

starting 16-electron square-planar complexes, as dictated by the trans-activating chloride or phosphine ligands. In other words, the development of a carbanionic character in Pt-C could help β -elimination.

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Registry No. *cis*-[Pt(PEt₃)₂(CH₃)Cl], 22289-46-9; *trans*-[Pt(PEt₃)₂(CH₃)Cl], 13964-96-0; *cis*-[Pt(PEt₃)₂(CH₂CH₃)Cl], 61009-44-7;

trans-[Pt(PEt₃)₂(CH₂CH₃)Cl], 54657-72-6; *cis*-[Pt(PEt₃)₂(CD₂CD₃)Cl], 117605-15-9; *trans*-[Pt(PEt₃)₂(CD₂CD₃)Cl], 97548-99-7; *cis*-[Pt(PEt₃)₂(CH₂CH₂CH₃)Cl], 89362-98-1; *trans*-[Pt(PEt₃)₂(CH₂CH₂CH₃)Cl], 17764-68-0; *cis*-[Pt(PEt₃)₂(CH₂(CH₂)₂CH₃)Cl], 89308-86-1; *trans*-[Pt(PEt₃)₂(CH₂(CH₂)₂CH₃)Cl], 90581-22-9; *cis*-[Pt(PEt₃)₂(CH₂Si(CH₃)₃)Cl], 33937-93-8; *trans*-[Pt(PEt₃)₂(CH₂Si(CH₃)₃)Cl], 117605-16-0; *cis*-[Pt(PEt₃)₂(CH₂(CH₂)₂CH₃)₂], 117559-19-0; *cis*-[Pt(PEt₃)₂(CH₂Si(CH₃)₃)₂], 33937-88-1; *cis*-[Pt(PEt₃)₂Cl₂], 15692-07-6; Me₃SiCH₂MgCl, 13170-43-9; *cis*-[Pt(PEt₃)₂(CH₂CH₃)₂], 75847-39-1; *cis*-[Pt(PEt₃)₂(CD₂CD₃)₂], 117605-17-1; *cis*-[Pt(PEt₃)₂(CH₂CH₂CH₃)₂], 17764-65-7.

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Thermodynamic Study of the Formation in Aqueous Solution of Cadmium(II) Complexes with Polyazacycloalkanes. Synthesis and Crystal Structure of the Dicationic Complex Na[Cd₂(L)Cl₂](ClO₄)₃ (L = 1,4,7,10,13,16,19,22,25,28-Decaazacyclotriacontane)

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Potentiometric and calorimetric studies on the equilibria between cadmium(II) and large polyazacycloalkanes of the series [3*k*]aneN_{*k*} (*k* = 6-11) have been carried out at 25 °C in 0.15 mol dm⁻³ NaClO₄ as ionic medium. Both mononuclear (*k* = 6-8) and dinuclear (*k* = 8-11) complexes are formed. The stability of these mononuclear complexes is compared with that, previously reported, of complexes formed by smaller macrocycles. Results indicate that the stability of the mononuclear complexes increases on going from the smallest macrocycle [9]aneN₃ to the pentadentate [15]aneN₅, then slightly decreases for [18]aneN₆ (log *k* = 18.80 (1)) and [21]aneN₇ (log *k* = 18.10 (1)), and finally sharply decreases for [24]aneN₈ (log *k* = 14.52 (7)). Ligand strain and formation of large, unstable chelate rings are invoked to explain this trend. The formation enthalpies of [Cd[18]aneN₆]²⁺ ($\Delta H^\circ = -15.3$ (1) kcal mol⁻¹) and [Cd[21]aneN₇]²⁺ ($\Delta H^\circ = -16.1$ kcal mol⁻¹) have been determined by microcalorimetry. Larger macrocycles of the series form stable dinuclear complexes: [Cd₂[24]aneN₈]⁴⁺ (log *k* = 18.21 (7)); [Cd₂[27]aneN₉]⁴⁺ (log *k* = 20.75 (1)); [Cd₂[30]aneN₁₀]⁴⁺ (log *k* = 23.21 (1)); [Cd₂[33]aneN₁₁]⁴⁺ (log *k* = 23.63 (2)). Many protonated species are formed, whose equilibrium constants have been measured, but no hydroxo species have been detected. The molecular structure of the dinuclear complex Na[Cd₂(L)Cl₂](ClO₄)₃ (L = 1,4,7,10,13,16,19,22,25,28-decaazacyclotriacontane ([30]aneN₁₀)) has been determined by single-crystal X-ray analysis. The compound crystallizes in the *Pbna* space group with *a* = 29.626 (7) Å, *b* = 13.790 (3) Å, *c* = 9.307 (3) Å, and *Z* = 4. Refinement of the atomic parameters by least squares gave a final *R* factor of 0.068 (*R*_w = 0.077) for 1428 unique reflections having *I* > 3σ(*I*). The structure consists of dimetallic [Cd₂(L)Cl₂]²⁺ and Na⁺ cations and of ClO₄⁻ anions. Both cadmium(II) ions are six-coordinated but with different environments: Cd(1) is surrounded by two chlorine atoms and by four nitrogen atoms of the macrocyclic ligand, whereas Cd(2) is coordinated by the other six ligand nitrogen atoms. The environment of Cd(2) is somewhat unusual, due to the constraints imposed by the intrachelate angles of 73-77°, and can be visualized as a distorted trigonal prism whose three lateral edges are spanned by the -NHCH₂CH₂NH- chains of the macrocycle. The same kind of environment may be present in other six-coordinated cadmium(II) macrocyclic complexes in solution.

Introduction

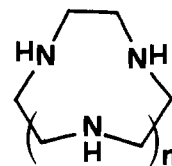
During the last few years much interest has been attracted by the metabolism of important non-iron elements such as copper and zinc, as well as of nonessential metals such as mercury and cadmium.

