the spectroscopic and structural results, the coordination mode of the nitrates can best be described as asymmetric didentate.

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Structure of a Complex of 1,4,8,11-Tetraazacyclotetradecane (Cyclam) with Zinc(II) Chloride

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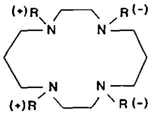
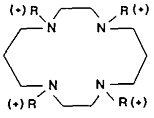
Abstract. Bis[μ-chloro-(1,4,8,11-tetraazacyclotetradecane)zinc(II)] tetrachlorozincate(II) hemihydrate, $[\mathrm{ZnCl(C_{10}H_{24}N_4)}]_{2n}^{+}.n[\mathrm{ZnCl_4}]^{2-}.(n/2)\mathrm{H_2O}$, $M_r = 818.5$ for $n = 1$, tetragonal, $I\bar{4}2d$, $a = 17.950\,(5)$, $c = 10.907\,(2)$ Å, $V = 3514\,(1)$ Å^3, $Z = 4$, $D_m = 1.52$, $D_x = 1.55$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 25.7$ cm^{-1}, $T = 290$ K, $R = 0.095$ for 750 unique observed $[I/\sigma(I) \geq 2.0]$ reflections. The structure consists of infinite —Cl—[Zn(cyclam)]$^{2+}$—Cl— chains interspersed with $[\mathrm{ZnCl_4}]^{2-}$ ions. The mean Zn—N and Zn—Cl (chain) distances are 2.13 (1) and 2.730 (4) Å, while the Zn—Cl bond length in the anion is 2.288 (5) Å.

Introduction. Complexes of the ligand 1,4,8,11-tetraazacyclotetradecane [cyclam (*A*), *R* = H] and its *N*-substituted derivatives have a number of possible conformations depending on the relative orientations of the N—*R* bonds and the metal-ion geometry (Bosnich, Poon & Tobe, 1965). The commonest conformation reported for complexes of first-row transition metals with cyclam itself is that known as *trans*-(III), in which the N—H bonds are oriented up and down as shown schematically in (*A*) [(+) and (−) represent the relative positions of the N—*R* groups above and below the macrocyclic ligand plane respectively]. The *trans*-(III) conformation was found in the octahedral [Ni(cyclam)Cl_2] (Bosnich, Mason, Pauling, Robertson & Tobe, 1965), and recently in [Zn(cyclam)(ClO_4)$_2$] (Tyson, Hodgson, Hedman & Clark, 1990). However, the factors determining the relative stability of these complexes are not always obvious, and for the related *N*-tetramethylcyclam (tmc) complexes isomerism between the *trans*-(I) and *trans*-(III) forms, and *vice versa*, has been observed in different solvents (Moore, Sachinidis & Willey, 1983). In the solid state, [Zn(tmc)Cl](ClO_4) [tmc = (*B*), *R* = CH_3] shows square-pyramidal geometry with the *trans*-(I) conformation (all N—*R* groups on the same side), but in solution it is fluxional betweent two identical trigonal bipyramids (Alcock, Herron & Moore, 1978). Therefore, it is of interest to examine the structures of other related complexes, and we here report that of the complex formed between $ZnCl_2$ and cyclam, and its isomerism in aqueous solution as observed by ^{13}C NMR.



(*A*)
trans-(III)



(*B*)
trans-(I)

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Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement parameters* ($Å^2 \times 10^3$)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	U_{eq}
Zn(1)	7500	7467 (2)	3750	96 (2)
Cl(1)	7562 (4)	7500	6250	49 (2)
Zn(2)	5000	5000	5000	30 (1)
Cl(2)	5718 (2)	5765 (2)	6192 (4)	43 (1)
O(1)	5000	5000	0	186 (24)
C(1)	7901 (10)	5929 (9)	3996 (15)	43 (6)
N(2)	8270 (7)	6613 (7)	3663 (11)	38 (4)
C(3)	8960 (11)	6738 (12)	4221 (15)	56 (7)
C(4)	9351 (9)	7426 (15)	3669 (23)	85 (10)
C(5)	9028 (12)	8145 (11)	4146 (16)	56 (7)
N(6)	8281 (8)	8343 (7)	3567 (14)	46 (5)
C(7)	7899 (13)	9000 (10)	3937 (26)	88 (11)

