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Nicotinate *N*-Oxide Complexes with Dipositive 3d Metal Ions¹

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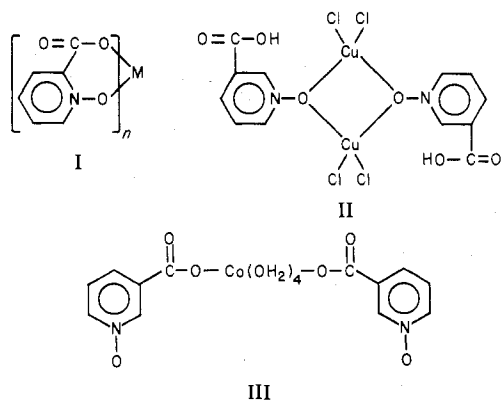
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Divalent 3d metal complexes with nicotinate *N*-oxide (*N*-nicO), of the type $M(N\text{-nicO})_2 \cdot x\text{H}_2\text{O}$ ($M = \text{Mn-Zn}$; $x = 4$ or 5), were synthesized by reaction of the corresponding metal(II) acetates or ferrous ammonium sulfate with ammonium nicotinate *N*-oxide. The characterization of the new metal complexes was based on spectral, magnetic, and x-ray powder diffraction studies and their solubility characteristics. These compounds appear to be hexacoordinated, linear, polynuclear complexes of the type $[M(N\text{-nicO})_2(\text{OH}_2)_2]_m \cdot n\text{H}_2\text{O}$ ($m = 2n$ for $M = \text{Mn, Fe, Co, Ni, Cu}$; $m = 3n$ for $M = \text{Zn}$), probably involving double $M(N\text{-nicO})_2M$ bridges. The *N*-nicO ligands coordinate through the N-O oxygen and one of the COO oxygens, while the other carboxylate oxygen is hydrogen bonded to water. Lattice water is also present in these complexes. Desiccation of the preceding compounds over P_2O_5 , under reduced pressure, leads to their partial or complete dehydration. Under these conditions, only lattice water is eliminated from the Mn(II), Ni(II), and Cu(II) complexes, without occurrence of any structural change. The Fe(II) and Co(II) complexes are completely dehydrated, while the Zn(II) complex loses the lattice water and one aquo ligand per Zn^{2+} ion. $\text{Co}(N\text{-nicO})_2$ seems to maintain coordination number 6, by the function of *N*-nicO as a tridentate bridging ligand, in a highly cross-linked polymeric structure. $\text{Fe}(N\text{-nicO})_2$ and $\text{Zn}(N\text{-nicO})_2 \cdot \text{H}_2\text{O}$ appear to be pentacoordinated, comprising chemically nonequivalent carboxylate groups; evidence favors the presence of both bi- and tridentate *N*-nicO bridging ligands in the Fe(II) complex and hydrogen-bonding of the uncomplexed COO oxygen of part of the bidentate ligands in the Zn(II) complex. *N*-nicO is a ligand of strength about equal to that of picolinate *N*-oxide.

Introduction

Several picolinate *N*-oxide (*N*-picO)-metal complexes have been reported in recent years.²⁻¹¹ This ligand acts, in most cases, as a bidentate O,O-chelating agent, coordinating through the -NO and one of the carboxylate oxygens.² Thus, metal chelates of type I have been reported for 3d metal, alkaline



earth, actinide, and B(III) ions.^{2-4,7-11} Complexes involving both anionic bidentate and unidentate or both anionic bidentate and neutral unidentate *N*-picO ligands have been also reported.⁴ In the case of trivalent lanthanide ion complexes with *N*-picO, the function of the ligand as uni- or bidentate has been in dispute.^{5,6}

Reactions of nicotinic acid *N*-oxide (*N*-nicOH) with metal salts have not been studied in any detail. A magnetically subnormal, binuclear adduct of CuCl_2 with the neutral ligand involves unidentate (NO oxygen-bonded), bridging ligands¹² (II). Co(II) ,¹³ Na(I) , and Mg(II) ¹⁴ salts of the anionic nicotinate *N*-oxide ligand (*N*-nicO) have been also reported. For the Co(II) salt, a structure involving coordination through one of the carboxylate oxygens was postulated¹³ (III). The Na(I) and Mg(II) salts were studied only in terms of their therapeutic properties.¹⁴

It was felt that the elucidation of the mode of coordination of the nicotinate *N*-oxide ligand would be of interest. In fact, several examples in the literature cite different modes of coordination of the parent amine ligand, i.e., the nicotinate

anion (nic). Thus, in $(\text{nic})_2\text{M}^{\text{II}}$ tetrahydrates ($M = \text{Co, Zn}$), this ligand appears to function as unidentate, N bonding,^{15,16} while some anhydrous analogues ($M = \text{Mn, Co, Ni, Cu, Ag, Zn}$) are bi- or polynuclear, involving bridging nic ligands, coordinated through nitrogen and one of the carboxylate oxygens.¹⁷⁻¹⁹ $(\text{nic})_2\text{Cd}^{\text{II}}$ has been characterized as a chelate, with the ligand coordinated through both the carboxylate oxygens,²⁰ whereas for the corresponding lanthanide(III) complexes, the presence of either chelating, O,O-bonded, or -O-C-O- bridging nic ligands was proposed.²¹⁻²³ Finally, $(\text{nic})_2\text{Cl}_2\text{Ge}^{\text{IV}}$ was characterized as a chelate involving O-, N-bonded nic ligands.²⁴ A similar mode of chelation was proposed for nicotinic acid in its adducts with lanthanide(III) hexathiocyanatochromates(III),²⁵ while the copper(II), cadmium(II), and mercury(II) chloride analogues appear to contain unidentate, N-bonded nicotinic acid groups.^{20,26,27} Accordingly, work aimed at the synthesis and characterization of *N*-nicO-M complexes was undertaken by these laboratories. The present paper deals with M(II) ($M = \text{Mn-Zn}$) complexes with this ligand.

