(20) B. E. Mann, *Adv. Organomet. Chem.*, **12**, 135 (1974).
(21) J. Evans, B. F. G. Johnson, J. Lewis, and R. Watt, *J. Chem. Soc., Dalton Trans.*, 2368 (1974).
(22) G. M. Bodner, B. N. Storhoff, D. Doddrell, and L. J. Todd, *Chem. Commun.*, 1530 (1970).
(23) H. C. Volger and H. Hogeveen, *Recl. Trav. Chim. Pays-Bas*, **86**, 1066 (1967).
(24) Monodentate coordination of a 1,3-diene to Rh(I) has been reported: M. G. B. Drew, S. M. Nelson, and M. Sloan, *J. Chem. Soc., Dalton Trans.*, 1484 (1973).

Contribution from the Department of Inorganic Chemistry, The Royal Institute of Technology, S-100 44 Stockholm 70, Sweden, and the Division of Physical Chemistry 1, University of Lund, S-220 07 Lund 7, Sweden

# Nitrito–Nitro Linkage Isomerization in the Solid State. 2. A Comparative Study of the Structures of Nitrito- and Nitropentaamminecobalt(III) Dichloride

INGMAR GRENTHE*[1a] and ELLIKA NORDIN[1b]

*Received September 15, 1978*

The mechanism of the isomerization in the solid state of nitritopentaamminecobalt(III) dichloride to the thermodynamically more stable nitro compound and of the reverse photochemical nitro → nitrito reaction have been investigated. Freshly synthesized crystals of $[Co(NH_3)_5ONO]Cl_2$ and crystals of the same compound aged for 1 half-life have been used for structure determinations. The intensity data were collected by a computer-controlled diffractometer. The two structures are orthorhombic, space group $P2_1nb$, with $Z = 4$. Monomeric cobalt complexes and chloride ions are linked by electrostatic forces and by a network of hydrogen bonds. The coordination around cobalt is close to octahedral. A comparison of the X-ray structures of the nitrito and nitro compounds and the changes in the powder diffractograms with time indicate that the thermal nitrito → nitro isomerization consists of two consecutive steps. The first step involves an intramolecular change of the coordination mode, most likely via a seven-coordinated transition state. The second step consists of a slow rearrangement which can be interpreted as a cooperative ~90° rotation of half of the number of the coordination polyhedra, or as a pseudo-$C_3$-rotation or an intramolecular twist. The nitro → nitrito photoisomerization gives a nitrito compound with a structure different from the one originally synthesized. The photoreaction is probably also intramolecular, proceeding via a seven-coordinated transition state.

## Introduction

It is well-known that the ambidentate $NO_2^-$ ligand can be coordinated either to oxygen or to nitrogen in cobalt(III) complexes. The latter mode is thermodynamically favored, at least for $[Co(NH_3)_5NO_2]Cl_2$ at room temperature, although heating the nitro compound in the solid seems to result in a slight formation of the nitrito form.[2] Nitrito complexes may be prepared,[3] but they isomerize both in solution and in the solid state to the more stable nitro form. Since Cr(III) prefers oxygen donors over nitrogen donors,[4] only the nitrito complexes of Cr(III) have been prepared so far.

A previous discussion[5] of the mechanism of the nitrito → nitro isomerization (eq 1) in the solid state was based on

$$trans\text{-}[Co(en)_2(NCS)ONO]X \rightarrow trans\text{-}[Co(en)_2(NCS)NO_2]X \quad (1)$$

structure determinations of the two isomers (en = ethylenediamine; $X^- = ClO_4^-$ or $I^-$). We will here extend the investigation by using structure determinations of the compounds $[Co(NH_3)_5ONO]Cl_2$, $[Co(NH_3)_5(ONO)_{1/2}(NO_2)_{1/2}]Cl_2$, and $[Co(NH_3)_5NO_2]Cl_2$. Crystals of the latter compound were prepared from an aqueous solution and the structure (space group $C2/c$) was investigated by Börtin.[6] The mechanism of the photochemical nitro → nitrito isomerization will also be briefly discussed.

In the following text we denote the compounds in the thermal reaction (2) as A, B, and C and the compounds in

$$\underset{A}{[Co(NH_3)_5ONO]Cl_2(s)} \rightarrow \underset{B}{[Co(NH_3)_5NO_2]Cl_2(s)} \rightarrow \underset{C}{[Co(NH_3)_5NO_2]Cl_2(s)} \quad (2)$$

the photoreaction (3) as D and E. F is the compound $[Co(NH_3)_5(ONO)_{1/2}(NO_2)_{1/2}]Cl_2$ formed by A during the first half-life of the thermal reaction A → B; cf. Table I.

$$\underset{D}{[Co(NH_3)_5NO_2]Cl_2(s)} \xrightarrow{h\nu} \underset{E}{[Co(NH_3)_5ONO]Cl_2(s)} \quad (3)$$

## Experimental Section

**Preparation.** Microcrystalline $[Co(NH_3)_5ONO]Cl_2$ (A) and $[Co(NH_3)_5NO_2]Cl_2$ (D) were prepared from aqueous solutions as described by Adell.[3a,c] The products were purified by dissolving them in water followed by a precipitation with solid ammonium chloride until satisfactory elemental analyses were obtained.

Single crystals of the nitrito compound, formed as slightly distorted octahedra, were obtained at 278 K from an aqueous solution by slow evaporation.

Isomerization in the solid state gives an intermediary nitro compound (B) with a structure different from C (cf. powder diffractograms (c) and (g) in Figure 1 and the section: Mechanism of the Reaction A → B → C). For the investigation of the structure of B, single crystals of A were aged at 283 K for 1 half-life ($t_{1/2} \approx$ 15 days at 283 K; cf. Adell[3c]) corresponding to the reaction A → B in eq 2. Fragmentation of the single crystal was reduced by the slow isomerization rate at 283 K. If the crystals were aged for longer periods of time, the amount of fragmentation increased resulting in poorer quality of the intensity data. The amount of the compound C formed after only 1 half-life is negligible; cf.: Mechanism of the Reaction A → B → C.

