

ing may well be due to the decrease in ligand-ligand repulsions which follows from the elongation of the central cobalt-nitrogen bond. In spite of the large range of values for individual distances, the average of $2.17 \pm 0.09 \text{ \AA}$ for the three cobalt-nitrogen bond lengths compares well with the corresponding value of 2.19 \AA for $\text{Co}(\text{Et}_4\text{dien})\text{Cl}_2$. Similarly, the intrachelate $\text{N}\cdots\text{N}$ distances average to 2.82 \AA in both compounds. The intrachelate N-Co-N angles average to $79.3 \pm 1.1^\circ$, close to the value of 80.3° found in $\text{Co}(\text{Et}_4\text{dien})\text{Cl}_2$.

The $\text{N}(1)\text{-Co-N}(3)$ angle, on the other hand, assumes quite different values in the two compounds. The increase from 120.4 to 135.4° on going from $\text{Co}(\text{Et}_4\text{dien})\text{Cl}_2$ to $\text{Co}(\text{Me}_5\text{dien})\text{Cl}_2$ may be ascribed to the pressures exerted both on the central part of the ligand molecule, through the $\text{Cl}(2)\cdots\text{C}(5)$ contact, and on the two ends, through the other chlorine-methyl carbon contacts.

Distances and angles in the rest of the molecule do not differ by more than 3σ from the expected values,

with the exception of the $\text{Co-N}(2)\text{-C}(5)$ angle considered before. The few significant differences which are found between the two crystallographically independent molecules may be related to their different environments in the crystal. These differences involve mainly the coordination polyhedron and reach a maximum (6σ) in the $\text{Cl}(2)\text{-Co-N}(1)$ angle. There are only two intermolecular contacts below 3.60 \AA : a 3.53-\AA contact between atoms $\text{Cl}(2)'$ (x, y, z) and $\text{C}(2)$ ($x + 1, 1/2 - y, 1/2 + z$) and a 3.58-\AA contact between atoms $\text{C}(2)'$ (x, y, z) and $\text{C}(7)$ ($x, 1/2 + y, 1/2 - z$).

The molecule of $\text{Co}(\text{Me}_5\text{dien})\text{Cl}_2$ is approximately symmetrical with respect to a plane passing through the atoms Co , $\text{Cl}(1)$, $\text{Cl}(2)$, and $\text{N}(2)$ (Table V). This pseudosymmetry is not present in the complex $\text{Co}(\text{Et}_4\text{dien})\text{Cl}_2$, where the ligand molecule assumes a different conformation.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING AND MATERIALS RESEARCH LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS 61801

The Crystal and Molecular Structure of N-Methyl-1,4-diazabicyclo[2.2.2]octonium Trichloroaquonickelate(II). A High-Spin Five-Coordinate Complex of Nickel(II) with Monodentate Ligands¹

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N-Methyl-1,4-diazabicyclo[2.2.2]octonium trichloroaquonickelate(II), $\text{C}_7\text{H}_{13}\text{N}_2(\text{H}_2\text{O})\text{NiCl}_3$, has been characterized by a three-dimensional X-ray diffractometer study. Refinement was carried out using full-matrix least-squares techniques on 1246 observed reflections to a final R value of 7.2%. The molecule crystallizes in the monoclinic space group $\text{P}2_1/\text{m}$ with unit cell dimensions $a = 8.173(4)$, $b = 9.393(5)$, $c = 7.769(4) \text{ \AA}$; $\beta = 96^\circ 40(2)'$; $Z = 2$; $\rho_{\text{calcd}} = 1.74$, $\rho_{\text{obsd}} = 1.73 \text{ g/cm}^3$. The complex is monomeric with the N-methyl-1,4-diazabicyclo[2.2.2]octonium ion, $\text{N}(\text{CH}_2\text{CH}_2)_3\text{N}^+\text{CH}_3$, coordinated to the nickel atom through the unquaternized nitrogen. The resulting zwitterion has crystallographic symmetry $m\text{-C}_s$ and is best described as a distorted trigonal bipyramid with equatorial chlorine atoms. Distortions are observed in the form of nonequivalent Ni-Cl bond lengths (one of $2.282 \pm 0.002 \text{ \AA}$ and two of $2.339 \pm 0.002 \text{ \AA}$) and an axial N-Ni-O bond angle of 171° . These result chiefly from steric repulsions between the chlorine atoms and the cation ligand (causing all N-Ni-Cl bond angles to be greater than 90°) combined with intermolecular hydrogen bonding. The observed crystal stability is attributed to the presence of infinite chains formed by the latter interaction.

Introduction

Structure and bonding in halogen complexes of first-row transition metals have been subjects of interest in our laboratory for some time.²⁻⁴ More recently, these interests have included complex stabilization by cation size and hydrogen-bonding effects.