Experimental Section

Synthetic Procedures. Nicotinic acid *N*-oxide (Aldrich product) was utilized as received. Reagent grade metal salts and NH_4OH were used. The new metal complexes were prepared by methods similar to those employed by Lever et al. for the syntheses of the corresponding *N*-picO metal complexes.⁴ Thus, nicotinic acid *N*-oxide was dissolved in water by adding NH_4OH dropwise, under stirring. The resulting ammonium nicotinate *N*-oxide aqueous solution was then heated to drive off any excess NH_3 present. An aliquot of this warm (50-60 °C) solution, containing 20 mmol of $(N\text{-nicO})\text{NH}_4$ in 10 ml of water, was allowed to react with a warm solution of 10 mmol of $\text{M}^{\text{II}}\text{OAc}$ ($M = \text{Mn, Co, Ni, Cu, Zn}$) or $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 9\text{H}_2\text{O}$ in 15 ml of water. Immediate precipitation was observed in all cases. The precipitates obtained by using $\text{M}^{\text{II}}\text{OAc}$ were found to be of the general type $M(N\text{-nicO})_2 \cdot n\text{H}_2\text{O}$ ($n = 4$ for Mn, Co, Ni, Cu ; $n = 5$ for Zn). Analytical results are given in Table I (C, H, and N analyses by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.; metal analyses by emission spectroscopy; water determination by Karl Fischer titration²⁸). The solid dark green reaction product between ferrous ammonium sulfate and $(N\text{-nicO})\text{NH}_4$ was found to analyze as $\text{FeSO}_4 \cdot 3(N\text{-nicO})\text{NH}_4 \cdot \text{H}_2\text{O}$. The characterization of this product is currently under way, together with that of two similar products of ferric ammonium sulfate and $(N\text{-nicO})\text{NH}_4$, and will be reported in a future communication. $\text{Fe}(N\text{-nicO})_2 \cdot 4\text{H}_2\text{O}$ was obtained as follows. $(N\text{-nicO})\text{NH}_4$ and ferrous ammonium sulfate aqueous solutions were mixed in the same amounts as above, but at 0 °C. A

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Table I. Analytical Data for *N*-nicO (L)-3d Metal Complexes

Complex	Color	% C		% H		% N		% metal		% water	
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
MnL ₂ ·4H ₂ O	Light tan	35.74	36.12	4.00	4.26	6.95	6.68	13.63	13.40	17.87	18.20
MnL ₂ ·2H ₂ O	Light tan	39.25	39.33	3.29	3.45	7.63	7.47	14.96	15.20	9.81	9.60
FeL ₂ ·4H ₂ O	Bright yellow	35.67	35.68	3.99	4.36	6.93	6.93	13.82	13.20	17.83	17.80
FeL ₂	Orange-yellow	43.41	43.12	2.43	2.66	8.44	8.40	16.82	17.40		0.30
CoL ₂ ·4H ₂ O	Pink	35.40	35.70	3.96	4.18	6.88	6.89	14.47	13.80	17.70	18.00
CoL ₂	Yellow-beige	43.01	42.76	2.41	2.37	8.36	8.58	17.58	16.90		0.20
NiL ₂ ·4H ₂ O	Light green	35.42	35.52	3.96	4.33	6.88	6.96	14.43	14.10	17.71	17.60
NiL ₂ ·3H ₂ O	Light green	37.06	36.92	3.63	3.75	7.20	7.07	15.09	14.80	13.89	13.50
CuL ₂ ·4H ₂ O	Blue	35.00	35.18	3.92	3.49	6.80	6.82	15.43	14.80	17.49	17.30
CuL ₂ ·3H ₂ O	Blue	36.60	36.49	3.58	3.41	7.11	6.86	16.13	16.50	13.72	14.10
ZnL ₂ ·5H ₂ O	White	33.39	32.72	4.20	3.95	6.49	6.19	15.14	14.70	20.87	21.00
ZnL ₂ ·H ₂ O	Off-white	40.08	39.73	2.80	2.74	7.79	8.02	18.18	18.50	5.01	4.80

slow precipitation of dark olive green solid occurred under these conditions. However, addition of 10–20 drops of glacial acetic acid to this reaction mixture led to the complete dissolution of the solid product. The resulting clear yellow solution deposited a bright yellow solid, after standing at 0 °C for a few minutes. This product analyzes as Fe(*N*-nicO)₂·4H₂O.

The new M(*N*-nicO)₂·*n*H₂O complexes were filtered, washed with water, allowed to dry in the atmosphere for 2–3 h, and then stored in a desiccator over calcium chloride. These complexes are insoluble in water and most common organic solvents. They dissolve with apparent dissociation, suggested by dramatic color changes, in pyridine and other aromatic amines. The Fe(II) and Co(II) complexes are also slightly soluble in dimethyl sulfoxide; the colors of the resulting solutions in this medium are again indicative of dissociation. Aqueous mineral acid solutions readily dissolve the new complexes.

The dehydration of the above complexes was attempted by storage in an evacuated desiccator over phosphorus pentoxide, for extended periods of time (1–3 weeks). (Heating of the complexes at 70–100 °C, under reduced pressure, seems to lead to some decomposition of these compounds, as was also the case with some *N*-picO analogues.⁴) Under these conditions, the Fe(II) and Co(II) complexes are converted to the anhydrous analogues M(*N*-nicO)₂; the Zn(II) complex yields the corresponding monohydrate, the Mn(II) compound yields the dihydrate, and the Ni(II) and Cu(II) complexes yield the trihydrates (Table I). These partially or completely dehydrated products exhibit the same solubility characteristics as those of the initially isolated tetra- or pentahydrates.

Spectral, Magnetic, and X-Ray Powder Diffraction Studies. Infrared spectra (Table II) were obtained on KBr disks (4000–500 cm⁻¹) and Nujol mulls of the complexes between high-density polyethylene windows (700–250 cm⁻¹) by using a Perkin-Elmer 621 spectrophotometer. Solid-state electronic spectra (Table III), magnetic susceptibility measurements (Table III), and x-ray powder diffraction patterns (Table IV, Figure 1) were obtained by methods described elsewhere.²⁹ The products of partial or complete dehydration are characterized by low crystallinity. In fact, their x-ray patterns exhibit only three to six bands (Table IV), which are substantially weaker and broader than those observed for the initially isolated complexes.

Discussion

Infrared Spectra and X-Ray Patterns. As is the case with many metal complexes of the pyridine monocarboxylic acids,^{15–19,30,31} the new metal complexes originally obtained contain four or five molecules of water. The x-ray powder diffraction patterns of the Mn(II), Fe(II), Co(II), and Ni(II) tetrahydrated complexes show considerable similarities (Table IV, Figure 1), as to allow the conclusion that these compounds have approximately similar structures. They cannot, nevertheless, be characterized as isomorphous. The Cu(II) analogue and the pentahydrated Zn(II) complex show different x-ray patterns from one another or from those of the above compounds. The overall evidence points to hexacoordinated structures for all of the initially isolated metal complexes (vide infra: electronic spectra and metal–ligand stretching modes). The difference of the x-ray pattern of the Cu(II) complex from those of the other tetrahydrates is presumably due to the Jahn–Teller effect.³² As far as the pattern of the Zn(II)