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Zn(1)—Cl(1)	2.730 (4)	Zn(1)—N(2)	2.066 (14)
Zn(1)—N(6)	2.117 (14)	Zn(1)—Cl(1*a*)	2.730 (4)
Zn(1)—N(2*a*)	2.066 (14)	Zn(1)—N(6*a*)	2.117 (14)
Cl(1)—Zn(1*a*)	2.730 (4)	Zn(2)—Cl(2)	2.288 (5)
Zn(2)—Cl(2*a*)	2.288 (5)	Zn(2)—Cl(2*b*)	2.288 (5)
Zn(2)—Cl(2*c*)	2.288 (5)	C(1)—N(2)	1.442 (21)
C(1)—C(1*a*)	1.535 (35)	N(2)—C(3)	1.398 (23)
C(3)—C(4)	1.543 (32)	C(4)—C(5)	1.507 (33)
C(5)—N(6)	1.525 (25)	N(6)—C(7)	1.423 (24)
C(7)—C(7*a*)	1.488 (46)		

Cl(1)—Zn(1)—N(2)	92.0 (4)	Cl(1)—Zn(1)—N(6)	92.9 (4)
N(2)—Zn(1)—N(6)	96.0 (5)	Cl(1)—Zn(1)—Cl(1*a*)	177.5 (2)
N(2)—Zn(1)—Cl(1*a*)	89.9 (4)	N(6)—Zn(1)—Cl(1*a*)	85.2 (4)
Cl(1)—Zn(1)—N(2*a*)	89.9 (4)	N(2)—Zn(1)—N(2*a*)	84.2 (7)
N(6)—Zn(1)—N(2*a*)	177.2 (5)	Cl(1*a*)—Zn(1)—N(2*a*)	92.0 (4)
Cl(1)—Zn(1)—N(6*a*)	85.2 (4)	N(2)—Zn(1)—N(6*a*)	177.2 (5)
N(6)—Zn(1)—N(6*a*)	84.0 (8)	Cl(1*a*)—Zn(1)—N(6*a*)	92.9 (4)
N(2*a*)—Zn(1)—N(6*a*)	96.0 (5)	Zn(1)—Cl(1)—Zn(1*a*)	175.3 (3)
Cl(2)—Zn(2)—Cl(2*a*)	110.8 (2)	Cl(2)—Zn(2)—Cl(2*b*)	108.8 (1)
Cl(2*a*)—Zn(2)—Cl(2*b*)	108.8 (1)	Cl(2)—Zn(2)—Cl(2*c*)	108.8 (1)
Cl(2*a*)—Zn(2)—Cl(2*c*)	108.8 (1)	Cl(2*b*)—Zn(2)—Cl(2*c*)	110.8 (2)
N(2)—C(1)—C(1*a*)	110.1 (10)	Zn(1)—N(2)—C(1)	108.2 (10)
Zn(1)—N(2)—C(3)	117.0 (12)	C(1)—N(2)—C(3)	115.7 (14)
N(2)—C(3)—C(4)	111.2 (15)	C(3)—C(4)—C(5)	112.2 (17)
C(4)—C(5)—N(6)	113.2 (15)	Zn(1)—N(6)—C(5)	111.7 (10)
Zn(1)—N(6)—C(7)	105.6 (12)	C(5)—N(6)—C(7)	120.0 (16)
N(6)—C(7)—C(7*a*)	112.7 (16)		

Experimental. Cyclam was prepared by the method of Barefield, Wagner, Herlinger & Dahl (1976). Addition of $ZnCl_2$ (0.68 g, 0.005 mol) in ethanol (20 cm^3), to a solution of cyclam (1.0 g, 0.005 mol) in ethanol (25 cm^3) gave a precipitate of the zinc(II) dichloride complex. This was filtered and washed with diethyl ether (yield 0.89 g, 53%). Recrystallization from methanol/nitromethane gave needle-shaped crystals. ^{13}C NMR spectra were obtained using a Bruker WH-180 spectrometer at 45.28 MHz.

