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Complexes of Nickel(II) with a Cyclic Tetradentate Secondary Amine

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The complexes of the nickel(II) halides and nickel(II) perchlorate with 1,4,8,11-tetraazacyclotetradecane have been prepared. The chloride and bromide are paramagnetic in the solid state, whereas the iodide and perchlorate are diamagnetic. All dissolve in methanol and water to give 2:1 electrolytes, and the solution spectra are independent of the nature of the anion and very similar to the diffuse reflectance spectrum of the perchlorate. The change in spin multiplicity on changing from chloride and bromide to iodide and perchlorate is ascribed to the increasing tetragonal distortion due to the axial ligands being prevented by steric reasons from exerting their full ligand field strength.

Introduction

The ligand 1,4,8,11-tetraazacyclotetradecane (cyclam) has been described in the previous paper,[1] and its complexes with cobalt(III) have been discussed. Although the cobalt(III) complexes were obviously octahedral and almost certainly *trans*, some problem remained about the configuration of the ligand system, and so the nickel complexes were prepared in order to obtain a simpler system for a structural analysis. Examination of these complexes, however, showed that they were of extreme interest in their own right and provided further information about spin multiplicity changes in a d^8 system. The structure of the chloride has been determined by X-ray diffraction.

Results and Discussion

The complexes were prepared by mixing equimolar quantities of the ligand and hydrated NiX_2 (where X = Cl, Br, I, ClO_4) in ethanol solution (or 1-butanol in the case of the iodide) and were precipitated by the addition of ether or acetone. The perchlorate is soluble in acetone and could be converted to the other derivatives by adding a solution of the appropriate lithium salt to the acetone solution. Some of the properties of these complexes are summarized in Table I.

TABLE I
PROPERTIES OF THE NICKEL(II) COMPLEXES OF 1,4,8,11-TETRAAZACYCLOTETRADECANE

Complex	Color	μ_{eff} at 20°, B.M.	Molecular conductivity (0.001 *M* solution) at 25°, ohm^{-1} Water	Methanol
$Ni(cyclam)Cl_2$	Mauve	3.09	247	106
$Ni(cyclam)Br_2$	Mauve	3.06	245	112
$Ni(cyclam)I_2$	Brown	Diamagnetic	244	105
$Ni(cyclam)(ClO_4)_2$	Orange	Diamagnetic	232	120

The complexes are soluble in water, methanol, and nitrobenzene, but insoluble in the other common organic solvents. The colors of these solutions are all yellow, and the spectra are independent of the nature of the anion and not very sensitive to the nature of the solvent. The conductivities of the aqueous solutions are those expected for a fully dissociated bi-univalent electrolyte, but the values obtained in methanol are considerably less than the value expected for a bi-univalent electrolyte (*ca.* 180 ohm^{-1}).[2] The similarity of the spectra suggests that the anion is not directly coordinated to the metal ion and that the two vacated coordination positions are not used for a strong interaction with the solvent. Nevertheless, there must be extensive outer-sphere ion association in methanol, even when the anion is perchlorate. The yellow color remains when these species are dissolved in 12 *F* hydrochloric acid, and the absence of any mauve color suggests that the chloride ion requires assistance from lattice forces before it can coordinate to the nickel. When lithium chloride is added to the yellow solution of the perchlorate in acetone the color immediately changes to mauve but, since this is followed immediately by the precipitation of the insoluble chloride, it is quite likely that the color is due to a fine suspension of the solid octahedral form. In aqueous solution the complexes are resistant to further change and the hydrochloric acid solution can be boiled for several minutes without any noticeable change taking place. A similar inertness is observed in alkaline solution. This lack of reactivity has been observed for other complexes of nickel(II) with cyclic multidentate ligands[3,4] and is consistent with the idea that the normal mode of displacement of an open multidentate ligand requires the displacement of one donor atom at a time[5] and that this unwrapping mechanism cannot be adopted by a cyclic ligand of this type. The rate-determining step here might be attack on the ligand leading to ring opening, but cyanide ions will displace the ligand fairly rapidly and it has been reported in a similar case[3] that the free cyclic ligand can be isolated from the reaction mixture. It is possible that we might encounter in the cyanide reaction a mechanism whereby the metal is displaced from the ligand in a single act of substitution that is rather akin to the entry and displacement of a metal ion in and from a porphyrin complex.[6]

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

[2] R. A. Krause and D. H. Busch, *J. Am. Chem. Soc.*, **82**, 4830 (1960).

