

acetonitrile/dichloromethane in the Fe structure. An absorption correction was applied.³² In the final cycles of refinement, only Cu, Cl, and S atoms were assigned anisotropic thermal ellipsoids. Hydrogen atoms were included in the structure factor calculation by use of a riding model, with C-H of 0.96 Å and $U_{\text{iso}} = 1.2U_{\text{iso}}^*$ for the bonded carbon. In the final difference map the largest feature was 1.2 e Å⁻³ in height, 1.14 Å from the nitrogen of the acetonitrile.

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Registry No. Fe^{II}(STPP)Cl-CH₃CN, 119145-08-3; Ni^{II}(STPP)Cl-C-H₂Cl₂, 119145-10-7; Cu^{II}(STPP)Cl-CH₃CN, 119145-12-9.

Supplementary Material Available: Tables of atomic coordinates, all bond distances, bond angles, hydrogen atom coordinates, anisotropic thermal parameters, and crystal data and data collection parameters for Ni^{II}(STPP)Cl-CH₂Cl₂, Cu^{II}(STPP)Cl-CH₃CN, and Fe^{II}(STPP)Cl-C-H₃CN (19 pages); tables of calculated and observed structure factors (71 pages). Ordering information is given on any current masthead page.

Notes

Contribution from the Departments of Chemistry and Energetic, University of Florence, 50144 Firenze, Italy, and Department of Inorganic Chemistry, University of Valencia, Valencia, Spain

Polynuclear Zinc(II) Complexes with Large Polyazacycloalkanes. 2.¹ Equilibrium Studies and Crystal Structure of the Binuclear Complex [Zn₂LCl₂](Cl)ClO₄·H₂O (L = 1,4,7,10,13,16,19,22-Octaazacyclotetrasane)

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In contrast to the very large amount of work that has been done on azamacrocycles in recent years,³⁻⁵ there have been only few investigations on "large" azamacrocycles.^{1,6-10} These macrocycles are very promising compounds that have been employed in anion coordination as well as in transition-metal complex studies. In other papers we have studied a series of large polyazacycloalkanes with the general formula [3*k*]aneN_{*k*} (with *k* = 7-12). One of the most interesting properties of these compounds is the ability to form polynuclear metal complexes. In the present paper, in order to complete the [3*k*]aneN_{*k*} series, we report studies on the formation equilibria between zinc(II) and the four polyazacycloalkanes 1,4,7,10,13,16-hexaazacyclooctadecane ([18]-aneN₆), 1,4,7,10,13,16,19-heptaazacycloheicosane ([21]aneN₇),

Table I. Crystallographic Data for [Zn₂([24]aneN₈)Cl₂](Cl)ClO₄·H₂O

formula	C ₁₆ H ₄₂ Cl ₄ N ₈ O ₅ Zn ₂
mol wt	699.13
<i>a</i> , Å	7.601 (7)
<i>b</i> , Å	14.079 (5)
<i>c</i> , Å	15.429 (7)
α, deg	63.17 (3)
β, deg	78.13 (8)
γ, deg	85.65 (8)
<i>V</i> , Å ³	1441.6
<i>Z</i>	2
space gp	P $\bar{1}$
<i>D</i> _{calcd} , g cm ⁻³	1.61
radiation	Mo Kα, graphite monochromated
λ, Å	0.7107
temp, °C	25
μ, cm ⁻¹	20.8
<i>R</i> ^a	0.071
<i>R</i> _w ^b	0.071

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

1,4,7,10,13,16,19,22-octaazacyclotetrasane ([24]aneN₈), and 1,4,7,10,13,16,19,22,25,28,31,34-dodecaazacyclohexatriacontane ([36]aneN₁₂) (see Chart I). The crystal structure of binuclear [Zn₂([24]aneN₈)Cl₂](Cl)ClO₄·H₂O is also reported.

