complex environment and in acetonitrile solution it shifts to lower energy relative to the solid-state transmission spectra. This is accompanied by a noticeable change in the color of the complexes in the solid state from green or red to yellow in solution. Substitution of axial ligands by solvent can be discounted on the basis of conductance measurements (Table I). Fackler, *et al.*,[20] have studied a series of octahedral Mn(III) complexes and have noted the same type of behavior for the lowest energy band. Since the d^4 system is subject to significant Jahn–Teller effects, they assumed a tetragonal distortion and assigned the lowest energy band to the ${}^5B_{1g} \rightarrow {}^5A_{1g}$ electronic transition. The same assignment is probably applicable to the near-infrared band of the Mn(III) macrocyclic complexes. In support of this assignment the energy of the ${}^5B_{1g} \rightarrow {}^5A_{1g}$ transition ($4Ds + 5Dt$) is observed to decrease with increasing axial ligand field strength.

The remaining d–d transitions appear as shoulders on an intense band (probably a charge-transfer transition) and thus are poorly resolved. Low-temperature mull spectra (77°K) showed only a slight enhancement in the resolution of these bands. However, circular dichroism studies on a series of optically active manganese(III) complexes[21] have provided additional insight as to the number, position, and probable assignment of these higher energy transitions.

Acknowledgment. We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Colgate Research Council for their support. We are also grateful to Dr. C. E. Forbes for helpful discussions concerning the interpretation of the esr data and to Mr. Jack H. Young, a Colgate Senior, for his assistance with the compound preparations. The electrochemical studies were carried out by Dr. M. Hughes.

Registry No. $[Mn^{II}[14]aneN_4(CF_3SO_3)_2]$, 53198-10-0; $[Mn^{II}[14]aneN_4(CH_3CO_2)_2]$, 53166-18-0; $[Mn^{III}[14]aneN_4(NCS)_2]NCS$, 53166-20-4; $[Mn^{III}[14]aneN_4(Cl)_2]BF_4$, 53166-22-6; $[Mn^{III}[14]aneN_4(Cl)_2]Cl$, 53166-23-7; $[Mn^{III}[14]aneN_4(Br)_2]PF_6$, 53166-25-9; $[Mn^{III}[14]aneN_4(Cl)_2]PF_6$, 53166-26-0.

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Transition Metal Complexes Containing an Optically Active Macrocyclic Ligand. Manganese(III), Nickel(II), and Copper(II)

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The synthetic macrocyclic ligand *rac*-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (*rac*-5,14-[14]aneN_4) has been resolved *via* its nickel(II) complex. The optically active ligand has been removed from Ni(II) and transferred to copper(II) and manganese(III). A circular dichroism analysis of (+)[Mn((–)5,14-[14]aneN_4)X_2]PF_6, where X^- is Cl^- or Br^-, has been very useful in interpreting the electronic spectrum of this tetragonally distorted high-spin d^4 system. The macrocyclic crystal field ($10Dq$) for Mn(III) as measured by the position of the ${}^5B_{1g} \rightarrow {}^5B_{2g}$ electronic transition was found to be about 23 kK.

Introduction

As part of an effort to explore the physical and chemical properties of manganese complexes incorporating synthetic macrocyclic ligands we have synthesized a number of high-spin six-coordinate manganese(III) complexes.[2] The compounds with the cyclic secondary amine *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (*ms*-[14]aneN_4),[3] Figure 1a, are pale and give electronic transitions which are likely of d–d origin. Although the electronic spectrum of Mn(III) has been examined by a number of workers,[4-6] the transition assignments and, in particular, a frequently observed low-energy absorption have caused some difficulty. We wish to report the resolution of *rac*-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (*rac*-5,14-[14]aneN_4),[3] Figure 1b, *via* its nickel(II) complex. It has been shown that the coordination geometry of this macrocycle is very similar to that of the more commonly encountered *ms*-[14]aneN_4 ligand[7,8] and as such the spectral results of the two systems should be related. The optically active ligand has been removed from the nickel(II) ion and incorporated into two manganese(III) complexes and one electronically related copper(II) compound. The narrow circular dichroism (CD) absorption has greatly facilitated the detection of transitions not readily observable in the absorption spectra of the complexes.

