

$\omega_2$ -phases in the  $\beta$ -phase (Sukedai, Hashimoto & Tomita, 1991) which can be expressed by the model shown in Fig. 8. In this model the  $\beta$ -phase containing only  $\omega_3$ - and  $\omega_4$ -phases gives the diffraction pattern for the  $\beta$ -phase only. Thus, if the  $\omega_2$ -phase in their model is replaced by the  $\omega_1$ -,  $\omega_3$ - or  $\omega_4$ -phase, the calculated diffraction patterns are similar to those calculated for the model shown in Fig. 4. The extra spots were observed for a specimen aged for 28 h (Fig. 9) in which the well developed  $\omega$ -phases are superimposed in the manner of the model. Fig. 10 shows the amplitudes of the characteristic and the extra diffraction spots for the model specimen and the arrows indicate the phase boundaries shown in Fig. 8. The intensities of the extra spots appear from the top surface of the  $\omega_2$ -phase and the intensity of the  $1/3 \bar{1}0\bar{1}$  beam is weaker than that of the  $2/3 \bar{1}0\bar{1}$  beam. This tendency does not change with the position of the  $\omega_1$ - $\beta$ - $\omega_2$  sandwich at depths of  $1/3$ ,  $1/2$  and  $2/3$  of the total thickness. This does not agree with the experimental result shown in Fig. 9 and it seems to be due to the difference in the number and modes of the sandwich realized in the specimen. There are also some intensity asymmetries in  $hkl$  and  $\bar{h}k\bar{l}$  in Fig. 10.

This may be due to differences in the superposition sequence of  $\omega_1$ - and  $\omega_2$ -phases.

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## Nitro–Nitrito Linkage Photoisomerization in Crystals of Pentaamminenitrocobalt(III) Dichloride

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#### Abstract

Photoisomerization in  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$  has been investigated by single-crystal X-ray diffraction:  $M_r = 261.0$ , monoclinic,  $C2/c$ ,  $Z = 4$ ,  $D_x = 1.83 \text{ Mg m}^{-3}$ ,  $\lambda(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$ ,  $\mu = 2.35 \text{ mm}^{-1}$ ,  $F(000) = 536$ ,  $T = 116 \text{ K}$ . Before illumination with an Xe lamp, (Ia),  $a = 10.176(2)$ ,  $b = 8.692(1)$ ,  $c = 10.746(2) \text{ \AA}$ ,  $\beta = 95.45(2)^\circ$ ,  $V = 946.2(3) \text{ \AA}^3$ ,  $R = 0.028$  for 1263 observed unique reflections. After illumination with an Xe lamp for 40 min, (Ib),  $R = 0.042$  for 1216 reflections. After illumination for 150 min, (Ic),  $R = 0.062$  for 730 reflections. Variation of the lattice constants was less than 0.6%. Nitrito coordination, induced by photochemical reaction, was detected on

electron density maps and the populations were refined to (Ib) 8.9 (5)% and (Ic) 14.5 (8)%. Thermodynamical linkage isomerization in  $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ , (II), was reinvestigated based on the X-ray intensity data measured by Grenthe & Nordin [*Inorg. Chem.* (1979), **18**(7), 1869–1874]. Linkage isomerization occurs in the original plane of  $\text{NO}_2^-$  in (I). However, the nitro plane is inclined during isomerization of (II) because of steric hindrance to rotation in the original plane.

#### Introduction

The nitrite ion is ambidentate and coordinates to metal atoms *via* an oxygen, nitrogen or two oxygen atoms (Finney, Hitchman, Raston, Rowbottom &

