angle is 101.8°. The Cl_2 atom further distorts the coordination geometry by moving N_3 drastically from the basal plane of the pyramid. It should also be noted that the distances between Cl_1 and the four CH_2 groups —C_2, C_3, C_6, and C_7—are all shorter than the van der Waals radii sum of 3.8 A.[17] We view the extremely distorted geometry of the complex as a direct result of these strong nonbonded repulsions. Six-coordination in $Co(Et_4dien)Cl_2$ is effectively suppressed by these same steric factors; the methylene group, C_2, completely blocks the sixth coordination site of the cobalt.

The importance of steric crowding in determining the coordination geometry of these types of complexes is confirmed on comparing the structures of the complexes $Co(Me_5dien)Cl_2$ and $Co(Et_4dien)Cl_2$. There are significant differences in the coordination geometries in these two cases, including a considerably larger (135°) N_1–Co–N_3 angle in the $Co(Me_5dien)Cl_2$ complex.[4] Replacement of the ethyl groups by the smaller methyl groups should decrease the repulsions between the chlorine atoms and the terminal alkyl groups. As a result, we expect a smaller displacement of N_3 from the plane determined by the atoms Co, N_1, N_2, and Cl_1, as is observed.[4] Furthermore, the complex $Ni(Me_5dien)Cl_2$ is known to be five-coordinate in the solid state, whereas $Ni(Et_4dien)Cl_2$ is four-coordinate in that state. Assuming that the electronic factors do not change in going from Me_5dien to Et_4dien, we attribute this different behavior to a steric effect, namely, an increase in steric crowding in the inner coordination sphere in the case of Et_4dien. In addition, in polar organic solvents where both the four- and five-coordinate forms of the complexes $Ni(Et_4dien)X_2$ are observed, the fractional concentration of the five-coordinate form decreases considerably in the X series $Cl^- > Br^- > I^-$.[8] We have previously suggested steric crowding as the principal explanation for this stability order, and the observed structure of $Co(Et_4dien)Cl_2$ provides strong support. We are now investigating the structure of the square-planar complex $[Ni(Et_4dien)Br]Br$ by X-ray techniques and we await the result of this study to discuss the mechanism of substitution reactions in these types of complexes.

It is of interest to compare the structure of high-spin $Co(Et_4dien)Cl_2$ with that of the low-spin five-coordinate complex $Ni(triars)Br_2$.[18] In the case of the latter, the As donor atoms and the central metal lie effectively in the same plane, and the geometry can be described as a distorted square pyramid. It seems reasonable to suggest that electronic factors assume a larger structural role in the low-spin complex and that the presence of heavy-donor As atoms capable of good σ(ligand) → p(metal)[19] and possibly d_π(metal) → d_π-(ligand) bonding will favor an arrangement in which the metal and the heavy-donor As atoms are accommodated in the same plane. The steric strain in this five-coordinate structure is then reduced by perturbing the metal–halogen bonds. Therefore, the molecular geometry adopted by $Ni(triars)Br_2$ can be viewed as a compromise between electronic and steric factors of comparable importance. This is in contrast to the case of the $Co(Et_4dien)Cl_2$ complex, where the *principal* determinant of molecular geometry is apparently the quest for relief of steric strain.

Acknowledgment.—We thank the National Science Foundation for support of this research.

[17] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, Table 7-20, p 260.

[18] G. A. Mair, H. M. Powell, and D. E. Henn, *Proc. Chem. Soc.*, 415 (1960).

[19] See the discussion in ref 11, pp 24–28.

Contribution from the Noyes Chemical Laboratory,
University of Illinois, Urbana, Illinois 61801

The Crystal Structure of Chloropentaamminecobalt(III) Hexafluorosilicate

By J. A. Stanko[1] and I. C. Paul

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The crystal structure of chloropentaamminecobalt(III) hexafluorosilicate, $[Co(NH_3)_5Cl]SiF_6$, has been studied by optical and single-crystal X-ray methods. The complex crystallizes in the monoclinic system with $a = 6.26 \pm 0.01$, $b = 8.22 \pm 0.01$, $c = 10.18 \pm 0.02$ A; and $\beta = 99° 40' \pm 30'$. The space group is $P2_1/m$ with two formula weights in the unit cell. The structure has been determined and refined to an R factor of 0.12 for 649 reflections. The cation and anion exist as octahedra, and the measured Co–N distances show no evidence for a "*trans* effect" induced by the presence of the Cl atom. A preliminary examination of the corresponding cyano derivative, $[Co(NH_3)_5CN]SiF_6$, indicates that it is isomorphous with the chloro compound.

