

Distortion of Crystal Structures of Some Co^{III} Ammine Complexes. II. Distortion of Crystal Structures of [Co(NH₃)₅NO₂]X₂ (X=Cl, Br) on Cooling

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Abstract

For two solid complexes, [Co(NH₃)₅NO₂]X₂ (X = Cl⁻, Br⁻), pentaamminenitrocobalt(III) dichloride/dibromide, the anisotropy of structural distortion on cooling the samples from 290 to 150 K was studied by variable-temperature single-crystal X-ray diffraction. The changes in lattice parameters were used to calculate the strain tensors and to scan linear strain in various crystallographic directions. The changes in different intra- and intermolecular distances in the structure were followed. Lattice strain on cooling was compared with lattice strain in the same structures under high hydrostatic pressure and with structural distortion in the course of homogeneous nitro–nitrito linkage isomerization. The effect of isomorphous substitution (Br⁻ for Cl⁻) with respect to structural strain was discussed. Structural strain in the monoclinic chloride and bromide was compared also with the previously obtained data [Boldyreva, Kivikoski & Howard (1997). *Acta Cryst.* B53, 394–404] on strain in the orthorhombic structure of another compound of the same Co^{III} nitropentaamine series, [Co(NH₃)₅NO₂]Cl(NO₃).

1. Introduction

Comparative studies of structural strain induced in the crystals of a series of Co^{III} nitropentaamine complexes by various actions are interesting, first with respect to understanding the interrelation between the solid-state reactivity of these compounds and the stresses and strains in their crystals (Boldyreva, Kivikoski & Howard, 1997a). Homogeneous linkage nitro→nitrito isomerization was shown, on one hand, to induce large anisotropic strain in the crystals (Boldyreva, Virovets, Burleva, Dulepov & Podberezhskaya, 1993) and, on the other hand, to be sensitive to compression of the crystals by some external loading (Boldyreva & Sidel'nikov, 1987; Boldyreva, 1994). In order to better understand which of the interactions in the crystals are mostly responsible for the observed anisotropy of strain, it is helpful to compare strain resulting from

different actions, in particular, from different *scalar* actions, such as cooling and increasing pressure (Boldyreva *et al.*, 1997a).

In our previous contribution (Boldyreva *et al.*, 1997a), we have considered in detail structural strain induced by cooling of the orthorhombic crystals of [Co(NH₃)₅NO₂]Cl(NO₃). In accordance with Neumann's principle (Nye, 1994), the orientation of the principal axes of strain tensors in orthorhombic crystals must coincide with the directions of crystallographic axes. Therefore, the differences in the anisotropy of contraction of the crystals of [Co(NH₃)₅NO₂]Cl(NO₃) resulting from different actions were limited by the different ratios of linear strain along the same principal directions.

The aim of the present contribution was to study structural distortion induced by a decrease in temperature in two other Co^{III} complexes of the same nitropentaamine series, namely in the chloride and the bromide. These two compounds crystallize as monoclinic structures (Börtin, 1968; Cotton & Edwards, 1968; Kubota & Ohba, 1992). Therefore, there are no restrictions imposed by Neumann's principle on the directions of two of the principal axes of the strain tensor. We aimed to compare the structural distortion of these two monoclinic complexes on cooling with the distortions of the same structures induced by hydrostatic pressure (another isotropic influence) and in the course of nitro–nitrito linkage isomerization (an anisotropic influence).^{*} We also aimed to compare these results with those reported previously for [Co(NH₃)₅NO₂]Cl(NO₃) (Boldyreva *et al.*, 1997a).

2. Experimental

X-ray diffraction data were collected on a Rigaku AFC6-S four-circle diffractometer with a Cryostream (Oxford Cryosystems) open-flow N₂ gas cryostat

^{*}The data on the lattice strain induced by hydrostatic pressure were taken from a powder X-ray diffraction study (Boldyreva, Ahsbahs & Uchtmann, 1994). The data on the lattice strain resulting from linkage isomerization were taken from powder X-ray diffraction studies (Boldyreva *et al.*, 1993; Masciocchi, Kolyshv, Dulepov, Boldyreva & Sironi, 1994).

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(Cosier & Glazer, 1986). The variable-temperature X-ray diffraction experiments were carried out in exactly the same way as described previously for [Co(NH₃)₅NO₂]Cl(NO₃) (Boldyreva *et al.*, 1997a).

Details on crystal growth, data collection, data reduction, data refinement, as well as the crystal data and the data on the refined structures of both compounds at two temperatures were reported elsewhere (Boldyreva, Kivikoski & Howard, 1997b).

The same software as described in the previous publication (Boldyreva *et al.*, 1997a) was used.

3. Results and discussion

The changes in lattice parameters and unit-cell volumes of [Co(NH₃)₅NO₂]Cl₂ and [Co(NH₃)₅NO₂]Br₂ with temperature are plotted in Fig. 1. Relative changes in the unit-cell volumes were comparable with those measured for [Co(NH₃)₅NO₂]Cl(NO₃) (Boldyreva *et al.*, 1997a), the chloride–nitrate being contracted slightly more with decreasing temperature than bromide and chloride. The molar volumes decreased linearly with decreasing temperature. The values of mean volume coefficients of thermal expansion from 150 to 290 K were equal to $87 \times 10^{-6} \text{ deg}^{-1}$ for chloride and $99 \times 10^{-6} \text{ deg}^{-1}$ for bromide.