Crystallographic data were collected with a Nicolet $P2_1$ four-circle diffractometer in ω–2θ mode. Maximum 2θ was 50° with scan range ± 1.2° (2θ) around the $K\alpha_1$–$K\alpha_2$ angles, scan speed 2.5–29° min^{-1}, depending on the intensity of a 2 s prescan; backgrounds were measured at each end of the scan for 0.25 of the scan time. *hkl* ranges were: 0/21; 0/21; 0/12. Three standard reflections were monitored every 200 reflections and showed a slight decrease during data collection (2%). The data were rescaled to correct for this. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 reflections ($20 < 2\theta < 26°$). The 2041 reflections examined (including 291 not satisfying the *I*-lattice condition) were processed using profile analysis. Merging in Laue group $4/mmm$ gave 877 unique reflections ($R_{int} = 0.025$) of which 750 were considered observed [$I/\sigma(I) \geq 2.0$]. These were corrected for Lorentz and polarization but not absorption effects. Crystal dimensions were $0.14 \times 0.12 \times 0.37$ mm.

Systematic conditions: *hkl*, $h + k + l = 2n + 1$; *hhl*, $2h + l = 4n$ are consistent with space groups $I4_1md$ or $I\bar{4}2d$; the latter was confirmed by refinement. Initially, structure solution was attempted by both

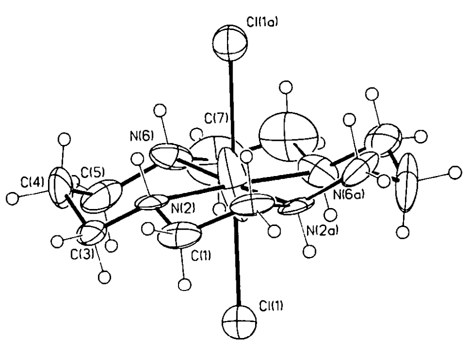

Fig. 1. Portion of the —Cl—[Zn(cyclam)]$^{2+}$ —Cl— cation showing the atomic numbering (50% probability ellipsoids).

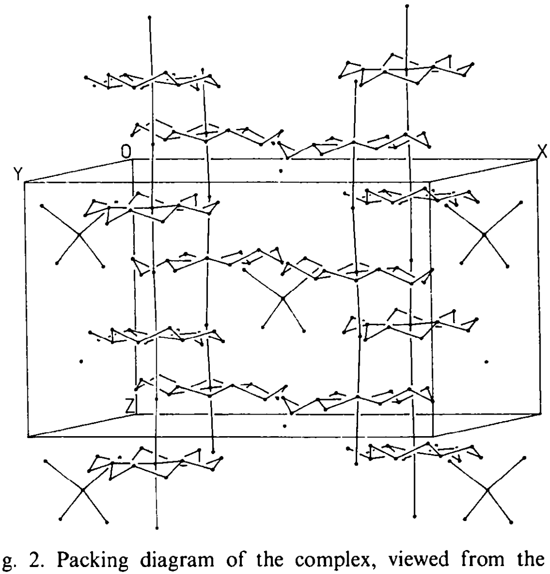

Fig. 2. Packing diagram of the complex, viewed from the 110 direction.