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White, 1981). In the synthesis of pentaamminenitro-cobalt(III) (I) from reaction of  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  with  $\text{NO}_2^-$ , the nitrito isomer is produced as a result of the reaction kinetics (Basolo & Hammaker, 1962). However, nitro coordination is thermodynamically favored and nitrito  $\rightarrow$  nitro linkage isomerization occurs in solution and even in the solid state (Jørgensen, 1984; Adell, 1944). On the other hand, nitro  $\rightarrow$  nitrito linkage isomerization occurs as a result of irradiation by light. The kinetics and mechanism of the spontaneous nitrito–nitro isomerization in  $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$  [here we refer to the most recent paper by Phillips, Choi & Larrabee (1990)] and the photochemical nitro–nitrito isomerization in  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$  (Heyns & De Waal, 1989) have been studied by means of IR spectroscopy. Crystallographic investigations of the nitrito–nitro isomerization have been reported for *trans*- $[\text{Co}(\text{en})_2(\text{NCS})\text{ONO}]\text{X}$  [en = ethylenediamine,  $\text{X}^- = \text{ClO}_4^-$  or  $\text{I}^-$  (Grenthe & Nordin, 1979*a*)] and  $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$  (Grenthe & Nordin, 1979*b*). However, information about the orientation of the reacting  $\text{NO}_2$  group was limited. In this article, the photochemical nitro–nitrito isomerization in (I) has been studied. Powder X-ray diffraction indicates a phase transition caused by the photochemical isomerization (Grenthe & Nordin, 1979*b*). Because the crystals gradually cracked during irradiation (Sysoev, 1983; Boldyreva, Sidel'nikov, Chupakhin, Lyakhov & Boldyrev, 1984; Boldyreva & Sidel'nikov, 1987), the initial stage of the reaction was investigated.

## Experimental

### Data collection

Crystals of  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$  were grown from aqueous solution and were twinned. The twinned cells were related by a twofold rotation about  $c^*$ , and the minor twin component made up at least a few percent of the total. Single crystals were obtained from an aqueous ethanol solution. A crystal,  $0.50 \times 0.33 \times 0.15$  mm, was mounted on a Rigaku AFC-5 four-circle diffractometer, and was cooled by a cold nitrogen stream in order to protect it against degradation by heat during the irradiation and to prevent the thermodynamical nitrito–nitro back reaction.

(Ia). Before irradiation, the typical peak half-width of the rocking curve was  $0.13^\circ$ . Lattice constants were determined based on 25  $2\theta$  values ( $20 < 2\theta < 30^\circ$ ). X-ray intensities were measured at 116 K with graphite-monochromatized Mo  $K\alpha$  radiation by  $\theta$ – $2\theta$  scan mode with scan width  $(1.3 + 0.36\tan\theta)^\circ$  and scan speed  $6^\circ \text{min}^{-1}$  in  $\theta$ . 1460 reflections were measured ( $-14 \leq h \leq 14$ ,  $0 \leq k \leq 12$ ,  $0 \leq l \leq 15$ ;  $4 < 2\theta \leq 60^\circ$ ) and 1325 reflections were observed with  $|F_o| > 3\sigma(|F_o|)$ . Mean ratio of  $|F_o|$  of five standard

reflections,  $\sum(|F_o|/|F_o|_{\text{initial}})/5$ , was in the range 0.997 to 1.002. After absorption correction by the Gaussian numerical integration method (Busing & Levy, 1957; transmission factors,  $A$ , 0.42–0.71), 1263 unique reflections were obtained ( $R_{\text{int}} = 0.016$ ).

(Ic). Peak searches of 25 reflections and refinement of the setting parameters were repeated during irradiation by a 150 W Xe lamp, without filtering after measurement of (Ia). Although the peak positions did not alter significantly, the peak profile broadened gradually owing to cracking of the crystal. After irradiation for 150 min, the peak half-width became as much as  $1.1^\circ$ , which may be the limit for crystal structure analysis. The Xe light was then turned off and X-ray intensities were measured by  $\omega$ -scan mode with scan width  $7.5^\circ$  and scan speed  $12^\circ \text{min}^{-1}$ . 2229 reflections were measured in a hemisphere of reciprocal space ( $-13 \leq h \leq 13$ ,  $-11 \leq k \leq 11$ ,  $0 \leq l \leq 13$ ;  $4 < 2\theta \leq 55^\circ$ ) and 1392 reflections were observed. Lattice constants were determined based on 25  $2\theta$  values ( $7 < 2\theta < 13^\circ$ );  $a = 10.191$  (5),  $b = 8.739$  (4),  $c = 10.682$  (4) Å,  $\beta = 95.38$  (6) $^\circ$ ,  $V = 947.1$  (7) Å<sup>3</sup>.  $0.997 \leq \sum(|F_o|/|F_o|_{\text{initial}})/5 \leq 1.001$ ;  $0.41 < A < 0.71$ ,  $R_{\text{int}} = 0.022$ .

