pected in that unlike Cu(II) all six binding sites of Ni(II) are essentially equivalent. Molecular models indicate that structure II is favored for these Ni(II) chelates on the basis of strain. Equilibrium constants for the addition of amino acidates to the Ni(II) *N*-mepyr-L-Asp and *N*-pyr-L-Asp chelates (log $K \simeq 3.7$) are considerably lower than those of the Ni(II) complexes of NTA (log $K \simeq 4.7$)[25] and dien (log $K \simeq 5.1$).[27]

The constants listed in Table I indicate that the Cu(II) and Ni(II) chelates of *N*-mepyr-L-Asp and *N*-pyr-L-Asp coordinate L enantiomers of amino acidates more strongly or equally as strongly as the D isomers except for the small opposite effect found in the Cu^{II}–*N*-mepyr-L-Asp–threonine system. The differences (Δ in Table I) between the K_X values for L- and D-amino acid enantiomers generally decrease with decreasing size of the α substituent of the amino acidate, *i.e.*, Phe > Try > Val > Leu ~ Thr ~ Ala, indicating that the stereoselectivity results from steric interactions and possibly the aromatic character of the side chain. The metal complexes of *N*-mepyr-L-Asp yield larger Δ values than those of *N*-pyr-L-Asp also indicating the importance of steric interactions.

The structure of the mixed-ligand chelate most compatible with the observed potentiometric data and steroselectivity is II. The α substituent (R) of the L enantiomer of the amino acid in II is pointing away from the bulky pyridyl residue while in the D isomer the R group is directed toward the aromatic ring. Thus, L-amino acids are bound more strongly than their D enantiomers.

Copper(II) complexes of *N*-mepyr-L-Asp exhibited the greatest amount of stereoselectivity. This is probably due to the increased crowding caused by the smaller size of Cu(II) as compared to Ni(II) and the 6-methyl group of the pyridyl group. The substantial preference of the metal chelates for the L enantiomers of Try and Phe are encouraging, and further studies are currently in progress in these laboratories.

Acknowledgment. We appreciate the support of this research by the U. S. Public Health Service through Grant No. GM-12626 of the National Institute of General Medical Sciences.