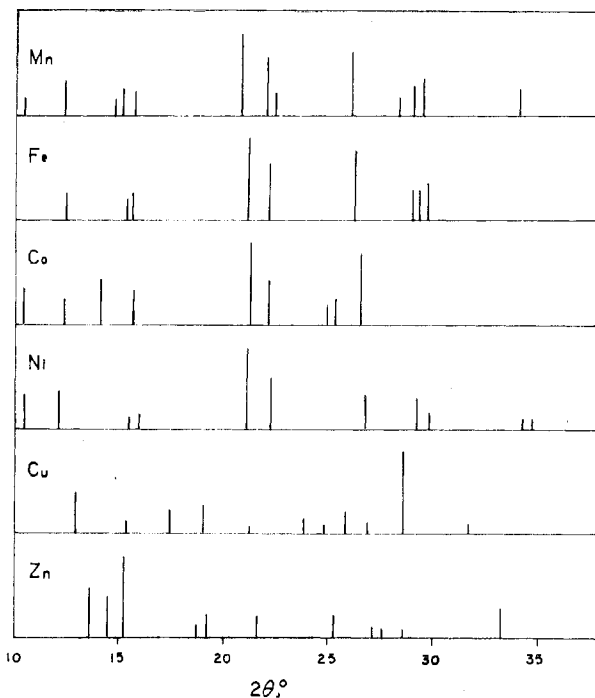


Figure 1. X-ray powder diffraction patterns of M(*N*-nicO)₂·*n*H₂O (M = Mn, Fe, Co, Ni, Cu) and Zn(*N*-nicO)₂·5H₂O complexes—schematic representation.

complex is concerned, its dramatic difference from the rest of the patterns shown in Figure 1 implies that its structure should differ considerably from those of the Mn(II)–Ni(II) complexes. Later in the text it is concluded that the above complexes are polynuclear of the type [M(*N*-nicO)₂(OH₂)₂]_x and involve also lattice water (three molecules of lattice water per metal ion in the case of Zn(II) and two in all other cases). The presence of one additional water molecule in the Zn(II) complex is apparently sufficient³³ to produce a significant change in its x-ray pattern, relative to those of the tetrahydrates. No comparisons of the poorly resolved x-ray patterns of the partial or complete dehydration products are attempted.

The coordination sites of the ligand can usually be deduced from characteristic shifts of ir bands associated with groups having coordinating ability (N–O and COO oxygens in the present case). Free nicotinic acid *N*-oxide exhibits the N–O stretch at 1270 cm⁻¹ and the N–O bend at 827 cm⁻¹.³⁴ In the spectra of the new metal complexes ν_{N-O} shows a negative frequency shift of 40–52 cm⁻¹, while δ_{N-O} appears as a split band (Table II). These features are indicative of coordination through the N–O oxygen.³⁵ On the other hand, the spectrum of the free ligand exhibits two bands at 1710 and 1436 cm⁻¹, corresponding, respectively, to ν_{CO_2} (asymmetric and symmetric) of the carboxylate ion.^{4,11,34,36} These modes undergo

Table II. Pertinent Infrared Data for $M(V-nicO)_2 \cdot xH_2O$ Complexes (cm^{-1})^a

$N-nicOH$	M = Mn		M = Fe		M = Co		M = Ni		M = Cu		M = Zn		Band assignment
	x = 4	x = 2	x = 4	x = 0	x = 4	x = 0	x = 4	x = 3	x = 4	x = 3	x = 5	x = 1	
3480 ms	3360 s, wb	3330 s, b	3350 vs, vb	3370 s, wb	3400 vs, vb	3400 vs, vb	3400 vs, vb	3400 vs, vb	3440 s, vb	3440 s, vb	3395 vs, vb	3370 vs, b	$\nu_{OH}(\text{hydroxyl})$ $\nu_{OH}(\text{water})^b$
3115 m	3120 s	3120 s	3115 vs	3120 s	3120 vs	3120 vs	3120 vs	3120 vs	3120 sh	3120 sh	3120 sh	3115 sh	} ν_{CH}
3088 ms	3075 s	3075 s	3080 vs	3080 s	3095 vs	3095 vs	3095 vs	3095 vs	3080 sh	3080 sh	3085 vs	3085 vs	
3079 vs	3055 s	3060 s	3060 vs	3060 s	3075 vs	3075 vs	3075 vs	3075 vs	3055 s, b	3055 s, b	3072 vs	3070 vs	
1710 vs	1624 vs	1624 vs	1620 vs	1621 vs	1630 vs	1630 vs	1630 vs	1630 vs	1616 vs	1618 vs	1633 vs	1649 vs	} $\nu_{CO_2}(\text{asym})$
			1637 s									1631 vs	
1610 ms	1630 s, sh	1633 s, sh	1632 s, sh	1628 s, sh	d	d	d	d	1624 s, sh	1625 s, sh	1629 vs, sh	1629 vs, sh	$\delta_{H-O-H}(\text{water})$
1572 s	1590 vs	1588 vs	1581 vs	1588 vs	1590 vs	1590 vs	1590 vs	1590 vs	1591 s	1595 s	1592 vs	1596 vs	} $A_1 + B_1 (\nu_{CC} + \nu_{CN})$
1480 m	1562 vs, b	1562 vs	1553 vs, b	1560 vs, b	1561 vs, b	1557 vs	1557 vs	1560 s, b	1560 s, b	1563 s, b	1565 vs, b	1565 vs	
1436 vs ^c	1481 m	1479 m	1480 m	1480 m	1480 m	1489 m	1489 m	1480 m	1477 w	1477 w	1481 w	1480 w	
1436 vs ^c	1432 m	1435 m	1429 m	1433 m	1436 m	1436 m	1436 m	1431 vs, sh	1435 s	1435 s	1437 ms	1438 ms	
1436 vs ^c	1393 vs	1392 vs	1391 vs	1392 vs	1401 vs	1401 vs	1401 vs	1401 vs	1402 vs	1402 vs	1395 vs, b	1395 vs, b	} $\nu_{CO_2}(\text{sym})$
			1367 vs						1369 vs	1369 vs	1365 vs	1365 vs	
1320 s, b													OH in-plane def + COOH
1270 vs	1219 vs	1223 vs	1222 vs	1220 vs	1230 vs	1230 vs	1230 vs	1230 vs	1221 vs	1223 vs	1230 vs	1221 vs	ν_{N-O}
827 s	850 m, b	850 m, sh	850 m, b	850 m, b	860 m, b	862 m, b	862 m, b	860 m, b	860 m, b	860 m, b	832 m	832 m	} δ_{N-O}
	826 m	828 m	829 m	830 m	836 m	835 m	835 m	829 m	829 m	829 m	810 ms, b	810 ms, b	
460 m	451 m	457 ms	460 s	466 m	470 m	466 m	466 m	466 m	482 ms	484 ms	462 ms	460 ms	} ν_{ligand} at 500–250 cm^{-1}
442 w, sh	422 ms	423 ms	421 s, sh	422 m, sh	420 m	420 m	420 m	420 m	468 ms	470 ms	419 m, sh	421 m	
421 w	395 m, sh	395 m, sh	399 ms, sh	397 ms, sh	401 m, sh	401 m, sh	401 m, sh	401 m, sh	427 m, sh	427 m, sh	388 m	389 m	
381 w													
349 vw	380 mw, sh	380 mw, sh	382 m, sh	385 m, sh	385 m, sh	385 m, sh	385 m, sh	385 m, sh	395 ms	397 ms	378 w, sh	378 w, sh	
332 vw, sh	350 w, sh	350 w, sh	372 w	372 w	372 w	372 w	372 w	372 w	379 m, sh	380 m, sh	360 vw	320 w, sh	
			349 w										
305 m, sh	330 w, sh	330 w, sh	340 w, sh	340 w, sh	350 ms	350 ms	350 ms	350 ms	338 w, sh	340 w	349 w	308 w	
280 ms	310 m	310 ms	315 w, b	336 w, sh	335 w, sh	335 w, sh	335 w, sh	335 w, sh	305 m	305 m	308 w	262 w	
250 ms	261 m	260 m	250 m	253 ms	248 ms	253 ms	253 ms	253 ms	252 w	250 w	261 m		
													} $\nu_{M-O}(\text{aq})$
417 ms	420 ms	420 ms	430 s	432 s	441 s	441 s	441 s	441 s	441 s	441 s	428 ms	443 ms	
343 m	343 m	343 m	333 w	362 m	362 m	362 m	362 m	362 m	360 m, sh	360 m, sh	330 m	352 m	
											320 mw		} $\nu_{M-O}(N-O)$
275 m	273 m	273 m	280 m	280 ms	281 ms	281 ms	281 ms	281 ms	288 m	288 m	275 m	299 m	
									281 ms	281 ms	275 m	285 m	} $\nu_{M-O}(COO)$
									279 ms	281 ms			