Experimental Section

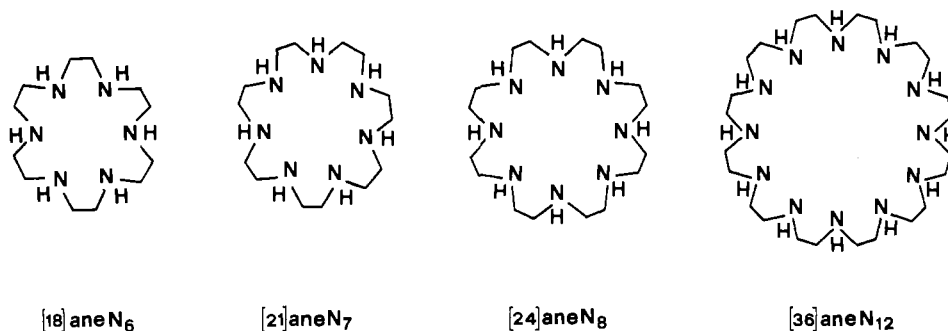
Synthesis of the Complex [Zn₂([24]aneN₈)Cl₂](Cl)ClO₄·H₂O. Good crystals, suitable for X-ray analysis, were obtained by slow evaporation at room temperature of a solution containing the octahydrochloride [24]aneN₈·8HCl (0.01 mol dm⁻³), Zn(ClO₄)₂ (0.02 mol dm⁻³), and NaClO₄ (3 mol dm⁻³). The pH of the solution was adjusted to 12 by adding NaOH. After a few days, crystals were collected, filtered, washed with ethanol, and dried under vacuum at room temperature. Anal. Calcd for C₁₆H₄₂N₈Zn₂Cl₄O₅: C, 27.49; H, 6.06; N, 16.03. Found: C, 27.4; H, 6.1; N, 16.0.

Emf Measurements. All potentiometric measurements were carried out in 0.15 mol dm⁻³ NaClO₄ (C. Erba ACS grade). Purification and standardization of solutions used in the potentiometric titrations were performed according to the procedure described in ref 11. Hydrochloride salts of [21]aneN₇, [24]aneN₈, and [36]aneN₁₂ have been obtained as described in ref 8, 7, and 10, respectively.¹² [18]aneN₆ was purchased from Fluka. The potentiometric titrations were carried out by using equipment that has been fully described.¹³ At least two titration curves for each system investigated were used. The experimental details of the emf measurements have been reported as supplementary material. The computer program SUPERQUAD¹⁴ was used to process emf data and cal-

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Chart I

**Table II.** Positional Parameters and Their Estimated Standard Deviations in Parentheses ($\times 10^4$; for Oxygen Atoms, $\times 10^3$)