$[Co(NH_3)_5ONO]Cl_2$ was also prepared photochemically by illumination of samples of D with light from a 100-W tungsten filament bulb. About 10 mg of D in powder form was placed in a thin layer between two parallel glass plates, cooled by a stream of cold air. After 6 h the isomerization was complete. An aqueous solution of the sample gave an absorption spectrum in the visible region identical with that of freshly prepared A. A powder diffractogram of the illuminated sample showed a different structure from that of the nitrito compound A (cf. diffractogram (a) in Figures 1 and 2). The new compound is denoted E.

**X-ray Study: Data Collection and Structure Determination and Refinement of $[Co(NH_3)_5ONO]Cl_2$ (A) and $[Co(NH_3)_5(ONO)_{1/2}(NO_2)_{1/2}]Cl_2$ (F).** Tables I and II contain crystal data and information on the collection and reduction of the sets of intensity data and the least-squares refinements; for further experimental details, see ref 7. The intensitites of three standard reflections were measured at regular time intervals during the data collections in order to obtain information about possible systematic changes in intensity due to deterioration of the crystal and to errors in the equipment used. The intensitites of these reflections showed no systematic variations, thus there was

0020-1669/79/1318-1869$01.00/0 © 1979 American Chemical Society

**Table I.** Crystal Data and Explanation of the Symbols A-F[e]

| | compd | symmetry<br>space group<br>*Z* | cell dimensions[a] | stability | annotations |
|---|---|---|---|---|---|
| A | $[Co(NH_3)_5ONO]Cl_2$ | orthorhombic<br>$P2_1nb$[b]<br>4 | $a = 10.349$ (2) Å[c]<br>$b = 13.228$ (3) Å<br>$c = 6.864$ (2) Å<br>$U = 939.5$ (6) Å$^3$ | unstable | synthesized according to ref 3a,c |
| B | $[Co(NH_3)_5NO_2]Cl_2$ | | | unstable | |
| C | $[Co(NH_3)_5NO_2]Cl_2$ | | | stable[d] | structure identical with D, except for a possible slight disorder |
| D | $[Co(NH_3)_5NO_2]Cl_2$ | monoclinic<br>$C2/c$<br>4 | $a = 10.327$ (5) Å<br>$b = 8.661$ (4) Å<br>$c = 10.729$ (9) Å<br>$\beta = 95.04$ (4)°<br>$U = 950.0$ Å$^3$ | stable[d] | crystallized from an aqueous solution |
| E | $[Co(NH_3)_5ONO]Cl_2$ | | | unstable | photochemically obtained, with a structure not identical with A |
| F | $[Co(NH_3)_5(ONO)_{1/2}(NO_2)_{1/2}]Cl_2$ | orthorhombic<br>$P2_1nb$<br>4 | $a = 10.376$ (1) Å<br>$b = 13.355$ (2) Å<br>$c = 6.8307$ (7) Å<br>$U = 946.6$ (4) Å$^3$ | unstable | A after 1$t_{1/2}$ |

[a] Structure A and F: calculated from 31 and 71 $\theta$ values, respectively, according to ref 33, using graphite-monochromated Cu K$\alpha$ radiation ($\lambda(\alpha_1)$ 1.540 562 Å), temperature 245 K. Structure D: values taken from ref 6, room temperature. [b] The set of equivalent sites is as follows: $x, y, z; \frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z; \frac{1}{2}+x, -y, -z; x, \frac{1}{2}+y, \frac{1}{2}-z$. The centrosymmetric space group *Pmnb* was rejected on the 0.005 level of significance according to Hamilton.[32] [c] Estimated standard deviations are given in parentheses throughout this paper. [d] According to ref 2 an equilibrium exists between the nitro and the nitrito forms, which lies very near the nitro compound at room temperature. [e] Cf. also the reaction schemes A(s) → B(s) → C(s) and

$$D(s) \overset{h\nu}{\rightleftharpoons} E(s)$$

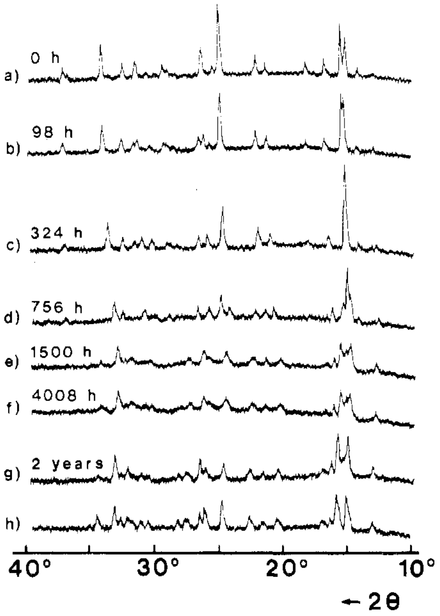

**Figure 1.** Powder diffractograms depicting the reactions A → B → C as a function of time; $t_{1/2}(A \rightarrow B) = 91$ h and $t_{1/2}(B \rightarrow C)$ = some months. The last diffractogram (h) shows the powder pattern of the D compound.

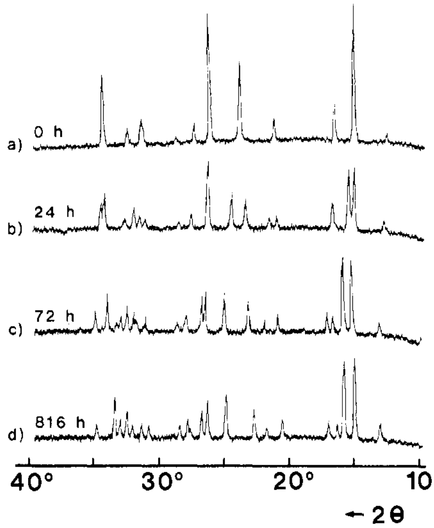

**Figure 2.** Powder diffractograms depicting the reaction E → D as a function of time.

no evidence for isomerization during the data collections at the temperature used (245 K).