The substitution of zinc(II) by cadmium(II) in zinc(II)-containing metalloenzymes offers the opportunity to use the experimental technique of ¹¹³Cd NMR in the study of enzymatic systems. It has been shown,² for instance, that the affinity of the alkaline phosphatase for cadmium(II) depends on the pH value and the presence of phosphate. At pH 6.5 two cadmium(II) ions are tightly bound whereas at higher pH values or in the presence of phosphate up to six cadmium(II) ions can be bound.

Polyazacycloalkanes, which produce polynuclear complexes with a number of metal ions in solution, can be a helpful tool in understanding some simple mechanisms occurring in biological systems. The polyammonium species formed by these ligands can efficiently and selectively bind nucleotide anions, catalyzing their dephosphorylation.³ The implication of metal ions in these

processes can alter the reaction pathway, providing positive or negative catalytic effects.⁴

We are presently looking for macrocyclic ligands able to produce metal complexes that may act as solution catalysts. In the present paper we report the results of a thermodynamic and structural study on the equilibria between cadmium(II) and the polyazacycloalkanes of the series [3*k*]aneN_{*k*} (*k* = 6-11).



$$k = n + 2$$

(1) (a) University of Florence. (b) University of Valencia.
(2) Gettins, P.; Coleman, J. E. *J. Biol. Chem.* **1983**, *258*, 396.

(3) Hosseini, M. W.; Lehn, J. M.; Mertes, M. P. *Helv. Chim. Acta* **1983**, *66*, 2454; **1985**, *68*, 818. Hosseini, M. W.; Lehn, J. M.; Maggiora, L.; Mertes, K. B.; Mertes, M. P. *J. Am. Chem. Soc.* **1987**, *109*, 537.
(4) Yohannes, P. G.; Plute, K. E.; Mertes, M. P.; Mertes, K. B. *Inorg. Chem.* **1987**, *26*, 1751.

Table I. Experimental Details of the Emf Measurements

| k | init quantity, mmol | | | pH range | | no. of data points |
|----|---------------------|-----------------------|----------------|--------------|----------|--------------------|
| | Cd ²⁺ | [3k]aneN _k | H ⁺ | investigated | computed | |
| 6 | 0.1010 | 0.0948 | 0.6663 | 3.0–11.0 | 3.9–4.8 | 40 |
| | 0.1010 | 0.0952 | 0.5712 | 3.2–10.8 | 4.0–4.8 | 33 |
| 7 | 0.0525 | 0.0532 | 0.3724 | 3.0–11.0 | 4.3–5.2 | 34 |
| | 0.0510 | 0.0531 | 0.3715 | 3.3–11.1 | 4.5–5.1 | 30 |
| | 0.0520 | 0.0644 | 0.3863 | 3.5–10.8 | 4.4–5.1 | 30 |
| 8 | 0.1011 | 0.0740 | 0.5916 | 3.3–8.0 | 4.6–6.2 | 33 |
| | 0.1011 | 0.0573 | 0.4585 | 3.0–8.0 | 4.4–6.3 | 51 |
| | 0.0820 | 0.0516 | 0.4126 | 3.1–8.0 | 3.9–7.5 | 46 |
| 9 | 0.1209 | 0.0631 | 0.5678 | 2.9–10.9 | 4.9–6.1 | 41 |
| | 0.0769 | 0.0424 | 0.3818 | 3.0–11.0 | 5.0–6.1 | 26 |
| 10 | 0.1101 | 0.0508 | 0.5076 | 2.9–11.1 | 4.7–6.1 | 40 |
| | 0.0729 | 0.0412 | 0.4122 | 3.2–11.2 | 4.6–5.9 | 35 |
| | 0.0921 | 0.0506 | 0.4813 | 3.1–11.1 | 4.4–10.8 | 53 |
| 11 | 0.0851 | 0.0473 | 0.5198 | 3.0–11.1 | 5.0–7.0 | 39 |
| | 0.0637 | 0.0382 | 0.4198 | 3.1–10.8 | 5.1–6.4 | 27 |

Experimental Section

Materials. The polyazacycloalkanes employed in this work have been obtained as hydrochloride salts by following previously reported procedures.^{5–7} The hydrogen perchlorate salts of the same compounds have been obtained by treating ethanolic solutions of the free amines with a concentrated perchloric acid aqueous solution. Satisfactory C, H, N analyses were obtained for all of these compounds. All potentiometric and calorimetric measurements were carried out in 0.15 mol dm⁻³ NaClO₄. NaClO₄ (Merck p.a.), used as supporting electrolyte, was purified according to the procedure already described.⁸ Stock solutions of cadmium(II) were prepared by dissolving Cd(NO₃)₂·4H₂O (Merck p.a.) in double-distilled water, and the concentration was determined by potentiometric titration with EDTA. CO₂-free NaOH solutions used as titrant and HCl solutions were prepared by following the procedure reported in ref 9. Stock solutions of HClO₄ were obtained by dilution of concentrated HClO₄ (Merck p.a.) in double-distilled water and standardized by potentiometric titration with THAM (Merck p.a.). Na[Cd₂([30]aneN₁₀)Cl₂](ClO₄)₃ was obtained as prismatic colorless crystals by slow evaporation at room temperature of a water solution of [30]aneN₁₀·10HCl (0.01 mol dm⁻³) and Cd(Cl)₂ (0.02 mol dm⁻³) containing 3 mol dm⁻³ NaClO₄ and maintained approximately at pH = 12. Anal. Calcd for C₂₀H₅₀Cd₂Cl₅NaN₁₀O₁₂: C, 22.93; H, 4.81; N, 13.37. Found: C, 23.0; H, 4.8; N, 13.3.