[3] N. F. Curtis, *J. Chem. Soc.*, 2644 (1964).

[4] M. C. Thompson and D. H. Busch, *J. Am. Chem. Soc.*, **86**, 3651 (1964).

[5] G. A. Melson and R. G. Wilkins, *J. Chem. Soc.*, 2662 (1963); D. W. Margerum, D. B. Rorabacher, and J. F. G. Clarke, Jr., *Inorg. Chem.*, **2**, 667 (1963).

[6] E. B. Fleischer and J. H. Wang, *J. Am. Chem. Soc.*, **82**, 3498 (1960)

The magnetic properties show a remarkable change on altering the nature of the anion. The moments found for the chloride and bromide (*ca.* 3.1 B.M.) are somewhat lower than those normally encountered in octahedral complexes of nickel(II) that are regular or have a weak axial distortion, where the usual value at room temperature is approximately 3.2 B.M. Goodgame and Venanzi[7] have observed a similar lowering of the moment in some of the bis(N,N′-dimethylethylenediamine)nickel(II) complexes and this is probably due to an increase in the axial distortion which removes the orbital triplet degeneracy of the first excited state. The changeover in magnetic behavior between bromide and iodide indicates that the axial distortion is sufficiently large to change the ground term from $^3A_{2g}$ to $^1A_{1g}$.[8] This is also identical with the observation of Goodgame and Venanzi,[7] although the complexes of the corresponding N,N′-diethylethylenediamine exhibit the change in spin multiplicity between chloride and bromide.[9] It is possible to invoke their argument and say that the iodide ion is too large to approach the metal closely enough to exert its maximum field, but one must be careful in invoking steric effects because the iodide is not isostructural with the chloride and it is not unlikely that lattice energy effects also play a considerable part in determining the extent of the axial distortion. Curtis[3] indicates a similar effect in his complexes of nickel(II) with the hexamethyl derivative of the cyclic ligand.

Qualitative magnetic measurements indicate that the complexes are diamagnetic in methanol, which lends support to the idea of only a weak axial interaction with the solvent. The inability of water to approach the nickel close enough to exert its full ligand field, which is normally greater than that of chloride, cannot be due to steric factors alone. The paramagnetic complexes of Goodgame and Venanzi[7,9] retain all or part of their paramagnetism on going into solution and the anion remains coordinated. The unusual instability of the aquo complexes of the cobalt(III) derivatives of the cyclic ligand suggests that the bonding of water is often enhanced by hydrogen-bonding effects that lead to a tightening of the structure[1] when there are other hydrogen-bonding ligands present in the complex that can interact directly and through the water in the solvation shell (*cf.* the "Royal Orb" suggested by Jørgensen[10]). In these complexes of the cyclic ligand there are only four suitable hydrogens and these, as will be seen below, are distributed two above and two below the plane of the complex.

The diffuse reflectance spectra of the complexes in magnesium carbonate mulls were measured between 350 and 1000 mμ. All four complexes show the beginning of a very intense band which starts at about 370 mμ. The mauve paramagnetic chloride and bromide have, in addition, two fairly broad bands at 520 and 670 mμ, which because of the analogy in position, intensity, and shape to the spectrum of $[Ni(NH_3)_6]^{2+}$ are probably derived from the transitions $^3A_{2g} \rightarrow {}^3T_{2g}$ and $^3A_{2g} \rightarrow {}^3T_{1g}$, of the O_h parentage. It seems likely that the splitting of the excited orbital triplet states due to the lower symmetry of the field is of the order of the band widths. The brown diamagnetic iodide and perchlorate, however, have only one band in this region, at about 460–480 mμ, and it is of interest to note that the solution spectra of all four complexes in water are virtually identical and very similar to the diffuse reflectance spectrum of the solid perchlorate.