Registry No. *N*-pyr-L-Asp, 41203-01-4; *N*-mepyr-L-Asp, 41203-02-5; Cu(*N*-pyr-L-Asp)$(H_2O)_2$, 41203-03-6; Ni(*N*-pyr-L-Asp)$(H_2O)_2$, 41203-04-7; Cu(*N*-mepyr-L-Asp)$(H_2O)_2$, 41203-05-8; Ni(*N*-mepyr-L-Asp)$(H_2O)_2$, 41203-06-9; Cu(*N*-pyr-L-Asp)$(OH)^-(H_2O)$, 41203-07-0; Cu_2(*N*-mepyr-L-Asp)$_2(OH)_2{}^{2-}$, 41203-08-1; Cu(*N*-pyr-L-Asp)(L-Phe)$^-$, 41203-09-2; Ni(*N*-pyr-L-Asp)(L-Phe)$^-$, 41203-10-5; Cu(*N*-mepyr-L-Asp)(L-Phe)$^-$, 41203-11-6; Ni(*N*-mepyr-L-Asp)(L-Phe)$^-$, 41203-12-7; Cu(*N*-pyr-L-Asp)(D-Phe)$^-$, 41203-13-8; Ni(*N*-pyr-L-Asp)(D-Phe)$^-$, 41212-29-7; Cu(*N*-mepyr-L-Asp)(D-Phe)$^-$, 41212-30-0; Ni(*N*-mepyr-L-Asp)(D-Phe)$^-$, 41212-31-1; Cu(*N*-pyr-L-Asp)(L-Try)$^-$, 41212-32-2; Ni(*N*-pyr-L-Asp)(L-Try)$^-$, 41212-33-3; Cu(*N*-mepyr-L-Asp)(L-Try)$^-$, 41212-34-4; Ni(*N*-mepyr-L-Asp)(L-Try)$^-$, 41212-35-5; Cu(*N*-pyr-L-Asp)(D-Try)$^-$, 41212-36-6; Ni(*N*-pyr-L-Asp)(D-Try)$^-$, 41212-37-7; Cu(*N*-mepyr-L-Asp)(D-Try)$^-$, 41212-38-8; Ni(*N*-mepyr-L-Asp)(D-Try)$^-$, 41212-39-9; Cu(*N*-pyr-L-Asp)(L-Val)$^-$, 41212-40-2; Ni(*N*-pyr-L-Asp)(L-Val)$^-$, 41212-41-3; Cu(*N*-mepyr-L-Asp)(L-Val)$^-$, 41212-42-4; Ni(*N*-mepyr-L-Asp)(L-Val)$^-$, 41212-43-5; Cu(*N*-pyr-L-Asp)(D-Val)$^-$, 41212-44-6; Ni(*N*-pyr-L-Asp)(D-Val)$^-$, 41212-45-7; Cu(*N*-mepyr-L-Asp)(D-Val)$^-$, 41385-45-9; Ni(*N*-mepyr-L-Asp)(D-Val)$^-$, 41212-46-8; Cu(*N*-pyr-L-Asp)(L-Thr)$^-$, 41212-47-9; Ni(*N*-pyr-L-Asp)(L-Thr)$^-$, 41212-48-0; Cu(*N*-mepyr-L-Asp)(L-Thr)$^-$, 41212-49-1; Ni(*N*-mepyr-L-Asp)(L-Thr)$^-$, 41212-50-4; Cu(*N*-pyr-L-Asp)(D-Thr)$^-$, 41212-51-5; Ni(*N*-pyr-L-Asp)(D-Thr)$^-$, 41212-52-6; Cu(*N*-mepyr-L-Asp)(D-Thr)$^-$, 41212-05-9; Ni(*N*-mepyr-L-Asp)(D-Thr)$^-$, 41212-06-0; Cu(*N*-pyr-L-Asp)(L-Leu)$^-$, 41212-07-1; Ni(*N*-pyr-L-Asp)(L-Leu)$^-$, 41212-08-2; Cu(*N*-mepyr-L-Asp)(L-Leu)$^-$, 41212-09-3; Ni(*N*-mepyr-L-Asp)(L-Leu)$^-$, 41212-10-6; Cu(*N*-pyr-L-Asp)(D-Leu)$^-$, 41212-11-7; Ni(*N*-pyr-L-Asp)(D-Leu)$^-$, 41212-12-8; Cu(*N*-mepyr-L-Asp)(D-Leu)$^-$, 41212-13-9; Ni(*N*-mepyr-L-Asp)(D-Leu)$^-$, 41212-14-0; Cu(*N*-pyr-L-Asp)(L-Ala)$^-$, 41212-15-1; Ni(*N*-pyr-L-Asp)(L-Ala)$^-$, 41212-16-2; Cu(*N*-mepyr-L-Asp)(L-Ala)$^-$, 41212-17-3; Ni(*N*-mepyr-L-Asp)(L-Ala)$^-$, 41385-46-0; Cu(*N*-pyr-L-Asp)(D-Ala)$^-$, 41212-18-4; Ni(*N*-pyr-L-Asp)-(D-Ala)$^-$, 41212-19-5; Cu(*N*-mepyr-L-Asp)(D-Ala)$^-$, 41212-20-8; Ni-(*N*-mepyr-L-Asp)(D-Ala)$^-$, 41212-21-9; L-aspartic acid, 56-84-8; 2-pyridinecarboxaldehyde, 1121-60-4; 6-methyl-2-pyridinecarboxaldehyde, 1122-72-1.

(27) N. E. Jacobs and D. W. Margerum, *Inorg. Chem.*, **6**, 2038 (1967).

Contribution from the W. A. Noyes Laboratory, School of Chemical Sciences,
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Metal Complexes of 1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane, *N*-Tetramethylcyclam

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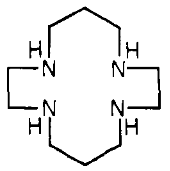
Received April 5, 1973

Preparations and properties of some nickel(II), copper(II), and zinc(II) complexes of the new 14-membered macrocyclic ligand 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane, II (*N*-tetramethylcyclam), are reported. Complexes of these metals are five-coordinate when a suitable anion or solvent molecule is available. Spectral data for a number of five-coordinate Ni(II) complexes are given. Nmr results on the Zn(TMC)Cl$^+$ ion indicate all four methyl groups are on the same side of the coordination plane. Qualitatively, the nickel(II) complex is kinetically labile compared to complexes of other ligands of the 14-membered class.

Investigations of metal complexes containing macrocyclic ligands has been an area of active research for several years.[1] Of the several tetradentate macrocyclic ligands known, by far the largest number of these contain 14 members and are perturbations on the simplest, 1,4,8,11-tetraazacyclotetradecane, which is commonly known as cyclam, I.[2] As a part of our own investigations on the redox chemistry of Ni(III) complexes of certain of these saturated 14-membered tetra-



I

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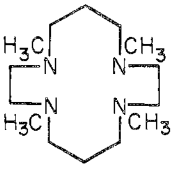
(1) Progress in this area is reviewed by L. F. Lindoy and D. H. Busch, *Prep. Inorg. React.*, **6**, 1 (1971).