Introduction

While searching for salts of acidopentaammine cations, $[M(NH_3)_5X]^{2+}$, useful for single-crystal spectroscopy we have found those of the hexafluorosilicate anion to have many suitable features. No crystallographic studies have been reported on this family of salts other than an early observation[2] on the external crystal habit and that the crystals were noticeably dichroic.

[1] (a) This paper is based in part on a thesis submitted by J. A. Stanko to the Graduate College of the University of Illinois in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Chemistry; (b) NSF Predoctoral Fellow, 1962–1965.

[2] S. M. Jorgensen, *J. Prakt. Chem.*, **18**, 230 (1878).

The crystal structure of a typical representative of the group, the hexafluorosilicate salt of chloropentaamminecobalt(III), has been carried out, principally to determine the orientation in the crystal of the $[Co^{III}(NH_3)_5Cl]^{2+}$ molecular ion. This information aids the interpretation of optical studies on band polarizations in pseudo-tetragonal chromophores.[3]

Experimental Section

Preparation of Compounds. **$[Co(NH_3)_5Cl]SiF_6$.**—This salt was readily obtained by the addition of hydrofluorosilicic acid to an aqueous solution of chloropentaamminecobalt dichloride or any other suitably soluble salt of this cation. If hydrofluorosilicic acid was present in excess, crystallization was immediate. The highly insoluble product so prepared could not be recrystallized to yield suitable material for spectroscopic and X-ray studies. It was found, however, that if the hexafluorosilicate anion was not present in excess of the stoichiometrically required amount, crystallization occurred much more slowly to give well-formed crystals. A typical procedure was to add, to a well-filtered, near-saturated solution of chloropentaamminecobalt dichloride, an equivalent amount (1:1) of $[Zn(H_2O)_6]SiF_6$, dissolved in a minimum amount of water. Within several hours, large, thin platelets were obtained, measuring 1–2 mm along the edges and 0.005–0.01 mm thick.

Alternatively, a diffusion method was employed, whereby saturated solutions of $[Co(NH_3)_5Cl]Cl_2$ and $[Zn(H_2O)_6]SiF_6$ were allowed to diffuse into a common container. The crystals obtained in this manner were characteristically thicker (0.01–0.05 mm) but showed evidence of twinning along the major diagonal of the rhomb-shaped growth face.

$[Co(NH_3)_5CN]SiF_6$.—Cyanopentaamminecobalt perchlorate was prepared by the method of Siebert.[4] This was converted to the chloride, and crystal growth was attempted under the condition of low concentration of hexafluorosilicate anion. In contrast to the chloro derivative, crystallization occurred very rapidly under these conditions and suitable crystals could not be obtained. The diffusion method, using the perchlorate salt and hydrated zinc hexafluorosilicate, was therefore employed. The crystals of cyanopentaamminecobalt hexafluorosilicate did not appear to be twinned when so prepared.

Microscopy. **$[Co(NH_3)_5Cl]SiF_6$.**—The reddish purple, rhomb-shaped crystal plates of chloropentaamminecobalt hexafluorosilicate were observed to give symmetric extinction along the major and minor diagonals of the rhomb. Crystallographic results (see below) identified the growth face of the rhomb as (001) and showed that it contains the unique monoclinic b axis and a axis along the major and minor diagonals, respectively. From an examination of the interference figure, the optic plane containing the two optic axes for the biaxial crystal may be assigned as parallel to (010). The crystals appear orange when light incident on (001) is polarized parallel to the unique b axis, and red-violet when the light is polarized parallel to the a axis.