Emf Measurements. The potentiometric titrations were carried out by using equipment (potentiometer, buret, stirrer, microcomputer, etc.) that has been fully described.¹⁰ The standard potential of the cell, E^o, was determined by the Gran method.¹¹ In Table I the initial concentrations of the reagents and the pH range explored for each titration are reported. The computer program SUPERQUAD¹² 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.

Microcalorimetry. All calorimetric measurements were carried out by using a BATCH 10700 LKB microcalorimeter. In a typical experiment 2 cm³ of a solution containing 0.01 mol dm⁻³ of the free amine and 0.15 mol dm⁻³ NaClO₄ was placed in one side of the calorimetric cell and the second side was filled with 1 cm³ of 0.01 mol dm⁻³ cadmium(II)

Table II. Crystallographic Data for Na[Cd₂([30]aneN₁₀)Cl₂](ClO₄)₃

| formula | C ₂₀ H ₅₀ Cd ₂ Cl ₅ NaN ₁₀ O ₁₂ | space group | Pbna ^a |
|-------------------|---|--|---|
| | | <i>d</i> _{calcd} , g cm ⁻³ | 1.83 |
| mol wt | 1047.74 | radiation | graphite monochromated Mo Kα (λ = 0.7107 Å) |
| a, Å | 29.626 (7) | temp, °C | 25 |
| b, Å | 13.790 (3) | μ, cm ⁻¹ | 15.4 |
| c, Å | 9.307 (3) | R ^b | 0.068 |
| V, Å ³ | 3802 (2) | R _w ^c | 0.077 |
| Z | 4 | | |

^a Alternative setting of space group *Pbcn* (No. 60 in ref 15a). ^b R = Σ||F_ol - |F_cl|/Σ|F_ol|. ^c R_w = [Σw(|F_ol - |F_cl|)²/Σw(F_o)²]^{1/2}.

Table III. Positional Parameters and Isotropic Thermal Parameters for Na[Cd₂([30]aneN₁₀)Cl₂](ClO₄)₃^a

| atom | x | y | z | U _{eq} /U _{iso} , Å ² |
|--------------------|--------------|-------------|-------------|--|
| Cd(1) ^b | 0.00869 (5) | 0.2500 | 0.5000 | 0.047 |
| Cd(2) ^b | -0.18539 (5) | 0.2500 | 0.5000 | 0.050 |
| Cl(1) | -0.0139 (2) | 0.4169 (4) | 0.5883 (8) | 0.113 |
| Cl(2) | 0.1109 (2) | 0.4683 (3) | 0.8445 (6) | 0.073 |
| Cl(3) ^b | 0.2519 (2) | 0.2500 | 0.5000 | 0.056 |
| O(1) | 0.1150 (6) | 0.3699 (9) | 0.8806 (17) | 0.126 |
| O(2) | 0.0985 (8) | 0.4818 (13) | 0.7059 (19) | 0.180 |
| O(3) | 0.0774 (10) | 0.5073 (14) | 0.921 (3) | 0.263 |
| O(4) | 0.1479 (7) | 0.5242 (14) | 0.8654 (25) | 0.200 |
| O(5) | 0.2799 (5) | 0.3182 (9) | 0.4318 (14) | 0.090 |
| O(6) | 0.2243 (5) | 0.3000 (10) | 0.6059 (17) | 0.114 |
| Na | 0.4866 (9) | 0.0398 (17) | 0.370 (3) | 0.170 (4) |
| N(1) | 0.0724 (5) | 0.2642 (10) | 0.3498 (15) | 0.065 (3) |
| N(2) | -0.0185 (4) | 0.3137 (8) | 0.2727 (13) | 0.046 (3) |
| N(3) | -0.1414 (4) | 0.2427 (10) | 0.2830 (14) | 0.055 (3) |
| N(4) | -0.1679 (5) | 0.0821 (10) | 0.4591 (14) | 0.062 (3) |
| N(5) | -0.2480 (5) | 0.1635 (11) | 0.5925 (17) | 0.082 (3) |
| C(1) | 0.0622 (6) | 0.3345 (12) | 0.2383 (18) | 0.071 (4) |
| C(2) | 0.0177 (5) | 0.3077 (12) | 0.1669 (18) | 0.063 (3) |
| C(3) | -0.0600 (5) | 0.2738 (11) | 0.2055 (18) | 0.060 (3) |
| C(4) | -0.0966 (4) | 0.2732 (10) | 0.3212 (16) | 0.047 (3) |
| C(5) | -0.1485 (7) | 0.1421 (14) | 0.2241 (19) | 0.080 (4) |
| C(6) | -0.1407 (7) | 0.0692 (13) | 0.3304 (19) | 0.077 (4) |
| C(7) | -0.2129 (7) | 0.0370 (15) | 0.4532 (21) | 0.088 (4) |
| C(8) | -0.2389 (7) | 0.0611 (14) | 0.5794 (22) | 0.093 (4) |
| C(9) | -0.2866 (9) | 0.2033 (15) | 0.518 (3) | 0.127 (4) |
| C(10) | 0.1123 (7) | 0.2813 (13) | 0.4386 (20) | 0.078 (4) |

^a Estimated standard deviations on the least significant digits are in parentheses. Isotropic temperature factors are of the form exp[-8π²U_{iso}(sin²θ)/λ²], and equivalent isotropic thermal parameters are of the form U_{eq} = 1/3Σ_iU_iρ_i*a_j*a_ra_j. ^b Atoms with population parameter 0.5.

solution, 0.15 mol dm⁻³ in NaClO₄. The heats of reaction obtained were corrected for the dilution of the reagents by blank experiments. The species present, and their percentages, before and after mixing, calculated by the computer program DISPOL,¹³ were respectively the free amine and the complex.