atom	x/a	y/b	z/c
Zn(1)	441 (1)	2271 (1)	1370 (1)
Zn(2)	-1545 (2)	-1880 (1)	2823 (1)
Cl(1)	-1782 (3)	2566 (2)	537 (2)
Cl(2)	-3219 (4)	-1164 (2)	1654 (2)
Cl(3)	2212 (3)	-501 (2)	3838 (2)
Cl(4)	6185 (4)	4776 (3)	2480 (2)
N(1)	2776 (10)	3070 (6)	250 (6)
N(2)	799 (11)	3572 (6)	1698 (6)
N(3)	-632 (10)	1485 (6)	2972 (6)
N(4)	-1858 (10)	-812 (6)	3535 (6)
N(5)	-3040 (11)	-2929 (6)	4250 (6)
N(6)	-750 (11)	-3404 (6)	2895 (6)
N(7)	1411 (10)	-1543 (6)	2220 (6)
N(8)	1944 (10)	863 (6)	1442 (6)
C(1)	3671 (13)	3672 (8)	602 (9)
C(2)	2242 (14)	4307 (8)	968 (9)
C(3)	1075 (15)	3033 (8)	2746 (8)
C(4)	-497 (15)	2256 (8)	3365 (8)
C(5)	-2508 (13)	1060 (8)	3271 (8)
C(6)	-2684 (13)	192 (7)	2967 (8)
C(7)	-2812 (14)	-1420 (8)	4564 (7)
C(8)	-2506 (15)	-2593 (9)	4940 (8)
C(9)	-2695 (14)	-4051 (8)	4487 (8)
C(10)	-862 (14)	-4154 (8)	3921 (8)
C(11)	1092 (14)	-3306 (8)	2273 (8)
C(12)	2272 (13)	-2577 (8)	2436 (8)
C(13)	1868 (13)	-773 (7)	1180 (7)
C(14)	1185 (12)	318 (7)	965 (7)
C(15)	3837 (12)	1232 (8)	967 (8)
C(16)	3893 (12)	2279 (8)	39 (8)
O(1)	618 (3)	414 (2)	351 (2)
O(2)	784 (2)	522 (1)	186 (1)
O(3)	484 (3)	549 (2)	214 (2)
O(4)	574 (3)	380 (2)	249 (2)
O(5)	725 (3)	440 (2)	324 (2)
O(6)	702 (4)	473 (2)	158 (2)
O(7)	611 (3)	594 (2)	209 (2)
O(8)	453 (5)	455 (3)	289 (3)
O(9)	272 (1)	700 (1)	475 (1)

culate the stability constants. For each ligand the titration curves either were treated as a single set or were treated separately without significant variation in the values of the equilibrium constants.

Collection and Reduction of X-ray Intensity Data. Investigations on a selected single crystal were carried out with an Enraf-Nonius CAD-4 X-ray diffractometer. A summary of the crystallographic data is reported in Table I. Unit cell parameters were determined by least-squares refinement of diffractometer setting angles for 25 carefully centered reflections. Intensities were corrected for Lorentz, polarization, and absorption effects (transmission factors ranged between 0.65 and 0.78). During data collection, three reflections were monitored periodically as a check of the stability of the diffractometer and of the crystal.

Solution and Refinement of the Structure. The structure was solved by the heavy-atom technique, which showed the positions of the two zinc atoms. Subsequent Fourier maps showed all non-hydrogen atoms. The oxygen atoms of the perchlorate anion are in a disordered array; two

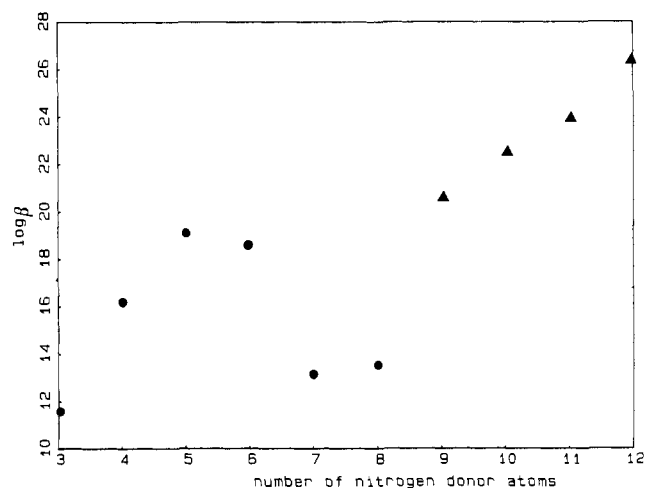


Figure 1. Logarithms of the formation constants of zinc(II) complexes of $[3k]aneN_k$ ($k = 3-12$) polyazacycloalkanes versus the number of nitrogen donor atoms: (●) mononuclear $[ZnL]^{2+}$ complexes; (▲) binuclear $[Zn_2L]^{4+}$ complexes.