Experimental Section

Reagents and Equipment. All of the solvents used were reagent grade unless otherwise noted. The CD spectra of the complexes from 220 to 700 nm were recorded in Spectroquality acetonitrile using a Durrum-Jasco spectropolarimeter (Model J-20). The recording of the near-infrared CD spectrum (700–1150 nm) was done using a homemade device similar to that described by Schnepp, *et al.*[9] Generation of the circularly polarized light was accomplished using a quarter-wave plate supplied by Morvue Electronic Systems, Tigard, Oreg. Cary spectrophotometers, Models 14 and 118C, were used for the absorption and first-derivative spectra. Solid-state mull spectra (4.5–30 kK) were done in the manner previously described.[3]

Conductivities at room temperature on 10^{-3}–10^{-4} M solutions were obtained using a Yellow Springs Instrument Co. Model 31 conductivity bridge. Conductances consistent with other 1:1 electrolytes in

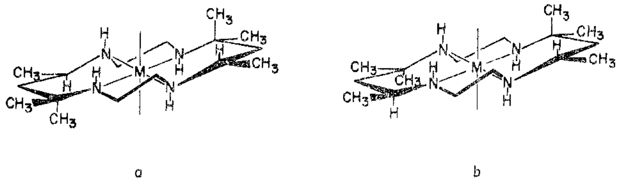

Figure 1. Coordination geometries of (a) *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (*ms*-[14]aneN$_4$) and (b) *rac*-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (*rac*-5,14-[14]aneN$_4$). The *SS* form is shown.

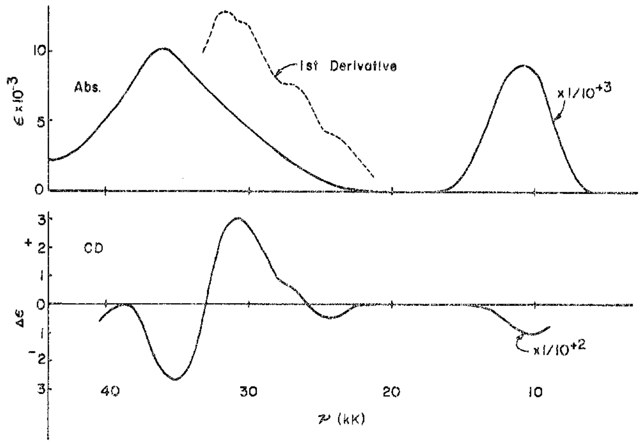

Figure 2. Absorption, first-derivative, and circular dichroism spectra of (+)[Mn^{III}((−)-5,14-[14]aneN$_4$)Cl$_2$]PF$_6$ in acetonitrile.

Table I. Absorption and Circular Dichroism Spectra of Some Optically Active Macrocyclic Complexes

	Abs[a]	CD[b]
(+)[Mn^{III}((−)-5,14-[14]aneN$_4$)Cl$_2$]PF$_6$	10.9 (9)	10.2 (−0.011)
	24.1 sh	24.4 (−0.55)
	26.5 sh	27.2 (+0.55)
	31.2 sh	30.8 (+3.03)
	36.1 (10,200)	35.1 (−2.75)
(+)[Mn^{III}((−)-5,14-[14]aneN$_4$)Br$_2$]PF$_6$	11.7 (17)	11.1 (−0.013)
	23.2 sh	22.4 (−0.33)
	27.0 sh	26.9 (+1.06)
	30.8 sh	30.0 (+2.36)
	34.8 (10,300)	34.3 (−2.02)
(+)[Cu^{II}((−)-5,14-[14]aneN$_4$)](ClO$_4$)$_2$	14.5 sh	~15.2 (+0.023)
	19.3 (138)	19.4 (+0.18)
	36.9 (6800)	33.5 (−4.20)
		38.8 (+7.00)
(+)[Ni^{II}((−)-5,14-[14]aneN$_4$)](ClO$_4$)$_2$	21.8 (94)	21.7 (+2.02)
	43.5 (11,300)	40.0 (−2.78)
		44.6 (+6.38)

[a] The band maximum in acetonitrile solution is given in kK followed by the molar extinction coefficient. [b] The band maximum in acetonitrile is given in kK followed by ($\epsilon_l - \epsilon_r$).