N-Methyl-1,4-diazabicyclo[2.2.2]octonium trichloroaquonickelate(II) first attracted our interest for several

reasons. The magnetic moment of 3.7 BM and the room-temperature diffuse reflectance spectrum were inconsistent with octahedral or tetrahedral coordination and appeared to be best explained by a high-spin five-coordinate geometry.⁵ This was consistent with the empirical formula if one assumed that the cation, $\text{N}(\text{CH}_2\text{CH}_2)_3\text{N}^+\text{CH}_3$, also functioned as a monodentate ligand. With this in mind, a structural investigation was undertaken to confirm the five-coordinate geometry, to investigate the source of stabilization in detail, and possibly to aid in the interpretation of the observed spectroscopic and magnetic data.

(1) Paper presented at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967. This work was supported by the Advanced Research Projects Agency under Contract SD-131.

(2) (a) G. Stucky, S. D'Agostino, and G. McPherson, *J. Am. Chem. Soc.*, **88**, 4828 (1966); (b) G. Stucky, J. Folkers, and T. Kistenmacher, *Acta Cryst.*, **23**, 1064 (1967).

(3) G. Stucky, *ibid.*, **24B**, 330 (1968).

(4) T. Kistenmacher and G. Stucky, *Inorg. Chem.*, **7**, 2150 (1968).

(5) V. L. Goedken, J. V. Quagliano, and L. M. Vallarino, *ibid.*, **8**, 2331 (1969).

Experimental Section

Crystals of $C_7H_{15}N_2(H_2O)NiCl_3$ were obtained from Dr. Virgil L. Goedken. They were well-formed transparent parallelepipeds of bright red color in transmitted light; preliminary investigation by precession photography indicated $2/m$ lattice symmetry. The systematic absence of $0k0$ for odd k on zero-layer photographs was consistent with the monoclinic space groups $P2_1$ and $P2_1/m$.

Further investigations were carried out on a crystal ground to a sphere of 0.22-mm diameter which was subsequently mounted in a 0.3-mm glass capillary. Lattice parameters were obtained from 21 carefully centered reflections measured on a Picker four-circle diffractometer. A least-squares refinement of these data using a diffractometer orientation and angle-setting program⁶ provided the following parameters and their corresponding standard deviations:⁷ $a = 8.173$ (4), $b = 9.393$ (5), $c = 7.769$ (4) Å; $\beta = 96^\circ 40$ (2)'; $V = 592.4$ Å³ (at 23° and $\lambda(\text{Cu K}\alpha)$ 1.5405 Å). The calculated density of 1.74 g/cm³ for two molecules per unit cell agrees with the measured value of 1.73 (3) g/cm³ obtained by the flotation method in a mixture of 1-bromopentane and iodobenzene.

Diffraction data were collected manually using Mo $K\alpha$ radiation to minimize absorption effects. Narrow-source, open-counter ω scans of several intense reflections indicated satisfactorily low mosaic dispersion. A takeoff angle of 0.7° provided 80% of the maximum intensity as a function of takeoff angle of a strong peak when incident beam and diffracted beam collimators of 1.0- and 2.0-mm diameter, respectively, were used. A 0.0005-in. zirconium foil filter was placed at the detector, a scintillation counter mounted 21 cm from the crystal, in order to reduce $K\beta$ radiation. The lower level discriminator of the pulse height analyzer was adjusted to minimize the detection of the white radiation. Error due to multiple diffraction was believed to be minimal because the ϕ axis did not coincide with any reciprocal lattice row.

Peaks were scanned for 100 sec (1.67°) by the θ - 2θ scan technique with stationary-crystal, stationary-counter background counts of 40 sec taken at each end of the scan. Two standard reflections were measured every 12 hr over a period of 8 days to ensure crystal and diffractometer stability. No changes in the intensities of these standard reflections were observed. One form of data ($2\theta_{\text{max}} = 60^\circ$) was collected providing 1936 unique reflections of which 682 were found to be unobserved ($I_{\text{obsd}} < 3\sigma(I)$) and were assigned intensities equal to the standard deviations of the background intensity in their respective locations. After correcting for background, absorption, Lorentz, and polarization factors,⁸ peaks for which $I_{\text{obsd}} < (I_{\text{bkg}} - 3\sigma(I_{\text{bkg}}))$, with I_{bkg} being the measured background intensity, were rejected. Eight such reflections were found and reference to the strip chart recorder (which recorded each reflection profile) indicated that these reflections were overlapped by streaking from large peaks immediately preceding them. The corrected data were refined using a modification⁹ of the full-matrix least-squares program ORFLS of Busing, Martin, and Levy⁹ with the program ERFR-2 of Sly, Shoemaker, and Van de Hende¹⁰ providing Fourier and Patterson calculations. Standard deviations of bond distances and angles were calculated using the function and error program ORFFE of Busing, Martin, and Levy.¹¹ Final diagrams of the

molecular and crystal structures were traced from computer-drawn plots generated by Johnson's program ORTEP.¹²

Anomalous dispersion corrections used for Ni and Cl were those of Cromer¹³ and were applied to the calculated structure factor while atomic form factors for neutral Ni, Cl, O, N, C, and H were taken from "International Tables for X-Ray Crystallography," 1962, Table 3.3.1.A.

