involvement of all the nitrogen atoms of the ligands in the coordination to the nickel(II) ions, the values of the stepwise protonation constants of the $[Ni_2L]^{4+}$ species accounting for the detachment of coordinated nitrogen atoms. The third protonation constant of the dinickel(II) complex of $[33]aneN_{11}$ and the fourth protonation constant of the corresponding complex of $[36]aneN_{12}$ are somewhat larger than the second and the third ones, respectively. This feature has already been observed in the dicadmium(II) complex of $[27]aneN_9$ and has been ascribed to the breaking of two metal–nitrogen donor bonds induced by protonation of one nitrogen atom of the ligand. Subsequent protonation takes place on this unbonded nitrogen.[14]

An interesting question was posed about the dimetal(II) complexes of $[30]aneN_{10}$ ligand concerning the distribution of the

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Table VI. Electronic Spectral Data for Nickel(II) Complexes of [3k]aneN$_k$ (k = 6–12) Ligands

compd	λ_{max} (ϵ)^a		
(Ni[18]aneN$_6$)$^{2+}$(aq)	835 (19)^b	530 (11)^b	345 (11)^b
(Ni[21]aneN$_7$)$^{2+}$(aq)	940 (15.7)	552 (11.2)	363 (14.3)
(NiH[21]aneN$_7$)$^{3+}$(aq)	940 (16.5)	554 (11.3)	363 (14.5)
(Ni[21]aneN$_7$)(ClO$_4$)$_2$(s)	948	555	361
(Ni$_2$[24]aneN$_8$)$^{4+}$(aq)	949 (9.8)	571 (6.1)	362 (12.5)
(Ni$_2$[24]aneN$_8$)(ClO$_4$)$_4$(s)	466		
(Ni$_2$[27]aneN$_9$)$^{4+}$(aq)	955 (9.4)	551 (6.0)	363 (12.1)
(Ni$_2$[27]aneN$_9$)(ClO$_4$)$_4$·3H$_2$O(s)	950	550	358
(Ni$_2$[30]aneN$_{10}$)$^{4+}$(aq)	965 (9.3)	557 (5.9)	357 (11.4)
(Ni$_2$[30]aneN$_{10}$)(ClO$_4$)$_4$·2H$_2$O(s)	976	583	343
(Ni$_2$[33]aneN$_{11}$)(ClO$_4$)$_4$·H$_2$O(s)	929	563	355
(Ni$_2$[33]aneN$_{11}$)$^{4+}$(aq)	928 (9.5)	557 (6.0)	348 (11.8)
(Ni$_2$[36]aneN$_{12}$)$^{4+}$(aq)	930 (10.1)	548 (6.1)	345 (11.6)
(Ni$_2$[36]aneN$_{12}$)(ClO$_4$)$_4$(s)	920	544	344

^{a} λ_{max} given in nm, ϵ in dm^3 mol^{-1} cm^{-1}. Molar extinction coefficients are given for a single nickel(II) ion. ^{b} Taken from ref 33.

nitrogen donor atoms between the two metal ions. The crystal structure of the complex [Cd$_2$([30]aneN$_{10}$)Cl$_2$]$^{2+}$ showed the 10-dentate [30]aneN$_{10}$ wrapping around one of the two cadmium(II) ions, coordinated by six donors of the ligand, and leaving only four nitrogens available for coordination to the second one.[14] Furthermore, [30]aneN$_{10}$ had already shown an asymmetrical coordination in [Zn$_2$([30]aneN$_{10}$)NCS](ClO$_4$)$_3$, in which one zinc(II) ion is coordinated by five nitrogen donor atoms of the macrocycle and the second one is bound by four donor atoms of the ligand and one thiocyanate anion, only nine nitrogens of the macrocycle involved.[12] On the other hand, the ligand disposes its donor atoms in a symmetrical fashion in [Cu$_2$([30]aneN$_{10}$)-Cl$_2$](ClO$_4$)$_3$·4H$_2$O, although in this case only eight nitrogens are involved in coordination to the copper(II) ions and one nitrogen is protonated.[10] The crystal structure of the centrosymmetric [Ni$_2$([30]aneN$_{10}$)(H$_2$O)$_2$]$^{4+}$ complexed cation, in which each nickel(II) ion is coordinated by five nitrogens of the macrocycle and one water molecule, answers the question on the ability of this ligand to distribute all its donor atoms between two symmetric coordination sites. Crystallographic data, up to now available for such complexes,[7,10,12–14] clearly show to what extent large [3k]-aneN$_k$ macrocyclic ligands can adapt themselves to different stereochemical requirements.