acetonitrile (120–160 ohm^{-1} cm^2 mol^{-1}) were found for [Mn^{III}((−)-5,14-[14]aneN$_4$)Cl$_2$]PF$_6$ and [Mn^{III}((−)-5,14-[14]aneN$_4$)Br$_2$]PF$_6$ while the Cu(II) and Ni(II) complexes exhibited 2:1 conductance values (220–300 ohm^{-1} cm^2 mol^{-1}).[10] Magnetic moment measurements were done on 10–20 mg of sample in the solid state using the Faraday method.[11] The analytical services of Instranal Laboratories, Rensselaer, N. Y., and Galbraith Laboratories, Knoxville, Tenn., were used for the elemental analyses.

Syntheses. (+)[Ni^{II}((−)-5,14-[14]aneN$_4$)](ClO$_4$)$_2$. To 350 ml of a solution containing 25.0 g of [Ni^{II}(*rac*-5,14-[14]aneN$_4$)](ClO$_4$)$_2$[12] at 80° was added 40 ml of an aqueous solution containing 50 g of NaI. The solution was set aside to cool and the [Ni^{II}(*rac*-5,14-[14]aneN$_4$)]I$_2$·H$_2$O which formed was removed by filtration and air-dried.

The following procedures involving silver salts were carried out in glassware shielded from the light.

The entire yield of the diiodide monohydrate, 22 g, was suspended in 300 ml of rapidly stirred water and 13.0 g of silver *d*-tartrate[13] added. The suspension was stirred for 15 min and AgI which formed was removed by filtration. The volume of the filtrate containing the yellow [Ni^{II}(*rac*-5,14-[14]aneN$_4$)](*d*-tart), was reduced to 100 ml and absolute ethanol added in a dropwise manner. After addition of a few milliliters of ethanol, a violet solid appeared which was the impure (+) diastereomer. Continued addition of ethanol and collection of additional fractions showed a smooth decrease in the optical purity with fraction number. Checks on the optical rotation of the filtrate revealed that it was being enriched with the *l* isomer. The (−) isomer was recovered in the manner described above using Ag$_2$(*l*-tart).[13] The highest value of [α] obtained in a fraction (2 g) containing the (+) diastereomer was [α]$_{546}$ 135°.

Anal. Calcd for Ni(C$_{16}$H$_{36}$N$_4$)(C$_4$H$_4$O$_6$): C, 48.90; H, 8.21; N, 11.40. Found: C, 48.60; H, 8.20; N, 11.34; μ_{eff} = 3.04 BM.

A small portion, 0.2 g, of the violet (+)[Ni^{II}((−)-5,14-[14]aneN$_4$)(*d*-tart)] was readily converted to the yellow diamagnetic ClO$_4^-$ salt by dissolving the (+) diastereomer in a minimum amount of water and adding excess concentrated HClO$_4$. The yield was about 0.1 g.

Anal. Calcd for (+)-Ni(C$_{16}$H$_{36}$N$_4$)(ClO$_4$)$_2$: C, 35.45; H, 6.69; N, 10.34. Found: C, 35.72; H, 6.79; N, 10.33. The compound is diamagnetic, [α]$_{546}$ 124°, Λ(CH$_3$CN) 282 ohm^{-1} cm^2 mol^{-1}.

Isolation of (−)-5,14-[14]aneN$_4$. The (−) ligand was obtained from 1.8 g of the best fraction of (+)[Ni^{II}((−)-5,14-[14]aneN$_4$)(*d*-tart)], [α]$_{546}$ 135°, in the manner outlined by Barefield[14] for [Ni^{II}(cyclam)](ClO$_4$)$_2$. Recrystallization from ethanol–water gave the ligand dihydrate. The yield was about 1.0 g.

Anal. Calcd for C$_{16}$H$_{36}$N$_4$·2H$_2$O: C, 59.96; H, 12.58; N, 17.48. Found: C, 59.88; H, 12.29; N, 17.12. The dry ligand was obtained by drying over P$_4$O$_{10}$ for 2 days; [α]$_D$(CH$_3$OH) −48°. Mass spectrum, *m/e*: calcd, 284; obsd, 284.