different models with population parameters of 0.5 were considered acceptable and were used in the refinement. 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 were included in calculated positions with an overall temperature factor U of 0.05. Anisotropic temperature factors were used for all the other atoms except for the oxygen atoms of the perchlorate anion and of the water molecule. All calculations were performed on an IBM Model 4361/3 computer with the SHELX-76 set of programs¹⁵ that use the analytical approximation for the atomic scattering factors and anomalous dispersion corrections for all the atoms from ref 16. Table II reports the list of the final atomic coordinates for non-hydrogen atoms with estimated standard deviations. The molecular plot was produced by the program ORTEP.¹⁷

Results and Discussion

Equilibrium Studies. In Table III are reported the formation constants of the zinc(II) complexes of the macrocycles $[18]aneN_6$, $[21]aneN_7$, $[24]aneN_8$, and $[36]aneN_{12}$. For the purpose of comparison, the stability constants of all other macrocycles belonging to the $[3k]aneN_k$ series (with $k > 6$) have been reported. With the only exception of the macrocycles $[18]aneN_6$ and $[21]aneN_7$, which form only mononuclear complexes, all the other macrocycles of the series form binuclear species. Only in the case of the macrocycle $[24]aneN_8$ are both mono- and binuclear species formed (see Table III). The stabilities of the mononuclear complexes $[Zn([18]aneN_6)]^{2+}$, $[Zn([21]aneN_7)]^{2+}$, and $[Zn([24]aneN_8)]^{2+}$ are compared with those of smaller macrocycles, $3 \leq k \leq 6$ in the $[3k]aneN_k$ series,¹⁸ and are reported in the left side

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Table III. Formation Constants for Zinc(II)/Large Polyazacycloalkane Systems in Aqueous Solution (25 °C in 0.15 mol dm⁻³ NaClO₄)

reaction	log K						
	[18]aneN ₆ ^a	[21]aneN ₇ ^a	[24]aneN ₈ ^a	[27]aneN ₉ ^b	[30]aneN ₁₀ ^b	[33]aneN ₁₁ ^b	[36]aneN ₁₂ ^a
Zn ^c + L = Zn(L)	18.70 (1) ^d	13.33 (1)	13.49				
Zn + L + H = Zn(L)H	22.63 (3)	20.2	22.07				
Zn + L + 2H = Zn(L)H ₂		25.15	27.60				
Zn + L + H ₂ O = Zn(L)OH + H		1.5	2.8				
2Zn + L = Zn ₂ (L)				20.55	22.51	23.91	26.27
2Zn + L + H = Zn ₂ (L)H				26.98			32.83
2Zn + L + 2H = Zn ₂ (L)H ₂				32.79	35.22	36.66	39.16
2Zn + L + 3H = Zn ₂ (L)H ₃					40.41	42.17	44.81
2Zn + L + 4H = Zn ₂ (L)H ₄							49.99
2Zn + L + H ₂ O = Zn ₂ (L)OH + H			12.60	13.56	14.16	15.40	16.09
2Zn + L + 2H ₂ O = Zn ₂ (L)(OH) ₂ + 2H			3.0	4.71	3.19	4.87	
Zn(L) + H = Zn(L)H		6.7	8.6				
Zn(L)H + H = Zn(L)H ₂		4.9	5.5				
Zn ₂ (L) + H = Zn ₂ (L)H				6.4			6.6
Zn ₂ (L)H + H = Zn ₂ (L)H ₂				5.8			6.3
Zn ₂ (L)H ₂ + H = Zn ₂ (L)H ₃					5.2	5.5	5.7
Zn ₂ (L)H ₃ + H = Zn ₂ (L)H ₄							5.2
Zn ₂ (L)H ₂ O = Zn ₂ (L)OH + H				-7.0	-8.4	-8.5	-10.1
Zn ₂ (L) + OH = Zn ₂ (L)OH				6.7	5.4	5.2	3.5
Zn ₂ (L)OH + OH = Zn ₂ (L)(OH) ₂			4.1	4.9	2.7	3.2	