^a Abbreviations: s, strong; m, medium; w, weak; v, very; b, broad; sh, shoulder; def, deformation. ^b The $\nu_{OH}(\text{water})$ bands in the tri- to pentahydrated complexes are very broad, characterized by continuous absorption at 3600–3150 cm^{-1} , indicative of the presence of many maxima. This broad absorption is not present in the spectra of the mono- and dihydrates. The values given as $\nu_{OH}(\text{water})$ in the table refer to the maximum of the relatively sharp $\nu_{OH}(\text{aq})$ band. ^c $\nu_{CO_2}(\text{sym})$ overlaps with the $B_1 (\nu_{CC} + \nu_{CN})$ modes in the spectrum of the free ligand. ^d Overlap between $\nu_{CO_2}(\text{asym})$ and $\delta_{H-O-H}(\text{water})$ bands.

Table III. Solid-State (Nujol Mull) Electronic Spectra and Magnetic Susceptibilities (300 K) of *N*-nicO (L)-3d Metal Complexes^a

Compd	λ_{\max} , nm	$10^6 \chi_M^{\text{cor}}$, cgsu	μ_{eff} , μ_B
(<i>N</i> -nicO)NH ₄	212 vs, 227 vs, 262 vs, 303 s, sh ^b		
MnL ₂ ·4H ₂ O	206 vs, 223 vs, sh, 270 vs, 300 s, sh, 357 s, sh	13 418	5.70
MnL ₂ ·2H ₂ O ^c		14 007	5.82
FeL ₂ ·4H ₂ O	208 vs, 223 vs, sh, 275 vs, b, 302 s, sh, 363 s, b, sh, 759 m, 776 m, sh, 980 w, sh	11 665	5.31
FeL ₂	209 vs, 222 vs, sh, 273 vs, b, 304 s, sh, 363 s, sh, 628 ms, sh, 827 ms, 933 m, sh, 1170 w	10 882	5.13
CoL ₂ ·4H ₂ O	206 vs, 225 vs, sh, 273 s, b, 312 s, b, 338 s, sh, 452 m, 500 m, 1200 w, b	8 658	4.58
CoL ₂	206 vs, 224 vs, sh, 273 s, b, 307 s, b, 360 s, b, 476 m, 511 m, 750 mw, sh, 1140 w, b	9 211	4.72
NiL ₂ ·4H ₂ O	209 vs, 227 vs, sh, 272 s, vb, 300 s, sh, 345 s, sh, 395 m, 676 mw, 712 mw, 1080 w, b	3 342	2.84
NiL ₂ ·3H ₂ O ^c		3 524	2.92
CuL ₂ ·4H ₂ O	206 vs, 224 s, sh, 278 s, b, 337 s, b, 709 m, b, 747 m, b, 953 mw, sh	1 856	2.12
CuL ₂ ·3H ₂ O ^c		1 822	2.10
ZnL ₂ ·5H ₂ O	205 vs, 225 vs, 274 vs, b		Diamagnetic
ZnL ₂ ·H ₂ O ^c			Diamagnetic

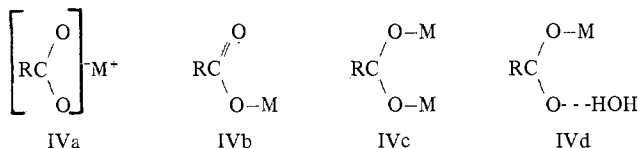
^a Abbreviations: s, strong; m, medium; w, weak; v, very; b, broad; sh, shoulder. ^b Uv spectra of nicotinic acid *N*-oxide from the literature⁴⁹⁻⁵¹ (nm): water solution, 220, 257.5-260, 306 sh; ethanol solution, 220, 268-269.5, 312. ^c The partial dehydration products of the Mn(II), Ni(II), Cu(II), and Zn(II) complexes exhibit solid-state electronic spectra identical with those of the corresponding tetra- or pentahydrates.