(2) B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, **4**, 1102 (1965).

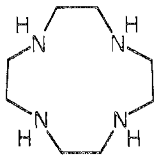
dentate ligands we desired a ligand which most likely could not undergo the process

$$Ni^{III}-N\langle-H + B \rightarrow Ni^{II}-N\langle\cdot + BH^+$$

which was found for nickel(III) complexes of secondary amines.[3] We chose as a possibility the previously unknown *N*-methylated tetramine, II, which we prepared by methylation of cyclam, hereafter designated as tetramethylcyclam or TMC. This is the first 14-membered macrocyclic ligand with four tertiary donors. Blinn earlier reported the preparation of a 12-membered tertiary tetramine ligand of the cyclen type, III, but these ligands can only bond to cis positions because of the small size of the "hole."[4] In fact, to our knowledge there are only two other examples of synthetic macrocyclic ligands containing tertiary donors and neither of these contains more than one tertiary center.[5] Because there is interest in the stereochemistry of complexes of the 14-membered family of secondary amine ligands bearing methyl substituents at carbon positions and because the stereochemistry of the new complexes would be of importance to their Ni(III) chemistry, we undertook an investigation of some general aspects of the coordination chemistry of this novel ligand with the divalent metal ions Ni, Cu, and Zu. Some of our findings are the subject of this report.



II



III

Experimental Section

All chemicals used in the following preparations were reagent grade where available and were used without further purification. Cyclam was prepared by a modification of a recently published synthesis.[6]

1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane (Tetramethylcyclam). A solution consisting of 9 g (0.045 mol) of cyclam, 48 ml of formic acid (98–100%), 40 ml of formaldehyde (40%), and 5 ml of water was refluxed for 24 hr. The reaction mixture was then transferred with 50 ml of water to a 500-ml beaker and cooled to *ca.* 5° in an ice bath. While stirring, a concentrated solution of sodium hydroxide (30 g of NaOH dissolved in 100 ml of water) was slowly added to pH >12. The temperature of the solution was kept below 25° during the addition. The solution was then extracted with five 100-ml portions of chloroform. The extracts were combined and dried over anhydrous sodium sulfate. The extracts were then filtered and reduced in volume to an oily residue. The residue was transferred to a 100-ml round-bottom flask. A small amount of chloroform was used to wash the remaining oil from the evaporation flask and then added to the 100-ml round-bottom flask containing the bulk of the oil. After removing the $CHCl_3$ the product distilled at 120° (0.1 mm). Care was taken in the initial stage of distillation to minimize foaming caused by the rapid evolution of the residual chloroform. The clear distillate solidified to a mat of long white needles; yield 6 g or 52%. Yields are sometimes as high as 80%.

The nmr spectrum of this material at 60 MHz in $CDCl_3$ consists of a multiplet at 1.62 ppm, $I = 1$, a singlet at 2.16 ppm, $I = 3$, and a singlet and overlapping triplet ($J = 5$–6 Hz) at 2.30 ppm, $I = 4$. Mass spectral analysis indicated the parent molecule ion at 256.

$Ni(TMC)(ClO_4)_2$. An aqueous solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (1 g, 27 mmol in 10 ml) was mixed with 10 ml of ethanol containing 0.4 g (15 mmol) of tetramethylcyclam. The mixture was stirred for 3 hr, filtered, and then taken to dryness on a rotary evaporator. The residue was transferred to a fritted funnel with absolute ethanol and the red product was washed with five 20-ml portions of ethanol. The product was finally washed with ether and dried *in vacuo* at 100° for 3 hr; yield 0.57 g or 70%.

$Zn(TMC)(ClO_4)_2$. This preparation was the same as that for the nickel complex. Care was taken in washing the product due to its increased solubility in ethanol; yield based on 1 g of zinc perchlorate—56%.

Five-Coordinate Nickel and Zinc Complexes. These complexes volunteered after addition of a slight excess of the appropriate sodium salt to concentrated aqueous solutions of the perchlorate complexes. The resulting materials could be recrystallized from water or water–ethanol mixtures if necessary. Solids were collected by suction and washed with ethanol and ether to dry. In the case of the thiocyanate 1 equiv of sodium thiocyanate was used and the green precipitate was recrystallized from $CHCl_3$.

$Ni(TMC)(NCS)_2$. This complex was prepared by treating the perchlorate complex with excess sodium thiocyanate in water. The blue precipitate was recrystallized from $CHCl_3$ by slow evaporation.