^aThis work. ^bTaken from ref 1. ^cCharges omitted for clarity. ^dValues in parentheses are the standard deviations in the last significant figure.

of Figure 1. The most stable mononuclear zinc(II) complex is [Zn([15]aneN₅)]²⁺; either an increase or a decrease in the number of available donor atoms yields less stable complexes (see Figure 1). We can explain the above trend by assuming that, at most, five nitrogen donor atoms can be involved in the mononuclear zinc(II) complex formation; in fact, the enthalpy of formation of [Zn([18]aneN₆)]²⁺¹⁹ ($\Delta H^\circ = -14.0 \pm 0.1$ kcal mol⁻¹) is identical with that reported for [Zn([15]aneN₅)]²⁺¹⁸ ($\Delta H^\circ = -14.0$ kcal mol⁻¹). With this assumption, [Zn([18]aneN₆)]²⁺, [Zn([21]aneN₇)]²⁺, and [Zn([24]aneN₈)]²⁺ contain an increasing number of unbound donor atoms that yield strained, large chelate rings, thus reducing the overall complex stability. In the case of [21]aneN₇ and [24]aneN₈, two and three nitrogen atoms, respectively, should remain uncoordinated. These nitrogens should be located either far from each other or in adjacent positions, yielding respectively the formation of separated 8- and 11-membered chelate rings or of unique 11- and 14-membered chelate rings. The high value of the protonation constant of [Zn([24]aneN₈)]²⁺ (log K = 8.6, see Table III) supports the second hypothesis.

The macrocycle [24]aneN₈ also forms stable binuclear species (see Table III). Undoubtedly, the most important binding characteristic of the series of large polyazacycloalkanes is the great tendency to form polynuclear species. As expected, macrocycle [36]aneN₁₂ forms the most stable binuclear complex of the series. There is a clear trend indicating an increase in the overall stability of the binuclear [Zn₂L]⁴⁺ species as the size of the macrocycle increases (see the right side of Figure 1). This trend can be explained in terms of the increase in the number of donor atoms involved in the coordination to the metal ions and the increase of the ligand flexibility as the ligand size increases. The diminution of the electrostatic repulsions between the two positive metal ions as the macrocyclic size increases is a further contribution to the above trend. Another binding characteristic, which is common to all large polyazamacrocycles, is the ability to form many protonated and hydroxo species (see Table III). It is well-known that zinc(II) tends to form hydroxo species in its amino complexes, but in the case of polyazacycloalkanes, these species are very stable and important. It is worthwhile to note that, in the case of [24]aneN₈, the only binuclear species formed is [Zn₂([24]aneN₈)OH]³⁺ (see Table III), confirming the importance of such species in zinc(II)/polyazamacrocyclic equilibria. The equilibrium constants relative to the ionization of the metal-bound water molecule in the binuclear species [Zn₂L(H₂O)]⁴⁺, reported in Table III, indicate that the water molecule dissociates more easily

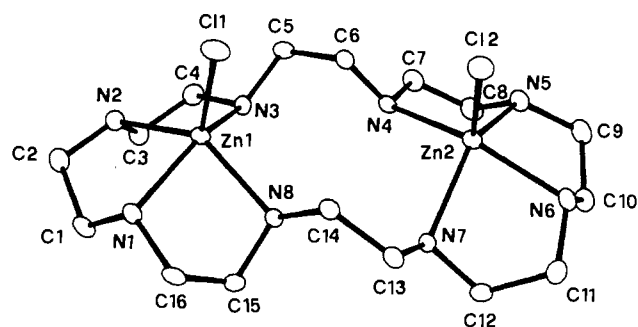


Figure 2. Perspective view of the [Zn₂([24]aneN₈)Cl₂]²⁺ cation with 50% probability ellipsoids.