Table IV. Main Bands in the X-Ray Powder Diffraction Patterns of *N*-nicO-M Complexes

Complex ^a	<i>d</i> spacings, Å (<i>I</i> in parentheses)
MnL ₂ ·4H ₂ O	8.50 (20), 7.19 (38), 6.02 (20), 5.86 (35), 5.64 (32), 4.27 (100), 4.04 (70), 3.97 (30), 3.41 (77), 3.11 (23), 3.08 (38), 3.03 (46), 2.63 (31), 2.39 (26), 2.34 (20)
FeL ₂ ·4H ₂ O	7.13 (32), 5.79 (27), 5.60 (32), 4.21 (100), 4.02 (70), 3.40 (85), 3.09 (37), 3.06 (39), 3.01 (44)
CoL ₂ ·4H ₂ O	8.50 (43), 7.19 (32), 6.28 (57), 5.68 (40), 4.19 (100), 4.02 (54), 3.57 (27), 3.52 (32), 3.36 (86)
NiL ₂ ·4H ₂ O	8.42 (38), 7.31 (45), 5.75 (15), 5.57 (15), 5.24 (18), 4.21 (100), 4.00 (62), 3.34 (44), 3.06 (39), 2.97 (20), 2.61 (14), 2.58 (13), 2.14 (31), 1.99 (18)
CuL ₂ ·4H ₂ O	6.86 (49), 5.77 (14), 5.09 (27), 4.67 (35), 4.19 (11), 3.74 (22), 3.59 (13), 3.45 (28), 3.31 (17), 3.12 (100), 2.82 (13), 2.37 (13), 2.35 (13)
ZnL ₂ ·5H ₂ O	18.39 (24), 9.71 (30), 6.51 (63), 6.10 (52), 5.82 (100), 4.74 (18), 4.62 (30), 4.11 (29), 3.52 (30), 3.29 (17), 3.23 (13), 3.12 (13), 2.69 (37)
MnL ₂ ·2H ₂ O ^b	3.96 (100), 3.60 (35), 3.41 (40), 3.05 (95), 2.99 (35), 2.06 (50)
FeL ₂ ^b	3.22 (100), 2.96 (60), 2.27 (60)
CoL ₂ ^b	6.05 (50), 5.75 (50), 3.49 (100), 3.33 (90), 2.37 (50), 2.16 (70)
NiL ₂ ·3H ₂ O ^b	4.51 (30), 4.12 (40), 3.51 (60), 3.31 (100), 3.01 (40), 2.14 (50)
CuL ₂ ·3H ₂ O ^b	4.69 (20), 4.35 (15), 3.09 (100), 3.05 (80), 2.86 (60)
ZnL ₂ ·H ₂ O ^b	3.99 (40), 2.89 (50), 2.19 (100)

^a L = *N*-nicO. ^b The x-ray patterns of these dehydration products are generally poorly resolved and show considerably weaker and more diffuse bands than those observed in the patterns of the tetra- or pentahydrated complexes.

the following changes in metal complexes with carboxylate ligands. In compounds with ionic carboxylate (IVa) they are



shifted to 1610-1550 and 1420-1300 cm^{-1} , respectively.⁴ When one of the COO oxygens forms a covalent bond to a metal ion (IVb), the band assigned as the asymmetric frequency in the free ion increases to ca. 1650 cm^{-1} , as the vibration takes on more ketonic character, while the frequency of the corresponding symmetric vibration decreases.^{4,37} And when both carboxylate oxygens are coordinated to metal ions (IVc) or one of these oxygens is coordinated to a metal ion and the other is hydrogen-bonded to water (IVd), the ν_{CO_2}

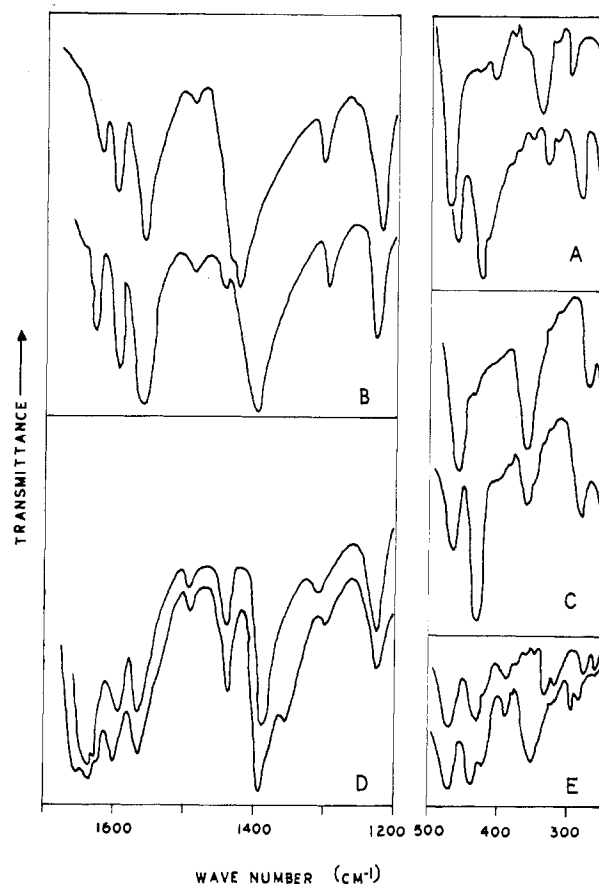


Figure 2. Infrared spectra (1700-1200 and/or 500-250 cm^{-1}): A, Fe(*N*-nicO)₂ (top) and Fe(*N*-nicO)₂·4H₂O (bottom); B and C, Co(*N*-nicO)₂ (top) and Co(*N*-nicO)₂·4H₂O (bottom); D and E, Zn(*N*-nicO)₂·5H₂O (top) and Zn(*N*-nicO)₂·H₂O (bottom).

bands are found at frequencies intermediate between those of the uncomplexed carboxylate ion and those of coordinated unidentate RCOO⁻ ligands.^{4,38} The tetra- or pentahydrated metal complexes exhibit $\nu_{\text{CO}_2}(\text{asym})$ at 1633-1616 cm^{-1} and the $\nu_{\text{CO}_2}(\text{sym})$ mode at 1402-1391 cm^{-1} (with a second band at 1369 cm^{-1} in the case of Cu(II)) (Table II, Figure 2). These data are consistent with both a configuration involving one COO oxygen bonded to the metal ion and the other hydrogen bonded to water (as in IVd), as is the case with the corresponding *N*-picO^{4,11} and picolate^{31,39} M(II) chelates and some nicotinate M(II) complexes,¹⁷⁻¹⁹ and a structure in which the carboxylate groups are ionic (IVa) (i.e., *N*-nicO coordinated only through the N-O oxygen), as in M(nic)₂-