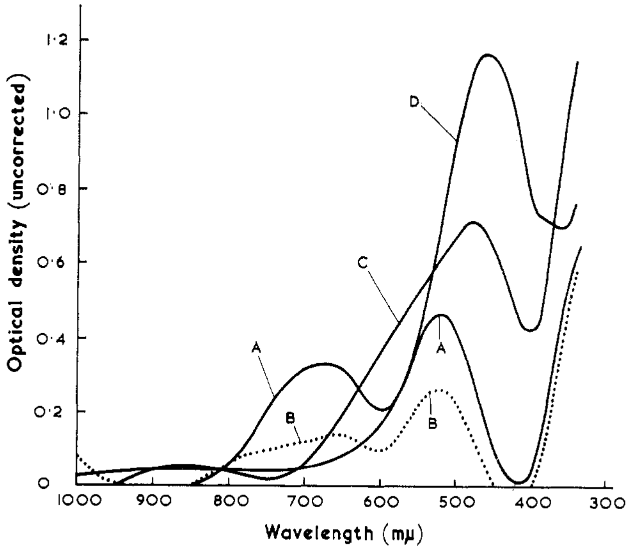

Figure 1.—Diffuse reflectance spectra of (A) Ni(cyclam)Cl_2, (B) Ni(cyclam)Br_2, (C) Ni(cyclam)I_2, (D) Ni(cyclam)$(ClO_4)_2$.

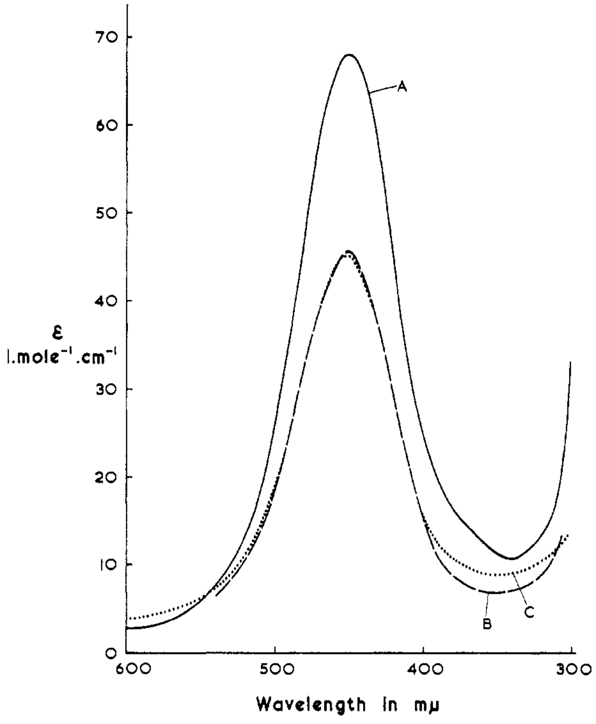

Figure 2.—Visible absorption spectra of (A) Ni(cyclam)$(ClO_4)_2$ in methanol (those of the other complexes are identical), (B) Ni(cyclam)Cl_2 in water, (C) Ni(cyclam)Br_2 in water.

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(8) C. J. Ballhausen and A. D. Liehr, *J. Am. Chem. Soc.*, **81**, 538 (1959).

(9) D. M. L. Goodgame and L. M. Venanzi, *J. Chem. Soc.*, 616 (1963).

(10) C. K. Jørgensen, "Inorganic Complexes," Academic Press Inc., New York, N. Y., 1963, p. 22.