(+)[Mn^{III}((−)-5,14-[14]aneN$_4$)X$_2$]PF$_6$, where X$^-$ = Cl$^-$, Br$^-$. These complexes were prepared in the manner outlined for [Mn^{III}(*ms*-[14]aneN$_4$)X$_2$]PF$_6$.[2] Each complex was synthesized using 0.3 g of the dry (−)-5,14-[14]aneN$_4$ to yield about 0.2 g of each of the Mn(III) complexes.

Anal. Calcd for the greenish yellow complex (+)[Mn(C$_{16}$H$_{36}$N$_4$)Cl$_2$]PF$_6$: C, 34.61; H, 6.54; N, 10.09. Found: C, 34.47; H, 6.46; N, 10.13; μ_{eff} = 4.94 BM; [α]$_D$(CH$_3$CN) 20°; Λ(CH$_3$CN) 148 ohm^{-1} cm^2 mol^{-1}.

Anal. Calcd for the yellow complex (+)[Mn(C$_{16}$H$_{36}$N$_4$)Br$_2$]PF$_6$: C, 29.83; H, 5.63; N, 8.70. Found: C, 29.51; H, 5.56; N, 8.65. μ_{eff} = 4.95 BM; [α]$_D$(CH$_3$CN) 23°; Λ(CH$_3$CN) 150 ohm^{-1} cm^2 mol^{-1}.

(+)[Cu((−)-5,14-[14]aneN$_4$)](ClO$_4$)$_2$. The (−) ligand, 0.3 g, was dissolved in 50 ml of methanol containing 0.4 g of [Cu(H$_2$O)$_6$](ClO$_4$)$_2$ and the resulting suspension heated at reflux for 30 min. After cooling, the copper complex was removed by filtration, washed with a few milliliters of methanol, and air-dried. The yield was about 0.2 g.

Anal. Calcd for the violet complex (+)[Cu^{II}(C$_{16}$H$_{36}$N$_4$)](ClO$_4$)$_2$: C, 35.14; H, 6.64; N, 10.25; Cl, 12.97. Found: C, 35.17; H, 6.72; N, 10.15; Cl, 13.25; μ_{eff} = 1.77 BM; [α]$_{436}$(CH$_3$CN) 57°; Λ(CH$_3$CN) 281 ohm^{-1} cm^2 mol^{-1}.

Results and Discussion

The Manganese(III) Complexes. Warner and Busch[7] and later Curtis, *et al.*,[8] have shown that the coordination geometries provided by the ligands shown in Figure 1 are similar. Primarily due to nonbonding interactions involving the methyl groups, both of the 14-membered cyclic amines prefer planar coordination. Moreover, the two six-membered chelate rings exist in a cyclohexane chair conformation with the two five-membered rings having enantiomeric, λ and δ conformations.[15] A single-crystal X-ray analysis of [Mn^{III}(*ms*-[14]aneN$_4$)Cl$_2$]Cl·3H$_2$O[16] has shown that the coordination sphere of the Mn(III) ion is slightly distorted but for the purposes of the following spectral arguments D_{4h} symmetry will be applied.

The absorption curve, its first-derivative, and the circular dichroism spectrum of (+)[Mn^{III}((−)-5,14-[14]aneN$_4$)Cl$_2$]PF$_6$ are shown in Figure 2. If the crystal field in the plane is greater than the crystal field on the *z* axis, $Dq_z < Dq_{xy}$, the relevant crystal field transitions for a high-spin d^4 metal ion[5] in order of increasing energy are ${}^5B_{1g} \rightarrow {}^5A_{1g}$ ($4Ds + 5Dt$) < ${}^5B_{1g} \rightarrow {}^5B_{2g}$ ($10Dq$) < ${}^5B_{1g} \rightarrow {}^5E_g$ ($3Ds - 5Dt + 10Dq$). Table I indicates that the acetonitrile solution spectra of both