$Cu(TMC)(ClO_4)_2$. Aqueous solutions of $Cu(ClO_4)_2 \cdot 6H_2O$ (1.85 g, 5 mmol in 20 ml) and tetramethylcyclam (1.28 g, 5 mmol in 30 ml) were mixed and the mixture was filtered. The blue solution was evaporated under a gentle stream of air to give dark blue crystals. These were collected and recrystallized from ethanol-water. This recrystallized material was dried *in vacuo* at 80° overnight; yield 80%.

$[Cu(TMC)Br]ClO_4$. $Cu(TMC)(ClO_4)_2$ was treated with 1 equiv of KBr in a small amount of water. The blue solution which resulted was evaporated to dryness and the residue was taken up in nitromethane, filtered to remove $KClO_4$, and evaporated to yield a blue complex which was collected and dried *in vacuo*. Yields were about 80%.

Analytical data for the new complexes are contained in Table I. These analyses were performed by the School of Chemical Sciences analytical laboratory. Infrared spectra were obtained on Nujol mulls or chloroform solutions (0.1-mm NaCl cells) using a Perkin-Elmer 457 spectrophotometer. Nmr spectra were obtained on a Varian 220-MHz spectrometer on CF_3CO_2H and CD_3NO_2 solutions. The Evans method[7] susceptibility measurements were done on aqueous solutions with a Varian A-60A spectrometer using *tert*-butyl alcohol as the standard. Electronic spectra were obtained using a Cary 14RI spectrophotometer using 1-cm quartz cells for solutions and Nujol mulls supported on filter paper for solids.

Results and Discussion

Syntheses and Properties of New Compounds. The new tetramine was prepared by direct methylation of cyclam, I, using formic acid and formaldehyde according to the general procedure in ref 8. Our recently developed synthesis of cyclam made this a convenient route.[6] The structure of II is supported by analytical and spectroscopic data (see Experimental Section and Table I). Reactions of aqueous or ethanolic solutions of II with aqueous solutions of nickel(II), copper(II), and zinc(II) perchlorates produce red-violet, blue, and colorless solutions, respectively. Depending upon the treatment of these solutions and the metal ion, complexes of stoichiometry $M(TMC)X_2$, $[M(TMC)X]Y$, and $[M(TMC)]Y_2$ (X is coordinating anion, Y is noncoordinating) can generally be isolated. A list of complexes prepared and data pertinent to their characterization are given in Tables I and II. Forma-

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(3) E. K. Barefield and M. T. Mocella, Abstracts, 165th National Meeting of American Chemical Society, Dallas, Tex., April 1973, No. INOR 139; submitted for publication.

(4) G. A. Kalligeros and E. L. Blinn, *Inorg. Chem.*, 11, 1145 (1972).

(5) L. L. Rusnak and R. B. Jordon, *Inorg. Chem.*, 10, 2686 (1971); R. Grigg and A. Sweeney, *Chem. Commun.*, 1273 (1970).

(6) E. K. Barefield, *Inorg. Chem.*, 11, 2273 (1972). We have found substantially improved yields are obtained if sodium borohydride is used as a reducing agent for this preparation (yield of cyclam—50%). This modified synthesis has been accepted for publication in *Inorg. Syn.*

(7) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

(8) "Organic Syntheses," Collect. Vol. 3, Wiley, New York, N. Y., 1955, p 723.

Table I. Analytical Data for *N*-Tetramethylcyclam and Its Metal Complexes

	% calcd				% found			
	C	H	N	M	C	H	N	M
$C_{14}H_{32}N_4 \equiv L$	65.55	12.58	21.86		65.61	12.60	21.57	
$NiL(ClO_4)_2$	32.69	6.27	10.90	11.42	32.40	6.15	10.88	11.15
$[NiLCl]ClO_4$	37.36	7.16	12.45	13.04	37.61	7.15	12.37	12.85
$[NiLBr]ClO_4$	33.98	6.52	11.33	11.88	33.98	6.35	11.10	11.78
$(NiLNCS)ClO_4$	38.12	6.92	14.81	12.41	38.15	7.09	14.75	12.35
$NiL(NCS)_2$	44.55	7.49	19.49		44.17	7.18	19.55	
$CuL(ClO_4)_2$	32.38	6.21	10.80	12.24	32.20	6.08	11.10	12.09
$[CuLBr]ClO_4$	33.65	6.46	11.22	12.73	34.09	6.60	10.95	12.69
$ZnL(ClO_4)_2$	32.27	6.19	10.76	12.55	32.25	6.20	10.85	12.53
$[ZnLCl]ClO_4$	36.79	7.06	12.27	14.32	37.00	6.83	12.36	14.30

Table II. Spectral, Magnetic, and Conductivity Data for Ni(II), Cu(II), and Zn(II) Complexes of *N*-Methylated Cyclam (L)