(Ib). A crystal,  $0.6 \times 0.3 \times 0.3$  mm, was mounted on the diffractometer and irradiated with the Xe light. After 40 min the peak half-width became  $0.45^\circ$ . X-ray intensities were measured by  $\omega$ -scan mode with scan width  $4^\circ$  and scan speed  $6^\circ \text{min}^{-1}$ ;  $a = 10.187$  (3),  $b = 8.704$  (3),  $c = 10.727$  (3) Å,  $\beta = 95.43$  (3) $^\circ$ ,  $V = 946.9$  (5) Å<sup>3</sup>. 2824 reflections were measured ( $-14 \leq h \leq 14$ ,  $-12 \leq k \leq 12$ ,  $0 \leq l \leq 15$ ;  $4 < 2\theta \leq 60^\circ$ ) and 2415 reflections were observed.  $0.999 \leq \sum(|F_o|/|F_o|_{\text{initial}})/5 \leq 1.004$ ;  $0.49 < A < 0.60$ ,  $R_{\text{int}} = 0.018$ .

### Refinement

(Ia). Coordinates of the non-H atoms reported by Bortin (1968) were utilized as the initial parameters and refined by full-matrix least squares with anisotropic thermal parameters using the *XTAL* program system (Hall & Stewart, 1990). The Co–N(3) bond axis lies on a crystallographic twofold axis and the  $\text{NH}_3$  group exhibits rotational disorder with two possible orientations as shown in Fig. 1. Six of the nine H atoms were located by difference syntheses and the others were calculated. The function  $\sum w(|F_o| - |F_c|)^2$  was minimized with weight  $w^{-1} = \sigma(|F_o|)$ .  $R(F) = 0.028$ ,  $wR(F) = 0.036$ ,  $S = 4.54$  for 1263 reflections.  $\Delta/\sigma < 0.12$ , number of reflections/number of parameters ( $r/p$ ) = 1263/55,  $-0.63 < \Delta\rho < 0.65 \text{ e Å}^{-3}$ . Complex neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The calculations were performed on a MIPS RS3230 computer. Atomic coordinates are listed in Table 1, and selected bond lengths and bond angles in Table 2.

(Ib) and (Ic). The nitro moiety was removed from the structural model of (Ia) and parameters of the other non-H atoms were converged. Difference synthesis at this stage of the refinement showed a superposition of the electron densities of the nitro and nitrito coordinations of the  $\text{NO}_2^-$  ion. The difference syntheses in the nitro plane for (Ib) and (Ic) are compared in Fig. 3. A positive peak appeared for (Ib) on extension of the Co—N bond axis. The peak height increased from (Ib) to (Ic), indicative of the

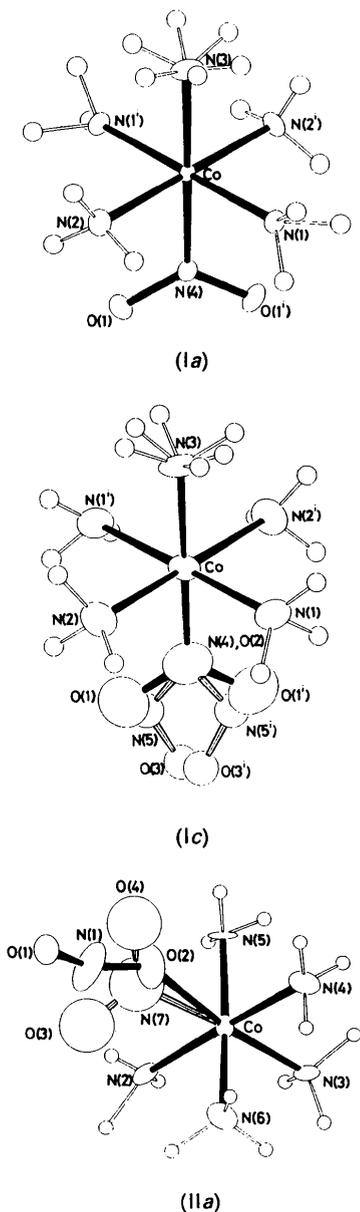


Fig. 1. ORTEP drawings (Johnson, 1965) of the complex cation  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+}$  with [(Ia) and (Ic)] 50% and (IIa) 30% probability ellipsoids. H atoms are represented by circles of radius 0.1 Å.