(+)[Mn^{III}((−)-5,14-[14]aneN_4)Cl_2]PF_6 and (+)[Mn^{III}((−)-5,14-[14]aneN_4)Br_2]PF_6 yield a weak absorption in the near-infrared region (~11 kK) of the spectrum. Solid-state mull spectra in the range of 4.5–30 kK show that this is the lowest energy absorption. In a study of the band origins for a number of Jahn–Teller distorted Mn(III) complexes, Fackler, *et al.*,[5] observed a similar low-energy transition. In their analysis they considered several assignments for this band, including the possibility of a charge-transfer or an electronic spin-forbidden transition but ultimately assigned it to the $^5B_{1g} \rightarrow {}^5A_{1g}$ crystal field band. The same assignment is given to the low-energy band of the Mn(III) macrocyclic complexes. In view of its low intensity, the assignment of this absorption to a charge-transfer band appears remote. Furthermore, the observation of a symmetrical low-energy CD envelope (out to 1150 nm) for both the chloride and bromide probably exclude the $^5E_g \rightarrow {}^3T_{1g}$ (O_h) spin-forbidden transition as a possibility. In a lower symmetry field (D_{4h}) this transition would split and very likely give rise to a more complex CD spectrum than is observed.

The higher energy crystal field transitions are difficult to detect but appear to be located on the side of an intense band centered at ~35 kK (Figure 2). A first-derivative spectrum of part of this absorption band suggests the presence of three additional absorptions which are easily resolved using CD. For (+)[Mn^{III}((−)-5,14-[14]aneN_4)Cl_2]PF_6 the CD intensities of the first two bands are about 5–6 times more intense than the bands at 30.8 and 35.1 kK. The absorptions at 24.4 and 27.2 kK are assigned to the crystal transitions $^5B_{1g} \rightarrow {}^5B_{2g}$ and $^5B_{1g} \rightarrow {}^5E_g$, respectively. The two most intense CD bands (Table I) are probably axial ligand-to-manganese(III) charge-transfer (CT) bands. Consistent with this assignment is the observed shift of this CT band to lower energy upon replacement of the axial chloride ions with bromide.

The positions of the CD absorptions may be helpful in assessing the magnitude of the crystal field (10*Dq*) generated by the bound ligands. Except for the low-energy absorption, the band positions of all of the CD transitions for (+)[Mn((−)-5,14-[14]aneN_4)Br_2]PF_6 are shifted to lower energy relative to the chloride complex. The shift of the infrared band to higher energy with decreasing crystal field on the *z* axis is consistent with the $^5B_{1g} \rightarrow {}^5A_{1g}$ assignment.

In view of the overlap of the high-energy transitions it is dangerous to discuss small changes in band position as a function of changes in the magnitude of the crystal field. However, the crystal field (10*Dq*, $^5B_{1g} \rightarrow {}^5B_{2g}$) of the macrocyclic ligand for both the chloride and bromide derivatives appears to be about 23 kK. This is significantly greater than that found for some recently reported optically active manganese(III) complexes.[17] The $10Dq_{xy}$ transition for these *N,N'*-bis(salicylidene)-*l*-propylenediaminomanganese(III) compounds[17] occurs at ~16 kK. The macrocyclic crystal field of the Mn^{III}[(−)-5,14-[14]aneN_4] complexes compares more favorably with the value obtained for [Co^{III}(cyclam)Cl_2]$^+$,[18] where cyclam is 1,4,8,11-tetraazacyclotetradecane. The crystal field strength of this cyclic secondary amine on cobalt(III) is 24.8 kK.

An attempt to establish the band assignments of the Mn(III) complexes using single-crystal techniques failed. Although large single crystals of [Mn^{III}(*ms*-[14]aneN_4)Cl_2]Cl·$3H_2O$ could be grown, they appeared to darken and decompose in the spectrometer beam. Even in the absence of decomposition severe overlap of the ligand field bands would probably exclude this approach as a useful one.

Attempts to synthesize [Mn^{III}((−)-5,14-[14]aneN_4)-$(NCS)_2$]NCS as was done for the Mn(III) complex incorporating the *meso* ligand[2] met with difficulty. The optically active thiocyanate complex appears to be unstable toward reduction, more soluble and hence more difficult to isolate than [Mn^{III}(*ms*-[14]aneN_4)$(NCS)_2$]$^+$.