$[Co(NH_3)_5CN]SiF_6$.—In general, the crystal habit of this compound is very similar to the chloro complex, but some of the crystals did show truncation of the vertices formed by the edges enclosing the larger oblique angle of the rhomb. Thus the habit becomes six sided. The crystals showed symmetric extinction along the major and minor diagonals of the growth face, as in the chloro derivative. They appear orange-yellow in light polarized along the b axis (see below) and very light yellow in light polarized along the a axis

Crystallographic Data. **$[Co(NH_3)_5Cl]SiF_6$.**—X-Ray examination of a crystal on the precession camera indicated that the crystals were monoclinic with the unique b axis (second setting) along the major diagonal of the rhomb. The a^* axis was found to make an angle of 10° 20′ ± 30′ with the plate face of the crystal, and as the c^* axis emerged normal to the plate face, the rhomb-shaped growth face was identified as (001). The cell parameters, determined from the $hk0$ and $0kl$ zones using Mo $K\alpha$ radiation (λ 0.7107 A), are $a = 6.26 \pm 0.01$, $b = 8.22 \pm 0.01$, $c = 10.18 \pm 0.02$ A, and $\beta = 99° 40' \pm 30'$. Systematic absences occur when $0k0$ has $k = 2n + 1$. The space group is either $P2_1$ or $P2_1/m$. A density measurement by flotation in a mixture of 1,2-dibromoethane and carbon tetrachloride is 2.08 g cm^{-3} as compared to 2.067 g cm^{-3} calculated assuming two molecules of $[Co(NH_3)_5Cl]SiF_6$ in the cell.

$[Co(NH_3)_5CN]SiF_6$.—Examination of a crystal of this compound on the precession camera (Mo $K\alpha$, λ 0.7107 A) led to the following crystallographic data: $a = 6.31 \pm 0.02$, $b = 8.03 \pm 0.02$, $c = 10.08 \pm 0.02$ A, and $\beta = 96° 40' \pm 30'$. Systematic absences, $0k0$ when $k = 2n + 1$, determine the space group as either $P2_1$ or $P2_1/m$. The measured density of 2.01 g cm^{-3} indicates that there are two molecules of $[Co(NH_3)_5CN]SiF_6$ in the unit cell ($\rho_{calcd} = 2.042$ g cm^{-3}). Examination of the intensity distribution of several zones leads to the conclusion that the chloro and cyano complexes are isomorphous.

Collection of X-Ray Data.—Multiple-film, equiinclination Weissenberg photographs ($h0l$–$h6l$) were taken with iron-filtered Co $K\alpha$ radiation (λ 1.792 A). There were distinct shaded and nonshaded background regions on the films owing to extremes of absorption accompanying surface and nonsurface reflections.[5] In addition, the shape of the diffraction maxima showed a continuous decrease in vertical width as the crystal turned in the X-ray beam from the position with the plate normal to the beam, giving the broadest spot, to the position where the plate face was parallel with the beam. Two standard reflections,[6] representative of the two different shapes, were used to make calibrated strips. By visual comparison with these strips, the intensities of 649 independent diffraction maxima were estimated. The raw data were corrected for absorption (Co $K\alpha$, μ 100 cm^{-1}),[7] and the levels $h0l$ to $h6l$ placed on the same relative scale according to X-ray exposure times.

Scattering curves for Co^{3+}, Cl^-, Si^{4+}, and F^- were taken from the compilation in "International Tables for X-Ray Crystallography."[8] The ammonia ligands were treated as nitrogen atoms and the N^0 curve was obtained from the same source. The cobalt-scattering curve was corrected for the effects of anomalous dispersion.[9]

Structure Determination.—As there are two molecules in the unit cell, the crystal belongs either to the space group $P2_1$ with all atoms in general positions or to $P2_1/m$ with crystallographic symmetry required for the $Co(NH_3)_5Cl^{2+}$ and SiF_6^{2-} groups. As both groups are presumed octahedral, the only ways of satisfying the symmetry constraint with an ordered structure require at least the Cl–Co–N axis and one F–Si–F axis to lie on a mirror plane.

The section $P(u, 0, w)$ of the three-dimensional Patterson synthesis contained a peak which was consistent with a Co–Cl vector between bonded atoms; as two further substantial maxima on this section could be interpreted in terms of the Co–Si and Si–Cl vectors, it was assumed that the Co, Si, and Cl atoms had almost identical y coordinates. The analysis thereafter proceeded on the assumption that $P2_1/m$ was the correct space group, with the Cl–Co–N and at least one of the F–Si–F axes lying on the mirror plane at $y = {}^1/_4$. Peaks on the section $P(u, {}^1/_2, w)$, corresponding to vectors between symmetry-related groups, were fully consistent with this assignment.

A Fourier synthesis based on signs calculated from the posi-

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[3] J. A. Stanko, *et al.*, to be published.

[4] H. Siebert, *Z. Anorg. Allgem. Chem.*, **327**, 63 (1964).