Methods. As cadmium(II) shows some tendency to form simple and/or mixed complexes with chloride ion, all potentiometric measurements were carried out in the presence and in the absence of Cl⁻. The titrations were carried out by using both the hydrochloride and the hydrogen perchlorate salts of the amines as starting materials, and HCl or HClO₄ was respectively added to adjust the initial pH. For each system (Cl⁻ or ClO₄⁻ medium) the titration curves were treated either as a single set or as separated entities without significant variation in the equilibrium constants. This treatment of the two sets of potentiometric data showed that the amount of chloride ion present in the working solutions did not affect the value of the stability constants. Furthermore, the two 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, by the procedure we have previously reported in footnote 18 of ref 6, were rejected.

Collection and Reduction of X-ray Intensity Data. Crystals of the compound [Cd₂([30]aneN₁₀)Cl₂](ClO₄)₂ contained NaClO₄ coprecipitated in a 1:1 ratio. A crystal in the form of a prism with approximate

- Bianchi, A.; Mangani, S.; Micheloni, M.; Nanini, V.; Orioli, P.; Paoletti, P.; Seghi, B. *Inorg. Chem.* **1985**, *24*, 1182.
- Micheloni, M.; Paoletti, P.; Bianchi, A. *Inorg. Chem.* **1985**, *24*, 3702.
- Bencini, A.; Bianchi, A.; Garcia-España, E.; Giusti, M.; Micheloni, M.; Paoletti, P. *Inorg. Chem.* **1987**, *26*, 681.
- Bencini, A.; Garcia-España, E.; Giusti, M.; Mangani, S.; Micheloni, M.; Orioli, P.; Paoletti, P. *Inorg. Chem.* **1987**, *26*, 1243.
- Bencini, A.; Bianchi, A.; Garcia-España, E.; Micheloni, M.; Paoletti, P. *Inorg. Chem.* **1988**, *27*, 176.
- Micheloni, M.; May, P. M.; Williams, D. R. *J. Inorg. Nucl. Chem.* **1978**, *40*, 1209.
- Micheloni, M.; Sabatini, A.; Vacca, A. *Inorg. Chim. Acta* **1977**, *25*, 41.
- Bianchi, A.; Bologni, L.; Dapporto, P.; Micheloni, M.; Paoletti, P. *Inorg. Chem.* **1984**, *23*, 1201.
- Gran, G. *Analyst (London)* **1952**, *77*, 661.
- Rossotti, F. J.; Rossotti, H. *J. Chem. Educ.* **1965**, *42*, 375.
- Gans, P.; Sabatini, A.; Vacca, A. *J. Chem. Soc., Dalton Trans.* **1985**, 1195.

(13) Vacca, A. Unpublished Fortran program.

Table IV. Selected Bond Distances (Å) and Angles (deg) for $\text{Na}[\text{Cd}_2(\text{[30]aneN}_{10})\text{Cl}_2](\text{ClO}_4)_3^a$

| Distances | | | | | |
|--------------------|-----------|------------------|-----------|--|--|
| Cd(1)–Cl(1) | 2.535 (6) | Cd(2)–N(3) | 2.41 (1) | | |
| Cd(1)–N(1) | 2.36 (1) | Cd(2)–N(4) | 2.40 (1) | | |
| Cd(1)–N(2) | 2.43 (1) | Cd(2)–N(5) | 2.37 (2) | | |
| Angles | | | | | |
| Cl(1)–Cd(1)–Cl(1)' | 149.3 (2) | N(3)–Cd(2)–N(4) | 73.1 (5) | | |
| Cl(1)–Cd(1)–N(1) | 109.2 (4) | N(3)–Cd(2)–N(5) | 135.1 (5) | | |
| Cl(1)–Cd(1)–N(1)' | 95.4 (4) | N(3)–Cd(2)–N(3)' | 114.4 (4) | | |
| Cl(1)–Cd(1)–N(2) | 82.3 (3) | N(3)–Cd(2)–N(4)' | 93.2 (5) | | |
| Cl(1)–Cd(1)–N(2)' | 87.6 (3) | N(3)–Cd(2)–N(5)' | 98.0 (5) | | |
| N(1)–Cd(1)–N(1)' | 73.6 (5) | N(4)–Cd(2)–N(5) | 75.0 (5) | | |
| N(1)–Cd(1)–N(2) | 73.7 (4) | N(4)–Cd(2)–N(4)' | 155.1 (5) | | |
| N(1)–Cd(1)–N(2)' | 144.3 (4) | N(4)–Cd(2)–N(5)' | 126.6 (5) | | |
| N(2)–Cd(1)–N(2)' | 141.2 (4) | N(5)–Cd(2)–N(5)' | 76.9 (5) | | |

^aPrimed atoms are referred to the unprimed ones through a 2-fold axis.

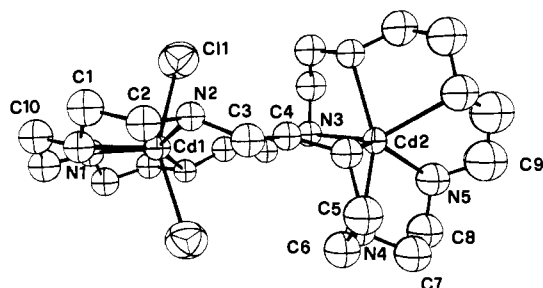


Figure 1. Perspective view of the $[\text{Cd}_2(\text{[30]aneN}_{10})\text{Cl}_2]^{2+}$ cation, with 50% probability ellipsoids. A 2-fold axis passes through atoms Cd(1) and Cd(2). Only symmetry-independent atoms are labeled.

dimensions $0.3 \times 0.2 \times 0.2$ mm was mounted on a Philips PW 1100 diffractometer and used for data collection. A summary of the crystallographic data is reported in Table II. Intensities were corrected for Lorentz, polarization, and absorption effects, the transmission factors ranging between 0.71 and 0.78 (numerical correction applied by the program SHELX-76¹⁴). The principal computer programs used in the crystallographic calculations are listed in ref 14. The intensities of three standard reflections, monitored periodically for stability control during data collection, did not show any systematic trend.