TABLE II

INFRARED ABSORPTION SPECTRA OF SOME 1,4,8,11-TETRAAZACYCLOTETRADECANE COMPLEXES IN NUJOL AND HEXACHLOROBUTADIENE MULLS[a]

Ni(cyclam)Cl_2	Ni(cyclam)Br_2	Ni(cyclam)I_2	[Co(cyclam)-Cl_2]Cl
722 w, b	722 w, b	722 w, b	719 w, b
800 w	804 w	813 w	813 w
875 vs	874 s	888 m	886 m
894 w	899 w	905 m	901 m
939 vs	945 vs	. . .	. . .
	992		
990 vs	1000 m		
		1010 vs	1010 vs
		1038 s	1033 s
1060 m	1053 m	1053 w	. . .
		1066 s	1064 s
1075 m	1075 m		
	1087 w	1089 m	
1097 vs	1101 s	1099 m	1097 s
1109 s	1111 sh	1105 sh	
		1127 m	1127 m
1233 m	1233 m	1233 m	1235 w
1255 w	1250 w	1245 m	. . .
1280 w	1280 m	1289 m	1284 m
1299 m	1300 m		
		1311 w	1311 w
1325 m	1325 m		
1337 m	1333 m		
1374 w	1379 w		
1418 s	1418 s	1418 m	1409 s
1429 sh	1429 m		
1447 s	1447 s	1447 s	1449 s
1466 s	1466 s	1453 sh	1471 sh
1481 w			
2817 s	2817 m	2817 s	2817 s
2874 s	2874 s	2874 s	2874 s
		3030 s	3096 s
		3106 sh	
3145 s	3145 s		

[a] vs, very strong; s, strong; m, medium; w, weak; b, broad; sh, shoulder. Frequencies in cm.$^{-1}$.

Changing the solvent from water to methanol does not affect the shape or position of the spectrum, but the molar extinction coefficients are higher. The reflectance spectra are shown in Figure 1 and the absorption spectra in Figure 2.

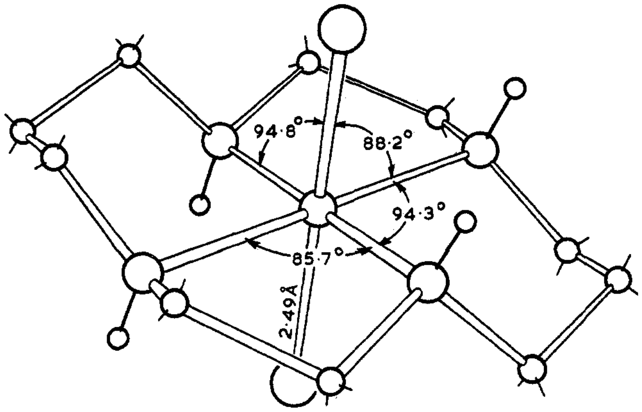

Figure 3.—Structure of Ni(cyclam)Cl_2 showing some of the bond angles.