Solution and Refinement of the Structure

As indicated by the precession photographs, the space group could be $P2_1$ (acentric) or $P2_1/m$ (centric). However, in the presence of anomalous scattering, the breakdown of Friedel's law can be used as a criterion for distinguishing between these two space groups.¹⁴ In this case, the following relationships should be observed: if acentric ($P2_1$), $F^2(hkl) = F^2(\bar{h}\bar{k}\bar{l}) \neq F^2(h\bar{k}l) = F^2(\bar{h}kl)$; if centric ($P2_1/m$), $F^2(hkl) = F^2(\bar{h}\bar{k}\bar{l}) = F^2(h\bar{k}l) = F^2(\bar{h}kl)$. A total of 192 reflections fulfilling the above symmetry relations and collected from all octants were compared in an attempt to distinguish between the centric and acentric space groups. First, reflections which are equivalent under both conditions were averaged and then these averages were compared to those of the possibly nonequivalent set. There was no evidence of any systematic variation in intensity between the sets of data. While it was recognized that the anomalous scattering of Mo $K\alpha$ radiation by nickel and chlorine may not be great enough to produce observable differences in observed intensities, the negative result was taken as sufficient reason to begin the refinement in the space group $P2_1/m$ rather than in $P2_1$.

A three-dimensional Patterson map indicated the coordinates of the Ni atom. Using these coordinates as the basis of a least-squares refinement and Fourier calculation, a value of R_w ($= [\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2]^{1/2} \times 100$) of 58.1% was obtained. From this Fourier map, chlorine atom coordinates were measured. The coordinates of all remaining nonhydrogen atoms were determined from a Fourier map computed after a second least-squares refinement in which only the scale factor was varied. One additional least-squares refinement on positional parameters followed by two least-squares refinements with varying isotropic temperature factors for all atoms led to a value of $R_w = 23.0\%$. At this point, 128 reflections which showed poor agreement were removed and remeasured. Three succeeding anisotropic thermal parameters gave a value of $R_w = 9.6\%$. A difference Fourier map based on the coordinates of the refinement revealed the positions of all hydrogen atoms as peaks of 2.0–2.8 times the largest background peaks. Inclusion of hydrogen atom coordinates followed by refinement of isotropic temperature factors and positional parameters for hydrogen

(6) H. Gvildys and M. Mueller, "B-101, Orientation and Angle Setting Generation Programs," Argonne National Laboratory, Argonne, Ill., 1960.

(7) Standard deviations in the last decimal place are indicated here and elsewhere in this paper by the immediately following number enclosed in parentheses.

(8) L. Guggenberger and C. Prewitt, "Program ACAC," E. I. du Pont de Nemours and Co., Wilmington, Del., 1966.

(9) W. Busing, K. Martin, and H. Levy, "ORFLS, a Fortran Crystallographic Least-Squares Program," U. S. Atomic Energy Commission Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(10) W. Sly, D. Shoemaker, and J. Van den Hende, "A Two- and Three-Dimensional Fourier Program for the IBM 709/7090, ERFR-2, Esso Research Corporation, Linden, N. J., 1962.

(11) W. Busing, K. Martin, and H. Levy, "ORFFE, a Fortran Crystallographic Function and Error Program," U. S. Atomic Energy Commission Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(12) C. Johnson, "ORTEP, a Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations," U. S. Atomic Energy Commission Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

(13) D. Cromer, *Acta Cryst.*, **13**, 17 (1965).

(14) S. Ramaseshan, *Current Sci.*, **36**, 87 (1966).