Solution and Refinement of the Structure. The structure was solved by a combination of direct methods and heavy-atom techniques, and refinement was performed by the full-matrix least-squares method. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with weights $w = [\sigma^2(F_o) + 0.002|F_o|^2]^{-1}$. Anisotropic thermal parameters were assigned to the Cd, Cl, and O atoms, whereas individual isotropic thermal parameters were assigned to all other atoms. Hydrogen atoms were included in calculated positions ($X-H = 1.00$ Å; $U_H \approx 1.2U_X$; $X = C, N$), and their parameters were not refined. Scattering factors and anomalous dispersion corrections were from ref 15b. The final atomic coordinates for non-hydrogen atoms are listed in Table III. The molecular plots were produced by the program ORTEP.¹⁴

Results and Discussion

Description of the Structure of the Compound $\text{Na}[\text{Cd}_2(\text{[30]aneN}_{10})\text{Cl}_2](\text{ClO}_4)_3$. The compound consists of dimetallic $[\text{Cd}_2(\text{[30]aneN}_{10})\text{Cl}_2]^{2+}$ and Na^+ cations and of ClO_4^- anions, the NaClO_4 salt from the reaction mixture being coprecipitated in a 1:1 ratio with the $[\text{Cd}_2(\text{[30]aneN}_{10})\text{Cl}_2](\text{ClO}_4)_2$ compound. A list of values of selected bond distances and angles appears in Table

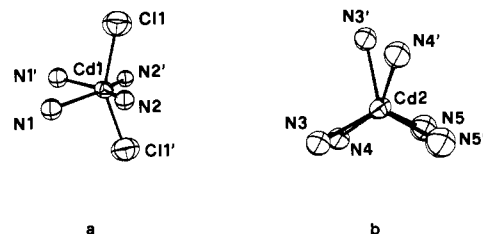


Figure 2. Skeletons of the coordination polyhedra about Cd(1) (a) and Cd(2) (b). Primed atoms are related to the unprimed ones through a 2-fold axis. The Cd(2) atom (b) is 1.39 Å from each of the basal faces of a distorted trigonal prism, respectively defined by N(3), N(4)', N(5)' and N(4), N(3)', N(5).

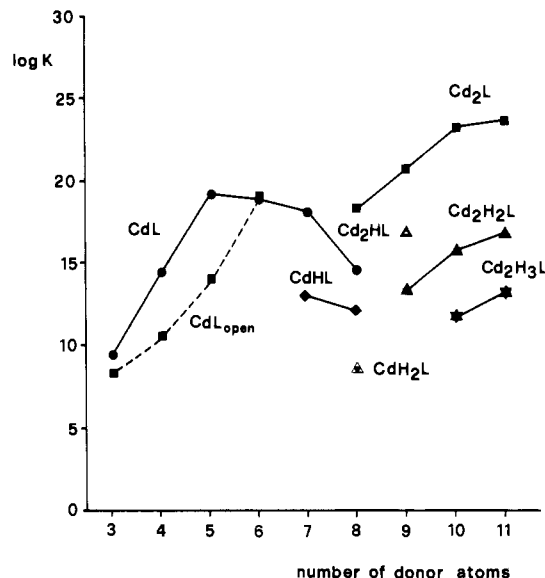


Figure 3. Logarithms of the formation constants of the cadmium(II) complexes of $[\text{3}k]\text{aneN}_k$ ($k = 3-11$) polyazacycloalkanes versus the number of nitrogen donor atoms. As a comparison, the formation constants of cadmium(II) complexes with some open-chain polyamines have been plotted (dashed line).

IV. The complex cation possesses a 2-fold symmetry axis, which passes through the metal atoms and bisects the C(9)–C(9)' and C(10)–C(10)' bonds. Also, a ClO_4^- anion lies on a 2-fold axis. A view of the dimetal cation appears in Figure 1. Both cadmium(II) ions, which lie 5.750 (2) Å apart, are six-coordinated. However, Cd(1) is surrounded by two Cl atoms and by four of the nitrogen atoms of the macrocyclic ligand, whereas Cd(2) is coordinated by the other six ligand N atoms. Although the environments of both metal sites are quite distorted with respect to the usual reference geometries for six-coordination, that of Cd(1) (Figure 2a) could be described as 4 + 2 pseudooctahedral, the main distortions from such geometry being due to the 149.3 (2)° angle (vs the ideal 180°) formed by the Cd(1)–Cl(1) and Cd(1)–Cl(1)' axial bonds and to the large equatorial N(2)–Cd(1)–N(2)' angle of 141.2 (4)°, which considerably exceeds the expected 90° value. The environment of Cd(2) is even more unusual, due to the constraints imposed by the intrachelate angles of 73–77°. Most simply, it may be visualized (Figure 2b) as a distorted trigonal prism, whose basal faces are defined by atoms N(3), N(4)', N(5)' and N(4), N(3)', N(5). Two basal and all three lateral edges of this prism are spanned by the ethylenediamine chains of the macrocycle.