(OH)₂)₄ complexes.^{15,16,40} Correlation of the above results to the frequencies of the ν_{CO_2} bands observed in the spectra of the partial or complete dehydration products is in favor of the former possibility. In fact, the ir spectra of Mn(*N*-nicO)₂·2H₂O and M(*N*-nicO)₂·3H₂O (M = Ni, Cu) are almost identical with those of the corresponding tetrahydrates. Hence, it may be concluded that in all of the initially obtained complexes, as well as the above three partially dehydrated products, the carboxylate groups behave in the same manner. In view of the hexacoordinated configuration of all of these complexes (vide infra), MO₆ moieties, involving coordination of two N–O groups, two unidentate COO groups, and two aquo groups and hydrogen bonding of the second carboxylate oxygen to water, can be postulated. In the case of Co(*N*-nicO)₂, ν_{CO_2} (asym) and ν_{CO_2} (sym) are shifted toward lower and higher frequencies (respectively), relative to the spectrum of Co(*N*-nicO)₂·4H₂O (Figure 2). This is probably due to coordination of both COO oxygens to Co²⁺ ions in the anhydrous Co(II) complex (IVc).¹⁷ Finally, in Fe(*N*-nicO)₂ and Zn(*N*-nicO)₂·H₂O, both the asymmetric and the symmetric ν_{CO_2} modes appear as doublets (Figure 2). This is suggestive of the presence of chemically nonequivalent carboxylate groups. The ν_{CO_2} (asym) band at 1666–1649 cm⁻¹ is attributed to the presence of COO groups coordinated through one oxygen (IVb), and that at 1637–1631 cm⁻¹, to bidentate bridging (IVc) (Fe(II)) or unidentate and hydrogen-bonded (IVd) (Zn(II)) carboxylate.

Other ligand absorptions, such as the A₁ and B₁ $\nu_{\text{CC}} + \nu_{\text{CN}}$ modes⁴¹ are affected to a much lesser extent by coordination. In the ν_{OH} (water) region, the tri- to pentahydrated complexes exhibit strong, relatively sharp maxima at 3400–3340 cm⁻¹ (shown in Table II), attributable to the presence of aquo ligands,⁴² as well as a very broad, weaker general absorption at 3600–3150 cm⁻¹, indicative of the presence of several maxima and apparently due to the simultaneous presence of lattice water.⁴³ This assignment is also supported by the fact that the spectra of Mn(*N*-nicO)₂·2H₂O and Zn(*N*-nicO)₂·H₂O show only the ν_{OH} bands corresponding to coordinated water (no broad absorption at 3600–3150 cm⁻¹ is observed).

In the lower frequency ir region several metal-sensitive bands appear. Tentative $\nu_{\text{M-O}}$ (aquo, NO, and COO) assignments (Table II) were based on similar assignments for carboxylate,⁴⁴ aquo,^{16,45} and aromatic amine *N*-oxide⁴⁶ 3d metal complexes. The assignment of $\nu_{\text{M-O}}$ (aquo) at 443–417 cm⁻¹ is supported by the disappearance of this band in the spectra of the anhydrous Fe(II) and Co(II) complexes (Table II, Figure 2). The $\nu_{\text{M-O}}$ modes in Fe(*N*-nicO)₂ and Zn(*N*-nicO)₂·H₂O occur at significantly higher frequencies than those in the corresponding tetra- or pentahydrate; this is probably suggestive of a coordination number lower than 6 for these two complexes.

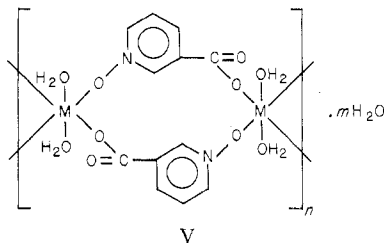
Electronic Spectra and Magnetic Moments. The magnetic moments of the new metal complexes (Table III) are generally normal for high-spin compounds of the metal ions studied.^{2,4,47} The moments of the two hexacoordinated Co(II) complexes are below the "octahedral" region for this metal ion (4.80–5.20 μ_{B}); this is not unexpected, since several low-symmetry hexacoordinated Co(II) complexes with aromatic amine *N*-oxides reportedly exhibit magnetic moments in the 4.50–4.70- μ_{B} region.^{2,47,48} The ultraviolet spectrum of the ligand is characterized by two bands due to $\pi \rightarrow \pi^*$ transitions (220, 257–270 nm) and one $n \rightarrow \pi^*$ transition band at 303–312 nm.^{49–51} In the spectra of the 3d metal complexes or the ammonium salt (Table III), the highest energy band is split into two components (205–212 and 222–227 nm), while the other $\pi \rightarrow \pi^*$ transition (257.5–260 nm in water) is shifted toward lower energies. Pyridine *N*-oxide and 4-picoline *N*-oxide also show red shifts of their $\pi \rightarrow \pi^*$ transition upon complex formation with the same metal ions.⁴ However, in

the corresponding *N*-picO–M chelates the $\pi \rightarrow \pi^*$ ligand band shows small (3–4 nm) blue shifts or remains unchanged.⁴ This is probably due to intramolecular hydrogen bonding in free picolinic acid *N*-oxide.⁵⁰ The absorptions at 300–312 nm in the spectra of the new metal complexes are attributed to the $n \rightarrow \pi^*$ ligand transition,^{4,50} while those at 337–363 nm are due to metal-to-ligand charge transfer.⁴ The energies of these charge-transfer bands increase along the series Fe(II) < Mn(II) < Ni(II) < Co(II) < Cu(II), in the spectra of the M(*N*-nicO)₂·4H₂O complexes (corresponding series for *N*-picO–M chelates is Fe(II) < Co(II) < Ni(II) < Mn(II) < Cu(II) and for hexakis(pyridine *N*-oxide) cationic M(II) complexes is Mn(II) < Ni(II) = Fe(II) = Co(II) < Cu(II)⁴). It is noteworthy that the charge-transfer bands in the new *N*-nicO–M complexes occur at higher energies than the corresponding absorptions in the spectra of either the *N*-picO–3d metal chelates or the pyridine *N*-oxide cationic metal complexes.⁴ Since *N*-picO and *N*-nicO appear to be ligands of about equal strength (vide infra), it is somewhat surprising that the charge-transfer bands in the transition metal complexes of the latter ligand occur at considerably higher energies.⁴ The presence of an electron-withdrawing group, such as the carboxylate, in the ortho or meta ring position (*N*-picO and *N*-nicO, respectively) would be expected to cause similar increases of the acceptor ability of the N–O site.^{4,52,53} Thus, it appears that, during 3d metal complex formation, the N–O group acts as a richer electron-donating site in *N*-nicO than in *N*-picO, while the reverse is true for the COO– group. In support of this argument is the fact that in the case of cyano-substituted pyridine *N*-oxides, which involve the electron-withdrawing CN group and behave as unidentate O ligands toward cobalt(II) and nickel(II) perchlorates, the meta-substituted *N*-oxide is a stronger ligand than the ortho derivative.⁵⁴