For both complexes, lattice strain on cooling from 290 to 150 K was clearly anisotropic. Since the structures are monoclinic, it would not be possible to analyse properly the anisotropy of strain without calculating the strain tensor. The linear strain in the directions of principal axes of strain tensors (*a*) on cooling, (*b*) when increasing pressure and (*c*) in the course of homogeneous linkage nitro→nitrito isomerization is plotted in Fig. 2. Despite the overall decrease in molar volume in all cases, lattice expansion in particular directions was measured for most types of contractions. In [Co(NH₃)₅NO₂]Cl₂, directions of expansion were observed for all three structural contractions (on cooling, with increasing pressure, and during isomerization). In [Co(NH₃)₅NO₂]Br₂, no directions of expansion were observed for structural contraction on cooling (in contrast to the case of the chloride), but, as in the chloride, there were directions of expansion during lattice contraction under pressure and in the course of linkage isomerization.

Fig. 3 shows the orientation of the principal axes of strain tensors with respect to crystallographic axes in the (*a*) chloride and (*b*) bromide. Although the chloride and bromide are isostructural, not only the values of lattice strain along the principal axes of strain tensors in these two complexes were different, but also the orientation of the principal axes with respect to the crystallographic axes. For example, the structure of the chloride expanded in the *b* direction on cooling, whilst the same *b* direction in the structure of the bromide coincided with the direction of axis 2 (medium

compression). At the same time, directions of maximum compression on cooling, as well as the relative lattice strain in these directions, were close (although not identical) in the chloride and bromide. For the series [Co(NH₃)₅NO₂]Cl₂, [Co(NH₃)₅NO₂]Br₂ and [Co(NH₃)₅NO₂]Cl(NO₃), the maximum cooling-induced linear strain (−1.30%) was observed in the structure of the chloride, although the overall volume contraction for this structure was the smallest. The anisotropy of lattice strain on cooling was different both from that induced by hydrostatic pressure and from lattice strain resulting from homogeneous nitro→nitrito isomerization. The relative linear strains along the principal axes of strain tensors, as well as the orientation of the

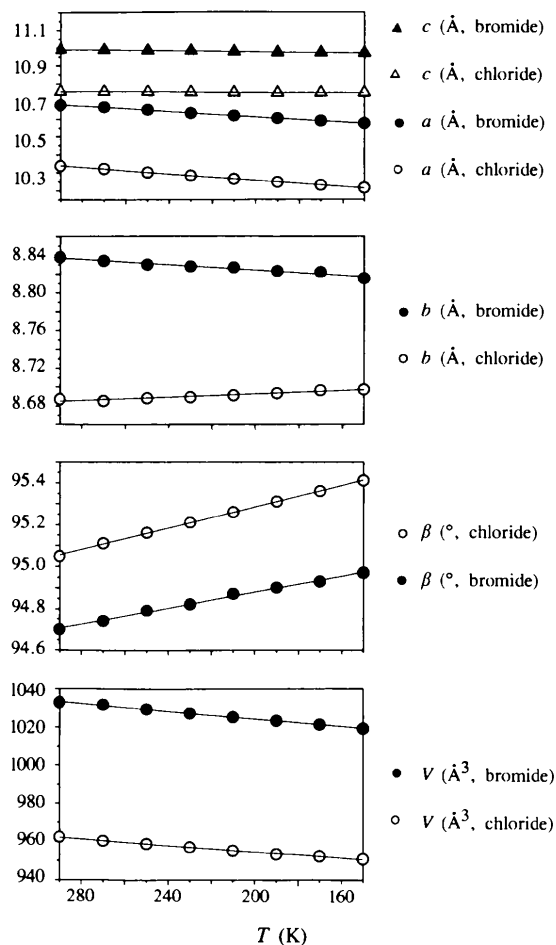


Fig. 1. Changes in lattice parameters and cell volume with decreasing temperature for [Co(NH₃)₅NO₂]Cl₂ and [Co(NH₃)₅NO₂]Br₂: (*a*) *a* (Å) and *c* (Å); (*b*) *b* (Å); (*c*) β (°); (*d*) V (Å³). Approximating linear relationships: [Co(NH₃)₅NO₂]Cl₂: $a = 10.080 + 8.9286 \times 10^{-4}T$ ($R^2 = 0.999$); $b = 8.7093 - 8.4524 \times 10^{-5}T$ ($R^2 = 0.927$); $c = 10.739 + 5.5952 \times 10^{-5}T$ ($R^2 = 0.974$); $\beta = 95.793 - 2.5417 \times 10^{-3}T$ ($R^2 = 0.999$); $V = 938.0 + 0.082T$ ($R^2 = 1.0$). [Co(NH₃)₅NO₂]Br₂: $a = 10.462 + 7.5417 \times 10^{-4}T$ ($R^2 = 1.000$); $b = 8.7953 + 1.4464 \times 10^{-4}T$ ($R^2 = 0.963$); $c = 10.947 + 1.4583 \times 10^{-4}T$ ($R^2 = 0.993$); $\beta = 95.262 - 1.9167 \times 10^{-3}T$ ($R^2 = 0.995$); $V = 1003.83 + 0.102T$ ($R^2 = 1.0$).

principal axes themselves with respect to the crystallographic axes, were different.