The infrared absorption bands of the halide complexes in the region 3–15 μ are listed in Table II. The spectra of the chloride and bromide are similar although there are significant differences in the relative intensity pattern. The iodide differs considerably both in the number of peaks and their relative intensities. The spectrum of the perchlorate, which is not listed, resembles that of the iodide rather than that of the chloride, except that the region 8.5–10 μ is obscured by the broad band of perchlorate. This absorption consists of a very broad strong band at 1093 cm.$^{-1}$ with a single strong side band at 1022 cm.$^{-1}$ which may possibly arise from the complex ion. There is no reason to believe that the perchlorate is coordinated. Also included in Table II is the spectrum of *trans*-[Co(cyclam)Cl_2]Cl, which has a very marked similarity to that of the iodide. The positions of the peaks and their relative intensities are so much alike that, apart from the splitting of the bands at 1097 and 1235 cm.$^{-1}$ in the iodide and the appearance of a very weak band at 1053 cm.$^{-1}$, the two spectra could easily be superimposed. It is reasonably clear that the cobalt(III) complex has a *trans* arrangement of the ligands, and the similarity of its visible absorption spectrum with that of *trans*-[Co(en)$_2$$Cl_2$]Cl and the inertness of the Co–Cl bond suggest that this bond is normal. The structure of Ni(cyclam)Cl_2 has been determined by X-ray diffraction and is shown in Figure 3.[11] The nickel–chlorine bonds are considerably longer than is usual for an undistorted octahedral complex, but there appears to be no distortion of the cyclic ligand. The structures of the other nickel complexes have not yet been determined and preliminary studies have shown that none of them is isostructural. The ease with which all of the three halides can be formed from the perchlorate in acetone solution by adding the appropriate lithium salt indicates that there can be no drastic changes in the configuration of the ligand in the complexes so that, even though the halides are not isomorphous and differ considerably in their infrared spectra, they must contain the same basic arrangement of the ligand. The differences in the unit cell and in the infrared spectrum must therefore arise from a combination of changes in the steric relationship between cation and anion, whether coordinated or free, changes in the conformation of the ligand, and possibly the extent to which the octahedron has been distorted. The very close similarity between the infrared spectra of the octahedral *trans*-[Co(cyclam)Cl_2]Cl and the grossly tetragonally distorted [Ni(cyclam)I_2] is rather intriguing, but the explanation must await the conclusion of the structural determinations that are now in progress.

Experimental

1,4,8,11-Tetraazacyclotetradecane (cyclam) was prepared by the method given in the preceding paper.[1]

Dichloro(1,4,8,11-tetraazacyclotetradecane)nickel(II).—Nickel(II) chloride hexahydrate (0.29 g.) dissolved in warm ethanol (20 ml.) was added to a solution of the ligand (0.25 g.) in ethanol (10 ml.). The resulting light brown solution was warmed on a water bath for a few minutes before ether was

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(11) B. Bosnich, R. Mason, P. Pauling, G. B. Robertson, and M. L. Tobe, *Chem. Commun.* (London), 97 (1965).

added. The resultant mauve precipitate was filtered off and washed with ether. It may be recrystallized by adding ether to the saturated solution in methanol; yield 0.25 g.

Anal. Calcd. for $C_{10}H_{24}N_4Cl_2Ni$: C, 36.3; H, 7.3; N, 17.0; Cl, 21.5. Found: C, 36.3; H, 7.4; N, 16.9; Cl, 21.5.

Dibromo(1,4,8,11-tetraazacyclotetradecane)nickel(II) was prepared from nickel(II) bromide hexahydrate in an analogous way.

Anal. Calcd. for $C_{10}H_{24}N_4Br_2Ni$: C, 28.7; H, 5.7; N, 13.3; Br, 38.2. Found: C, 28.9; H, 6.0; N, 13.3; Br, 38.3.

Diiodo(1,4,8,11-tetraazacyclotetradecane)nickel(II).—Nickel (II) iodide (0.39 g.) was dissolved in hot 1-butanol (200 ml.) and added to a solution of the ligand (0.25 g.) in ethanol (10 ml.). The brown solution was heated for 2 min. at 100°, filtered while hot, and allowed to cool. Brown crystals were deposited (0.4 g.), filtered off, and washed with ether.

Anal. Calcd. for $C_{10}H_{24}N_4I_2Ni$: C, 23.4; H, 4.7; N, 10.9; I, 49.5. Found: C, 23.5; H, 4.8; N, 10.9; I, 49.7.

(1,4,8,11-Tetraazacyclotetradecane)nickel (II) Perchlorate.—Nickel(II) perchlorate (0.45 g.) dissolved in ethanol (20 ml.) was added to a solution of the ligand (0.25 g.) in ethanol (10 ml.). The solution turned brown and golden yellow crystals began to separate. The solution was evaporated to a small volume (5 ml.), and the crystals were dissolved by adding acetone (20 ml.) and reprecipitated by adding ether. The complex (0.4 g.) was filtered off and washed with ether.