Table 3. ^1H *decoupled* ^{13}C *NMR chemical shifts* (δ; *reference* 1,4-*dioxane at* δ 67.4 *in* D_2O, *and* CD_3NO_2 *at* δ 62.8 *in* CD_3NO_2)

Species	Cyclam in CD_3NO_2	$ZnCl_2$/ cyclam complex in CD_3NO_2	$ZnCl_2$/ cyclam complex in D_2O (fresh solution)	$ZnCl_2$/ cyclam complex in D_2O (after 24 h), major species	$ZnCl_2$/ cyclam complex in D_2O (after 24 h), minor species
C—*C*H₂—C	29.6	29.5	28.7	28.7	28.3
N—*C*H₂—C—C—N	49.5	48.9	48.4	48.4	49.0
N—*C*H₂—C—N	50.8	51.0	50.7	49.8	51.0

Patterson and direct methods in both space groups, without success. The problems of Patterson interpretation were compounded by the unexpected stoicheiometry (Zn:*L* 3:2 rather than 1:1), and by the disorder affecting one of the Zn atoms. Eventually a solution was obtained from the Patterson synthesis in $I\bar{4}2d$, with Zn(1) and Cl(1) of the cation in position 8(*d*) (symmetry 2) and Zn(2) of the anion in 4(*a*) (symmetry $\bar{4}$). The light atoms were then found on successive Fourier syntheses. After refinement to *R* = 0.105, a large residual peak remained at 0.5, 0.5, 0.0 [4(*b*)]; following inclusion of the O atom of a presumed solvent water molecule at this point, the only substantial residuals (2 e Å^{-3}) were near Zn(1) and Cl(1) in the cation. Zn(1) has anomalous thermal parameters indicative of disorder (see below); this disorder almost certainly affects the ligand and C(1), though we were not able to model their behaviour. This imperfect modelling probably accounts for the relatively high *R* value. Refinement was also attempted in space group $I\bar{4}$ but not surprisingly (in view of the good merging *R* already mentioned) this failed to produce any improvement.

Anisotropic thermal parameters were used for all non-H atoms. H atoms were given fixed isotropic temperature factors, $U = 0.07$ Å^2, and were inserted at calculated positions and not refined. Final refinement was on *F* by cascaded least-squares method refining 86 parameters. A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ with $g = 0.0008$ was used and shown to be satisfactory by a weight analysis. Final $R = 0.095$, $wR = 0.100$. Maximum shift/e.s.d. in final cycle was 0.18. Computing was with *SHELXTL-Plus* (Sheldrick, 1986) on a DEC MicroVAX II. Scattering factors in the analytical form and anomalous-dispersion factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Final atomic coordinates are given in Table 1, and bond lengths and angles in Table 2.* The molecular structure and packing diagram are in Figs. 1 and 2.

Discussion. The structure determination shows that the product of the reaction of $ZnCl_2$ and cyclam is not the expected 1:1 complex but has a 3:2 stoicheiometry. It comprises infinite —Cl—[Zn(cyclam)]$^{2+}$—Cl— chains interspersed with $[ZnCl_4]^{2-}$ ions. This is in contrast to $[Ni(cyclam)Cl_2]$ which contains discrete molecules with octahedrally coordinated Ni (Bosnich, Mason, Pauling, Robertson & Tobe, 1965). However, the cyclam molecule shows the same *trans*-(III) conformation in both complexes. A similar infinite-chain structure is found for $HgCl_2$ in its complex with the analogous 16-membered ring tetrazamacrocycle, 1,5,9,13-tetraazacyclohexadecane, though this ligand has all its N—H bonds on the same side of the ring (Alcock, Curzon & Moore, 1984). Such chains also occur for Zn in [ZnCl(tetrahydrofuran)(μ-Cl)], but with tetrahedrally coordinated metal atoms (Bottomley, Ferris & White, 1989).

The distinction between Zn and Ni may arise from the greater propensity of Zn to form an $[MCl_4]^{2-}$ ion, though such ions are of course known for Ni. The size difference may also contribute. The Zn—N bonds are rather variable, but their mean [2.13 (1) Å] is longer than for Ni (2.06 Å); the Zn—Cl bonds are also longer [2.730 (4) compared to 2.492 Å], though those in the anion are considerably shorter [2.288 (5) Å]. The Zn—N bonds in the tetramethylcyclam complex are significantly longer still [2.20 (1) Å]. Furthermore, Zn(1) has anomalous thermal parameters, with a large component lying nearly along the chain axis (see Fig. 1). This is indicative of its being unable to fit comfortably at the centre of the cyclam ring. We conclude that the small size difference between Ni^{2+} and Zn^{2+} is just sufficient to cause the switch from a simple octahedral complex to that observed.