Anisotropic structural distortion resulting from isomorphous substitution of some atoms in the structure by larger (or smaller) ones has been described in a number of publications by the 'tensor of compositional deformation' (Chanh, Clastre, Gaultier, Haget & Meresse, 1988); Hazen & Finger, 1982; Zotov & Petrov, 1991). Calculation of the tensor of compositional deformation was suggested as a method of identifying the directions of the strongest and weakest modifications of the intermolecular interactions due to the substitution process (Chanh *et al.*, 1988; Zotov &

Petrov, 1991). Homogeneous solid-state linkage nitro→nitrito isomerization can also be considered as a substitution of $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+}$ for $[\text{Co}(\text{NH}_3)_5\text{ONO}]^{2+}$, with a decrease in the overall molar volume. For the chloride-nitrate (Boldyreva *et al.*, 1997a), as well as for the chloride and bromide (the present study), the anisotropy of structural strain resulting from this 'substitution' is very different from those measured for cooling or pressure-induced contraction of the same structures. This can be explained mainly by a large difference in the shapes and electronic structures of complex cations with the N (nitro) and O (nitrito) coordinated NO_2 ligand and, consequently, by very

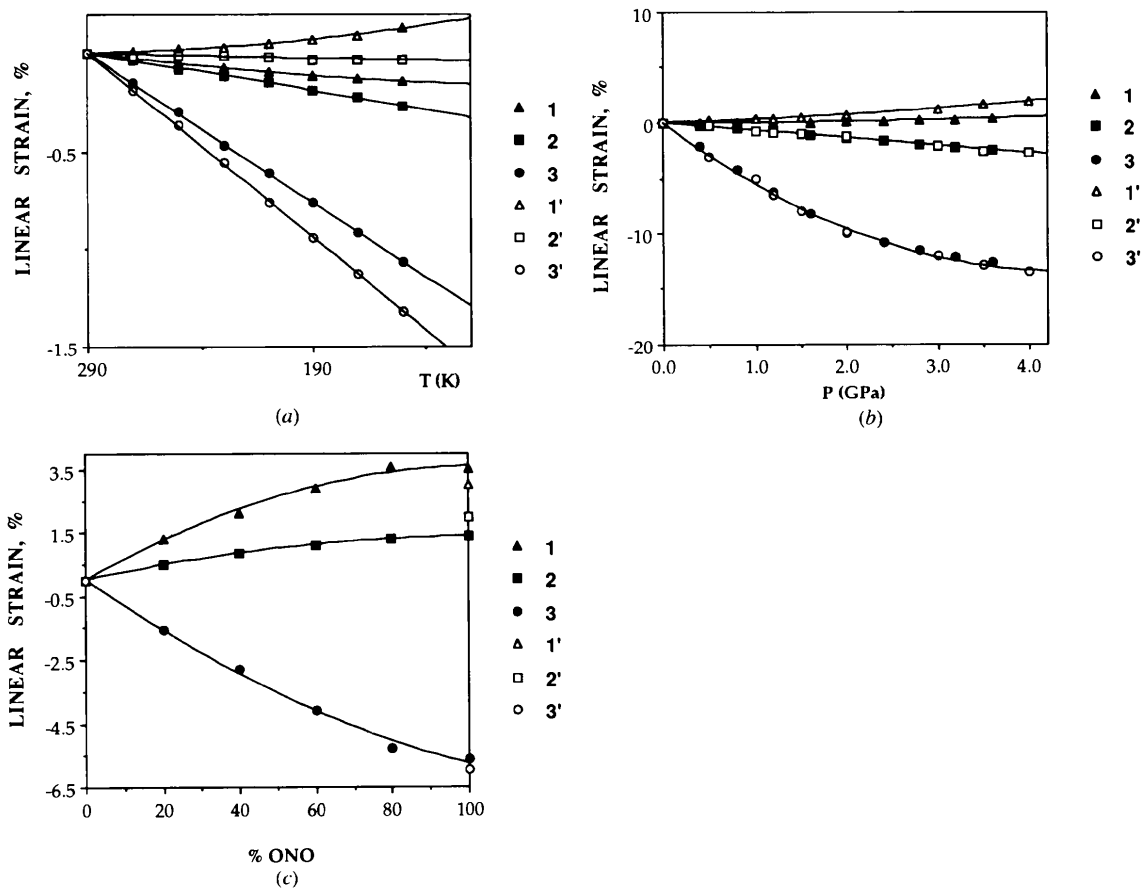


Fig. 2. Linear strain (%) in the directions of three principal axes of strain tensors for $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ (axes 1', 2' and 3') and $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Br}_2$ (axes 1, 2 and 3); compression of the structure resulting from: (a) a decrease in temperature from 290 to 150 K; (b) an increase in pressure from ambient to 4.0 GPa; (c) nitro→nitrito linkage isomerization. Here, and also in Fig. 3, in accordance with the generally accepted system of notation (Nye, 1994), 1, 2 and 3 are the principal axes, along which the strain *ellipsoid* (not to be confused with a strain *quadratic*!) has maximum, medium and minimum linear dimensions. $\Delta l_i/l_i$ = linear strain in the direction of the principal axis i ($i = 1, 2, 3$). Approximating relationships: (a) Temperature-induced strain. $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$: $\Delta l_1/l_1(\Delta b/b) = 0.48 - 0.003T + 5.06 \times 10^{-6}T^2$ ($R^2 = 0.995$), $\Delta l_2/l_2 = -0.067 + 0.00023T$ ($R^2 = 0.902$), $\Delta l_3/l_3 = -2.739 + 0.00945T$ ($R^2 = 