[5] M. J. Buerger, "Crystal Structure Analysis," John Wiley and Sons, Inc., New York, N. Y., 1960, pp 204–231.

[6] The reflections chosen were $\bar{1}09$ and 603. After a series of measurements with a Nonius microdensitometer, these reflections were found to have the same intensity.

[7] Using a modification of an absorption program, GNABS, suitable for a crystal bound by n plane faces. The program was written by C. W. Burnham, Geophysical Laboratory, Carnegie Institute, Washington, D. C.

[8] J. A. Ibers in "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, pp 201–207.

[9] R. W. James, "Optical Principles of Diffraction of X-Rays," G. Bell and Sons, London, 1962, pp 148–154, 608–610.

tions of the Co, Cl, and Si atoms revealed the complete octahedron of fluorine atoms surrounding the Si atom and the five nitrogen atoms completing the octahedron around the Co atom. The crystallographic R factor, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, on this calculation was 0.55. Inclusion of the 14 atoms other than hydrogen in a structure factor calculation reduced the R factor to 0.34. Least-squares refinement, using a program[10] which allowed full-matrix treatment of the parameters, was commenced at this stage. Two weighting schemes were used in the course of the analysis. The first scheme set all weights equal to unity, the other had $\sqrt{w} = 1/\sigma$, where $\sigma = |F_{av}|/|F_o|$ for $|F_{av}| > |F_o|$ and $\sigma = |F_o|/|F_{av}|$ where $|F_{av}| \leq |F_o|$. Only slight differences were noted in the use of either scheme and the final refinement was based on unit weights. The function minimized was $\Sigma w||F_o| - |F_c||^2$. Refinement was initially attempted in the space group P2$_1$, constraining the y coordinate of the Co atom to fix the origin in this direction. The results were not satisfactory, and all further calculations were based on the space group P2$_1$/m. The atomic coordinates and isotropic temperature factors of all ten atoms were refined in four cycles of least-squares treatment. The R factor was 0.22. At this stage in the analysis, absorption corrections were applied to the observed data. Introduction of anisotropic thermal motion to the Co, Si, and Cl atoms reduced R to 0.18. When the remaining seven atoms were varied anisotropically, the refinement converged to a final R factor of 0.12. In the final least-squares cycle, the shifts in parameters were in every case less than one-fifth of the esd. The inaccuracies in intensity measurement introduced by wide variation in spot shape led us to believe that further refinement on the present data is not justified. The major aim of the analysis, that of determining the orientation of the Co–Cl bond in the crystal, has been achieved. The final positional parameters and anisotropic thermal parameters of the atoms, together with their standard deviations, are listed in Tables I and II. Table III contains the final list of observed and calculated structure amplitudes.

TABLE I

FINAL ATOMIC PARAMETERS, WITH ESTIMATED STANDARD DEVIATIONS (×10^4) IN PARENTHESES, IN FRACTIONS OF THE UNIT CELL EDGE

	x	y	z
Co	0.2350 (5)	0.2500	0.2168 (3)
Si	0.3342 (10)	0.2500	0.6974 (6)
Cl	−0.1080 (9)	0.2500	0.0921 (5)
F(1)	0.5728 (23)	0.2500	0.7976 (16)
F(2)	0.0962 (19)	0.2500	0.5933 (13)
F(3)	0.2506 (21)	0.3903 (19)	0.7913 (12)
F(4)	0.4261 (20)	0.3922 (18)	0.6024 (11)
N(1)	0.5317 (33)	0.2500	0.3287 (23)
N(2)	0.1487 (22)	0.4256 (21)	0.3344 (13)
N(3)	0.3245 (22)	0.4142 (22)	0.0953 (12)

Results and Discussion

A schematic drawing of the crystal structure viewed down the b axis is shown in Figure 1 and viewed along the a axis in Figure 2. The Cl–Co–N(1) and F(1)–Si–F(2) axes lie on the mirror plane perpendicular to b at $y = {}^1/_4$. The octahedra are completed by two pairs of nitrogen and fluorine atoms which are related to each other by reflection through this mirror plane. Within the accuracy of the analysis, the SiF_6^{2-} anion and the $[Co(NH_3)_5Cl]^{2+}$ cation are perfect octahedra and the bond distances, uncorrected for the effects of thermal motion, agree with expected values. From an analysis,[11] based on projection data, on the salt $[Co(NH_3)_5Cl]Cl_2$, Shigeta, *et al.*, reported a significantly shorter Co–N bond (1.91 A) in the position *trans* to the chloro sub-