In structure A the positions of the cobalt and chlorine atoms were deduced from three-dimensional vector maps. Successive difference electron density maps gave the positions of the remaining nonhydrogen atoms and all but one of the hydrogen atoms.[34] The hydrogen atoms were included in the final refinement with fixed positional and thermal parameters ($B = 5.0$ Å$^2$). Final structural parameters for all atoms of structure A are listed in Tables III and IV.

A final difference electron density map had its largest residuals (0.6 e Å$^{-3}$) irregularly scattered in the vicinity of O(2) and N(1). A $\delta R$ normal probability plot comparing the model with experiment[8] is shown in Figure 3. The slope and intercept of the least-squares line fitted to all data (twice the unique data set) are 1.19 and 0.08, respectively. Neglecting systematic errors in $|F_o|$, the value of the slope indicates that $\sigma(|F_o|)$ is underestimated by about 20% but is still in good agreement with the value of the standard deviation of an observation of unit weight ($S = 1.25$; cf. Table II). The structure is very nearly centrosymmetric (space group $P2_1nb$). This fact made it impossible to determine the absolute configuration. There was no evidence of extinction.

After 1 half-life there was no sign of a change of space group. For the refinement of structure F, preliminary atomic coordinates for the nonhydrogen atoms were taken from structure A. A least-squares refinement including these atoms with anisotropic temperature factors on the cobalt and chlorine atoms and with occupancy 0.5 for the O(1), O(2), and N(1) atoms of the $ONO^-$ ligand gave the $R$ and $R_w$ values of 0.108 and 0.143, respectively. The structural parameters for these atoms are given in Table III. An attempt to locate the nitro group in a following difference electron density map was not successful, since only scattered peaks with a maximum electron density of 2.2 e Å$^{-3}$ in the vicinity of O(2) and N(1) were found. There was no resemblance of a nitro ligand (with occupancy 0.5). It is obvious that the $NO_2^-$ ligand is noticeably disordered after isomerization during 1 half-life.

**Table II.** Crystal Data, Intensity Data Collection, and Least-Squares Refinement[f]

| | $[Co(NH_3)_5ONO]Cl_2$ (A) | | $[Co(NH_3)_5(ONO)_{1/2}(NO_2)_{1/2}]Cl_2$ (F) | |
|---|---|---|---|---|
| $M$ | 261.00 | | 261.00 | |
| $F(000)$ | 536 | | 536 | |
| $D_m$,[a] g cm$^{-3}$ | 1.77 | | | |
| $D_c$, g cm$^{-3}$ | 1.84 | | 1.83 | |
| cryst vol, mm$^3$ | $8.13 \times 10^{-4}$ | | $4.76 \times 10^{-4}$ | |
| temp, K | 245 | | 245 | |
| no. of data sets | 2 | | 2 | |
| $\theta$ interval of data sets, deg | 5–50 | 50–70 | 5–50 | 50–70 |
| $\Delta\omega$ interval ($\omega$–$2\theta$ scan), deg | $1.00 + 0.50 \tan\theta$ | $1.00 + 0.50 \tan\theta$ | $1.20 + 0.70 \tan\theta$ | $1.80 + 0.70 \tan\theta$ |
| $\mu$(Cu K$\alpha$), cm$^{-1}$ | 202.6 | | 201.1 | |
| range of transmission factors | 0.141–0.313 | | 0.225–0.450 | |
| no. of rflctns used in the refinement, $m$ | 1693[b] | | 867 | |
| no. of rflctns with zero wt ($I < 0$) | 101 | | 85 | |
| no. of parameters refined, $n$ | 100 | | 60 | |
| $R$,[c] $R_0$,[d] $R_w$[e] | 0.050, 0.059, 0.054 | | 0.108, 0.130, 0.143 | |
| $S = \{\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(m-n)\}^{1/2}$ | 1.25 | | 1.32 | |
| $a$ (const in wtng fctn) | 0.0008 | | 0.0064 | |

[a] Room temperature. [b] Twice the unique data have been refined. [c] $R = \Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$. [d] $R_0 = R$ (including zero weight data). [e] $R_w = \{\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert^2)/\Sigma w\lvert F_o\rvert^2\}^{1/2}$. [f] The data were recorded by using graphite-monochromated Cu K$\alpha$ radiation ($\lambda$ 1.541 838 Å).

**Table III.** Positional and Thermal Parameters for the Nonhydrogen Atoms in $[Co(NH_3)_5ONO]Cl_2$ (A) and in $[Co(NH_3)_5(ONO)_{1/2}(NO_2)_{1/2}]Cl_2$ (F)[a]

Complex A

| atom | $x$ | $y$ | $z$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{22}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Co | 1/4 | 0.10885 (5) | 0.18674 (9) | 54 (1) | 21 (1) | 84 (1) | −2 (1) | −13 (2) | −5 (1) |
| Cl(1) | −0.0017 (3) | 0.3569 (2) | 0.1650 (3) | 60 (3) | 38 (1) | 174 (5) | −6 (1) | 4 (3) | 2 (2) |
| Cl(2) | 0.5003 (3) | 0.3563 (2) | 0.1627 (3) | 68 (3) | 36 (1) | 125 (4) | −2 (1) | 8 (3) | 1 (2) |
| O(1) | 0.2404 (12) | −0.1090 (3) | −0.1961 (5) | 131 (5) | 39 (2) | 169 (8) | −36 (7) | −32 (13) | −25 (4) |
| O(2) | 0.2306 (15) | −0.0116 (4) | 0.0315 (7) | 326 (14) | 76 (4) | 223 (11) | −42 (10) | 119 (19) | −74 (6) |
| N(1) | 0.2665 (13) | −0.0304 (6) | −0.1047 (10) | 258 (21) | 88 (5) | 351 (19) | −28 (10) | 190 (21) | −92 (9) |
| N(2) | 0.2522 (11) | 0.1993 (3) | −0.0384 (6) | 104 (7) | 45 (3) | 111 (8) | 35 (7) | 32 (12) | 27 (4) |
| N(3) | 0.2527 (11) | 0.2255 (3) | 0.3600 (6) | 58 (5) | 36 (2) | 140 (8) | 15 (6) | −3 (10) | −16 (4) |
| N(4) | 0.2536 (11) | 0.0176 (3) | 0.4103 (6) | 66 (6) | 38 (2) | 151 (9) | −4 (6) | −10 (11) | 18 (4) |
| N(5) | 0.0651 (8) | 0.1058 (7) | 0.1863 (12) | 56 (7) | 51 (4) | 200 (16) | −28 (6) | −31 (9) | −18 (9) |
| N(6) | 0.4401 (8) | 0.1057 (7) | 0.1817 (12) | 59 (7) | 45 (4) | 203 (17) | 1 (5) | 26 (10) | 28 (9) |