Complex	Color	μ_{eff}, BM	Λ_M[a]	Electronic spectral data,[b] λ (ϵ)
$NiL(ClO_4)_2$	Red	Diamag	155	519 (184), 520[c]
				1130 (23), 800 sh (44), 654 (29), 511 (71), 392 (104)[d]
				1480 (9), 981 (3), 790 sh (7), 610 (34), 390 (118)[e]
$[NiLCl]ClO_4$	Green	3.3	92	1785 (9), 1110 (4), 869 sh (11), 820 (54), 602 sh (9), 524 (12), 406 (170)
$[NiLBr]ClO_4$	Green	3.2	94	1896 (10), 1170 (4), 881 sh (11), 726 (50), 619 sh (13), 540 (11), 433 (172)
$[NiLNCS]ClO_4$	Green	3.3	78	1495 (11), 1060 (3), 901 sh (8), 657 (55), 573 sh (14), 495 sh (8), 400 (147)
$NiL(NCS)_2$	Blue	3.1	Nonelec	975 (10), 820 sh (5), 610 (13), 390 (23)
$CuL(ClO_4)_2$	Blue		154	583 (214), 627 (227),[d] 580[c]
$[CuLBr]ClO_4$	Blue		100	787 (122)
$[ZnLCl]ClO_4$	White		152	
$ZnL(ClO_4)_2$	White		83	

[a] Ohm^{-1} cm^{-2} M^{-1}; CH_3NO_2 solutions, *ca.* 10^{-3} *M*. [b] CH_3NO_2 solutions unless otherwise specified; wavelength in nm, extinction coefficient in parentheses in M^{-1} cm^{-1}. [c] Solid state; diffuse transmittance. [d] H_2O solution. [e] Acetonitrile solution.

tion of the nickel complex is qualitatively much slower than that of the copper complex and is hampered by hydroxide formation in aqueous solution.

Infrared spectra for these complexes show that no NH absorptions are present but little further information can be gained from this source. Magnetic susceptibility data given in Table II indicate all the nickel complexes except Ni(TMC)-$(ClO_4)_2$ are high spin in the solid state. These remain high spin in nonionizing solvents. Ni(TMC)$(ClO_4)_2$ is diamagnetic in the solid state but is at least partially paramagnetic in most solvents except CF_3CO_2H. Conductivity measurements (Table II) indicate the acido perchlorate complexes of nickel, copper, and zinc to be 1:1 electrolytes in nitromethane while the bis(perchlorates) are 2:1 electrolytes. Ni(TMC)$(NCS)_2$ is a nonelectrolyte in nitromethane.

Absorption spectral data for the copper and nickel complexes are given in Table II. Spectra of the nickel(II) acido perchlorate complexes are characterized by six or seven observable bands in their solution absorption spectra, ranging in energy from about 6000 to 25,000 cm^{-1}. Spectra with similar features are obtained on solid samples by the diffuse-transmittance technique. Spectra of this type with very low energy transitions are not typical of octahedral or tetragonal complexes but are similar to those observed for five-coordinate species.[9] These data do not distinguish between square-pyramidal and trigonal-bipyramidal geometries (the latter could result from folding of the macrocyclic ligand). Other information obtained on these complexes suggests that the geometry is square pyramidal, *vide infra,* and the spectra appear to be consistent with those expected for this geometry although no calculations have been performed.

The electronic spectrum of Ni(TMC)$(ClO_4)_2$ in the solid state consists of a single absorption at 515 nm but its solution spectrum is highly solvent dependent. A single absorption at 519 nm is observed in nitromethane but in acetonitrile a spectrum consistent with a high-spin, five-coordinate species is obtained (Table II). In water the observed spectrum consists of absorptions at 1130, 800, 654, 511, and 392 nm which are expected for high-spin five- or six-coordinate species (the near-infrared region of the spectrum cannot be obtained because of the solvent) but the absorption at 511 nm is probably due to the same species present in the solid state and in nitromethane or trifluoroacetic acid solution. Susceptibility measurements on more concentrated solutions (by the Evans method)[7] indicate that the equilibrium constant for the reaction

$$Ni(TMC)^{2+} + nH_2O \rightleftharpoons Ni(TMC)(H_2O)_n{}^{2+}$$

is about 1. The nature of the species actually present in solution is difficult to ascertain but a conversion of diamagnetic (planar), four-coordinate complex to paramagnetic, five-coordinate complex is most likely considering the obvious propensity of the $Ni(TMC)^{2+}$ ion for formation of five-coordinate species.