TABLE II

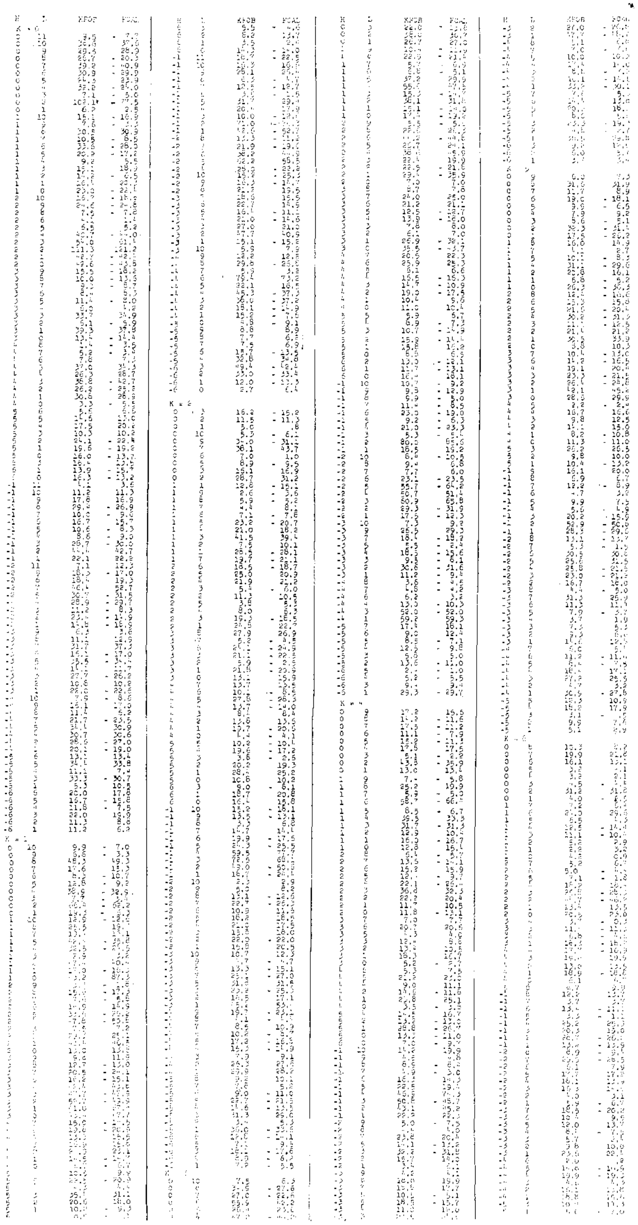
FINAL ANISOTROPIC THERMAL PARAMETERS (×10^3) EXPRESSED IN THE FORM $\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$[a]

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Co	11 (1)	6 (1)	3 (0.3)	. . .	2 (1)	. . .
Si	12 (2)	4 (1)	3 (0.6)	. . .	3 (2)	. . .
Cl	13 (2)	7 (1)	5 (0.6)	. . .	4 (2)	. . .
F(1)	20 (5)	17 (4)	13 (2)	. . .	28 (5)	. . .
F(2)	6 (3)	15 (3)	9 (2)	. . .	5 (4)	. . .
F(3)	52 (5)	33 (4)	12 (2)	56 (7)	−13 (4)	−30 (4)
F(4)	48 (5)	25 (4)	11 (1)	−46 (7)	−17 (4)	18 (3)
N(1)	15 (6)	11 (5)	12 (3)	. . .	8 (7)	. . .
N(2)	23 (4)	10 (3)	7 (2)	5 (6)	6 (4)	−9 (4)
N(3)	24 (5)	14 (3)	4 (1)	−5 (6)	0 (4)	5 (4)

[a] Dots in a column indicate that this term was constrained to zero during the refinement. Standard deviations (×10^3) are given in parentheses.

TABLE III

FINAL LIST OF h, k, l, F_o, AND F_c



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(10) P. K. Gantzel, R. A. Sparks, and K. N. Trueblood, "I.U.C. World List of Crystallographic Programs," International Union of Crystallography, 1962, No. 384.

(11) Y. Shigeta, Y. Komiyama, and H. Kuroya, *Bull. Chem. Soc. Japan*, **36**, 1159 (1963).