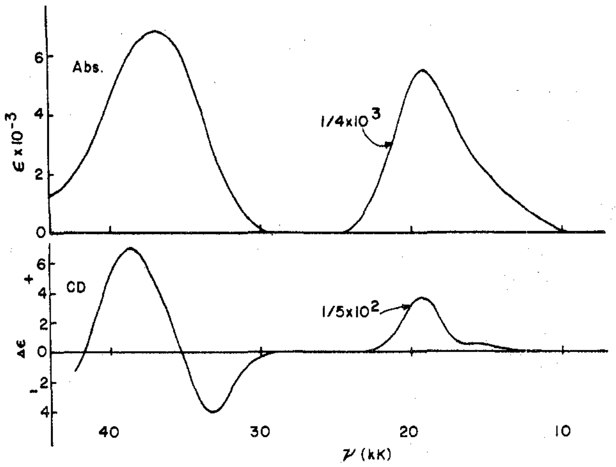

Figure 3. Absorption and circular dichroism spectra of (+)[Cu^{II}((−)-5,14-[14]aneN_4)]$(ClO_4)_2$ in acetonitrile.

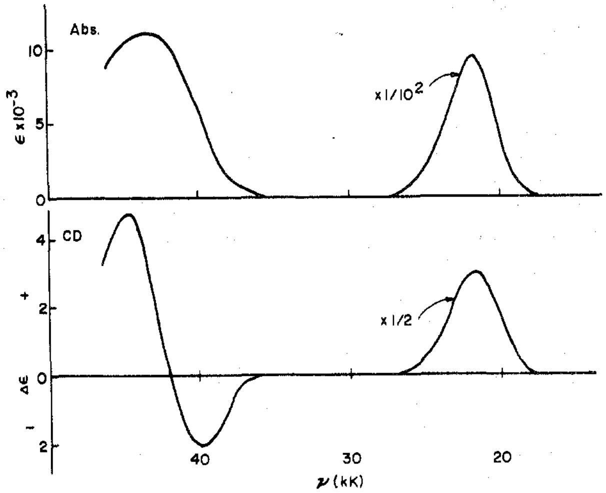

Figure 4. Absorption and circular dichroism spectra of (+)[Ni^{II}((−)-5,14-[14]aneN_4)]$(ClO_4)_2$ in acetonitrile.

The Copper(II) and Nickel(II) Complexes. To aid in the spectral analysis of the Mn(III) complexes a Cu(II) complex containing (−)-5,14-[14]aneN_4 was synthesized. Although the crystal field term diagrams for high-spin d^4 and d^9 are the same, the spectral analysis for (+)[Cu((−)-5,14-[14]aneN_4)]$(ClO_4)_2$ proved to be more complicated than that for the manganese(III) complexes. Figure 3 shows the absorption and CD spectra for the copper complex in acetonitrile. Only two transitions are evident from the absorption curve while CD indicates the presence of at least four. The position and intensity of the high-energy CD bands (~40 kK) label them as CT transitions. The low-energy absorption envelope which is common to many square-planar Cu(II) complexes[19] is partially resolved. This band contains all three crystal field transitions and interpretation is further complicated by the large value of the spin–orbit coupling constant.[19] Spectral assignments without further data such as band position as a function of solvent are tenuous.

Figure 4 shows the absorption and CD spectra of the nickel complex used to resolve the ligand. Except for the CD intensities the absorptions are identical with those of the partially resolved nickel complex reported by Warner and Busch.[7] Two charge-transfer transitions are observed at high energy (~40 kK) and one symmetrically shaped CD absorption is observed at 21.7 kK. The latter is probably the $^1A_{1g} \rightarrow {}^1A_{2g}$ electronic transition.[20]

Acknowledgment. We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Colgate Research Council for their support. We are also grateful to Mr. Jeffrey B. Kessler, a Colgate student, for his assistance with the compound preparations.

Registry No. (+)[Mn^{III}((−)-5,14-[14]aneN_4)Cl_2]PF_6, 53228-45-8; (+)[Mn^{III}((−)-5,14-[14]aneN_4)Br_2]PF_6, 53228-47-0; (+)[Cu^{II}((−)-5,14-[14]aneN_4)](ClO_4)$_2$, 53447-11-3; (+)[Ni^{II}((−)-5,14-[14]aneN_4)](ClO_4)$_2$, 52553-45-4; (+)[Ni^{II}((−)-5,14-[14]aneN_4)(*d*-tart)], 53166-27-1; (−)-5,14-[14]aneN_4, 53187-81-8.