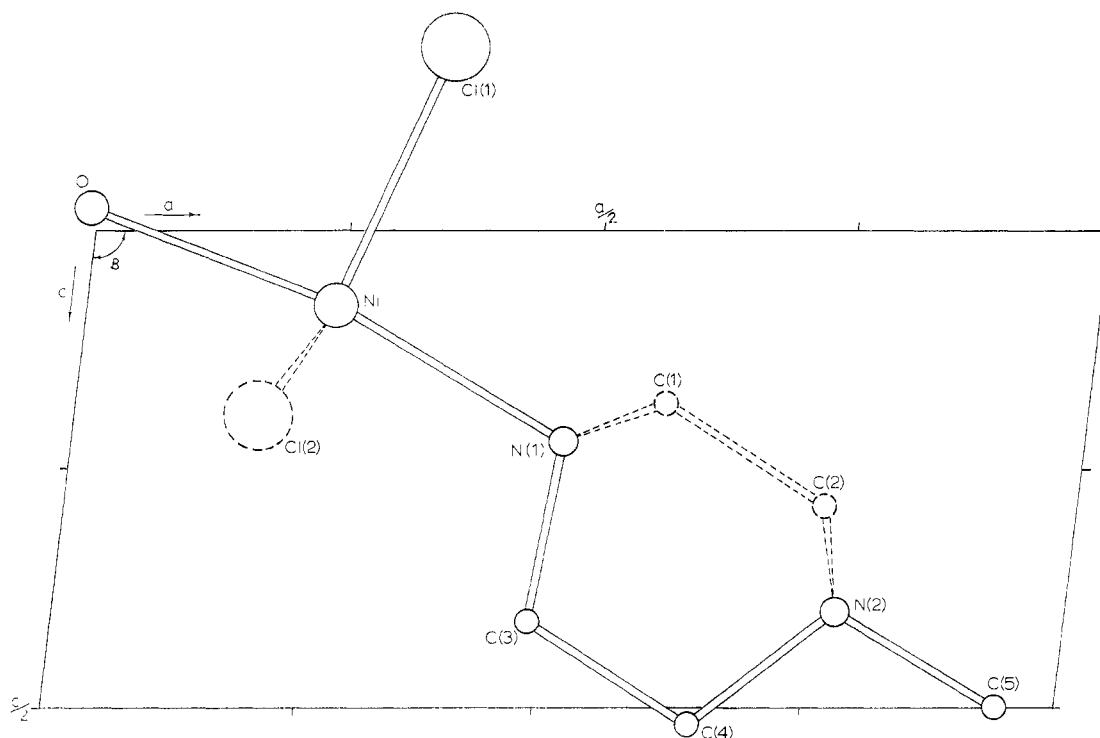


Figure 1.—View of crystallographic mirror plane ($y = 1/4$); dashed lines indicate atoms reflected across the mirror.

atoms led to an R_w of 7.6%. These final cycles were based on a weighting scheme calculated as

$$\sigma(F) = \frac{F}{2I} [I_p + (T_p/T_b)^2(B_a + B_b) + (kI)^2]^{1/2}$$

where I_p is the integrated peak count, T_p is the time of peak scan, T_b is the total background count time, and B_a and B_b are background counts at either end of the peak scan. The contributions to the error in the structure factor are, respectively, peak counting error, background counting error, and errors which depend linearly on the observed intensity (kI). Errors associated with absorption correction, Lp corrections, and diffractometer instability are found to be of the "linearly dependent on I " type. Since the crystal used in this study was quite spherical (as viewed under a microscope), errors in the absorption correction were believed to be minimal. The value of k was then set equal to 0.01—the lower limit for an experiment in which the approximate X-ray beam stability is 1%. The estimated standard deviation for an observation of unit weight was 2.47 indicating that the choice of $k = 0.01$ was too small. The additional error probably results from other sources which also are intensity dependent.

From the final cycle of refinement an unweighted "R" value ($(\sum(|F_o| - |F_c|)/\sum|F_o|) \times 100$) of 7.2% was calculated. A final difference Fourier map was calculated and was found to be free of peaks larger than four-tenths the magnitude of those chosen as hydrogen atom peaks. No systematic reduction of intense peaks was observed indicating that extinction is not an important factor in this crystal.

To check the coordinates obtained for hydrogen atoms, a computer program was written to calculate theoretical hydrogen coordinates. This program assumed sp^3 bond character about the carbon atoms and used a crystallographic carbon-hydrogen bond distance of 0.95 Å. It was observed that the average deviation between the calculated coordinates and those obtained by refinement of the positional parameters originally obtained from the difference Fourier map was less than 0.09 Å. When the theoretical hydrogen atom coordinates were used as a basis for refinement, the coordinates obtained agreed closely (within 0.04 Å) with the previously refined coordinates. Hydrogen atom coordinates used for the final least-squares refinements were those obtained by refinement of the theoretical coordinates. These coordinates led to an average C-H crystallographic bond distance of 0.94 Å and thermal parameters ranging from 0.45 to 10.7.

On the basis of the absence of any observed breakdown of Friedel's law, the results of a statistical test,¹⁵ failure of an attempt to refine the structure in the acentric space group, and the lack of abnormally high β_{22} values, the assignment of the crystal to the space group $P2_1/m$ is considered correct.

Results and Discussion

The relative orientation of the molecule within the unit cell is shown in Figure 1. The view is that of the mirror plane ($y = 1/4$) with solid lines representing atoms lying in the plane and dashed lines indicating atoms projected onto it. Deviations from idealized

(15) B. Dewar, A. Stone, and E. Fleischer, "A Fortran Program for the Automatic Manufacturing of Unitary Structure Factors," private communication.