1.000$). $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Br}_2$: $\Delta l_1/l_1 = -0.17 - 2.607 \times 10^{-4}T + 2.9 \times 10^{-6}T^2$ ($R^2 = 0.997$), $\Delta l_2/l_2(\Delta b/b) = -0.59 + 0.0023T$ ($R^2 = 0.999$), $\Delta l_3/l_3 = -2.23 + 0.008T$ ($R^2 = 1.000$). (b) Pressure-induced strain. $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$: $\Delta l_1/l_1 = 0.22P + 0.07P^2$ ($R^2 = 0.997$), $\Delta l_2/l_2 = -0.63P - 0.013P^2$ ($R^2 = 0.997$), $\Delta l_3/l_3(\Delta b/b) = -6.5P + 0.78P^2$ ($R^2 = 0.996$). $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Br}_2$: $\Delta l_1/l_1 = -0.02P + 0.036P^2$ ($R^2 = 0.978$), $\Delta l_2/l_2 = -0.63P - 0.013P^2$ ($R^2 = 0.997$), $\Delta l_3/l_3(\Delta b/b) = -6.5P + 0.78P^2$ ($R^2 = 0.996$). (c) Strain induced by nitro-nitrito isomerization. $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$: Only extremes (100% NO_2 isomer and 100% ONO isomer) were studied and are shown on the plot. $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Br}_2$: $\Delta l_1/l_1 = 0.069(\% \text{ONO}) - 3.31 \times 10^{-4}(\% \text{ONO})^2$ ($R^2 = 0.994$), $\Delta l_2/l_2(\Delta b/b) = 0.025(\% \text{ONO}) - 1.16 \times 10^{-4}(\% \text{ONO})^2$ ($R^2 = 0.999$), $\Delta l_3/l_3 = -0.086(\% \text{ONO}) + 2.84 \times 10^{-4}(\% \text{ONO})^2$ ($R^2 = 0.996$).

large changes in the interactions of a complex cation with the crystalline environment resulting from the linkage isomerization. In this respect, it is interesting to compare the structures of $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Br}_2$. The structure of the chloride can be considered as a 'contracted structure of the bromide', in which the Br^- ions are substituted by smaller and less polarizable Cl^- ions. One can notice the qualitative similarity of the anisotropy of distortion of the structure of $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Br}_2$ on cooling and resulting from substitution of Br^- for Cl^- .

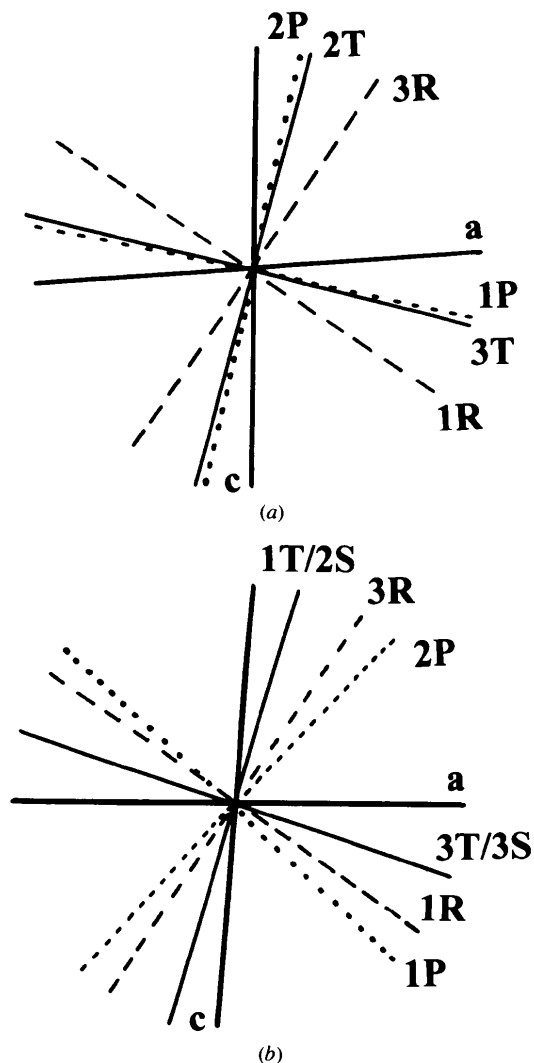


Fig. 3. Orientation of the principal axes of strain tensors with respect to crystallographic axes in the (a) chloride and (b) bromide. Strain induced by a decrease in temperature from 290 to 150 K (1T, 2T, 3T), by hydrostatic pressure 2 GPa (1P, 2P, 3P), by linkage nitro→nitrito isomerization (1R, 2R, 3R) or by isomorphous substitution of Br^- for Cl^- (1S, 2S, 3S). All the axes shown are in the crystallographic plane (ac). The remaining axis is perpendicular to this plane (parallel to the crystallographic axis b).