Complex F

| atom | $x$ | $y$ | $z$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Co | 1/4 | 0.1094 (2) | 0.1849 (3) | 53 (3) | 25 (2) | 106 (7) | 3 (3) | 29 (6) | −11 (2) |
| Cl(1) | 0.0014 (5) | 0.3522 (4) | 0.1641 (8) | 46 (6) | 50 (4) | 121 (12) | 0 (3) | −6 (7) | 25 (5) |
| Cl(2) | 0.5013 (7) | 0.3593 (5) | 0.1589 (10) | 85 (8) | 39 (4) | 239 (18) | 12 (4) | −8 (9) | −7 (6) |

| atom | $x$ | $y$ | $z$ | $B$, Å$^2$ | atom | $x$ | $y$ | $z$ | $B$, Å$^2$ |
|---|---|---|---|---|---|---|---|---|---|
| O(1) | 0.272 (2) | −0.107 (1) | −0.192 (2) | 0.7 (3) | N(3) | 0.256 (2) | 0.220 (1) | 0.362 (2) | 2.9 (2) |
| O(2) | 0.256 (4) | −0.012 (2) | 0.018 (3) | 3.7 (4) | N(4) | 0.255 (2) | 0.015 (2) | 0.410 (2) | 2.9 (2) |
| N(1) | 0.284 (3) | −0.029 (2) | −0.108 (5) | 3.8 (7) | N(5) | 0.069 (2) | 0.103 (1) | 0.175 (3) | 2.8 (4) |
| N(2) | 0.258 (2) | 0.198 (1) | −0.039 (2) | 3.5 (3) | N(6) | 0.445 (3) | 0.113 (2) | 0.183 (4) | 4.3 (5) |

[a] The anisotropic temperature factor used is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + \ldots)]$. Values of $\beta_{ij}$ are multiplied by $10^4$.

**Table IV.** Positional Parameters for the Hydrogen Atoms in $[Co(NH_3)_5ONO]Cl_2$ (A)

| atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| H(12)[a] | 0.181 | 0.180 | −0.143 |
| H(22) | 0.223 | 0.252 | −0.037 |
| H(32) | 0.316 | 0.187 | −0.132 |
| H(13) | 0.184 | 0.216 | 0.474 |
| H(23) | 0.239 | 0.271 | 0.332 |
| H(33) | 0.300 | 0.211 | 0.464 |
| H(14) | 0.174[b] | −0.012[b] | 0.425[b] |
| H(24) | 0.262 | 0.032 | 0.511 |
| H(34) | 0.301 | −0.042 | 0.402 |
| H(15) | 0.022 | 0.041 | 0.204 |
| H(25) | 0.004 | 0.180 | 0.246 |
| H(35) | 0.017 | 0.219 | 0.128 |
| H(16) | 0.455 | 0.048 | 0.177 |
| H(26) | 0.476 | 0.145 | 0.226 |
| H(36) | 0.473 | 0.129 | 0.058 |

[a] H(12) denotes that the hydrogen atom is bonded to N(2) etc. [b] The parameter has been calculated geometrically.

Tables of observed and calculated structure factors are available.[9] The atomic scattering factors as well as the correction for anomalous scattering of cobalt and chlorine were taken from ref 10.

## Description of the Structures

**$[Co(NH_3)_5ONO]Cl_2$ (A).** The structure consists of nitritopentaamminecobalt(III) complexes and chloride ions in a fluorite-like arrangement. The structure is nearly identical with that of the corresponding chromium(III) compound $[Cr(NH_3)_5ONO]Cl_2$ (space group $P2_1/n$).[7,11,12] The anions and cations are held together by electrostatic forces and a network of hydrogen bonds; cf. Table V and Figure 4.

The symmetry of the $CoN_5O$ group in the complex is close to octahedral. The distortions are given by the tilt angle, range of twist angles, range of edge lengths, and the displacement of the metal ion from the center of the coordination polyhedron.[13] The tilt angle is the angle between the planes defined by O(2), N(2), N(5) and N(3), N(4), N(6). The values are 0.8(0.0)°, 53.8–65.4(60.0)°, 2.54–2.86(constant) Å, and

**Table V.** Possible Hydrogen Bonds in $[Co(NH_3)_5ONO]Cl_2$ (A)[a]

| N–H···Cl | N···Cl | N–H | H···Cl | N–H ...Cl |
|---|---|---|---|---|
| N(5)–H(25)···Cl(1) | 3.395 (9) | 1.23 | 2.41 | 135 |
| N(2)–H(32)···Cl($1^{i}$) | 3.344 (9) | 0.93 | 2.42 | 171 |
| N(4)–H(14)···Cl($1^{ii}$) | 3.431 (9) | 0.92 | 2.59 | 153 |
| N(5)–H(15)···Cl($1^{ii}$) | 3.516 (9) | 0.97 | 2.61 | 155 |
| N(3)–H(33)···Cl($1^{iii}$) | 3.468 (9) | 0.89 | 2.63 | 158 |
| N(6)–H(36)···Cl($1^{i}$) | 3.631 (8) | 0.96 | 2.72 | 158 |
| N(2)–H(12)···Cl($2^{iv}$) | 3.398 (9) | 1.07 | 2.34 | 171 |
| N(3)–H(13)···Cl($2^{v}$) | 3.508 (9) | 1.06 | 2.49 | 160 |
| N(4)–H(34)···Cl($2^{ii}$) | 3.365 (9) | 0.94 | 2.50 | 154 |
| N(6)–H(16)···Cl($2^{ii}$) | 3.523 (10) | 0.78 | 2.80 | 155 |

[a] Cl···H distances shorter than 2.8 Å are included in the table. Distances are in angstroms and angles in degrees. Superscripts refer to the following transformations of the coordinates $x, y, z$: (i) $\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$; (ii) $x, -\frac{1}{2}+y, \frac{1}{2}-z$; (iii) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; (iv) $-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$; (v) $-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$.