Table 1. Positional parameters, equivalent isotropic temperature factors and populations

$$U_{\text{eq}} = (1/3) \sum_i U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{\text{eq}}$ (Å <sup>2</sup> )	Population
(I) First row (Ia); second row (Ib); third row (Ic)					
Co	0	0.28867 (7)	½	0.0076 (1)	
	0	0.2872 (1)	½	0.0115 (2)	
	0	0.2855 (3)	½	0.0216 (7)	
N(1)	0.0252 (3)	0.2906 (3)	0.4337 (2)	0.0129 (7)	
	0.0227 (3)	0.2899 (5)	0.4346 (3)	0.017 (1)	
	0.0191 (7)	0.289 (1)	0.4363 (8)	0.028 (3)	
N(2)	0.1927 (3)	0.2923 (3)	0.2427 (3)	0.0158 (8)	
	0.1932 (3)	0.2901 (5)	0.2440 (4)	0.021 (1)	
	0.1937 (7)	0.288 (1)	0.2462 (8)	0.032 (3)	
N(3)	0	0.0591 (5)	½	0.020 (1)	
	0	0.0579 (6)	½	0.022 (2)	
	0	0.058 (1)	½	0.029 (4)	
Cl	0.20674 (7)	0.02015 (9)	0.01540 (7)	0.0134 (2)	
	0.2075 (1)	0.0192 (1)	0.0137 (1)	0.0180 (3)	
	0.2092 (2)	0.0175 (3)	0.0114 (3)	0.028 (1)	
N(4)	0	0.5102 (5)	½	0.011 (1)	1
	0	0.5080 (7)	½	0.021 (2)	0.911 (5)
	0	0.501 (2)	½	0.048 (6)	0.855 (8)
O(1)	0.0738 (2)	0.5812 (3)	0.1852 (2)	0.0179 (7)	1
	0.0753 (4)	0.5798 (4)	0.1851 (4)	0.027 (1)	0.911 (5)
	0.074 (1)	0.575 (2)	0.187 (1)	0.063 (4)	0.855 (8)
N(5)	—	—	—	—	0
	0.042 (7)	0.6077 (9)	0.199 (5)	0.06 (1)	0.911 (5)
	0.040 (7)	0.606 (9)	0.201 (8)	0.033 (8)	0.855 (8)
O(2)	—	—	—	—	0
	0	0.5080 (7)	½	0.06 (1)	0.089 (5)
	0	0.501 (2)	½	0.033 (8)	0.145 (8)
O(3)	—	—	—	—	0
	0.011 (7)	0.732 (1)	0.228 (6)	0.06 (1)	0.089 (5)
	0.00 (1)	0.729 (5)	0.233 (7)	0.033 (8)	0.145 (8)
(II) First row (IIa); second row (IIb)					
Co	½†	0.10887 (7)	0.1870 (1)	0.0229 (3)	
	½	0.1091 (1)	0.1844 (3)	0.0269 (5)	
Cl(1)	0.0031 (4)	0.3555 (3)	0.1628 (3)	0.0337 (9)	
	0.0018 (6)	0.3556 (3)	0.1591 (5)	0.043 (1)	
Cl(2)	0.5050 (4)	0.3576 (3)	0.1644 (3)	0.0338 (9)	
	0.5018 (5)	0.3556 (4)	0.1666 (5)	0.040 (1)	
N(2)	0.249 (1)	0.1999 (6)	-0.0372 (9)	0.048 (2)	
	0.252 (2)	0.2001 (9)	-0.038 (2)	0.051 (4)	
N(3)	0.249 (1)	0.2272 (5)	0.360 (1)	0.036 (2)	
	0.253 (2)	0.2222 (7)	0.365 (2)	0.040 (3)	
N(4)	0.258 (1)	0.0171 (5)	0.412 (1)	0.040 (2)	
	0.252 (2)	0.0163 (8)	0.407 (1)	0.040 (3)	
N(5)	0.0628 (9)	0.1112 (6)	0.180 (1)	0.030 (3)	
	0.061 (2)	0.112 (1)	0.187 (2)	0.049 (5)	
N(6)	0.437 (2)	0.1013 (8)	0.185 (2)	0.052 (4)	
	0.440 (1)	0.103 (1)	0.172 (2)	0.039 (4)	
O(1)	0.266 (2)	-0.1082 (4)	-0.1956 (9)	0.037 (3)	0.86 (2)
	0.253 (3)	-0.1078 (8)	-0.192 (2)	0.047 (4)	0.77 (2)
N(1)	0.235 (2)	-0.0312 (8)	-0.112 (2)	0.078 (6)	0.86 (2)
	0.273 (4)	-0.035 (2)	-0.107 (5)	0.16 (2)	0.77 (2)
O(2)	0.230 (2)	-0.013 (1)	0.036 (2)	0.071 (4)	0.86 (2)
	0.227 (4)	-0.011 (2)	0.024 (5)	0.087 (9)	0.77 (2)
N(7)	0.252	0.002	0.000	0.15 (3)	0.14 (2)
	0.251	0.002	0.000	0.07 (1)	0.23 (2)
O(3)	0.319	0.012	-0.125	0.15 (3)	0.14 (2)
	0.318 (5)	0.012 (4)	-0.126 (6)	0.07 (1)	0.23 (2)
O(4)	0.199	-0.074	0.016	0.15 (3)	0.14 (2)
	0.198 (5)	-0.073 (2)	0.016 (8)	0.07 (1)	0.23 (2)