Similarly, as has been carried out for $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}(\text{NO}_3)$ in our previous contribution (Boldyreva *et al.*, 1997a), we have also calculated linear strain in the directions collinear with vectors linking different

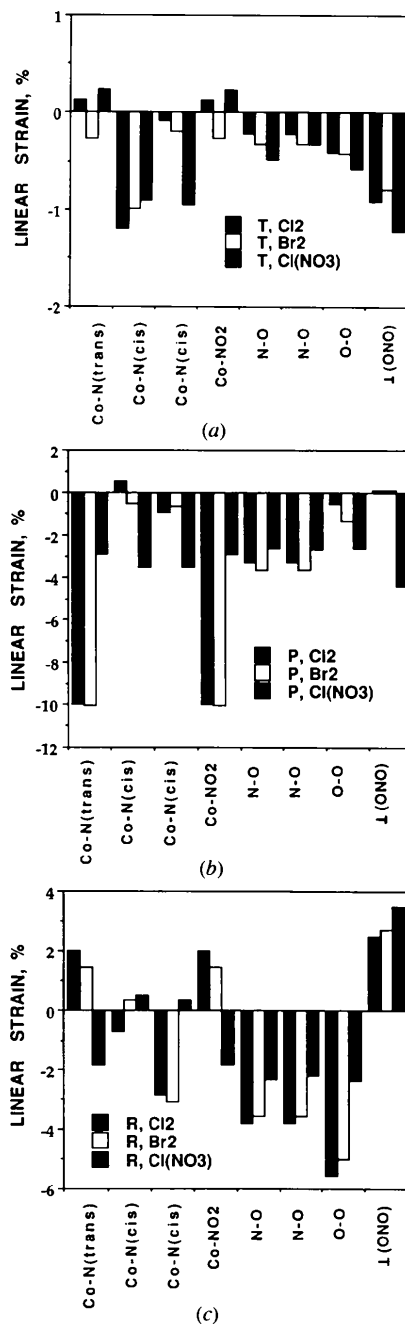


Fig. 4. Linear strain in the directions collinear with vectors linking different atoms in complex cations in the structures of the three Co^{III} nitroamine complexes, $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$, $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Br}_2$ and $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}(\text{NO}_3)$. (a) Lattice distortion induced by a decrease in temperature from 290 to 150 K (T); (b) lattice strain at hydrostatic pressure 2 GPa (P); (c) lattice strain resulting from nitro→nitrito linkage isomerization (R).

Table 1. Selected intramolecular distances (Å) and angles (°) in $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{X}_2$ ($\text{X}=\text{Cl}, \text{Br}$) at 290 and 150 K

	$[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$		$[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Br}_2$	
	290 K	150 K	290 K	150 K
Co(1)—N(1) (<i>trans</i> - NH_3)	1.989 (2)	1.985 (2)	1.990 (4)	1.990 (3)
Co(1)—N(2) (<i>cis</i> - NH_3)	1.959 (1)	1.960 (1)	1.966 (2)	1.960 (2)
Co(1)—N(3) (<i>cis</i> - NH_3)	1.957 (1)	1.959 (1)	1.967 (2)	1.966 (2)
Co(1)—N(4) (NO_2 ligand)	1.925 (2)	1.919 (2)	1.930 (3)	1.925 (3)
N(4)—O(1)	1.231 (1)	1.238 (1)	1.231 (3)	1.240 (2)
Co(1)—N(4)—O(1)	120.15 (9)	120.08 (8)	119.8 (2)	120.0 (2)
O(1)—N(4)—O(1A)	119.7 (2)	119.8 (2)	120.4 (3)	120.1 (3)

atoms in complex cations $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+}$. This allowed us, in particular, to compare the anisotropy of strain in the chloride–nitrate with that in the chloride and bromide in the same ‘reference system’, despite the different space-group symmetries of these structures. The results of this comparison for different types of structural contraction are plotted in Fig. 4.

In the chloride and bromide, the directions of maximum contraction on cooling were close to the directions of ‘Co—*cis*- NH_3 ’ bonds and with the direction perpendicular to the plane of the ONO group. This is similar to that observed previously for cooling-induced strain in the chloride–nitrate (Boldyreva *et al.*, 1997a). The slightly expanding direction in the chloride was collinear with the direction ‘*trans*- NH_3 —Co— NO_2 ’. This is also similar to the result previously observed for the chloride–nitrate (Boldyreva *et al.*, 1997a).

The orientation of complex cations with respect to the directions of contraction and the directions of expansion in the structures was different for different methods of decreasing the molar volume (low temperature, high pressure, homogeneous linkage isomerization). For example, for both the chloride and the bromide, the direction of major compression under pressure was different from that on cooling and was close to the direction of ‘Co—*trans*- NH_3 ’ and ‘Co— NO_2 ’ bonds. The same structures *expanded* in these directions and contracted mainly in the direction linking the two oxygens of the NO_2 ligand as a result of the isomerization. The direction perpendicular to the ONO plane was close to the direction of maximum contraction on cooling and to the direction of maximum expansion during linkage isomerization in all three complexes. The direction of maximum contraction under pressure in the chloride–nitrate was the same, whilst it slightly *expanded* under pressure in the chloride and bromide. Lattice strain induced by the same action was *qualitatively* similar, even for the structures with different space-group symmetry. At the same time, it was *quantitatively* different for all three complexes, even for the isostructural chloride and bromide.