(increasing acidity) as the macrocycle becomes smaller ($pK_a = 10.1$ for [36]aneN₁₂, through 7.0 for [27]aneN₉). This trend may be explained by taking into account that [Zn₂L]⁴⁺ species will become more strained and that one zinc ion will bind the water molecule more tightly as the macrocycle becomes smaller. Indeed, the absence of the [Zn₂([24]aneN₈)]⁴⁺ species, coupled with the existence of a very stable [Zn₂([24]aneN₈)OH]³⁺ hydroxo species, present in a wide range of pH, is in agreement with the previous hypothesis. Looking at the regular diminution of the stability of binuclear [Zn₂L]⁴⁺ complexes (Table III and right side of Figure 1), we can predict a $pK_a < 7$ for the ionization of the metal-bound water molecule in the [Zn₂([24]aneN₈)H₂O]⁴⁺ complex. In other words, this species hydrolyzes at such a low pH that, in the experimental conditions employed in the potentiometric measurements, it is always present as the hydrolyzed species [Zn₂([24]aneN₈)OH]³⁺.

Description of the Structure. The structure of [Zn₂([24]aneN₈)Cl₂](Cl)ClO₄·H₂O consists of [Zn₂([24]aneN₈)Cl₂]²⁺ cations (see Figure 2) and chloride and perchlorate anions. The structure is completed by interposed water molecules. Both zinc atoms are five-coordinate, each one bound to four nitrogen atoms of the macrocycle and to a chloride anion. The two coordination polyhedra are very similar and can be better described as distorted square pyramids with the apical positions occupied by chloride anions, both of them on the same side with respect to the macrocycle plane. The zinc atoms are above the basal plane by 0.729 (2) and 0.724 (2) Å for Zn(1) and Zn(2), respectively. The eight Zn–N distances are within the range 2.144–2.245 Å, whereas the two Zn–Cl distances are almost identical: Zn(1)–Cl(1) = 2.233 (3) and Zn(2)–Cl(2) = 2.234 (3) Å. The macrocycle is disposed in an elongated form in order to allow the eight nitrogens to be placed at the vertices of two squares. The angles at the nitrogen atoms within the macrocyclic framework are all significantly larger

(19) Determined in our laboratory by direct batch microcalorimetry.

Table IV. Selected Bond Lengths (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses