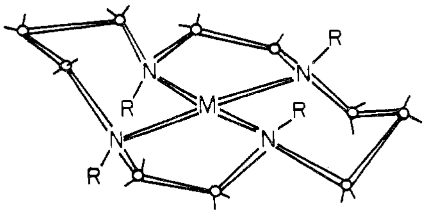
The single six-coordinate nickel complex, Ni(TMC)$(NCS)_2$, prepared by treating Ni(TMC)$(ClO_4)_2$ with excess NaNCS in water had an absorption spectrum similar to those of other six-coordinate complexes of this general type. The infrared spectrum of this complex in chloroform solution contained two C≡N stretching absorptions at 2080 and 2095 cm^{-1}.

Spectral data for copper(II) are not as diagnostic of coordination number and geometry as those for nickel but the single rather low energy absorption for [Cu(TMC)Br]ClO_4 in nitromethane and for Cu(TMC)$(ClO_4)_2$ in water are consistent with five-coordination. This conclusion is supported by conductivity measurements. The data for Cu(TMC)$(ClO_4)_2$ in nitromethane and in the solid state indicate that the ion is most likely four-coordinate.

Stereochemistry. The fact that complexes of *N*-methylated cyclam tend to be five-coordinate in the solid state if a coordinating anion is present is well established by the just described spectral, conductivity, and magnetic data. It also appears that in solution the nickel and possibly the copper complex of the tertiary macrocycle coordinate solvents readily to yield five-coordinate species. This behavior was

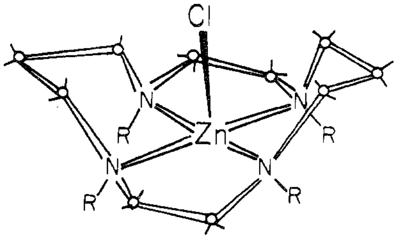
(9) C. Furlani, *Coord. Chem. Rev.*, **3**, 141 (1968), and references therein.

not observed for Ni(cyclam)$^{2+}$ which is planar (as detected by absorption spectroscopy) in every ordinary solvent (the complex is solvated in liquid ammonia to give a six-coordinate species). The aforementioned data do not distinguish between square-pyramidal and trigonal-bipyramidal geometries nor do they bear on the problem of the donor nitrogen configurations. Both nickel(II) (NiLCl$_2$)[10a] and lithium (LiLClO$_4$)[10b] complexes of cyclam have structure IV (the trans III structure according to the designation of Bosnich, *et al.*[2]), and this structure has been inferred for certain other C-substituted cyclam-like complexes.[10c] However, methyl substituents on the ring can have a pronounced effect on the sets of donor configurations which can be obtained in isomerization reactions.[10c]



IV

The facile formation of five-coordinate complexes for the present ligand suggested that the trans III set of configurations might not be present. The nmr spectra of Ni(TMC)(ClO$_4$)$_2$ in CF$_3$CO$_2$H and Zn(TMC)(ClO$_4$)$_2$ in CD$_3$NO$_2$ show only one sharp methyl resonance even at 220 MHz. This indicates these complexes are isomerically pure and it also eliminates one of the five sets of nitrogen configurations available for a planar arrangement of donors[2] and presumably all nonplanar arrangements. The nmr spectrum of [Zn(TMC)Cl]ClO$_4$ at 220 MHz is shown in Figure 1. The most interesting and important feature of this spectrum is the single methyl resonance which is observed at −2.62 ppm. This result is consistent with the stereochemical arrangement of donors shown as V.[11] If the chloride ion was on the same side of the plane as the methyl groups, the nmr result would be the same but this seems unreasonable because molecular models indicate there should be a large "hole" on the side opposite the methyls. Although the remaining features of the spectrum are complicated, they can in large part be assigned on the basis of couplings and chemical shifts. The following assignment of resonances is based on the assumption of a chair conformation for the six-membered chelate rings. This must be the case, since the methyl groups are constrained to approximate axial positions; a boat conformation would lead to severe steric interaction between the methyl groups and the α hydrogens. The following numbering scheme is useful for assigning the protons of the six-membered ring.



V

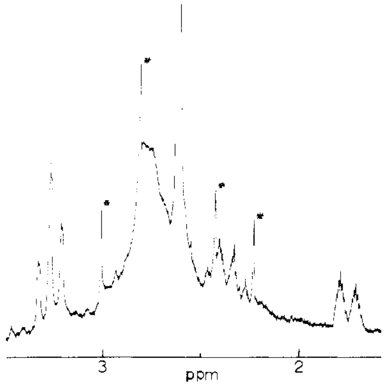
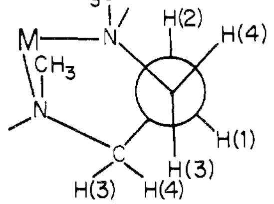
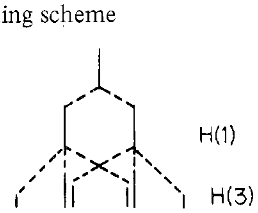


Figure 1. Nmr spectrum of [Zn(TMC)Cl]ClO$_4$ in CD$_3$NO$_2$ at 220 MHz. Spinning side bands are denoted by asterisks.