The d–d transition spectra of the M(*N*-nicO)₂·4H₂O (M = Fe, Co, Ni, Cu), M(*N*-nicO)₂·3H₂O (M = Ni, Cu) (which have spectra identical with those of the corresponding tetrahydrates), and Co(*N*-nicO)₂ complexes are characteristic of hexacoordinated configurations. Splittings of the ⁵T_{2g} → ⁵E_g (759–980 nm) and ²E_g → ²T_{2g} (709–953 nm) transitions in the spectra of the above Fe(II) and Cu(II) complexes, respectively, are suggestive of low effective symmetries for the central metal ions.^{47,55} In view of the similarities of the x-ray patterns of the tetrahydrated complexes, it follows that all of these compounds, including the Mn(II) complexes, are characterized by symmetries lower than O_h. The d–d transition bands in the spectra of the Co(II) and Ni(II) complexes are assigned as follows (nm):^{54,56} Co(*N*-nicO)₂·4H₂O: ⁴T_{1g}(F) → ⁴T_{1g}(P), 452; ⁴A_{2g}(F), 500; ⁴T_{2g}(F), 1200. Co(*N*-nicO)₂: ⁴T_{1g}(F) → ⁴T_{1g}(P), 476; ⁴A_{2g}(F), 511; ⁴T_{2g}(F), 1140. Ni(*N*-nicO)₂·xH₂O (x = 3 or 4): ³A_{2g}(F) → ³T_{1g}(P), 395; ³T_{1g}(F), ¹E_g(D) 676, 712; ³T_{2g}(F), 1080. Approximate *Dq* and β value calculations from the spectra of the hydrated complexes suggest that *N*-nicO is a slightly weaker ligand than *N*-picO; viz., for *N*-nicO toward hexacoordinated Co(II), *Dq* = 1026 cm⁻¹, β = 0.83; for Ni(II), *Dq* = 926 cm⁻¹; β = 0.84. The corresponding *Dq* values for *N*-picO, in M(*N*-picO)₂·2H₂O chelates, are 1030 and 935 cm⁻¹, respectively.⁴ For the anhydrous Co(II) complex a higher *Dq* value (1050 cm⁻¹) for *N*-nicO is calculated, while β is 0.84. Finally, the spectrum of Fe(*N*-nicO)₂ is richer in d–d band maxima than that of the hydrated Fe(II) complex; this spectrum may be interpreted in terms of a pentacoordinated structure,⁵⁷ which is also supported by the lower frequency ir evidence.

Nature of the New Metal Complexes. As already mentioned the *N*-nicO–M complexes are generally insoluble in water and most organic media (cf. Experimental Section). In contrast, the corresponding *N*-picO–M chelates dissolve in water and/or

methanol.⁴ These differences in solubility are suggestive of bi- or polynuclear structures for the new *N*-nicO-M complexes. Furthermore, since both the N-O and COO groups are involved in coordination, it is more likely that *N*-nicO would function as a bridging rather than chelating ligand.¹⁷⁻²⁷ On the basis of the overall evidence, the most likely structure for the $M(N\text{-nicO})_2 \cdot x\text{H}_2\text{O}$ ($x = 2-5$) complexes is $[M(N\text{-nicO})_2(\text{OH}_2)_2]_n \cdot m\text{H}_2\text{O}$ (m varies between 0 and $3n$) (see also structural formula V). In these complexes, the carboxylate



oxygens, which are not coordinated to the metal ions, form hydrogen bonds to water, as discussed above.^{4,15-17,31,39} The linear, polynuclear, hexacoordinated structure V involves double *N*-nicO bridges between neighboring metal ions and aquo ligands at the axial positions (trans to each other). In the case of $\text{Co}(N\text{-nicO})_2$, coordination number 6 is apparently preserved, after the complete elimination of water, by formation of covalent bonds between the Co(II) ions of one unit of type V and the uncomplexed COO oxygens from adjacent polymeric units, and vice versa; this leads to a highly cross-linked polymeric structure, similar to that proposed by Kleinstein et al. for $M(\text{nic})_2$ complexes.¹⁷ $\text{Fe}(N\text{-nicO})_2$ seems to differ from the Co(II) analogue in that only two units of type V are cross-linked in the above manner, after removal of the water; thus, one *N*-nicO ligand per Fe(II) ion acts as tridentate and one as bidentate, the carboxylate groups coordinating as in IVc and IVb, respectively. Finally, $\text{Zn}(N\text{-nicO})_2 \cdot \text{H}_2\text{O}$ appears to be linear and polymeric, differing from V in that only one aquo ligand is coordinated to each Zn^{2+} ion and lattice water is absent. The COO groups in this complex are apparently nonequivalent; presumably only one COO group per Zn^{2+} ion is hydrogen bonded to water. The proposed structures for $\text{Fe}(N\text{-nicO})_2$ and $\text{Zn}(N\text{-nicO})_2 \cdot \text{H}_2\text{O}$ require coordination number 5, which is consistent with the ir and electronic spectral evidence.

Registry No. $\text{MnL}_2 \cdot 4\text{H}_2\text{O}$, 59015-61-1; $\text{MnL}_2 \cdot 2\text{H}_2\text{O}$, 59015-58-6; $\text{FeL}_2 \cdot 4\text{H}_2\text{O}$, 59015-56-4; FeL_2 , 58894-74-9; $\text{CoL}_2 \cdot 4\text{H}_2\text{O}$, 59015-60-0; CoL_2 , 58894-72-7; $\text{NiL}_2 \cdot 4\text{H}_2\text{O}$, 59015-54-2; $\text{NiL}_2 \cdot 3\text{H}_2\text{O}$, 59015-55-3; $\text{CuL}_2 \cdot 4\text{H}_2\text{O}$, 59015-57-5; $\text{CuL}_2 \cdot 3\text{H}_2\text{O}$, 59015-59-7; $\text{ZnL}_2 \cdot 5\text{H}_2\text{O}$, 59015-53-1; $\text{ZnL}_2 \cdot \text{H}_2\text{O}$, 59015-52-0; (*N*-nicO) NH_4 , 58894-70-5.

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University of Massachusetts at Boston, Boston, Massachusetts 02125**Metal Complexes of Cyclic Triamines. 1. Complexes of 1,4,7-Triazacyclononane ([9]aneN₃) with Nickel(II), Copper(II), and Zinc(II)**

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The equilibria which exist between the potentially tridentate cyclic amine 1,4,7-triazacyclononane, [9]aneN₃, and Ni(II), Cu(II), and Zn(II) ions have been investigated in 0.1 M KNO₃ at 25.0 °C. The bis complexes Cu([9]aneN₃)₂X₂ and Ni([9]aneN₃)₂X₂ as well as Ni([9]aneN₃)X₂ (where X⁻ = NO₃⁻ and/or Cl⁻) have also been isolated and characterized. The unexpectedly large formation constants determined for the 1:1 metal-ligand complexes and the large value of *Dq* for Ni([9]aneN₃)₂²⁺ suggest that this ligand imposes rather severe steric constraints on coordination.