Spectral and Magnetic Properties. The electronic spectral data for the nickel(II) complexes of [3k]aneN$_k$ (k = 6–12) polyazacycloalkanes obtained, both in solid state and in aqueous solution, in the range 300–1200 nm are reported in Table VI. Data related to [Ni([18]aneN$_6$)]$^{2+}$(aq) have been taken from ref 33. The complex [Ni([21]aneN$_7$)]$^{2+}$ presents, in aqueous solution, a three-band electronic spectrum typical for an octahedral high-spin nickel(II) chromophore, analogous to that reported for [Ni([18]aneN$_6$)]$^{2+}$(aq), in which full octahedral coordination of the 6-dentate ligand to nickel(II) is also reached.[31,33] The main difference between the electronic spectral features of these two complexes is the low-energy shift experienced by [Ni([21]-aneN$_7$)]$^{2+}$(aq) with respect to [Ni([18]aneN$_6$)]$^{2+}$(aq), the stronger ligand field interaction shown by the latter complex coinciding with its higher thermodynamic stability. As above noted, the structure of [Ni([21]aneN$_7$)]$^{2+}$ can be derived from that of [Ni([18]aneN$_6$)]$^{2+}$ by replacing an ethylenic chain of the ligand

by a five-termed one, containing an uncoordinated nitrogen, giving rise to a large eight-membered ring, which reduces the overall interaction of the ligand with the nickel(II) ion. Protonation of this uncoordinated nitrogen atom does not affect the electronic spectral feature of the [Ni([21]aneN$_7$)]$^{2+}$(aq) complex. An analogous spectrum has been obtained in the solid state for [Ni([21]aneN$_7$)](ClO$_4$)$_2$. The macrocycle [24]aneN$_8$ forms, in water solution, a dinickel(II) complex whose electronic spectrum is again characteristic for a paramagnetic octahedral nickel(II) species; the nickel(II) ions bound to the 8-dentate ligand complete their coordination spheres with water molecules. However, in the handling of solutions containing this blue complex, a fleeting appearance of a reddish species was sometimes observed. The formation of this species was favored by increasing temperature or by the presence of high concentrations of inert electrolyte or of nonaqueous solvents. The isolation of the dark orange dia-magnetic [Ni$_2$([24]aneN$_8$)](ClO$_4$)$_4$ solid compound (see synthesis of compounds) explained these observations. The solid complex presents an electronic spectrum, typical of a square low-spin nickel(II) chromophore, with a single band in the d–d region having a maximum at 466 nm (Table VI). This compound dissolves in water to produce solutions that initially maintain the spectral features of the low-spin square complex and then completely convert, over a period of some hours, to possessing the spectral features of the high-spin blue form. In the case of [27]aneN$_9$, [30]aneN$_{10}$, [33]aneN$_{11}$, and [36]aneN$_{12}$, typical spectra for octahedral high-spin nickel(II) complexes have been again observed. The spectral features for solid complexes of each ligand are respectively similar to that of their solutions. This suggests that no substantial changes in the coordination sphere of nickel(II) ions take place, in solution, with respect to the solid complexes. The electronic spectra, the microanalysis of solid complexes, and the crystal structure of [Ni$_2$([30]-aneN$_{10}$)(H$_2$O)$_2$](NO$_3$)$_4$ agree with the involvement of water molecules, in completing the octahedral coordination sphere of the nickel(II) ions, bound to these macrocycles. So, in [Ni$_2$-([27]aneN$_9$)](ClO$_4$)$_4$·3H$_2$O, the ligand would coordinate all its nine nitrogen donors to the two nickel(II) ions, leaving three coordination sites available for water molecules. Likewise, one molecule of water must be coordinated by one of the two nickel(II) ions enclosed in the 11-dentate [33]aneN$_{11}$, while the 12-dentate [36]aneN$_{12}$ fulfills the coordination sphere of both nickel(II) ions.