Solution Equilibria of Cadmium(II) Complexes. The equilibrium constants related to the formation reactions in aqueous solution of cadmium(II) complexes of polyazacycloalkanes of the $[\text{3}k]\text{aneN}_k$ ($k = 6-11$) series are reported in Table V. These macrocycles form mononuclear complexes when $k = 6-8$ (6–8 nitrogen atoms as donors) and binuclear complexes when $k = 8-11$ (8–11 nitrogen donors). In Figure 3 the logarithms of the formation constants of these complexes, as well as of those previously reported for the macrocycles $[\text{9]aneN}_3$,¹⁶ $[\text{12]aneN}_4$,¹⁷ and $[\text{15]aneN}_5$,¹⁶

- (14) Sheldrick, G. M. "SHELX-76, Program for Crystal Structure Determination"; University of Cambridge, Cambridge, England, 1976. Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. "MULTAN 11/82, A System of Computer Programs for the Automatic Solution of Crystal Structure from X-ray Diffraction Data"; University of York, York, England, and University of Louvain, Louvain, Belgium, 1982. Johnson, C. K. "ORTEP"; Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1971. Nardelli, M. PARST. *Comput. Chem.* **1983**, *75*, 95.
- (15) (a) *International Tables for Crystallography*; Reidel: Dordrecht, Holland, 1983; Vol. A. (b) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

Table V. Formation Constants of Cadmium(II) Complexes of Macrocycles [3*k*]aneN_{*k*} (*k* = 6–11) in 0.15 mol dm⁻³ NaClO₄ Aqueous Solution at 25 °C

| reacn | log <i>K</i> | | | | | |
|---|------------------------|-----------------------|-----------------------|-----------------------|------------------------|------------------------|
| | [18]aneN ₆ | [21]aneN ₇ | [24]aneN ₈ | [27]aneN ₉ | [30]aneN ₁₀ | [33]aneN ₁₁ |
| Cd + L = CdL ^a | 18.80 (1) ^b | 18.10 (1) | 14.52 (7) | | | |
| Cd + L + H = CdLH | | 22.59 (2) | 21.67 (2) | | | |
| CdL + H = CdLH | | 4.49 | 7.15 | | | |
| CdLH + H = CdLH ₂ | | | 5.86 | | | |
| 2Cd + L = Cd ₂ L | | | 18.21 (7) | 20.75 (1) | 23.21 (1) | 23.63 (2) |
| 2Cd + L + H = Cd ₂ LH | | | | 26.38 | | |
| 2Cd + L + 2H = Cd ₂ LH ₂ | | | | 32.21 (1) | 35.07 (1) | 36.06 (2) |
| 2Cd + L + 3H = Cd ₂ LH ₃ | | | | | 39.94 (3) | 41.39 (4) |
| Cd ₂ L + H = Cd ₂ LH | | | | 5.63 | | |
| Cd ₂ LH + H = Cd ₂ LH ₂ | | | | 5.83 | | |
| Cd ₂ LH ₂ + H = Cd ₂ LH ₃ | | | | | 4.88 | 5.3 |

^a Charges omitted for clarity. ^b Values in parentheses are standard deviations in the last significant figure.

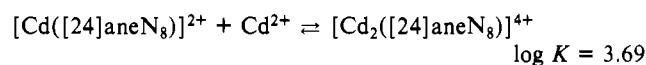
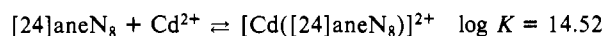
forming only mononuclear complexes, are plotted versus the number of nitrogen atoms in each ligand. The stability of the mononuclear complexes increases on passing from the smallest macrocycle, containing only three nitrogen donors, to the pentadentate [15]aneN₅ and then slightly decreases for [18]aneN₆ and [21]aneN₇, finally dropping down markedly for [24]aneN₈. Two hypotheses can be advanced to explain the small decrease in stability experienced by [18]aneN₆ (log *K* = 18.8) with respect to that of [15]aneN₅ (log *K* = 19.2): (i) a nitrogen atom is not coordinated to cadmium(II), forming a large chelate ring that lowers the stability of the complex; (ii) all six nitrogen atoms of [18]aneN₆ are involved in coordination to the cadmium(II) ion, at the expense, however, of severe strains. The crystal structure of the complex cation [Cd₂([30]aneN₁₀)Cl₂]²⁺ reported here shows that six contiguous nitrogen atoms of the ligand can be bound to one cadmium(II) ion, but, at least in that case, six-coordination is achieved by arranging the donor atoms at the vertices of a very strained and irregular trigonal prism (see Figure 2). The use of a stick and ball molecular model reveals that also in the case of [Cd([18]aneN₆)]²⁺ a similar six-coordinate environment might be attained. Moreover, [Cd([18]aneN₆)]²⁺ does not present any tendency to undergo protonation, indicating that upon coordination to cadmium(II) none of the nitrogen atoms of the ligand are available for protonation. For the next complex of the series, [Cd([21]aneN₇)]²⁺, in which at least one nitrogen atom is definitely uncoordinated, the stability decreases further (log *K* = 18.1) and the formation of a monoprotonated species, [Cd(H[21]aneN₇)]³⁺, is observed. All of these results support the second hypothesis above. The six-coordination of [18]aneN₆ and [21]aneN₇ can, on the other hand, readily explain the enthalpy changes related to the formation of their cadmium(II) complexes: -15.3 (1) and -16.1 (1) kcal mol⁻¹, respectively. Although the free energy terms for the same reactions, -25.6 and -24.7 kcal mol⁻¹, respectively, point to a smaller tendency of [21]aneN₇ to coordinate to cadmium(II), the above enthalpy contributions clearly indicate that the overall interaction between cadmium(II) and [21]aneN₇ is somewhat stronger than that between cadmium(II) and [18]aneN₆. The enthalpy increment (-0.8 kcal mol⁻¹) is too small to account for coordination of a further nitrogen atom and may arise from the fact that the [21]aneN₇ macrocyclic ring, being larger and more flexible than that of [18]aneN₆, allows six donor atoms to achieve a better arrangement about cadmium(II), forming stronger bonds with the metal ion. Such a mechanism would imply a larger entropy gain for the smaller [18]aneN₆ in the complexation reaction than for [21]aneN₇, in agreement with the experimental results (*T*Δ*S*^o = 10.3 kcal mol⁻¹ for [Cd([18]aneN₆)]²⁺ and 8.6 kcal mol⁻¹ for [Cd([21]aneN₇)]²⁺). Then if both [18]aneN₆ and [21]aneN₇ are six-coordinated to cadmium(II), the lower stability of [Cd([21]aneN₇)]²⁺ with respect to that of [Cd([18]aneN₆)]²⁺ may be ascribed to the presence of an 8-membered chelate ring whose stability is lower than that of the 5-membered ones. For [24]aneN₈, assuming that six-co-