C_{3v} symmetry about the metal atom are noted primarily in the nonlinearity (171.4°) of the O–Ni–N(1) axial bonds and in nonequivalent angles between equatorial ligands. Least-squares planes calculated for trigonal-bipyramidal symmetry (plane includes Ni, Cl(1), Cl(2), and Cl(2)') and for square-pyramidal symmetry (Cl(2), Cl(2)', O, and N(1) atoms used) are given in Table I. These calculations indicate significant devia-

TABLE I
LEAST-SQUARES PLANES^a FOR $C_7H_{15}N_2(H_2O)NiCl_3$

Square Pyramid: $0.4251X - 0.9052Z - 0.3335 = 0$					
Atom	N	C(1)	Cl(2)	O	N(1)
Dist from plane, Å	0.592	2.870	-0.432	0.467	0.397
Trigonal Bipyramid: $0.8874X + 0.4611Z + 1.9028 = 0$					
Atom	Ni	Cl(1)	Cl(2)	O	N(1)
Dist from plane, Å	0.0827	-0.0257	-0.0285	-2.0117	2.2250

^a Equation given by $AX + BY + CZ + D = 0$, where X , Y , and Z are orthogonal coordinates related to fractional coordinates in the monoclinic cell by $X = xa + zc \cos \beta$, $Y = yb$, and $Z = zc \sin \beta$.

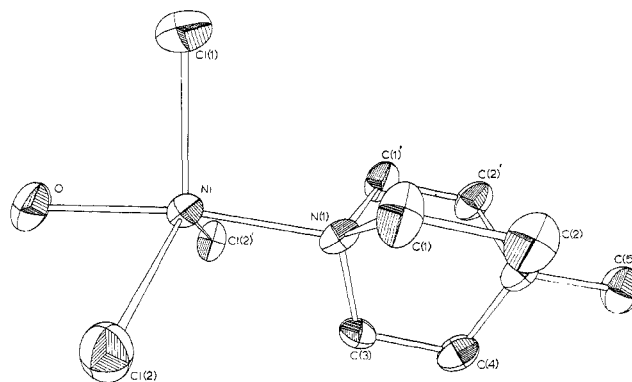


Figure 2.—Perspective view of the molecular structure of $C_7H_{15}N_2(H_2O)NiCl_3$ with root-mean-square displacements indicated (hydrogen atoms omitted).

chiefly to vibrations roughly normal to the plane while atoms lying on the mirror are subject primarily to in-plane vibration. Caution should be exercised in analysis of thermal motion from perspective drawings such as Figure 2, but the above trend is evident in spite of the distortion induced. The thermal parameters used

TABLE II
POSITIONAL AND THERMAL PARAMETERS FOR $C_7H_{15}N_2(H_2O)NiCl_3$

Atom	x	y	z	β_{11}^a	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	0.2430 (1)	0.2500	0.0797 (1)	0.0082 (2)	0.0043 (1)	0.0067 (2)	...	-0.0013 (1)	...
Cl(1)	0.3315 (3)	0.2500	-0.1883 (3)	0.0161 (4)	0.0082 (3)	0.0073 (3)	...	0.0017 (3)	...
Cl(2)	0.1846 (2)	0.0268 (2)	0.1913 (2)	0.0102 (2)	0.0060 (2)	0.0152 (3)	-0.0020 (2)	-0.0023 (2)	0.0026 (2)
O	-0.0068 (8)	0.2500	-0.0213 (9)	0.0109 (10)	0.0049 (7)	0.0115 (12)	...	-0.0047 (9)	...
N(1)	0.4842 (8)	0.2500	0.2201 (7)	0.0107 (10)	0.0027 (6)	0.0063 (9)	...	-0.0008 (8)	...
N(2)	0.7723 (8)	0.2500	0.3968 (8)	0.0092 (10)	0.0048 (6)	0.0078 (10)	...	-0.0012 (9)	...
C(1)	0.5825 (8)	0.1224 (7)	0.1805 (9)	0.0106 (10)	0.0070 (7)	0.0141 (12)	0.0031 (7)	-0.0024 (9)	-0.0050 (7)
C(2)	0.7507 (8)	0.1193 (6)	0.2869 (9)	0.0127 (10)	0.0055 (6)	0.0127 (11)	0.0008 (7)	-0.0015 (9)	-0.0025 (7)
C(3)	0.4724 (10)	0.2500	0.4086 (10)	0.0078 (12)	0.0090 (10)	0.0071 (12)	...	-0.0032 (10)	...
C(4)	0.6396 (11)	0.2500	0.5156 (10)	0.0022 (14)	0.0097 (11)	0.0056 (12)	...	-0.012 (10)	...
C(5)	0.9396 (10)	0.2500	0.4983 (12)	0.0062 (12)	0.0016 (13)	0.0126 (16)	...	-0.0036 (12)	...
H(1) ^b	-0.008 (11)	0.175 (9)	-0.084 (11)	5.10					
H(2)	0.605 (8)	0.135 (7)	0.050 (10)	2.07					—
H(3)	0.503 (13)	0.085 (12)	0.178 (16)	9.75					
H(4)	0.788 (13)	0.053 (13)	0.396 (16)	10.70					
H(5)	0.829 (7)	0.114 (7)	0.212 (8)	0.62					
H(6)	0.412 (6)	0.176 (6)	0.441 (7)	0.43					
H(7)	0.658 (6)	0.162 (6)	0.591 (7)	0.74					
H(8)	0.018 (13)	0.250	0.428 (15)	2.68					
H(9)	0.961 (7)	0.158 (7)	0.552 (8)	1.28					