The differences in intramolecular bond distances and angles in chloride and bromide on cooling were within experimental error (Table 1), similar to those

previously observed for cooling-induced strain in the chloride–nitrate (Boldyreva *et al.*, 1997a). Therefore, the observed large lattice strain is attributed to the changes in the contact distances between the atoms of complex cations and their nearest neighbours in the structure.

The nearest environment of a complex cation in the structures of $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Br}_2$ is shown in Fig. 5. Symmetry codes for generating the atoms of the environment are given in Table 2 and the values of contact distances (at 290 K and ambient pressure) are summarized in Table 3.

Despite the different space-group symmetries of the crystal structures, the nearest environment of the complex cations in the structures of the three Co^{III} nitroammine complexes $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$, $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Br}_2$ and $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}(\text{NO}_3)$ turned

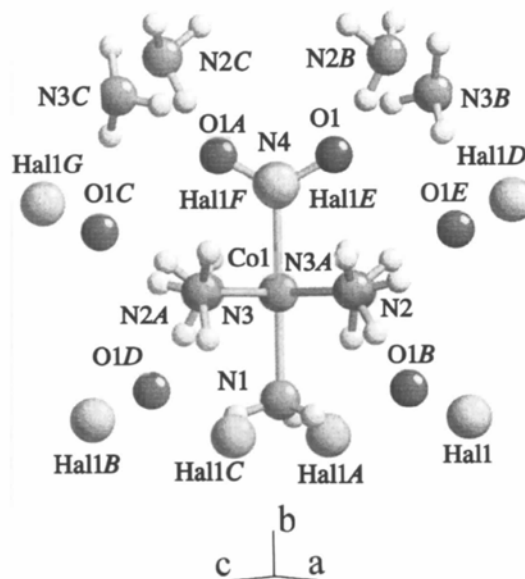


Fig. 5. The nearest environment of the complex cations in the structures of $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Br}_2$. Projections on the plane of the NO_2 group are shown. Symmetry codes for the generation of symmetry-equivalent atoms and the distances of atoms from the projection plane are given in Table 2. The contact distances in the structures at 290 K and ambient pressure are summarized in Table 3. N(1) = nitrogen of *trans*- NH_3 , N(2) and N(3) = nitrogens of *cis*- NH_3 , and N(4) = nitrogen of NO_2 ligand.

Table 2. Symmetry codes of atoms and the distances of atoms of a complex cation and its nearest environment from the projection plane in Fig. 5 at 290 K and ambient pressure

Atom	Symmetry code	Distance (Å)	
		Chloride	Bromide
Atoms in the environment			
Nitrogens of <i>cis</i> -NH ₃			
N(2B)	$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$	2.083 (2)	2.170 (2)
N(3B)	$x, 1 - y, z - \frac{1}{2}$	-2.294 (2)	-2.415 (2)
N(2C)	$x - \frac{1}{2}, \frac{1}{2} + y, z$	-2.084 (2)	-2.170 (2)
N(3C)	$-x, 1 - y, 1 - z$	2.294 (2)	2.415 (2)
Oxygens of NO ₂ ligand			
O(1B)	$\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$	3.317 (2)	3.429 (2)
O(1C)	$x, 1 - y, \frac{1}{2} + z$	3.805 (2)	3.910 (2)
O(1D)	$x - \frac{1}{2}, y - \frac{1}{2}, z$	-3.317 (2)	-3.429 (2)
O(1E)	$-x, 1 - y, -z$	-3.805 (2)	-3.910 (2)
Halide anions			
Hal(1)	x, y, z	-0.422 (1)	-0.450 (1)
Hal(1A)	$-x, -y, -z$	-3.383 (1)	-3.460 (1)
Hal(1B)	$-x, y, \frac{1}{2} - z$	0.422 (1)	0.450 (1)
Hal(1C)	$x, -y, \frac{1}{2} + z$	3.383 (1)	3.460 (1)
Hal(1D)	$\frac{1}{2} - x, \frac{1}{2} - y, -z$	-0.066 (1)	-0.031 (1)
Hal(1E)	$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$	3.739 (1)	3.878 (1)
Hal(1F)	$x - \frac{1}{2}, \frac{1}{2} + y, z$	-3.739 (1)	-3.878 (1)
Hal(1G)	$x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$	0.066 (1)	0.031 (1)
Atoms of a complex cation			
Nitrogens of <i>cis</i> -NH ₃			
N(2)	x, y, z	1.234 (2)	1.258 (2)
N(3)	x, y, z	1.511 (2)	1.494 (2)
N(2A)	$-x, y, \frac{1}{2} - z$	-1.234 (2)	-1.258 (2)
N(3A)	$-x, y, \frac{1}{2} - z$	-1.511 (2)	-1.494 (2)
Nitrogen of <i>trans</i> -NH ₃			
N(1)	x, y, z	0.0	0.0
Nitrogen of NO ₂ ligand			
N(4)	x, y, z	0.0	0.0
Oxygens of NO ₂ ligand			
O(1)	x, y, z	0.0	0.0
O(1A)	$-x, y, \frac{1}{2} - z$	0.0	0.0
Cobalt			
Co(1)	x, y, z	0.0	0.0

The coordinates for atoms O(1) used in this work are related to the coordinates for atoms O(1) in Boldyreva, Kivikoski & Howard (1997b) by the transformation $-x, y, \frac{1}{2} - z$.

out to be similar.* In all the structures, negatively charged halide anions are located directly below and above the N atoms of the NO₂ ligands; O atoms of the NO₂ ligands form weak hydrogen bonds with *cis*-NH₃ ligands of the neighbouring cations and *trans*-NH₃ ligands form hydrogen bonds with the anions. The absolute values of the contact distances were quantitatively different in all three structures, even for the same chemical species,† thus reflecting slightly different non-covalent interactions between the same chemical species in different structures of the Co^{III} nitropentaamine series.