Anal. Calcd. for $C_{10}H_{24}N_4Cl_2O_8Ni$: C, 26.2; H, 5.3; N, 12.2; Cl, 15.5. Found: C, 26.2; H, 6.0; N, 12.2; Cl, 15.5.

Visible absorption spectra were measured with a Unicam SP-500 quartz spectrophotometer; infrared spectra of Nujol and hexachlorobutadiene mulls between rock salt plates were measured with a Perkin-Elmer PE 137 spectrometer. Magnetic susceptibility measurements were made by the Gouy method and conductivities were measured with a Wayne-Kerr universal bridge, the solutions being contained in a cell fitted with shiny platinum electrodes.

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Preparations and Properties of Chromium(II) Complexes. II. Complexes with Pyridine[1]

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Reactions between pyridine and chromium(II) halides have resulted in the isolation of the complexes $CrCl_2 \cdot 2py$, $CrBr_2 \cdot 2py$, $CrBr_2 \cdot 6py$, $CrI_2 \cdot 4py$, and $CrI_2 \cdot 6py$ (where py = pyridine), which are all relatively stable in air. The room temperature magnetic susceptibilities indicate the presence of four unpaired electrons. Low-temperature reflectance spectra show two bands, one near 10,000–12,000 cm.$^{-1}$ and another at ~17,000 cm.$^{-1}$. X-Ray powder patterns have been compared, where possible, with those of the corresponding copper(II) complexes. These data all indicate that the complexes are extensively distorted from octahedral symmetry.

Introduction

Pyridine forms a very large number of complexes with many divalent first-row transition metal salts,[2] particularly the simple halides.[2,3] Many of these compounds date back to the very early literature.[4] As expected, information on chromium(II)–pyridine systems is scarce, with few definite and well-characterized complexes having been reported. Relatively stable complexes are formed with the formate[5] and acetate,[6] $[Cr(HCOO)_2py]_2$ and $[Cr(CH_3CO_2)_2py]_2$, the pyridine probably occupying the same position as water in[7] the well-known $[Cr(CH_3CO_2)_2H_2O]_2$. This type of structure is found[8] in $[Cu(CH_3CO_2)_2py]_2$.

Recent work has shown pyridine to coordinate with chromium(II) phthalocyanine[9] and bis(benzoylacetonato)chromium(II).[10] The little information which is available on chromium(II) halide complexes with pyridine is contradictive and inaccurate. The complex $CrCl_2 \cdot 2py \cdot 2H_2O$ was obtained from the reaction between aqueous chromium(II) chloride solution and pyridine,[5] and later[3,11] $CrCl_2 \cdot 2py$ was obtained from the same reaction and also from the reaction between anhydrous chromium(II) chloride and pyridine.[12,13] The latter complex is high-spin[3] and isomorphous[13] with the corresponding copper(II) complex, the crystal structure of which is known.[14,15] Attempts to prepare $CrBr_2 \cdot 2py$ have also been made,[3] but no analytical data were reported. Magnetic measurements on the sample indicated that the complex was in a very impure state. To our knowledge, no spectral studies have been carried out on any of these complexes.

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[1] Part I: J. P. Fackler, Jr., and D. G. Holah, *Inorg. Chem.*, **4**, 954 (1965).

[2] See, for example, the articles by N. S. Gill, R. H. Nuttall, D. E. Scaife, and D. W. A. Sharp, *J. Inorg. Nucl. Chem.*, **18**, 79 (1961), and P. C. H. Mitchell, *ibid.*, **18**, 382 (1961), which list a number of such complexes.

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[4] For example, F. Reitzenstein, *Z. anorg. allgem. Chem.*, **11**, 254 (1895); **18**, 253 (1898).

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[8] J. Hanic, D. Stempelova, and K. Hanicova, *ibid.*, **17**, 633 (1964).

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[14] E. G. Cox, E. Sharratt, W. Wardlaw, and K. C. Webster, *J. Chem. Soc.*, 129 (1936).

[15] J. D. Dunitz, *Acta Cryst.*, **10**, 307 (1957).