The ^{13}C NMR spectra (Table 3) show that the complex undergoes a slow isomerization in aqueous solution, though it is stable in nitromethane. The species in nitromethane solution is probably $[ZnCl(cyclam)]^+$ derived from the break up of the

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* Lists of anisotropic thermal parameters, H-atom coordinates and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54460 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU0269]

chloride chain, *i.e.* with the *trans*-(III) conformation and with an axially coordinated chloride ligand. As the spectra show only three ^{13}C resonances this chloride must be in rapid exchange between the two axial positions on the NMR timescale; a six-coordinate structure cannot be ruled out, with coordinated nitromethane in the remaining axial position. In aqueous solution an analogous *trans*-(III) structure is likely upon first dissolution of the complex, probably with water replacing the axial chloride, but a minor isomer forms after 24 h (Table 3). This isomer has the same number of resonances as the original species, and only the *trans*-(I) isomer satisfies this requirement. Isomerism from *trans*-(III) to *trans*-(I) forms has been observed previously for nickel(II) complexes of tetramethylcyclam (Moore, Sachinidis & Willey, 1983). By analogy with the nickel(II) complexes, it is likely that in the *trans*-(I) form the Zn atom is five coordinate, with the axial position occupied by a water molecule or chloride ion. In water, the *trans*-(III) form is most probably six coordinate with two axially bonded water molecules.

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Structure of Disodium Methyl Phosphate Hexahydrate

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Abstract. $2Na^+.CH_3O_4P^{2-}.6H_2O$, $M_r = 264.09$, monoclinic, Pc, $a = 7.277$ (1), $b = 6.298$ (2), $c = 11.477$ (4) Å, $\beta = 92.44°$, $V = 525.5$ Å^3, $Z = 2$, $D_x = 1.669$ g cm^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, $\mu = 35.26$ cm^{-1}, $F(000) = 276$, $T = 298$ K, $R = 0.028$ for 781 independent reflections. Three P—O bond lengths are the same (1.513 Å) within experimental error, with the ester P—O bond length significantly longer [1.626 (3) Å]. The Na ions are octahedrally coordinated by water O atoms and have no direct interaction with the phosphate O atoms. Water molecules form three hydrogen bonds with each phosphate O atom, except the ester O atom which at most forms one weak interaction.

Introduction. Because the phosphodiester linkage is important for the structure and electrostatic properties of nucleic acids and phospholipids, we decided to carry out an experimental study of the charge density distribution of this group, using the crystal structure of a suitable salt of dimethyl phosphate as a model system. Although we have recently achieved this objective (Klooster & Craven, unpublished results), our initial efforts to obtain the monosodium salt by hydrolysis of trimethyl phosphate, gave the disodium salt. The composition of the disodium methyl phosphate hexahydrate crystals was determined by the X-ray structure determination which we now report.

Experimental. Hydrolysis of trimethyl phosphate (Aldrich Chemical Company, Inc.) with an equimolar amount of sodium hydroxide in ethanol (McIvor, McCarthy & Grant, 1956), after evaporation to dryness, gave only a few crystals suitable for X-ray study. A crystal 0.5 × 0.2 × 0.2 mm elongated along the c axis, showing the forms {100}, {010} and {001}, was mounted with the c axis close to the φ axis of an Enraf–Nonius CAD-4 diffractometer. Cell dimensions were obtained from 20 centered reflections ($12 < 2\theta < 114°$), Ni-filtered Cu $K\alpha$ radiation. Bragg intensities were measured to $2\theta \leq 120°$, ω–2θ scans,

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