Similar nearest environments of complex cations in different structures can serve as an additional argument in favour of the hypothesis, that the interactions between the cations and the anions in the structures of

* Compare Fig. 5 of the present contribution with Fig. 4 from Boldyreva *et al.* (1997a).

† Compare Table 3 of the present contribution with Table 3 of Boldyreva *et al.* (1997a).

Co^{III} nitropentaamine complexes are no less important in determining crystal structures than the close packing of complex cations alone (Boldyreva *et al.*, 1997a). A 'structure forming unit' or a 'synthon' (Desiraju, 1995) for these structures should include a complex cation *and* its nearest environment. Any analysis of the anisotropy of structural strain under various actions should also consider the linear strain in the directions of contacts of a complex cation with its nearest environment, as well as the changes in the contact distances.

Lattice strains in the directions of the contacts of a complex cation with the nearest neighbours in the crystal structures of the chloride and bromide are plotted in Fig. 6 [contraction results from (a) cooling, (b) increasing pressure and (c) nitro→nitrito linkage isomerization]. The strain in the directions of the intermolecular contacts in [Co(NH₃)₅NO₂]Br₂ (and the changes in the contact distances) for structural distortion resulting from isomorphous substitution of Br⁻ for Cl⁻ are shown in Fig. 6(d).

Table 3. The contact distances (Å) between complex cations and the nearest neighbours at 290 K and ambient pressure

Number of contact	Pair of atoms	Distance	
		Chloride	Bromide
1	N(NH ₃)—Hal ⁻		
2	N(2)—Hal(1E)	3.353 (2)	3.436 (3)
3	N(2A)—Hal(1F)	3.353 (2)	3.436 (3)
4	N(3)—Hal(1C)	3.357 (2)	3.496 (3)
5	N(3A)—Hal(1A)	3.357 (2)	3.496 (3)
6	N(3)—Hal(1B)	3.406 (2)	3.505 (3)
7	N(3A)—Hal(1)	3.406 (2)	3.505 (3)
8	N(1)—Hal(1A)	3.460 (2)	3.543 (1)
9	N(1)—Hal(1C)	3.460 (2)	3.543 (1)
10	N(2)—Hal(1)	3.458 (2)	3.594 (3)
11	N(2A)—Hal(1B)	3.458 (2)	3.594 (3)
12	N(3)—Hal(1E)	3.465 (2)	3.585 (0)
13	N(3A)—Hal(1F)	3.465 (2)	3.585 (0)
14	N(1)—Hal(1)	3.485 (2)	3.605 (1)
15	N(1)—Hal(1B)	3.485 (2)	3.605 (1)
16	N(2)—Hal(1D)	3.525 (2)	3.618 (3)
17	N(2A)—Hal(1G)	3.525 (2)	3.618 (3)
	N(cis-NH ₃)—O(NO ₂ ⁻)		
18	N(3)—O(1C)	2.973 (2)	3.078 (4)
19	O(1)—N(3B)	2.973 (2)	3.078 (4)
20	N(3A)—O(1E)	2.973 (2)	3.078 (4)
21	N(3C)—O(1A)	2.973 (2)	3.078 (4)
22	N(2)—O(1B)	3.090 (2)	3.242 (4)
23	O(1)—N(2B)	3.090 (2)	3.242 (4)
24	N(2A)—O(1D)	3.090 (2)	3.242 (4)
25	O(1A)—N(2C)	3.090 (2)	3.242 (4)
	O(NO ₂)—Hal ⁻		
26	O(1)—Hal(1D)	3.361 (2)	3.432 (3)
27	O(1A)—Hal(1G)	3.361 (2)	3.432 (3)
28	O(1)—Hal(1E)	3.816 (2)	3.949 (3)
29	O(1A)—Hal(1F)	3.816 (2)	3.949 (3)
	N(NO ₂)—Hal ⁻		
30	N(4)—Hal(1E)	3.776 (2)	3.917 (2)
31	N(4)—Hal(1F)	3.776 (2)	3.917 (2)

Results of the measurements of linear strain for the chloride and bromide were qualitatively similar with minor quantitative differences. For lattice compression induced by cooling or by increasing pressure, linear strains in the directions of all the intermolecular contacts were negative. The only exceptions were a small positive strain on cooling in the directions of two of the NH₃—Cl⁻ contacts in [Co(NH₃)₅NO₂]Cl₂, and a small positive strain with increasing pressure in the direction of N(NO₂)—Hal⁻ contacts in both the chloride and bromide.* In contrast to this, the structures of the chloride and bromide, as well as that of the previously studied chloride–nitrate (Boldyreva *et al.*, 1997a), noticeably expanded in the directions of many intermolecular contacts as a result of linkage nitro–nitrito isomerization, despite an overall decrease

in molar volume. Relative values of linear strain in various directions were noticeably different for different contacts, but rather similar for the same type of contact in the chloride and bromide. For all the non-covalent contacts in [Co(NH₃)₅NO₂]Cl₂ and [Co(NH₃)₅NO₂]Br₂, the values of strain in the direction of a contact were smaller than the maximum linear strain in the structure.