^a The form of the anisotropic ellipsoid is: $\exp(-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl))$. ^b Isotropic thermal parameters are given for H atoms.

tion from square-pyramidal geometry in that each of the four atoms involved in the determination of the plane lies more than 0.39 Å from the plane. Agreement is better in the case of a calculated equatorial plane (Cl(1), Cl(2), and Cl(2)') lie 0.03 Å on one side of the plane while the nickel atom is 0.08 Å on the other side). However, the atomic displacements indicated above suggest that the best description is that of a molecular geometry somewhat distorted from that of a trigonal bipyramid.

Vibrational motion, as observed from the plotted thermal ellipsoids of Figure 2, is strongly influenced by the crystallographically imposed mirror symmetry. The motion of atoms lying off the mirror is limited

and the positional parameters are given in Table II and bond lengths corrected for thermal motion are given in Table III. These values are observed to agree well with the respective uncorrected values and probably give good estimation of the relative accuracy of the bond lengths. This is not surprising for N(1),

TABLE III
COMPARISON OF BOND LENGTHS (Å) WITH CORRECTION FOR THERMAL MOTION

Bond	Uncor	Riding model
Ni–Cl(1)	2.282 (2)	2.291 (2)
Ni–Cl(2)	2.339 (2)	2.348 (2)
Ni–O	2.100 (6)	2.107 (6)
N–N(1)	2.140 (6)	2.139 (6)

TABLE IV

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR C₇H₁₆N₂(H₂O)NiCl₂^a

Table with columns for h, k, l indices, F_o (observed), and F_c (calculated) structure factors. The table contains multiple rows of data points, with some entries marked with an asterisk (*) to indicate unobserved reflections.

^a Unobserved reflections are indicated by an asterisk.

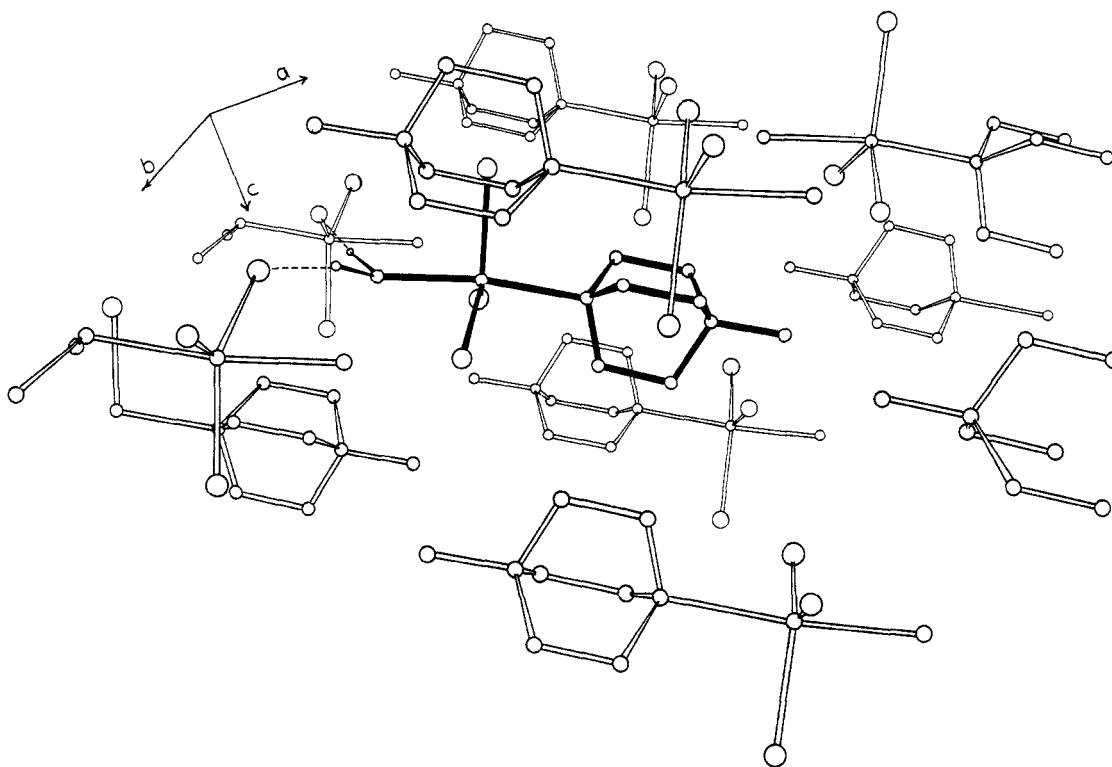


Figure 3.—Molecular packing of $C_7H_{15}N_2(H_2O)NiCl_3$; the environment of the shaded molecule is shown with the $O-H \cdots Cl$ interaction indicated by dashed lines (all other H atoms are omitted).