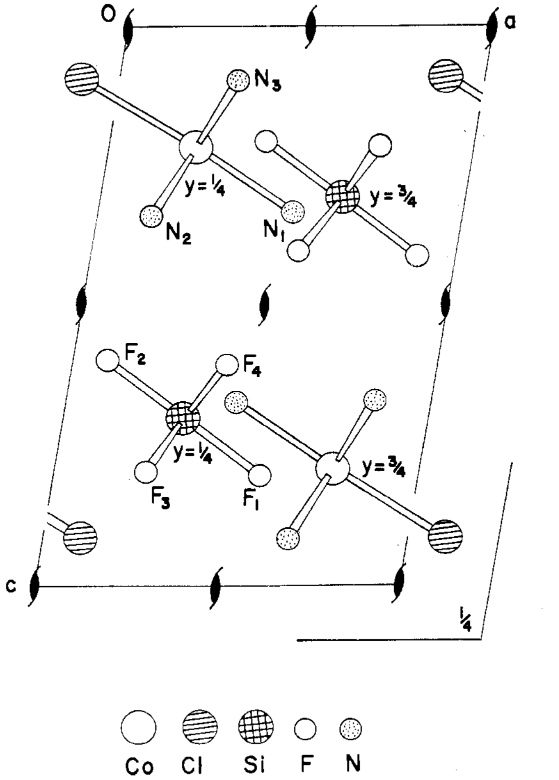

Figure 1.—A view of the crystal structure looking down the *b* axis. The octahedra are completed by mirror reflection of the N(2), N(3), F(3), and F(4) atoms lying above the planes $(x, {}^1/_4, z)$ and $(x, {}^3/_4, z)$ to an equivalent distance below. The *y* coordinates of the central atoms of each octahedron are indicated.

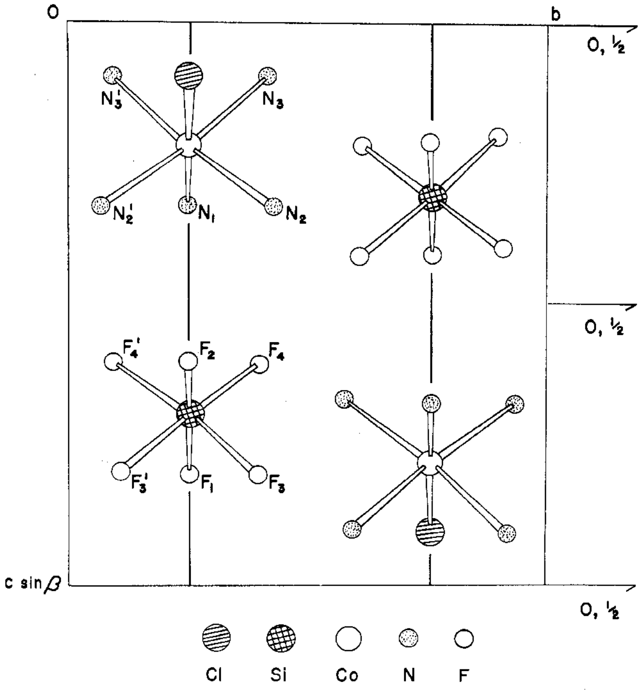

Figure 2.—The contents of a unit cell viewed along the *a* axis.

TABLE IV

BOND DISTANCES AND ANGLES

Distances, A		Angles, deg	
Co–Cl	2.303 ± 0.006	N(2)–Co–N(2′)	91.7 ± 0.6
Co–N(1)	2.009 ± 0.023	N(3)–Co–N(3′)	86.6 ± 0.6
Co–N(2)	2.007 ± 0.015	N(2)–Co–N(3′)	177.1 ± 0.6
Co–N(3)	1.974 ± 0.015	N(1)–Co–N(2)	88.7 ± 0.7
Si–F(1)	1.661 ± 0.017	N(1)–Co–N(3)	91.3 ± 0.7
Si–F(2)	1.677 ± 0.014	F(1)–Si–F(2)	178.7 ± 0.5
Si–F(3)	1.639 ± 0.015	F(3)–Si–F(4′)	178.6 ± 0.7
Si–F(4)	1.679 ± 0.014	F(1)–Si–F(3)	89.1 ± 0.6
		F(1)–Si–F(4)	89.7 ± 0.6
Angles, deg		F(3)–Si–F(4)	91.1 ± 0.7
Cl–Co–N(1)	178.9 ± 0.4	F(3)–Si–F(3′)	89.5 ± 0.7
Cl–Co–N(2)	90.5 ± 0.4	F(4)–Si–F(4′)	88.5 ± 0.7
Cl–Co–N(3)	89.5 ± 0.4	F(2)–Si–F(3)	91.8 ± 0.6
N(2)–Co–N(3)	90.8 ± 0.6	F(2)–Si–F(4)	89.6 ± 0.6