ordination is still reached, two nitrogen atoms should remain uncoordinated. These nitrogens should be located either far from each other or in adjacent positions, yielding respectively the formation of two 8-membered chelate ring or of one 11-membered chelate ring. Both possibilities could account for the lower stability of [Cd([24]aneN₈)]²⁺ with respect to that of [Cd([21]aneN₇)]²⁺, but the second one is in contrast to the fact that the two stepwise protonation constants of [Cd([24]aneN₈)]²⁺ have similar values.

It is noteworthy that a decrease in the values of the equilibrium constants similar to that observed for the formation of cadmium(II) complexes with [18]aneN₆ and [21]aneN₇ has also been found for the reactions of cadmium(II) with monoprotonated [21]aneN₇ and [24]aneN₈, where six and seven nitrogen donor atoms, respectively, are again available for coordination.

In Figure 3 are also shown (dashed line) the logarithms of the stability constants of the cadmium(II) complexes with the linear polyamines den, trien, tetren,¹⁸ and penten,¹⁹ which can be considered as the noncyclic counterparts of the polyazacycloalkanes [3*k*]aneN_{*k*} where *k* = 3–6, respectively. It is notable that the "macrocyclic effect", namely the greater stability of the macrocyclic complexes with respect to that of the noncyclic counterparts, shown by [9]aneN₃, [12]aneN₄, and [15]aneN₅, vanishes for [18]aneN₆.

[Cd([24]aneN₈)]²⁺ can bind a second cadmium(II) ion, forming a binuclear complex. The values of the stability constants related to the equilibria



clearly indicate that while this ligand forms a stable mononuclear complex its tendency to form a binuclear complex is low. By use of the equilibrium data obtained for the Cd²⁺/[24]aneN₈ system the distribution of the complexes formed as a function of pH has been calculated for 1:1 and 2:1 Cd²⁺: [24]aneN₈ molar ratios. The results are plotted in Figure 4. For the 1:1 ratio the percentage of binuclear complex is very low (ca. 6%; Figure 4a). For the 2:1 ratio, at variance with what happens for larger macrocycles (see Figure 5), the percentage of binuclear species reaches only a value of ca. 60% (Figure 4b). As shown in Figure 4b, owing to the low tendency of [24]aneN₈ to form binuclear complexes, some of the metal ion still remains uncoordinated and precipitation of cadmium(II) hydroxide occurs as the pH is increased. A different behavior was observed for copper(II), which forms only binuclear complexes.⁵ Under the experimental conditions used in this work, polyazacycloalkanes with nine or more nitrogen donor atoms form only binuclear cadmium(II) complexes. The stability of these complexes increases from [24]aneN₈ to [30]aneN₁₀ and remains essentially unchanged from the latter to [33]aneN₁₁. On the other hand, only passing to [33]aneN₁₁ one of the two cad-

(16) Kodama, M.; Kimura, E. *J. Chem. Soc., Dalton Trans.* **1978**, 1081.
 (17) Kodama, M.; Kimura, E. *J. Chem. Soc., Dalton Trans.* **1977**, 2269.

(18) Smith, M.; Martell, A. E. *Critical Stability Constants*; Plenum: New York, 1975; Vol. 2.
 (19) Jacobsen, E.; Schroder, K. *Acta Chem. Scand.* **1961**, 16, 1393.

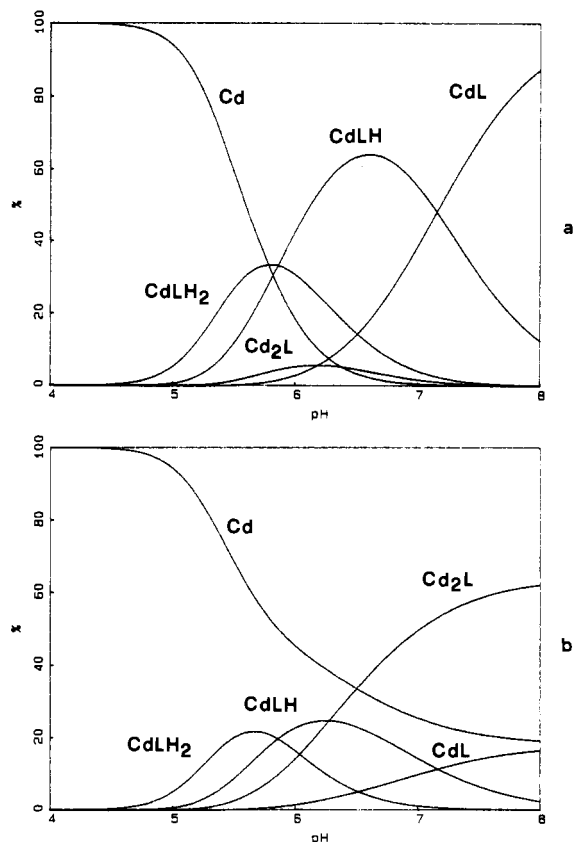


Figure 4. Calculated distribution of the equilibrium species formed in the system $\text{Cd}^{2+}/[24]\text{aneN}_8$ in $0.15 \text{ mol dm}^{-3} \text{ NaClO}_4$ aqueous solution at 25°C : (a) $10^{-3} \text{ mol dm}^{-3} \text{ Cd}^{2+}$ and $[24]\text{aneN}_8$; (b) $2 \times 10^{-3} \text{ mol dm}^{-3} \text{ Cd}^{2+}$, $10^{-3} \text{ mol dm}^{-3} [24]\text{aneN}_8$.