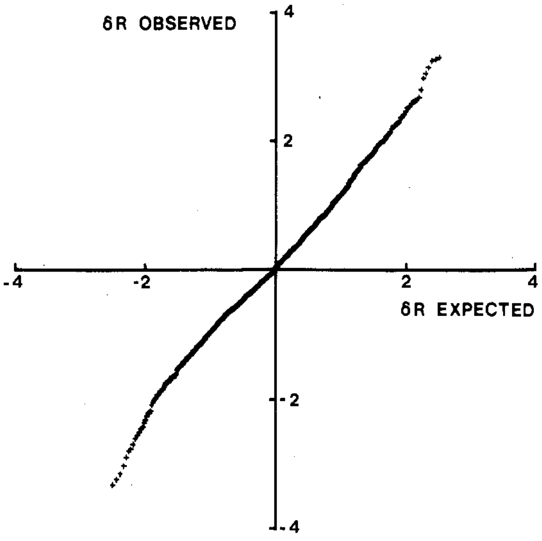

**Figure 3.** $\delta R$ normal probability plot. Only every other point is plotted.

0.029(0.0) Å, respectively. The values for octahedral symmetry are given within parentheses. A comparison with the corresponding values in the chromium(III) structure (1.2°, 55.8–63.9°, 2.73–2.94 Å, 0.028 Å) shows that the deviations from octahedral geometry are somewhat larger in the cobalt complex.

**Table VI.** Bond Lengths (Å) and Angles (deg) in $[Co(NH_3)_5ONO]Cl_2$ (A) and $[Co(NH_3)_5ONO)_{1/2}(NO_2)_{1/2}]Cl_2$ (F)

| atoms | A | F |
|---|---|---|
| | Bond Lengths | |
| Co–O(2) | 1.927 (5) | 1.98 (2) |
| –N(2) | 1.954 (4) | 1.94 (1) |
| –N(3) | 1.948 (4) | 1.91 (1) |
| –N(4) | 1.952 (4) | 1.99 (1) |
| –N(5) | 1.913 (8) | 1.88 (2) |
| –N(6) | 1.968 (9) | 2.02 (3) |
| N(1)–O(1) | 1.244 (9)[a] | 1.19 (4) |
| –O(2) | 1.037 (10)[a] | 0.94 (4) |
| N(2)–H(12) | 1.07 | |
| –H(22) | 0.75 | |
| –H(32) | 0.93 | |
| N(3)–H(13) | 1.06 | |
| –H(23) | 0.65 | |
| –H(33) | 0.89 | |
| N(4)–H(14) | 0.92 | |
| –H(24) | 0.72 | |
| –H(34) | 0.94 | |
| N(5)–H(15) | 0.97 | |
| –H(25) | 1.23 | |
| –H(35) | 0.71 | |
| N(6)–H(16) | 0.79 | |
| –H(26) | 0.71 | |
| –H(36) | 0.96 | |
| | Bond Angles | |
| Co–O(2)–N(1) | 131.3 (9)[a] | 138 (3) |
| O(1)–N(1)–O(2) | 125.3 (11)[a] | 128 (4) |

[a] Probably disordered positions.

Selected bond distances and angles are given in Table VI and a stereo drawing of the coordination polyhedron is given in Figure 5. The cobalt–nitrogen bond distances (with the possible exception of Co–N(5)) are compatible with known structure data.[6,14,15] No structural trans effect is noticed in A, and this is found neither in D nor in $[Co(NH_3)_5NO_2]Br_2$.[16] The average nitrogen–metal bond distances in the cobalt(III) and chromium(III) complexes differ slightly more (0.11 Å)

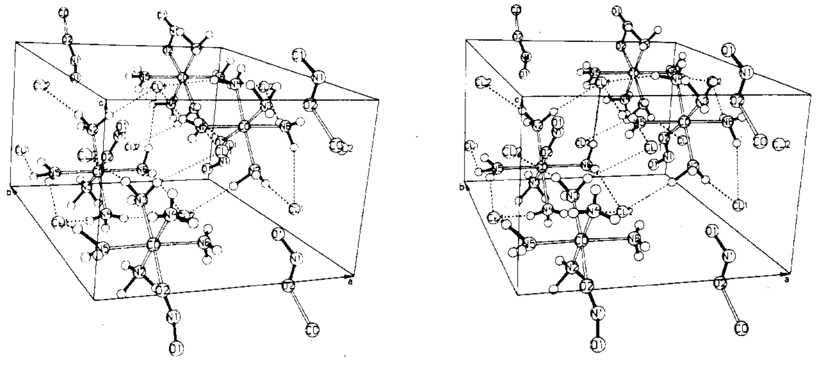

**Figure 4.** Crystal packing of $[Co(NH_3)_5ONO]Cl_2$ (A). Dashed lines represent hydrogen bonds.

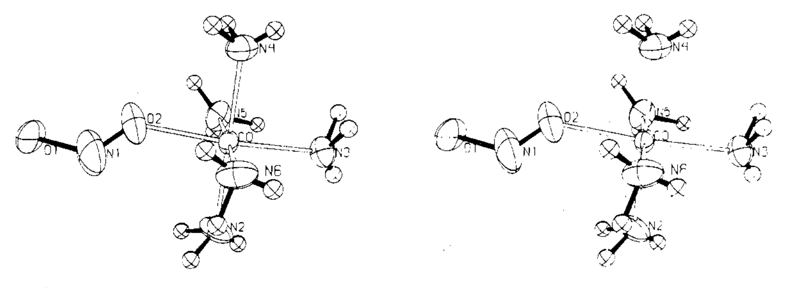

**Figure 5.** The $[Co(NH_3)_5ONO]^{2+}$ cation. The ellipsoids for the nonhydrogen atoms represent 50% of the probability distribution.