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Stability of Some Transition Metal Ion Complexes with a Linear Aliphatic Triamine Potentially Forming a Five-Membered Chelate Ring Fused with a Seven-Membered Chelate Ring: 1,4,9-Triazanonane (2,4-tri). II[1]

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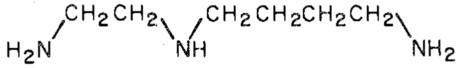
The triamine $H_2N(CH_2)_2NH(CH_2)_4NH_2$ (2,4-tri) has been investigated as chelating agent for copper(II), nickel(II), and zinc(II) ions. These divalent metal ions form a large number of complexes with 2,4-tri in aqueous solution. The relative stability constants were determined potentiometrically in 0.5 *M* KNO_3 at 25°. Five complexes having the formulas ML, MHL, ML_2, $M(HL)_2$, and MHL_2 (where L = 2,4-tri) are common to all the three metal ions. In addition to the simple and protonated complexes, Cu^{2+} and Zn^{2+} give the hydroxo complexes $[Cu(OH)L]^+$, $[Zn(OH)L]^+$, and $[Zn(OH)_2L]$. With regard to the simple complex ML, the amine acts as a bidentate chelate agent toward Ni^{2+} and Zn^{2+} while it acts as a tridentate chelate toward Cu^{2+}, the latter forming two fused chelate rings, one five-membered and the other seven-membered. The ML_2 complexes contain only two five-membered chelate rings, both the molecules of 2,4-tri acting as bidentates. The protonation constants have been measured and compared with those of some other triamines previously investigated.

Introduction

Recently it has been clearly demonstrated that the coordinating power of ligands which form complexes with a sequence of alternating five- and six-membered rings is greater than that of ligands forming complexes with all five-membered or all six-membered chelate rings. This has been verified both for linear aliphatic tetramines[2] and for linear aliphatic triamines.[3] This enhanced coordinating power is made evident by the thermodynamic functions $\Delta G°$ and $\Delta H°$ relative to the reaction of complex formation in aqueous solution.[4]

In order to determine the coordinating properties of the 1,4,9-triazanonane ligand (2,4-tri)[5] in aqueous solution



$$H_2N-CH_2CH_2-NH-CH_2CH_2CH_2CH_2-NH_2$$

we have measured the stability constants of its complexes with copper(II), nickel(II), and zinc(II). The full coordination of the three nitrogen atoms would give rise to the formation of a five-membered chelate ring fused with a seven-membered chelate ring. A chelate ring of such size is unusual, especially in aqueous solution. The equilibria between the ligand 2,4-tri and the ions have been studied in aqueous solution (0.5 *M* KNO_3) at 25° using a potentiometric method.

Also the protonation constants have been measured and the effect on the three nitrogens' basicity of the progressive and systematic extension of one aliphatic chain in going from 2,2-tri[6] to 2,3-tri[3] to 2,4-tri has been investigated.

Table I. Experimental Details of the Potentiometric Measurements (Initial Concentrations, $M \times 10^2$)

Cation	L:M ratio	[L]	[M^{2+}]	[H^+]	pH range
H^+		0.2641		0.943	3.5–11.6
		0.2885		1.032	3.5–11.1
		0.2799		1.003	3.5–11.2
Ni^{2+}	1:0.14	0.4169	0.0599	1.491	3.3–10.9
	1:0.40	0.3681	0.1454	1.317	3.4–11.1
	1:0.23	0.3724	0.0855	1.329	3.4–10.8
Cu^{2+}	1:0.26	0.4287	0.1127	1.532	3.6–11.2
	1:0.14	0.4244	0.0598	1.518	3.6–11.2
	1:0.70	0.4036	0.2812	1.443	3.7–11.2
Zn^{2+}	1:0.27	0.4263	0.1151	1.520	3.5–10.8
	1:0.43	0.4088	0.1758	1.457	3.4–8.4
	1:0.22	0.4206	0.0934	1.504	3.4–11.1

Experimental Section

Materials. 2,4-tri is commercially available (Eastman Organic Chemicals). The product was purified as the hydrochloride which was recrystallized twice from ethanol and dried *in vacuo* at 60°. *Anal.* Calcd for $C_6H_{20}N_3Cl_3$: Cl, 44.2. Found: Cl, 44.2.

The potassium hydroxide solution ($\simeq$0.5 *M*) was prepared from KOH pellets. The pellets were washed with twice distilled and decarbonated H_2O (under a N_2 flow); the last addition of water was