since its motion is restricted by the ring system. For the O atom, however, the lack of "riding" thermal motion suggests the presence of hydrogen bonding. The fact that the Ni-Cl(1) distance is shorter than the Ni-Cl(2) distance is consistent with the observation that hydrogen-bonded chlorine atoms, in this case Cl(2) in Ni-Cl(2)-H(1), apparently form longer metal-chlorine bonds than nonhydrogen-bonded chlorine atoms in metal-chlorine bonds. For example, in a structure containing the $Ni_2Cl_5^{4-}$ anion,¹⁶ the hydrogen-bonded Ni-Cl distances are 2.371 (2) and 2.336 (2) Å, while the nonhydrogen-bonded Ni-Cl distances are 2.283 (2) Å. One can also consider the chlorine atom to be bridging between two electronegative centers in Ni-Cl(2)-H(1). Systems of this type are well known to form longer metal-halogen bonds. An example of this is $[CH_3AlCl_2]_2$ ¹⁷ with Al-Cl distances of 2.25 Å (bridging) and 2.05 Å (terminal).¹⁷

Several interesting observations can be made from the bonded and nonbonded distances and angles of Table V. First, the sum of the interior bond angles around N(1) is about 4° less than the sum of similar angles around N(2). Also, the distances between chlorine atoms and ring carbon atoms are all greater for Cl(1) than for Cl(2). The first observation, considered in light of the fact that the equatorial plane containing Cl atoms is forced toward the oxygen atom by 0.1 Å, indicates significant steric repulsion between the ring and equatorial ligands. The second feature indicated above suggests a model involving an inter-

TABLE V

SELECTED DISTANCES (Å) AND ANGLES (DEG)

Bonded Distances		Bonded Angles	
Ni-Cl(1)	2.281 (2)	Cl(1)-Ni-Cl(2)	115.99 (5)
Ni-Cl(2)	2.339 (2)	Cl(2)-Ni-Cl(2) ^a	127.35 (9)
Ni-O	2.100 (6)	Cl(1)-Ni-O	93.21 (21)
Ni-N(1)	2.140 (6)	Cl(2)-Ni-O	84.67 (10)
N(1)-C(1)	1.494 (6)	Cl(1)-Ni-N(1)	95.43 (18)
N(1)-C(3)	1.487 (9)	Cl(2)-Ni-N(1)	91.53 (8)
N(2)-C(2)	1.502 (6)	O-Ni-N(1)	171.41 (25)
N(2)-C(4)	1.494 (9)	Ni-N(1)-C(1)	112.39 (26)
N(2)-C(5)	1.489 (9)	Ni-N(1)-C(3)	109.60 (23)
C(1)-C(2)	1.518 (7)	C(1)-N(1)-C(1) ^a	106.40 (73)
C(3)-C(4)	1.512 (10)	C(2)-N(2)-C(2) ^a	109.57 (64)
O-H(1)	0.854 (77)	N(1)-C(1)-C(2)	112.18 (48)
		N(1)-C(3)-C(4)	112.53 (63)
Nonbonded Distances		Nonbonded Angles	
Ni-Ni	>5.0	C(1)-N(1)-C(3)	107.72 (42)
Ni-Cl(2)	4.658 (2)	C(1)-C(2)-N(2)	109.71 (48)
O-O	4.709 (3)	C(3)-C(4)-N(2)	109.87 (60)
O-N(2)	3.908 (10)	C(2)-N(2)-C(4)	107.83 (42)
O-Cl(2)	3.189 (4)	C(2)-N(2)-C(5)	109.92 (41)
N(2)-Cl(2)	4.092 (4)	C(4)-N(2)-C(5)	111.70 (63)
C(5)-Cl(2)	3.768 (5)	Ni-O-H(1)	101.1 (49)
H(1)-Cl(2)	2.424 (70)	H(1)-OH(1) ^a	110.8 (69)
Intramolecular Distances			
O-Cl(2)	2.995 (5)	Cl(2)···H(1)-O	144.9 (34)
O-Cl(1)	3.187 (7)	Cl(1)···H(1)-O ^b	88.7 (48)
H(1)-Cl(2)	2.881 (71)	Cl(2)···H(1)-O ^b	89.3 (52)
H(1)-Cl(1)	3.096 (75)		
Cl(1)-C(1)	3.534 (7)		
Cl(1)-C(3)	4.646 (8)		
Cl(2)-C(1)	3.387 (7)		
Cl(2)-C(3)	3.443 (7)		

(16) F. K. Ross and G. D. Stucky, to be submitted for publication.

(17) G. Allegra, G. Perago, and A. Immirzi, *Makromol. Chem.*, **61**, 69 (1963).