**Table VII.** IR Group Frequencies for the $ONO^-$ Group in Various Nitrito Complexes

| | $\nu_{as}$, $cm^{-1}$ | $\nu_s$, $cm^{-1}$ | $\delta$, $cm^{-1}$ |
|---|---|---|---|
| $[Co(NH_3)_5ONO]Cl_2$ (A) | 1445 | 1055 | 835 |
| $[Cr(NH_3)_5ONO]Cl_2$ | 1455 | 1040 | 835 |
| *trans*-$[Co(en)_2(NCS)ONO]ClO_4$ | 1440 | 1050 | |
| *trans*-$[Co(en)_2(NCS)ONO]I$ | 1425 | 1045 | 845 |

than the difference in ionic radii,[17] 0.07 Å.

The two N–O lengths in the nitrito ligand differ widely from those found in other nitrito complexes. Usually the bond to the oxygen atom coordinated to the central ion is the longer of the two,[18] but the difference is not large, less than 0.06 (1) Å. The large $\beta_{ij}$ values of the atoms in the $ONO^-$ group (these $\beta_{ij}$ values are much larger in the cobalt complex than in the chromium complex) indicate a slight positional disorder, resulting in erroneous bond distances. Additional information must be used to give evidence about the geometry of the coordinated $ONO^-$ group. We have determined the IR group frequencies of the $ONO^-$ ligand in a number of different nitrito complexes; see Table VII. If large differences in bond distances exist, changes in these frequencies are expected.[19] The data in Table VII indicate that the $ONO^-$ group in A is not different from that in other nitrito complexes and agree with the values given by Nakamoto.[20] Also, ESCA measurements of A and of $[Cr(NH_3)_5ONO]Cl_2$ give the same difference in charge between the nitrito nitrogen and the ammine nitrogens. Hence the two nitrogen–oxygen bond distances ought to be similar. The N–O bond distances in $[Cr(NH_3)_5ONO]Cl_2$ are equal and have values in close agreement with those found in other structures containing the $ONO^-$ ion. In neither of the complexes does the nitrito ligand seem to be hydrogen bonded to any of the ammine ligands. There is a slight change in the orientation of the nitrito ligand between the two complexes. We can describe the orientation by the torsion angle N(1)–O(2)–Co–N(2) which is 35 (1)° in the cobalt compound as compared to 48.3 (3)° in the chromium compound.

**$[Co(NH_3)_5(ONO)_{1/2}(NO_2)_{1/2}]Cl_2$ (F).** In the partially isomerized compound the bond distances and angles agree well with those of A; cf. Table VI. The torsion angle N(1)–O(2)–Co–N(2) for the remaining $ONO^-$ ligand is equal to 24 (5)°.

### Mechanism of the Reaction A → B → C

The reaction $[Co(NH_3)_5ONO]Cl_2 \rightarrow [Co(NH_3)_5NO_2]Cl_2$ was studied by powder diffractometry at 293 K. Just as in the case of *trans*-$[Co(en)_2(NCS)ONO]ClO_4$,[5] a gradual shift of the powder pattern and, consequently, of the cell dimensions occurs as the solid is changed from the nitrito to the nitro form. There are reasons to believe that the reaction proceeds via the formation of a solid solution, since powder patterns from both phases could not be observed simultaneously; see Figure 1. Figure 1 indicates that the reaction in the solid state takes place via two consecutive steps. With Adell's rate constant the nitrito → nitro isomerization A → B should be almost complete in Figure 1c (only 10% of A left; $t_{1/2}$ = 91 h at 293 K). Since the diffractograms continue to change with time, a slow reaction must occur, involving the first-formed nitro compound B. Due to the methods of investigation[3a,21,22] only the faster step A → B, i.e., the nitrito → nitro linkage isomerization, was recognized earlier. Figure 1c–g shows that B very slowly changes into stable C, with a half-life of some months. A comparison between g and h in Figure 1 indicates that the structure of C is very similar to D, and the two structures may only differ by a possible slight disorder in C. The reaction B → C is accompanied by a change of space group from $P2_1nb$ to $C2/c$.