stituent when compared to the other Co–N distances (1.97 A),[12] thus increasing the credibility of a report[13] of a similar effect in an early structure determination of $Co(NH_3)_3(NO_2)_2Cl$. Within the accuracy of the present analysis, the measured bond lengths (Table IV) do not indicate any shortening of the Co–N(1) distance relative to the other Co–N distances.

Intermolecular distances are listed in Table V. There are a number of N···F contacts in the range 2.99–3.06 A which are indicative of N–H···F hydrogen bonding.[14]

TABLE V

INTERMOLECULAR CONTACTS IN A (≤3.50 A)

N(2)–F(2)	3.02	F(4)–N(2′)[a]	3.03
N(2)–F(4)	2.99	Cl–N(3′)[b]	3.50
N(1)–F(4)	3.19	N(3)–N(3′)[c]	3.47
F(1)–N(3′)[a]	3.00	Cl–F(3′)[d]	3.36
F(3)–N(3′)[a]	3.16	F(2)–N(2′)[d]	3.22
F(4)–F(4′)[a]	3.00	F(3)–N(2′)[d]	3.02
F(4)–N(1)[a]	3.02	N(3)–F(3)[e]	3.06

[a] $1 - x, {}^1/_2 + y, 1 - z$. [b] $-x, {}^1/_2 + y, -z$. [c] $1 - x, {}^1/_2 + y, -z$. [d] $-x, {}^1/_2 + y, 1 - z$. [e] $x, y, -1 + z$.

The observed optical dichroism is fully consistent with the crystal structure since the pseudo-tetragonal axes (Cl–Co–N) of the two $Co(NH_3)_5Cl^{2+}$ ions in the unit cell each lie in a plane parallel to (010) and are both equally inclined at 32° to the *a* axis. With light, polarized parallel to the *b* axis, and incident on the growth face (001), the electric vector would be perpendicular to all Co–Cl bond directions. For other directions of the electric vector, the absorption can be resolved into components parallel and perpendicular to the pseudo-tetragonal axis. In the case of light polarized along the *a* axis, the intensity would be made up of a 75% contribution from the component with the electric vector parallel to the pseudo-tetragonal axis

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(12) Shigeta, Komiyama, and Kuroya[11] apparently did not refine the structural parameters of the $[Co(NH_3)_5Cl]Cl_2$ salt by least-squares methods, nor did they quote standard deviations for bond distances or angles. As the occurrence of a "*trans* effect" in $[Co(NH_3)_5X]^{2+}$ octahedra is of great interest, we have carried out a least-squares refinement on the data of Shigeta, *et al.*, using initially isotropic temperature factors and finally anisotropic temperature factors. On isotropic refinement, the *R* factor dropped to 0.08, with distances: Co–N(1), 1.91 ± 0.03; Co–N(2), 1.91 ± 0.04; Co–N(3), 1.96 ± 0.03; and Co–N(4), 1.95 ± 0.04 A. Introduction and refinement of anisotropic thermal parameters gave an *R* factor of 0.07, with the distances being Co–N(1), 1.92 ± 0.04; Co–N(2), 1.91 ± 0.04; Co–N(3), 1.93 ± 0.04; and Co–N(4), 1.95 ± 0.04 A. We therefore feel that the differences in the Co–N distances reported by Shigeta, *et al.*, cannot be considered significant and that the occurrence of a "*trans* effect" in these complexes still awaits experimental verification.

(13) Y. Tanito, Y. Saito, and H. Kuroya, *Bull. Chem. Soc. Japan*, **26**, 420 (1953).

(14) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, p 290.

and a 25% contribution from the component with the vector perpendicular to this axis.