Introduction

Metal complexes of cyclic amines have been extensively investigated during the last 15 years. Most studies have focused upon macrocyclic complexes which contain cyclic tetraamine ligands¹⁻³ and to a lesser extent complexes containing cyclic diamines.⁴ The few studies of complexes containing cyclic triamines indicate that these complexes exhibit thermodynamic and kinetic stability normally associated with macrocyclic complexes.^{5,6} Busch and co-workers⁷ suggested that the unusual stability of macrocyclic complexes is due to the fixed geometrical placement of ligand donor atoms (the MJF effect). The MJF effect, however, was first illustrated with a cyclic triamine, tris(anhydro-*o*-aminobenzaldehyde) (TRI).⁷ Our preliminary studies with a series of saturated cyclic triamines indicated that these compounds form unusually stable metal complexes.⁶

In this study we present further evidence of the complexing strength of cyclic tridentate amines. Formation constants for the mono complexes of 1,4,7-triazacyclononane ([9]aneN₃)⁸ with nickel(II), copper(II), and zinc(II), as well as the acidity constants of the triprotonated species H₃([9]aneN₃)³⁺ are presented. The mono and bis complexes of [9]aneN₃ with nickel(II) and the bis complex of copper(II) have been isolated and characterized. The unusual stability of the [9]aneN₃ complexes is demonstrated by comparison of the formation constants obtained in this study with those of other potentially tridentate amines.

The permutation of the normal Irving-Williams⁹ order of stability for the copper(II) and nickel(II) complexes and the unusually large value for the ligand field parameter (*Dq*) for [Ni([9]aneN₃)₂]²⁺ are presented as evidence to support our conclusion that the stability of the [9]aneN₃ complexes is due largely to the stereorestrictive mode of coordination imposed by this ligand.

Experimental Section

Materials. All reagents and solvents used were reagent grade and were used without further purification. Standard solutions of nickel(II), copper(II), and zinc(II) as the nitrates were standardized by complexometric titration techniques.¹⁰

1,4,7-Triazacyclononane *N,N',N''*-Tri-*p*-tosylate. A solution of 6.58 g (0.035 mol) of 1,2-dibromoethane in 80 ml of dimethylformamide (DMF) was added dropwise to a hot (100 °C) solution containing 21.34 g (0.035 mol) of disodiiodiethylenetriamine *N,N',N''*-tri-*p*-tosylate¹¹ in 180 ml of DMF. After stirring and heating of the solution at 100 °C for 16 h, it was cooled to room temperature. Concentration to one-tenth of the original volume followed by the addition of 1 l. of water gave a white gummy solid which was extracted with 300 ml of hot benzene. After treatment with activated carbon the benzene

solution was dried over anhydrous sodium sulfate. The benzene was then removed to give a yellow-brown oil which was dissolved in hot ethanol. After cooling and standing of the mixture for 24 h, 4.14 g (0.007 mol), 20% yield, of 1,4,7-triazacyclononane *N,N',N''*-tri-*p*-tosylate was collected as colorless needles, mp 222–223 °C.¹¹ NMR: δ_{TMS}(CDCl₃) 7.60 (q, 12 H, phenyl), 3.45 (s, 12 H, methyl), 2.40 (s, 9 H, ethylene).

1,4,7-Triazacyclononane Trihydrobromide. The procedure of Koyama and Yoshino¹² was employed for the hydrolysis of the cyclic tosylate. A solution containing 3.55 g (6.01 mmol) of 1,4,7-triazacyclononane *N,N',N''*-tri-*p*-tosylate in 180 ml of 30% hydrobromic acid-acetic acid was refluxed with stirring for 48 h. The solution was filtered while hot and concentrated to one-tenth its original volume. Addition of 150 ml of 25% ether-ethanol solution gave 1.65 g (4.44 mmol), 74% yield, of the amine trihydrobromide, mp 277–278 °C dec.¹² NMR: δ_{TMS}(D₂O) 4.1 (s).

1,4,7-Triazacyclononane Trihydrochloride. A slurry of 1.12 g (3.01 mmol) of the hydrobromide salt in 3–4 ml of concentrated hydrochloric acid was heated until all solid dissolved. Sometimes several drops of water had to be added to produce complete solution. Upon cooling, this solution gave colorless crystals of the trihydrochloride salt. Two additional recrystallizations from hydrochloric acid gave 0.64 g (2.69 mmol), 89% yield, of the pure salt, mp 280–281 °C dec. Anal. Calcd for C₆H₁₈N₃Cl₃·0.5H₂O: C, 29.10; H, 7.73; N, 16.97; Cl, 42.96. Found: C, 29.19; H, 7.25; N, 17.08; Cl, 42.93. NMR: δ_{TMS}(D₂O) 4.0 (s).

Metal Complexes. All metal complexes were synthesized by the following procedure.

Ethanolic slurries of the amine hydrochloride (ca. 0.1 M) were neutralized with potassium hydroxide, cooled, and filtered. Then solutions containing a stoichiometric amount of the appropriate metal salt in ethanol (ca. 0.05 M) were added to the filtrate. Crystals of the metal complex were isolated after partial evaporation of the solvent. In some cases excess of ligand was added to the solutions. The crude product was usually recrystallized from ethanol. The analytical data are reported in Table I.

Spectroscopic and Magnetic Measurements. Solution and solid-state spectra were obtained with a Cary Model 14 recording spectrophotometer. Diffuse transmittance spectra were obtained using the Nujol mull technique.¹³ Infrared spectra were recorded on a Perkin-Elmer 137 spectrophotometer employing KBr disks containing the sample. The NMR spectra were recorded with a Varian A-60 NMR spectrometer, using CDCl₃ or D₂O as solvent.

Magnetic susceptibilities were measured by the Faraday method at 20 °C on a Cahn Model 7600 system. The instrument was calibrated using Hg(Co(NCS)₄)₂.

Potentiometric Titrations. Solutions of H₃([9]aneN₃)Cl₃ were prepared and standardized by titration with standard sodium hydroxide solution. Metal-ligand titrations were performed with equimolar quantities of metal and ligand. Three titrations were performed for each metal system with concentration ranging from 3 × 10⁻³ to 9 × 10⁻³ M. Because several weeks were required for equilibrium to be established in the nickel(II) system, the titration was performed out