^a Symmetry-related atom. ^b Intramolecular angle.

molecular interaction forcing the ring system down toward Cl(2) and Cl(2)' rather than one in which it settles into a position of minimum repulsion after the geometry of the coordination sphere is determined. An inspection of molecular packing in the unit cell (Figure 3) and appropriate distances indicates that the interaction is probably an electrostatic attraction of the quaternized nitrogen atom for oxygen atoms (3.91 Å) and possibly Cl(2) atoms (4.43 Å) on neighboring molecules. This interaction appears to be at least partly responsible for the nonlinearity of the O-Ni-N(1) bond angle. No bond lengths in the ring structure are observed to be affected by these interactions; all C-N bonds agree with the average value of 1.493 Å within 1.5σ while the two independent C-C bonds agree closely with their average value of 1.515 Å.

Even though hydrogen atoms could be located with relative ease, the refinement of their positional parameters did not offer additional information concerning interactions of the ring system. The terminal methyl protons appear to be in well-defined potential minima as hydrogen peaks were located in a staggered configuration with respect to the ring. The over-all average

C-H bond distance is 0.94 (11) Å and the average error in H-C-H bond angles is 6.1° . A peak corresponding to the hydrogen atom of the water molecule was also located and refined. It was found to be 2.42 Å from Cl(2) of a neighboring molecule and 0.854 (77) Å from the oxygen atom. The over-all Cl(2)-O distance of 3.189 (4) Å and the O-H...Cl(2) angle of 145° are in reasonable agreement with the wide variety of distances and angles reported for hydrogen bonds.^{18,19} The coordinates determined for the hydrogen atom (and its mirror image) are consistent with a water molecule of tetrahedral geometry with one pair of electrons coordinated to the metal in a σ -type bond.

Electrostatic interactions appear to be the major forces leading to the stability of this complex. The hydrogen bonding mentioned previously provides rows of staggered interacting molecules (as shown for the shaded molecule in Figure 3) while the interactions of the quaternized nitrogen atoms cross-link these chains into sheets running diagonally through the unit cell.

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(19) W. Hamilton and J. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin Inc., New York, N. Y., 1968.

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The Crystal Structure of Bis(2-amino-2-methyl-3-butanoneoximato)platinum(II) Chloride Monohydrate

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The crystal structure of bis(2-amino-2-methyl-3-butanoneoximato)platinum(II) chloride monohydrate, $C_{10}H_{23}N_4O_2PtCl \cdot H_2O$, has been determined from three-dimensional X-ray diffraction data. Unit cell dimensions are $a = 12.83 \pm 0.02$ Å, $b = 11.03 \pm 0.02$ Å, $c = 12.62 \pm 0.02$ Å, and $\beta = 93.0 \pm 0.2^\circ$. The space group is $P2_1/c$. The density by flotation is 1.94 g/cm³; four formula units in the unit cell give a calculated density of 1.95 g/cm³. The structure is isomorphous with that of the corresponding nickel complex. Refinement by full-matrix least squares led to a conventional R factor of 8.9% using 1324 visually estimated reflections. The complex has approximate symmetry (C_s) with the four nitrogen atoms in square-planar coordination about platinum with average bond distances: Pt-N(oxime), 1.98 (3) Å; Pt-N(amine), 2.03 (3) Å. The intermolecular O...O hydrogen-bond distance is 2.48 (4) Å. Intermolecular hydrogen bonding involving the chloride ion, the water molecule, and the amine nitrogens of the cation plays a major role in stabilizing the crystal structure.

Introduction

Several metal-glyoxime complexes with short intramolecular hydrogen bonds have been studied by X-ray diffraction.¹⁻⁵ The shortest intramolecular O...O distance was observed for bis(dimethylglyoximato)nickel(II)¹ (2.40 (4) Å) while the longest was found for bis(dimethylglyoximato)platinum(II)⁵ (3.03 (6) Å), suggesting a large difference in hydrogen-bond strength.

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(4) E. Frasson, R. Bardi, and S. Bezzi, *Acta Cryst.*, **12**, 201 (1959).

(5) E. Frasson, C. Panattoni, and R. Zannetti, *ibid.*, **12**, 1027 (1959).

The crystal structure of bis(2-amino-2-methyl-3-butanoneoximato)nickel(II) chloride monohydrate was reported recently.⁶ In that complex there is one intramolecular O...O hydrogen bond (2.38 (2) Å) rather than the two found in the glyoxime complexes. With only one intramolecular hydrogen bond, a short, possibly symmetrical O...O hydrogen bond might be found even with the larger platinum cation. For that reason the structure of bis(2-amino-2-methyl-3-butanoneoximato)platinum(II) has been determined.

Experimental Section

Crystal Preparation.—The compound was kindly provided by Murmann.⁷ The crystals used for this study were obtained by crystallization from dichloromethane-heptane solution.

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