Bond Lengths			
Zn(1)-Cl(1)	2.233 (3)	Zn(1)-N(1)	2.165 (7)
Zn(1)-N(2)	2.158 (10)	Zn(1)-N(3)	2.200 (8)
Zn(2)-Cl(2)	2.236 (4)	Zn(2)-N(4)	2.203 (10)
Zn(2)-N(5)	2.147 (7)	Zn(2)-N(6)	2.144 (9)
Zn(2)-N(7)	2.246 (7)	N(1)-C(1)	1.461 (18)
N(1)-C(16)	1.462 (14)	C(1)-C(2)	1.535 (17)
C(2)-N(2)	1.468 (12)	N(2)-C(3)	1.498 (14)
C(3)-C(4)	1.524 (14)	C(4)-N(3)	1.481 (17)
N(3)-C(5)	1.488 (13)	C(5)-C(6)	1.517 (19)
C(6)-N(4)	1.460 (11)	N(4)-C(7)	1.474 (11)
C(7)-C(8)	1.499 (16)	C(8)-N(5)	1.478 (19)
N(5)-C(9)	1.467 (14)	C(9)-C(10)	1.519 (15)
C(10)-N(6)	1.442 (12)	N(6)-C(11)	1.502 (13)
C(11)-C(12)	1.543 (19)	C(12)-N(7)	1.472 (13)
N(7)-C(13)	1.460 (11)	C(13)-C(14)	1.492 (14)
C(14)-N(8)	1.488 (16)	N(8)-C(15)	1.487 (11)
C(15)-C(16)	1.518 (12)		
Angles			
Cl(1)-Zn(1)-N(1)	105.0 (2)	Zn(1)-N(3)-C(5)	115.7 (6)
Cl(1)-Zn(1)-N(3)	110.0 (3)	Cl(1)-Zn(1)-N(8)	111.4 (3)
N(1)-Zn(1)-N(2)	79.5 (4)	N(1)-Zn(1)-N(3)	144.4 (3)
N(1)-Zn(1)-N(8)	81.8 (4)	N(2)-Zn(1)-N(3)	81.4 (3)
N(2)-Zn(1)-N(8)	136.0 (4)	N(3)-Zn(1)-N(8)	91.7 (3)
Cl(2)-Zn(2)-N(4)	104.7 (3)	Cl(2)-Zn(2)-N(5)	113.4 (3)
Cl(2)-Zn(2)-N(6)	106.1 (3)	Cl(2)-Zn(2)-N(7)	113.2 (2)
N(4)-Zn(2)-N(5)	80.7 (3)	N(4)-Zn(2)-N(6)	147.8 (3)
N(4)-Zn(2)-N(7)	95.1 (4)	N(5)-Zn(2)-N(6)	78.9 (4)
N(5)-Zn(2)-N(7)	132.7 (4)	N(6)-Zn(2)-N(7)	81.0 (4)
Zn(2)-N(7)-C(12)	106.8 (7)	Zn(2)-N(7)-C(13)	114.9 (7)
C(12)-N(7)-C(13)	113.2 (8)	N(7)-C(13)-C(14)	114.0 (8)
C(13)-C(14)-N(8)	115.3 (9)	Zn(1)-N(8)-C(14)	112.3 (7)
Zn(1)-N(8)-C(15)	106.2 (7)	C(14)-N(8)-C(15)	112.5 (8)
N(8)-C(15)-C(16)	110.4 (9)	C(15)-C(16)-N(1)	111.1 (9)
Zn(1)-N(1)-C(1)	107.8 (7)	Zn(1)-N(1)-C(16)	108.8 (7)
C(1)-N(1)-C(16)	114.8 (9)	N(1)-C(1)-C(2)	108.1 (9)
C(1)-C(2)-N(2)	108.8 (9)	Zn(1)-N(2)-C(2)	111.4 (7)
Zn(1)-N(2)-C(3)	103.9 (7)	C(2)-N(2)-C(3)	116.0 (9)
N(2)-C(3)-C(4)	107.7 (9)	C(3)-C(4)-N(3)	110.7 (9)
Zn(1)-N(3)-C(4)	107.8 (6)	C(4)-N(3)-C(5)	110.0 (8)
N(3)-C(5)-C(6)	111.9 (9)	C(5)-C(6)-N(4)	114.5 (9)
Zn(2)-N(4)-C(6)	112.3 (6)	Zn(2)-N(4)-C(7)	107.4 (7)
C(6)-N(4)-C(7)	114.9 (9)	N(4)-C(7)-C(8)	111.9 (9)
C(7)-C(8)-N(5)	107.9 (9)	Zn(2)-N(5)-C(8)	104.5 (7)
Zn(2)-N(5)-C(9)	111.8 (7)	C(8)-N(5)-C(9)	114.1 (9)
N(5)-C(9)-C(10)	110.0 (9)	C(9)-C(10)-N(6)	108.0 (9)
Zn(2)-N(6)-C(10)	108.2 (7)	Zn(2)-N(6)-C(11)	109.4 (7)
C(10)-N(6)-C(11)	113.6 (9)	N(6)-C(11)-C(12)	108.7 (9)
C(11)-C(12)-N(7)	110.3 (9)		