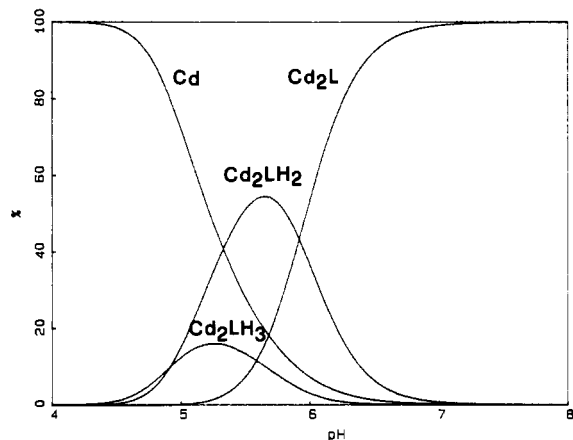


Figure 5. Calculated distribution of the equilibrium species formed in the system $\text{Cd}^{2+}/[30]\text{aneN}_{10}$ in $0.15 \text{ mol dm}^{-3} \text{ NaClO}_4$ aqueous solution at 25°C ($2 \times 10^{-3} \text{ mol dm}^{-3} \text{ Cd}^{2+}$ and $10^{-3} \text{ mol dm}^{-3} [30]\text{aneN}_{10}$).

mium(II) ions may reach six-coordination, whose attainment, as already discussed above for $[18]\text{aneN}_6$, does not involve a gain in stability. It is interesting to note that if the trend observed for the stability of the binuclear complexes were extended toward the $[21]\text{aneN}_7$ side, the stability of its binuclear complex would drop below that of the mononuclear complex, so that a second metal ion could not be bound, as is indeed found experimentally. It seems reasonable to expect that in these binuclear complexes all nitrogen atoms are involved in coordination to the metal ions, as suggested by the absence of monoprotonated species for most of the mac-

rocyclic derivatives that have been studied. The low stability of the binuclear complex of $[24]\text{aneN}_8$ and the structure of the complex $[\text{Cd}_2([30]\text{aneN}_{10})\text{Cl}_2]^{2+}$ suggest that in this series of binuclear complexes the nitrogen donors are not evenly shared, even though the conditions under which crystallization occurs are very different from those under which the complexation equilibria have been studied.

The facile protonation characterizing these compounds reveals a remarkable flexibility in the coordination sphere of the metal ions, which can easily undergo changes in the number of coordinated nitrogens. Thus, diprotonated binuclear complexes are formed by $[27]\text{aneN}_9$, $[30]\text{aneN}_{10}$, and $[33]\text{aneN}_{11}$ and even triprotonated ones are formed by the last two. The stability of these protonated complexes increases with the number of nitrogen donor atoms present in the macrocyclic framework. The fact that most of the dicadmium(II) complexes do not form monoprotonated species can be explained in terms of a rearrangement of the ligand, induced by the first protonation, followed by detachment of a second nitrogen and consequent protonation of the same. This could account for the fact that the stepwise protonation constant of $[\text{Cd}_2(\text{H}[27]\text{aneN}_9)]^{5+}$ is somewhat larger than that of $[\text{Cd}_2([27]\text{aneN}_9)]^{4+}$. The low stability of the binuclear complex of $[24]\text{aneN}_8$ and the structure of the complex $[\text{Cd}_2([30]\text{aneN}_{10})\text{Cl}_2]^{2+}$ suggest that in this series of binuclear complexes the nitrogen donors are not evenly shared, even through the conditions under which crystallization occurs are very different from those under which the complexation equilibria have been studied.

Comparing the behaviors of cadmium(II) and zinc(II) ions is of interest. Despite the different sizes of the two metal ions, the species formed in solution with $[27]\text{aneN}_9$, $[30]\text{aneN}_{10}$, and $[33]\text{aneN}_{11}$ are very similar,²⁰ the differences being due to the additional formation of hydroxo species by zinc(II). Moreover, the stabilities of the complexes are very similar, being only slightly higher for cadmium(II). In spite of these similarities, significant structural differences should occur between the cadmium(II) and zinc(II) complexes, however, due to the greater tendency of cadmium(II) to exhibit higher coordination numbers. There are indeed differences between the structure of the complex here reported and that of the compound formed by zinc(II) with the same $[30]\text{aneN}_{10}$ ligand.²⁰ In the zinc(II) complex one of the metal ions is five-coordinated by nitrogen atoms of the ligand, while the other one is coordinated by four nitrogens and one exogenous unidentate ligand, one nitrogen atom of $[30]\text{aneN}_{10}$ being uncoordinated. Furthermore, protonated cadmium(II) complexes result to be more acidic than the corresponding complexes of zinc(II).

The similarity between the stabilities of zinc(II) and cadmium(II) binuclear complexes suggests the possibility of obtaining mixed cadmium(II)-zinc(II) complexes. Potentiometric measurements on systems in which these ligands were employed have proved the existence of such complexes as predominant species in solution.²¹

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Registry No. $\text{Na}[\text{Cd}_2([30]\text{aneN}_{10})\text{Cl}_2](\text{ClO}_4)_3$, 118017-55-3.

Supplementary Material Available: Tables of all crystallographic data (Table S1), anisotropic thermal parameters (Table S2), hydrogen atom coordinates (Table S3), and all bond distances (Table S4) and angles (Table S5) (5 pages); a listing of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

(20) Bencini, A.; Bianchi, A.; Garcia-España, E.; Mangani, S.; Micheloni, M.; Orioli, P.; Paoletti, P. *Inorg. Chem.* **1988**, *27*, 1104.

(21) Work in progress.