† x coordinate of Co was fixed to define the origin.

terminal O atom of the nitrito coordination produced by the photochemical reaction. On the other hand, the electron density of the nitro coordination broadened from (Ia), (Ib) to (Ic) as a result of the loss of crystal periodicity, which is reflected in the significantly greater thermal parameters. The Co and nitro N(4) atoms lie on a crystallographic twofold axis (see Fig. 1). Consequently the nitrito coordination caused by the photoisomerization should have two possible orientations. Since the electron densities

Table 2. Selected bond lengths (Å) and bond angles (°)

	(Ia)	(Ib)	(Ic)
Co—N(1)	1.966 (2)	1.972 (3)	1.982 (9)
—N(2)	1.970 (3)	1.975 (3)	1.978 (7)
—N(3)	1.995 (4)	1.996 (5)	1.988 (9)
—N(4)	1.926 (4)	1.922 (6)	1.883 (18)
—O(2)	—	1.922 (6)	1.883 (18)
N(4)—O(1)	1.237 (3)	1.251 (5)	1.239 (16)
N(5)—O(2)	—	1.13 (4)	1.15 (8)
—O(3)	—	1.18 (4)	1.21 (10)
Co—N(4)—O(1)	119.9 (2)	120.0 (4)	121.5 (11)
O(1)—N(4)—O(1')	120.1 (4)	120.1 (6)	117.1 (16)
Co—O(2)—N(5)	—	140 (2)	143 (4)
O(2)—N(5)—O(3)	—	117 (6)	116 (7)

Symmetry code: (i)  $-x, y, -z + \frac{1}{2}$ .

	(IIa)	(IIb)
Co—N(2)	1.954 (7)	1.946 (13)
—N(3)	1.965 (7)	1.950 (11)
—N(4)	1.966 (7)	1.962 (9)
—N(5)	1.938 (9)	1.962 (21)
—N(6)	1.938 (21)	1.975 (10)
—O(2)	1.928 (14)	1.957 (30)
—N(7)	1.910	1.906
N(1)—O(1)	1.21 (1)	1.15
—O(2)	1.05 (2)	1.06 (5)
N(7)—O(3)	1.11	1.11
—O(4)	1.15	1.15
Co—O(2)—N(1)	135 (1)	132 (3)
O(2)—N(1)—O(1)	132 (1)	127 (4)
Co—N(7)—O(3)	116	115
Co—N(7)—O(4)	125	126
O(3)—N(7)—O(4)	118	119