These six protons should exhibit (AB)$_2$XY behavior. However, chemical shift differences are large enough so that an approximate first-order analysis is sufficient to assign the resonances observed. The higher field multiplets centered at 1.75 and 2.37 ppm, respectively, are assigned on the basis of integrated intensity and field position to the center methylene protons, H(1) and H(2). Decoupling experiments indicate the protons at 1.75 ppm are coupled to those occurring at 3.27 ppm ($J \approx 1$ Hz) and to those at about 2.8 ppm ($J \approx 2$ Hz). These very small couplings suggest that they are to vicinal protons which are gauche. In a chair conformation protons H(3) and H(4) are both gauche only to H(1). Thus the resonance centered at 1.75 ppm is assigned to H(1) (the major splitting into the doublet is a result of the gem coupling to H(2)). The apparent quartet at 2.37 ppm is then assigned to H$_2$. The coupling scheme accounts for the major quartet structure. Additional smaller coupling is to H(4). The apparent triplet at 3.27 ppm is then assigned to H(3). Protons H(4) and the protons in the five-membered chelate ring account for the featureless resonance at 2.8 ppm.



The question of whether the observed stereochemistry is a

[10] (a) B. Bosnich, R. Mason, P. Pauling, G. B. Robertson, and M. L. Tobe, *Chem. Commun.*, 97 (1965); (b) D. E. Fenton, C. Nave, and M. R. Truter, *J. Chem. Soc., Chem. Commun.*, 1303 (1972); (c) L. G. Warner and D. H. Busch, *J. Amer. Chem. Soc.*, 91, 4092 (1969).

[11] This is not the only possible interpretation of this observation, although it seems most likely. It is possible that a single methyl resonance could arise as a result of the equilibrium Zn(TMC)Cl$^+ \rightleftharpoons$ ZnTMC^{2+} + Cl$^-$. Conductivity data for this system indicate K_{eq} for such a process must be small. However, if the rates of the forward and reverse reactions are high enough, any isomer with a set of nitrogen configurations which places two methyls on each side of the coordination plane would exhibit only one methyl resonance in its nmr spectrum. A spectrum obtained at −20° showed no broadening of the methyl resonance. Chemical evidence, *vide infra*, is consistent with structure V.

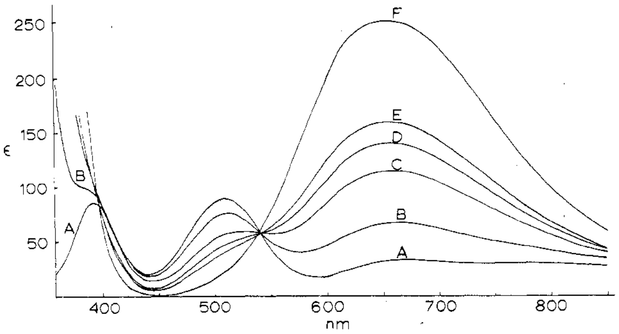
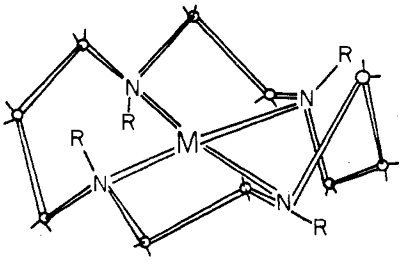


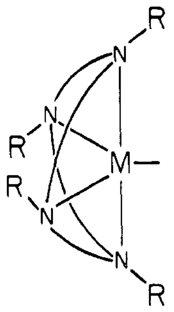
Figure 2. Absorption spectra obtained on a solution initially 3.35 × 10^{-3} *M* in both $Ni(TMC)(ClO_4)_2$ and $Cu(H_2O)_6(NO_3)_2$ at (A) 0, (B) 13, (C) 28, (D) 40, (E) 74, and (F) 294 hr.

result of kinetic control or whether it is in fact the thermodynamically most stable, remains to be answered. Powder pattern data suggest that $[Zn(TMC)Cl]ClO_4$ and $[Ni(TMC)Cl]ClO_4$ are isomorphous. Since there is no reason to suspect that the formations of the Ni, Zn, and Cu complexes occur by different mechanisms which could give different sets of nitrogen configurations we assume the ligand to be positioned similarly in all of these complexes. We have been unable to produce any complex which appears to have a different set of donor configurations. However, the usual methods for inverting secondary amines are not available here.[12]