than the theoretical ones for sp^3 hybridization (medium value 113.7°). Wide angles are also found between the carbon atoms of the different polyhedra. Bond lengths and angles in the coordination polyhedra are reported in Table IV. The basal planes of the two polyhedra form a dihedral angle of just 20° . If the present structure is compared with that of the analogous binuclear complex¹ $[Zn_2([30]aneN_{10})(NCS)](ClO_4)_3$, it can be seen that in this case the 24-membered macrocycle is much more flattened than the 30-membered macrocycle. This situation reflects the different geometries of both polyhedra: a trigonal bipyramid in the case of $[Zn_2([30]aneN_{10})(NCS)](ClO_4)_3$ and a square pyramid in the present case. The Zn-Zn distance, 5.44 Å, is shorter than that found for the larger macrocycle $[30]aneN_{10}$, 6.40 Å. Several hydrogen bonds are formed between the oxygen atoms of the perchlorate ions and both the hydrogen atoms of the water molecules and the hydrogen atoms linked to the N-H groups. The comparison of the structure of $[Zn_2([24]aneN_8)Cl_2]^{2+}$ with that of the copper(II) complex⁷ $[Cu_2([24]aneN_8)Cl_2]^{2+}$ leads to some interesting considerations. In both structures the metal ions are five-coordinated with the same set of donor atoms, four nitrogen atoms and one chloride anion. The coordination polyhedra are in both cases slightly distorted square pyramids. However, besides these similarities, there are also significant differences between the two structures. The larger zinc(II) ions in the $[Zn_2([24]aneN_8)Cl_2]^{2+}$ complex are much more displaced from the least-squares basal plane (0.72 Å) than copper(II) ions (0.34 Å) in the $[Cu_2([24]aneN_8)Cl_2]^{2+}$ complex. As a result, the two complexes

have different M-N bond orientations with respect to the basal plane; this situation is also reflected in the different conformations, adopted by the macrocycle in the two complexes and demonstrates the high flexibility of large macrocycle to adapt themselves to metal ion stereochemical requirements.

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Registry No. $[Zn_2([24]aneN_8)Cl_2](Cl)ClO_4 \cdot H_2O$, 118977-74-5; $[18]aneN_6$, 296-35-5; $[21]aneN_4$, 296-85-5; $[24]aneN_8$, 297-11-0; $[36]aneN_9$, 24904-24-3.

Supplementary Material Available: Tables of thermal parameters and complete bond lengths and angles and a table containing the initial quantities of reactant, pH range, number of data points for each titration curve, and the computer output of the program SUPERQUAD giving individual data points for emf measurements (52 pages); a listing of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

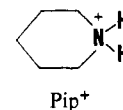
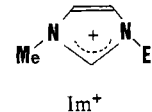
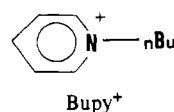
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X-ray Crystallographic Characterization of Hydrogen-Bonding Interactions in Piperidinium Chloride and Piperidinium Tetrachloroaluminate: Relevance to the Structure of Room-Temperature Melts

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That certain bulky organic cation halides may become room-temperature melts when mixed with aluminum trichloride (in compositions up to 70 mol % $AlCl_3$) has fostered much activity in recent years.^{1,2} The prototypal melt, *N*-ethylpyridinium bromide/ $AlCl_3$, was first reported in 1951,³ and the analogous methylpyridinium halides have also been investigated.⁴ In more recent years, however, two other bulky organic cations, *N*-butylpyridinium,¹ Bupy⁺, and 1-methyl-3-ethylimidazolium, Im⁺, (and several related alkyl derivatives),^{1,2} have been the subject of detailed investigation.



Our interest in this field has evolved as a result of the unusual interaction that another class of low melting point salt, $M[Al_2R_6X]$ (M = a wide variety of cations ranging from alkali-metal cation to tetraalkylammonium; R = Me, Et, ...; X = halide, azide, thiocyanate, or indeed most anions capable of bridging two aluminum atoms), exhibits when contacted with excess aromatic hydrocarbon. Such mixtures do not form classic solutions but form two liquid phases, the denser of which is salt-rich and has been called a "liquid clathrate" by their original discoverer, J. L. Atwood.⁵ That room-temperature melts dissolve in benzene and

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