of the atoms coordinated to the Co did not split, the positions of the nitro N(4) and nitrito O(2) atoms were constrained to be the same. The terminal nitrito O(3) atom was not restricted on the twofold axis, because the single peak which appeared on the twofold axis seemed to be the result of superposition of the densities related by the crystallographic twofold axis. No other significant electron density of the nitrite ion existed. The nitrito N(5) atom was expected to be hidden behind the electron density of the nitro O(1) atom. The minor nitrito group was refined with a common isotropic thermal parameter and with a weak constraint to keep the geometry reasonable. The major nitro group was refined with anisotropic thermal parameters. H atoms were included in the refinement. The occupancy of the nitrito coordination of (Ib) was estimated to be 8.9 (5)%,  $R = 0.042$ ,  $wR = 0.036$ ,  $S = 7.09$  for 1216 reflections,  $\Delta/\sigma < 0.32$ ,  $r/p = 1216/62$ ,  $-0.56 < \Delta\rho < 0.80 \text{ e } \text{Å}^{-3}$ . The nitrito occupancy of (Ic) was 14.5 (8)%,  $R = 0.062$ ,  $wR = 0.052$ ,  $S = 8.24$  for 730 reflections,  $\Delta/\sigma < 0.46$ ,  $r/p = 730/62$ ,  $-1.18 < \Delta\rho < 1.38 \text{ e } \text{Å}^{-3}$ .

(IIa) and (IIb). The reflection data measured by Grenthe & Nordin (1979b) were used. A freshly synthesized crystal, (IIa), orthorhombic,  $P2_1nb$  (cab setting of  $Pna2_1$ ),  $a = 10.349$  (2),  $b = 13.228$  (3),  $c = 6.864$  (2) Å,  $V = 939.7$  (6) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.85 \text{ Mg m}^{-3}$ ,  $F(000) = 536$ ,  $T = 245 \text{ K}$ . A crystal aged for 15 days at 283 K, (IIb),  $a = 10.376$  (1),  $b = 13.355$  (2),  $c = 6.8307$  (7) Å,  $V = 946.5$  (4) Å<sup>3</sup>,  $T =$

245 K. Although Grenthe & Nordin (1979b) recognized the disorder due to the linkage isomerization of  $\text{NO}_2^-$ , only the nitrito coordination was tentatively included and the nitro coordination was not introduced in the refinement. Therefore, the disorder was analyzed in the present study. From the atom list reported by Grenthe & Nordin (1979b), the nitrite moiety was omitted and other non-H atoms were refined with anisotropic thermal parameters. A difference synthesis of (IIb) after this refinement showed two small peaks, 1.91 Å distant from each other, which appeared to be attributable to the nitro oxygen atoms. They were therefore labelled O(3) and O(4), since the O...O distance in  $[\text{Co}(\text{NO}_2)_6]^{3-}$  is 2.088 (2) Å (Ohba, Toriumi, Sato & Saito, 1978). The position of the corresponding nitro N(7) atom was assumed to be on the line connecting the Co and the midpoint between the O(3) and O(4) atoms. The nitro N(7) and nitrito O(2) atoms were separated by 0.35 Å. The coordinates of the O(2) atom could not be refined correctly by fixing the N(7) position. Therefore, the coordinates of the N(7) and O(2) atoms were fixed at the initial values. The major nitrito group was refined anisotropically and H atoms were included in the refinement. The minor nitro group was refined with a common isotropic thermal parameter and a weak constraint of the geometry for (IIb). Positions of the O(3) and O(4) atoms were fixed in the refinement of (IIa). The occupancy of the nitro coordination in (IIa) was estimated to be 14 (2)%,  $R = 0.044$ ,  $wR = 0.075$ ,  $S = 0.28$  for 915 reflections,  $\Delta/\sigma < 0.26$ ,  $r/p = 915/101$ ,  $-0.64 < \Delta\rho < 0.73 \text{ e } \text{Å}^{-3}$ . The nitro occupancy in (IIb) was 23 (2)%,  $R = 0.068$ ,  $wR = 0.116$ ,  $S = 0.42$  for 867 reflections,  $\Delta/\sigma < 0.29$ ,  $r/p = 867/107$ ,  $-1.27 < \Delta\rho < 1.09 \text{ e } \text{Å}^{-3}$ .\* The polar direction of the crystal was checked: when the sign of  $\Delta f''$  was inverted,  $R$  values increased by 0.004.