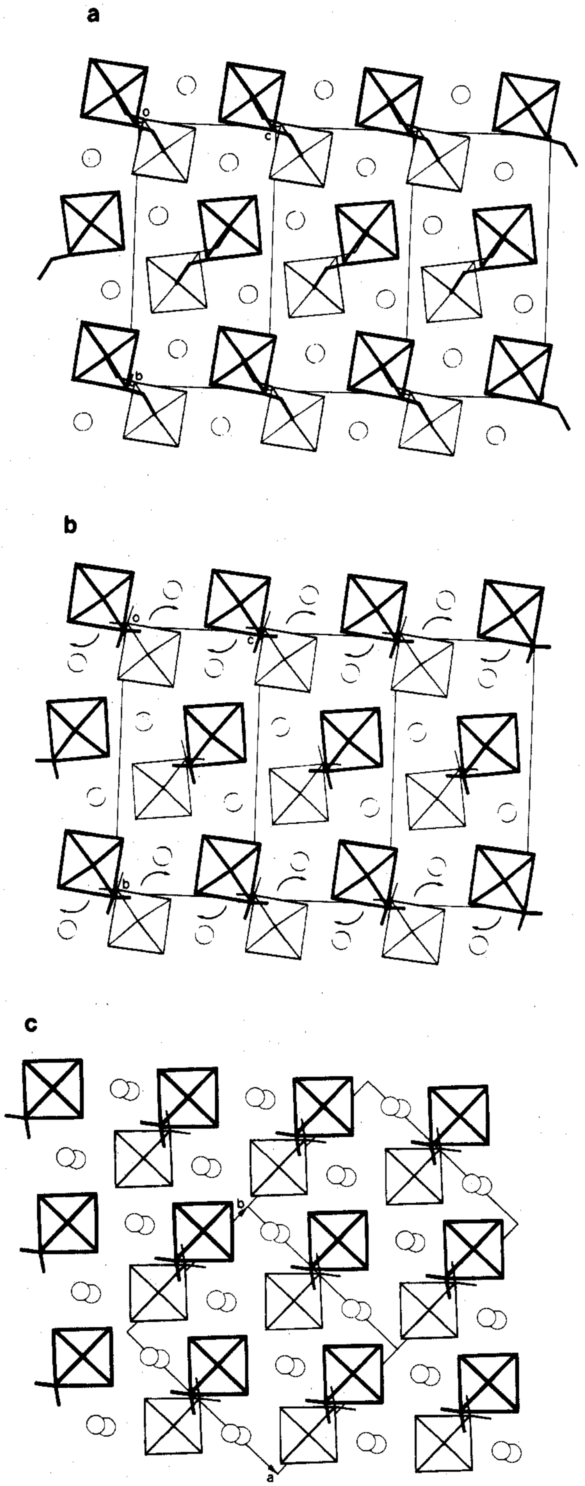

**Figure 6.** Projections showing the orientation of the polyhedra: (a) structure A, along *a*; (b) structure B, along *a*; (c) structure D, along *b* × *a*.

The isomerization A → B → C may be described by using Figure 6a–c. Figure 6a shows the original nitrito compound A. The $ONO^-$ ligand is inclined to the paper plane. Figure 6b depicts a structure model of the nitro compound B obtained (by extrapolation) from the investigation of a single crystal of A aged for 1 half-life. Since we could not locate the nitro group in the electron density maps, we tried to place the group by using geometrical considerations (van der Waals contact distances). The isomerization cannot take place in the plane of the original $ONO^-$ group (as in the case of the *trans*-$[Co(en)_2(NCS)ONO]X \rightarrow$ *trans*-$[Co(en)_2(NCS)NO_2]X$ reactions), since in the final state the contact distances

O(2)–Cl(1)[35] ≈ 2.5 Å and O(2)–N(3)[35] ≈ 2.7 Å would then be too short in comparison with the sum of the van der Waals radii (3.2 and 2.9 Å, respectively). The corresponding distances after 1 half-life would be 2.9 and 2.6 Å, respectively, still on the short side. In view of this it seems reasonable to assume that the $NO_2^-$ ligand is forced out of the $ONO^-$ plane. There are several possible locations which lead to approximately the same contact distances. We have selected a position with a torsion angle O(1)–N(1)–Co–N(2) equal to 45°. Inclusion of the $NO_2^-$ group in this position results in values of $R$ and $R_w$ equal to 0.104 and 0.118 respectively. The corresponding values for torsion angles 0° and 90° are $R = 0.125$, $R_w = 0.162$ and $R = 0.127$, $R_w = 0.170$, respectively. The $R$ values without the $NO_2^-$ ligand are $R = 0.108$ and $R_w = 0.143$. Structures A and B are very similar, apart from the nitrito/nitro ligand. The structure models indicate that the isomerization is intramolecular, just as in solution;[23,24] otherwise the nitrogen atom of the nitrito ligand would have to move about 4.8 Å. Most likely the reaction proceeds by a seven-coordinated transition state, where the cobalt atom is bonded to both O(2) and N(1).

The second step B → C is probably induced by the first, A → B, due to van der Waals repulsion between the O(2) atom in its new position with its immediate surroundings. This step consists of a slow rearrangement of half of the number of the complexes and can be interpreted as an ~90° rotation of the coordination polyhedra in the same direction in the *bc* plane as shown in Figure 6b. Besides the pseudo-$C_4$-rotation, some other mechanisms may also give the same result, such as a pseudo-$C_3$-rotation or an intramolecular twist, e.g., proposed for the solid-state racemization of some (+)-$[Co(en)_3]X_3 \cdot nH_2O$ compounds.[25] The first two mechanisms are probably the most likely ones, because the barriers for the reorientation of the whole complex ion in both hexaammine and some trans tetraammine complexes in the solid state are known to be low.[26,27] At the same time a small change of the atomic positions and in the orientation of half the $NO_2^-$ groups occurs. Hence all nitro ligands now lie in parallel planes as distinguished from structure B. In structure A, adjacent nitrito ligands are inclined 102°. The torsion angle N(1)–O(2)–Co–N(2) in A and the corresponding angle in D only differ by 4° (=3$\sigma$). Figure 6c shows the compound D (=C) after the cooperative rotation. The cell parameters of A and D are approximately given by the relationships

$$a_D = \tfrac{1}{2}b_A + c_A \qquad b_D = -\tfrac{1}{2}b_A + c_A \qquad c_D = a_A \qquad (4)$$

## Photochemical Isomerization of D → E Studied by Powder Diffractometry

It is known that the photoreaction of solid $[Co(NH_3)_5NO_2]Cl_2$ produces the isomeric nitrito compound.[28-30] Since the thermal nitrito → nitro reaction is a two-step reaction and results not only in a motion of the nitrito ligand but also in a cooperative rotation of half of the complexes, it was of interest to see if the photoreaction would give back the A structure or if a new nitrito complex could be obtained from D by the isomerization of the $NO_2^-$ group only. From the photochemical experiment described previously we obtained a sample of pure nitrito complex. The powder diffractogram of this sample is shown in Figure 2a. It is obvious from the diffractogram that the structure of this nitrito compound (E) is not identical with that of the one originally synthesized (A); cf. Figure 1a. Figure 2 also shows that the photochemically produced nitrito compound, which was kept at 293 K, isomerizes thermally to the original D compound; cf. Figures 1h and 2d. The rate constant for this process has been determined by Adell[28] and was found to be identical with the rate of linkage isomerization of the nitrito compound A. The $NO_2^- \rightarrow ONO^-$ photoisomerization is probably also an intramolecular process proceeding via a seven-coordinated transition state. It is not probable that the reaction takes place in the plane of the $NO_2^-$ group. A smaller van der Waals repulsion is obtained if the $ONO^-$ ligand is tilted with respect to the original $NO_2^-$ plane.