Five-coordinate complexes of macrocyclic secondary amine ligands are known but these have the planar ligand structure shown as VI.[13] In each case the five-coordinate complex contains the ligand in a folded form VII.[13]



VI



VII

The single six-coordinate complex which was prepared, $Ni(TMC)(NCS)_2$, exhibits two C≡N stretching absorptions consistent with a cis arrangement of thiocyanates and is probably formed by folding of the ligand to accommodate the sixth ligand. Although the presence of two C≡N stretches in the infrared spectrum is also in agreement with a trans structure, this seems unlikely because of interaction with the methyl groups.

Kinetic Stability. Complexes of the 14-membered family of ligands are in general among the most kinetically inert of coordination compounds.[14] The resistance of these complexes to ligand protonation (in 12 *M* HCl and HNO_3) and to metal ion sequestering by S^{2-} or OH^- is a direct reflection of the very low rate of ligand dissociation. This in turn is a result of the macrocyclic chelate effect rather than an unusual metal-ligand interaction. In contrast to the aforementioned behavior, the nickel complex of II is very susceptible to acid, it being destroyed after a few hours in trifluoroacetic acid or more quickly in dilute mineral acids. Such reactivity and relative stability is not unlike that for nickel and copper complexes of linear tetramines. An interesting result of the kinetic lability of the nickel complex (and our first evidence for such) is demonstrated by

$$Ni(TMC)(H_2O)_n{}^{2+} + \text{excess } Ag^+ \xrightarrow{H_2O} Ag^0 + Ag(TMC)^{2+} + Ni(H_2O)_6{}^{2+}$$

This rapid reaction with silver was found to occur for a number of *free* macrocyclic amines.[15] But the importance of this observation in the present case was a vivid illustration of kinetic lability. Similar observations were made with $Zn(TMC)^{2+}$. Further experiments with copper revealed that the ligand is transferred completely after a few days (see Figure 2) to Cu^{2+} to form $Cu(TMC)H_2O^{2+}$ and $Ni(H_2O)_6{}^{2+}$. This again indicates that the complex is labile and further that the formation constant for $Cu(TMC)H_2O^{2+}$ is at least 10^2 times greater than that for $Ni(TMC)(H_2O)_n{}^{2+}$.

This dramatic difference in kinetic stability observed for complexes of II compared with that for complexes of I and its analogs is not expected on the basis of differences in donor strength alone and must be due to a poor stereochemical arrangement of the tertiary amine macrocycle and the metal ion. The ligand stereochemistry shown as V probably forces the metal above the nitrogen plane and the apparent low formation constant must be due to the ease with which the tetradentate can be "pushed" from the metal by competing ligands such as water. It is difficult to assess the strain incorporated in such a structure but this may also contribute to the ease of dissociation of the ligand.

Research in this area is continuing. We are attempting to obtain other (hopefully more stable) isomers of TMC by methylation of $Ni(cyclam)^{2+}$. A promising area of alkali metal chemistry with TMC is developing. Finally an unstable Ni(III) complex can be generated with TMC. Investigations into its chemistry are under way.

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Registry No. Cyclam, 295-37-4; TMC, 41203-22-9; H_2CO, 50-00-0; $[Ni(TMC)](ClO_4)_2$, 41296-56-4; $[Ni(TMC)Cl](ClO_4)$, 41203-14-9; $[Ni(TMC)Br](ClO_4)$, 41203-15-0; $[Ni(TMC)NCS](ClO_4)$, 41203-16-1; $[Ni(TMC)(NCS)_2]$, 41203-17-2; $[Cu(TMC)](ClO_4)_2$, 41203-18-3; $[Cu(TMC)Br](ClO_4)$, 41203-19-4; $[Zn(TMC)](ClO_4)_2$, 41203-20-7; $[Zn(TMC)Cl](ClO_4)$, 41203-21-8.

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(12) This involves deprotonation of the amine and subsequent inversion of the coordinated amide ion. Protonation should then yield the thermodynamically most stable product(s).

(13) L. G. Warner, Ph.D. Thesis, The Ohio State University, 1970.

(14) N. F. Curtis, *Coord. Chem. Rev.*, 3, 1 (1968); D. K. Cabbiness and D. W. Margerum, *J. Amer. Chem. Soc.*, **92**, 2151 (1970); also see ref 1.

(15) E. K. Barefield and M. T. Mocella, submitted for publication.