## Discussion

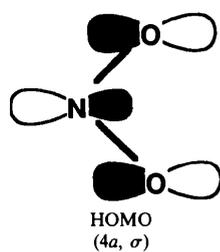
### Nitro → nitrito photoisomerization

The structures of the complex cation are shown in Fig. 1 with the atom-numbering schemes. The reaction cavity (see Appendix) of  $\text{NO}_2^-$  in (I) is shown in Fig. 2(a). The isomerization takes place nearly in the nitro plane and the nitrito group is accommodated in the cavity. Populations of the nitrito coordination after irradiation for 40 and 150 min were estimated to be 8.9 (5) and 14.5 (8)%, respectively. However,

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55116 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS0597]

the photochemical reaction was 88% complete in 150 min for the powder specimen distributed in a KBr disk and monitored by IR spectroscopy (Heyns & De Waal, 1989). In (Ic) (Fig. 3), the electron density of the nitrito coordination is apparently lower than that of the initial nitro coordination. When a needle-shaped crystal 10–20  $\mu\text{m}$  in thickness is irradiated with UV light, the crystal turns towards the light source (Boldyreva *et al.*, 1984). These facts indicate that photoisomerization occurs only near the surface of the crystal. The possibility of the occurrence of a metastable state with seven coordination, *i.e.* N—O attachment of  $\text{NO}_2^-$  to the Co atom, was claimed from low-temperature photolysis experiments (Johnson & Pashmann, 1975). However, it is difficult to detect the metastable state in electron density maps, because the population must be low and the electron density will be hidden behind that of the initial nitro coordination.

In the solid state, UV light causes the nitro–nitrito linkage isomerization and minor oxidation–reduction decomposition to occur simultaneously. The precursor to the photoreactions is expected to be an  $\text{NO}_2^- \rightarrow \text{Co}^{3+}$  charge-transfer state (Balzani, Ballardini, Sabbatini & Moggi, 1968). The Co—N coordination bond may be weakened by depopulation of the HOMO of the nitrite ion (see the scheme below). A driving force of the linkage isomerization seems to be the electrostatic attraction between the Co and O atoms, because the negative charge of  $\text{NO}_2^-$  is located almost totally on the O atoms (Kikkawa, Ohba, Saito, Kamata & Iwata, 1987; Okuda, Ohba, Saito, Ito & Shibuya, 1990).



#### Nitrito $\rightarrow$ nitro thermal isomerization

The reaction cavity of the nitrito group in (II) is shown in Fig. 2(b). The nitro plane is inclined by *ca* 60° to the original plane after the isomerization. The torsion angle O(3)—N(7)—Co—N(2) is nearly 45° as expected from the work of Grenthe & Nordin (1979b). Although they did not assign the nitro group in difference syntheses, they predicted, based on the van der Waals contact distances, that the isomerization cannot take place in the original plane. The population of the nitro coordination is already 14 (2)% for a freshly prepared crystal. The occupation factors of the nitro coordination after aging at

283 K for 15 days were estimated to be 23 (2)%. However, the reaction is expected to be 50% complete based on the observed half-life (Adell, 1952). The underestimation of the nitro population in this work may be partly due to rotational disorder of the nitro group.