It may be remarked that Johnson and Pashman[31] claim that a metastable compound, which is believed to involve a bidentate N–O attachment of the $NO_2^-$ ligand has been observed on low-temperature photolysis of D.

**Acknowledgment.** Professor I. Leden and Drs. J. Albertsson, S. Andersson, and Å. Oskarsson have supported this work with valuable discussions and advice. The ORTEP drawings were made by B.S. M. Molund. The ESCA and IR spectra were recorded by Dr. B. Folkesson and Mrs. K. Trankell. The Swedish Natural Science Research Council and the Royal Physiographical Society of Lund gave financial support, which is also gratefully acknowledged.

**Registry No.** $[Co(NH_3)_5ONO]Cl_2$, 54734-10-0; $[Co(NH_3)_5NO_2]Cl_2$, 13782-02-0; $[Cr(NH_3)_5ONO]Cl_2$, 16480-88-9; *trans*-$[Co(en)_2(NCS)ONO]ClO_4$, 36452-54-7; *trans*-$[Co(en)_2(NCS)ONO]I$, 69102-48-3.

**Supplementary Material Available:** Listings of structure factor amplitudes for A and F (15 pages). Ordering information is given on any current masthead page.

## References and Notes

(1) (a) The Royal Institute of Technology. (b) University of Lund.
(2) (a) V. Doron, *Inorg. Nucl. Chem. Lett.*, **4**, 601 (1968); (b) I. R. Beattie and D. P. N. Satchell, *Trans. Faraday Soc.*, **52**, 1590 (1956).
(3) (a) B. Adell, *Z. Anorg. Chem.*, **252**, 272 (1944); (b) B. Adell, *Acta Chem. Scand.*, **5**, 941 (1951); (c) B. Adell, *Z. Anorg. Allg. Chem.*, **271**, 49 (1952); (d) R. G. Yalman and T. Kuwana, *J. Phys. Chem.*, **59**, 298 (1955), and references therein.
(4) S. Ahrland, J. Chatt, and N. R. Davies, *Q. Rev., Chem. Soc.*, **12**, 265 (1958).
(5) I. Grenthe and E. Nordin, *Inorg. Chem.*, **18**, 1109 (1979).
(6) O. Börtin, *Acta Chem. Scand.*, **22**, 2890 (1968).
(7) E. Nordin, *Acta Crystallogr., Sect. B*, **34**, 2285 (1978).
(8) S. C. Abrahams and E. T. Keve, *Acta Crystallogr., Sect. A*, **27**, 157 (1971).
(9) Supplementary material.
(10) "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974.
(11) M. Hansson and O. Börtin, *Acta Chem. Scand.*, **22**, 1689 (1968).
(12) O. Börtin, Thesis, Gothenburg, 1971.
(13) K. R. Dymock and G. J. Palenik, *Inorg. Chem.*, **14**, 1220 (1975).
(14) E. F. Epstein and I. Bernal, *J. Chem. Soc. A*, 3628 (1971).
(15) J. Alberto, P. Bonapace, and N. S. Mandel, *Acta Crystallogr., Sect. B*, **31**, 2540 (1975).
(16) F. A. Cotton and W. T. Edwards, *Acta Crystallogr., Sect. B*, **24**, 474 (1968).
(17) R. D. Shannon, *Acta Crystallogr., Sect. A*, **32**, 751 (1976).
(18) (a) K. A. Klanderman, W. C. Hamilton, and I. Bernal, *Inorg. Chim. Acta*, **23**, 117 (1977); (b) A. Camus, N. Marsich, and G. Nardin, *Acta Crystallogr., Sect. B*, **33**, 1669 (1977), and references therein.
(19) N. B. H. Jonathan, *J. Mol. Spectrosc.*, **4**, 75 (1960).
(20) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", Wiley, New York and London, 1963, p 155.
(21) B. Adell, *Z. Anorg. Allg. Chem.*, **275**, 106 (1954).
(22) R. B. Penland, T. J. Lane, and J. V. Quagliano, *J. Am. Chem. Soc.*, **78**, 887 (1956).
(23) R. G. Pearson, P. M. Henry, J. G. Bergmann, and F. Basolo, *J. Am. Chem. Soc.*, **76**, 5920 (1954).
(24) K. Murmann and H. Taube, *J. Am. Chem. Soc.*, **78**, 4886 (1956).
(25) C. Kutal and J. C. Bailar, Jr., *J. Phys. Chem.*, **76**, 119 (1972).
(26) G. R. Murray, Jr., and J. S. Waugh, *J. Chem. Phys.*, **29**, 207 (1958).
(27) S. E. Ulrich and B. A. Dunell, *Inorg. Nucl. Chem. Lett.*, **9**, 85 (1973).
(28) B. Adell, *Z. Anorg. Allg. Chem.*, **279**, 219 (1955).
(29) W. W. Wendlandt and J. H. Woodlock, *J. Inorg. Nucl. Chem.*, **27**, 259 (1965).
(30) V. Balzani, R. Ballardini, N. Sabbatini, and L. Moggi, *Inorg. Chem.*, **7**, 1398 (1968).
(31) D. A. Johnson and K. A. Pashman, *Inorg. Nucl. Chem. Lett.*, **11**, 23 (1975).
(32) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).
(33) S. Danielsson, I. Grenthe and Å. Oskarsson, *J. Appl. Crystallogr.*, **9**, 14 (1976).
(34) The positional parameters of the atom not found were calculated from the known geometry of $NH_3$, and it is marked with *b* in Table IV.
(35) $x, -\frac{1}{2} + y, \frac{1}{2} - z$.