Acknowledgment.—We wish to acknowledge our indebtedness to Professor R. L. Belford, Professor T. L Brown, and the late Professor T. S. Piper for their interest and encouragement during the various stages of this investigation. In particular, Professor Belford suggested the need for an X-ray investigation to aid the interpretation of the optical results. Dr. M. G. Newton and Mr. J. S. McKechnie assisted at various stages of the X-ray study. Fourier computations were carried out by the ERFR-2 program written by W. G. Sly, D. P. Shoemaker, and J. H. van den Hende. We acknowledge partial support from the National Institutes of Health (GM 12470-02 and 5T1 GM 722-05) and a grant of computer time from the Graduate College of the University of Illinois. The detailed computations were carried out on the IBM 7094 at the University of Illinois.

Contribution from the Istituto di Chimica Generale e Inorganica
Università di Firenze, Florence, Italy

Molecular and Crystal Structure of the Octahedral Nickel(II) Complex with N-γ-Dimethylaminopropylsalicylaldimine

By M. Di Vaira and P. L. Orioli

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The crystal structure of bis(N-γ-dimethylaminopropylsalicylaldiminato)nickel(II) has been determined by three-dimensional X-ray analysis. Cell dimensions are: $a = 10.226 \pm 0.008$ A, $b = 15.254 \pm 0.012$ A, $c = 15.333 \pm 0.008$ A, $\beta = 107° 12' \pm 4'$, $Z = 4$, space group $P2_1/c$. The structure consists of discrete molecules in which nickel(II) exhibits a distorted octahedral coordination. Although the nickel atom does not lie on a crystallographic center of symmetry, the molecules are almost centrosymmetrical, the average deviations of the atomic positions from exact centrosymmetry being of the order of magnitude of the standard deviations.

Introduction

N-Substituted salicylaldimines form, with first-row transition metals, complexes with a large variety of stereochemistries. The structures of planar, tetrahedral, and square-pyramidal nickel(II) salicylaldimine complexes have been determined by X-ray diffraction.[1]

However, no structure of an octahedral nickel(II) complex with this type of ligand has been so far described, although it would seem interesting to compare the results with those of the four- and five-coordinated complexes.

Complexes of nickel(II) with Schiff bases formed from ring-substituted salicylaldehydes and N,N-substituted derivatives of 1,3-diaminopropane have been recently studied.[2] Diamagnetic planar or paramagnetic octahedral complexes are obtained depending on the nature of the N substituent.

N-γ-Dimethylaminopropylsalicylaldimine forms with nickel(II) a complex of the formula $[OC_6H_4CHN(CH_2)_3N(CH_3)_2]_2Ni$, in which the ligand is tridentate. Spectral and magnetic measurements suggest for this complex an octahedral configuration, although somewhat distorted.[3]

A further point of interest for the determination of this structure was to establish whether the salicylaldimine residues would assume a *cis* configuration as in the complex bis(N-β-diethylaminoethyl-5-chlorosalicylaldiminato)nickel(II)[1d] or a *trans*-planar configuration.

We report here the results of the three-dimensional X-ray analysis on this compound.

Experimental Section

Collection of the X-Ray Data.—The complex was prepared by the reaction between nickel salicylaldehydate and N,N-dimethyltrimethylenediamine in ethanol solution. Crystals suitable for X-ray analysis were grown from ethanol solutions.

Cell dimensions were determined from two equatorial Weissenberg photographs taken around the *a* and *b* axes, using Cu Kα radiation (λ 1.5418). An NaCl rotation pattern ($a = 5.6273$ A) was superimposed on each film for calibration. 2θ values were measured for about 20 reflections and the data were treated by a least-squares technique. The results are: $a = 10.226 \pm 0.008$ A, $b = 15.254 \pm 0.012$ A, $c = 15.333 \pm 0.008$ A, $\beta = 107° 12' \pm 4'$, $d_c = 1.37$ g cm^{-3}, $Z = 4$.

Systematic absences of $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$ indicated the space group to be $P2_1/c$. A few weak reflections violated the space group conditions: 103, 105, $10\bar{3}$, 205, $30\bar{9}$, $50\bar{7}$, $70\bar{9}$. These reflections were clearly Renninger spots, since their occurrence depended on the wavelength and on the technique used in taking the photographs. The successful determination of the structure in $P2_1/c$ confirmed this assumption.

The crystal chosen for the collection of the data had the shape of a truncated six-sided bipyramid, with dimensions 0.25 × 0.25 × 0.15 mm. $0kl$ through $8kl$ double integrated Weissenberg photographs were taken on a Nonius integrating camera, using

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