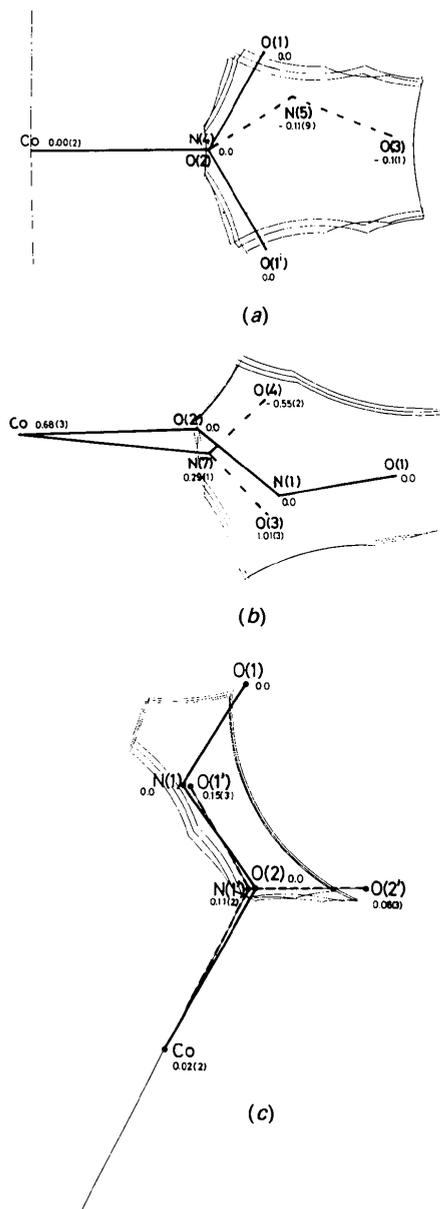


Fig. 2. Section of the reaction cavity of the  $\text{NO}_2^-$  group in the original nitrite plane and those of the parallel planes shifted by  $\pm 0.1$  Å in (a) (I), (b) (II) and (c)  $[\text{Co}(\text{en})_2(\text{NCS})\text{ONO}]\text{ClO}_4$ . The orientation of the  $\text{NO}_2^-$  after the linkage isomerization is also drawn with broken lines, and distances from the original plane are indicated by numbers near the atom labels. One of the two possible positions of the nitrito group in (I) is omitted for clarity.

Spontaneous nitrito–nitro isomerization also occurs in crystals of  $[\text{Co}(\text{en})_2(\text{NCS})\text{ONO}]X$  [(III)  $X = \text{ClO}_4^-$  or  $\text{I}^-$  (Grenthe & Nordin, 1979a)]. The reaction cavity of  $\text{NO}_2^-$  in the perchlorate salt is shown in Fig. 2(c). Terminal O atoms of  $\text{NO}_2^-$  in (III) are connected to the N atoms of en ligands by intermolecular hydrogen bonds. No hydrogen bond involving the nitrite ion in (I) and (II) exists. Linkage isomerization of (III) takes place in the original nitrite plane in contrast to that of (II). It is expected that the  $\text{NO}_2^-$  group rotates in the original plane if no steric hindrance exists.

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### APPENDIX

The space around the reacting group in the crystal is called the reaction cavity (Ohashi, Yanagi, Kurihara,

Sasada & Ohgo, 1981). The reaction cavity of the  $\text{NO}_2^-$  group is defined in this paper as the concave space limited by the envelope surfaces of spheres placed at the positions of neighboring atoms, each sphere having a radius 1.0 Å greater than the corresponding van der Waals radius,  $r_w$ . In calculating the reaction cavity for the cyanoethyl group of cobaloxime complexes, the  $r_w$  of H (1.2 Å) is selected as the incremental radius,  $\Delta r$  (Ohashi *et al.*, 1981). However, the reaction cavity for the nitrite anion is apparently underestimated if the  $r_w$ 's of N and O atoms, 1.5–1.6 Å (Bondi, 1964), are used as  $\Delta r$ . Therefore, the  $\Delta r$  for  $\text{NO}_2^-$  was empirically determined to be 1.0 Å. At any rate, the nitro group must be accommodated in the cavity in a crude approximation which takes no account of electrostatic interactions like hydrogen bonds. Positions of the H atoms are idealized for this calculation.

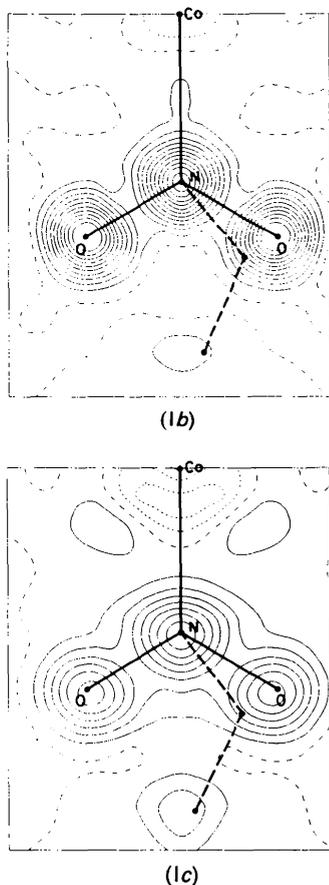


Fig. 3. The difference syntheses in the nitro coordination plane for (1b) and (1c). Contour intervals at  $0.1 \text{ e } \text{Å}^{-3}$ . One of the two possible positions of the nitro group is omitted for clarity.

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