The changes in the contact distances in the structures of chloride and bromide on cooling are plotted in Fig. 7. The difference between the two structures is noticeably more pronounced than could be anticipated from a comparison of linear strain in Fig. 6. The largest discrepancy was observed for the changes in the contact distances 'NH₃—O', although they can be only indirectly affected by the nature of the halide anion (Cl⁻ or Br⁻) in the structure.

We have also compared more generally the relative changes in contact distances between the same chemical species in the structures of the chloride, bromide and chloride–nitrate:

In the structure of the chloride, the contact distances 'NH₃—O(NO₂)' changed very little. In the structure of the bromide, however, a large (up to -0.056 Å or -1.73%) shortening of the 'NH₃—O(NO₂)' contacts was measured. In the structure of [Co(NH₃)₅NO₂]Cl(NO₃), the changes measured for the 'NH₃—O(NO₂)' contacts were somewhat smaller than in the structure of the bromide, but still large [in the range -0.03 to -0.04 Å or -1.2 to -1.0% (Boldyreva *et al.*, 1997a)].

The changes in contact distances 'NH₃—Cl' in the structure of the chloride–nitrate were in the range -0.41 to -1.02% [from -0.014 to -0.035 Å (Boldyreva *et al.*, 1997a)]. In the structure of the chloride, the changes in the contact distances 'NH₃—Cl' were in the range from +0.09% (+0.003 Å) to -1.70% (-0.059 Å).

The contact distances 'N(NO₂)—Cl' changed by -1.2% (-0.05 Å), both in the chloride–nitrate and the chloride. The change in the contact distance 'N(NO₂)—Br' in the bromide was somewhat smaller, -0.04 Å (-0.9%). The changes in the 'N(NO₂)—Hal⁻' contact distances in the structures of the chloride–nitrate, chloride and bromide were, respectively, 100, 94 and 86% of the maximum linear strain measured with a decrease in temperature in these three structures.

The changes in the contact distances 'O(NO₂)—Cl' were -0.23% (-0.008 Å) in the chloride–nitrate and -0.86% (-0.033 Å) in the chloride, although even the starting (at *T* = 290 K) values of these contact distances were much smaller in the chloride than in the chloride–nitrate.

Finally, a few words can be said about the changes in the contact distances 'N(NH₃)—Br' in the structure of the bromide. We have no better reference point for a comparison with them than the reported changes in the

* The structure of the chloride–nitrate contracted in the directions of the N(NO₂)—Cl contacts on cooling or with increasing pressure (Boldyreva *et al.*, 1994, 1997a). Also in the structures of the chloride and bromide the same directions were strongly contracted on cooling.

' $\text{N}(\text{NH}_4)\text{—Br}^-$ ' distances during the thermal expansion of NH_4Br^* (Hovi, Heiskanen & Varteva, 1964; Hovi, Paavola & Urvas, 1968*a,b*; Jaakkola, Pöyhönen & Simola, 1968; Pöyhönen, 1960; Pöyhönen, Mansikka & Heiskanen, 1964), which are of the same magnitude.

Similar to that observed in the case of the chloride-nitrate (Boldyreva *et al.*, 1997*a*), the vectors linking atoms rotated (not more than $0.5\text{--}1^\circ$) with respect to the crystallographic axes and to the principal axes of the strain tensor as a result of structural distortion. The angles between various vectors also changed slightly. For example, the angle between the normal to the (ONO) plane and the direction ' $\text{N}(\text{NO}_2)\text{—Hal}^-$ ' decreased at 0.6° in the structure of the chloride and increased at 0.3° in the structure of the bromide as the temperature decreased from 290 to 150 K. In our previous publication (Boldyreva *et al.*, 1997*a*), we

* Since the measurements of thermal expansion of ammonium halides were carried out in different temperature intervals, such a comparison could be done only 'per one degree of temperature change' and should be treated with caution only as an approximate estimate.

have already mentioned that a 'bond-angle' expansion [or contraction (Megaw, 1939)] can contribute to the overall expansion (or contraction) in addition to 'bond-length' expansion (or contraction). It is worth noting this once again with respect to strain in the chloride and the bromide.

For understanding the anisotropy of strain, it may also be helpful to consider a larger fragment of crystal structure than just a complex cation and its nearest environment. A fragment of the structures of the $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{X}_2$ complexes ($\text{X} = \text{Cl}^-, \text{Br}^-$), showing hydrogen bonds between the halide anions and the *trans*- NH_3 ligands of the complex cations, forming 'bands' in the *c* direction,* is plotted in Fig. 8.

Interpretation of the anisotropy of lattice distortion of $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Br}_2$ is even more complicated than in the case of the chloride-nitrate. Two principal axes of the strain ellipsoids also lie in the *ac* plane, but their directions do not coincide

* Contacts $\text{N}(1)\text{—Hal}(1\text{A})$, $\text{N}(1)\text{—Hal}(1\text{C})$, $\text{N}(1)\text{—Hal}(1)$, $\text{N}(1)\text{—Hal}(1\text{B})$ in Table 3.

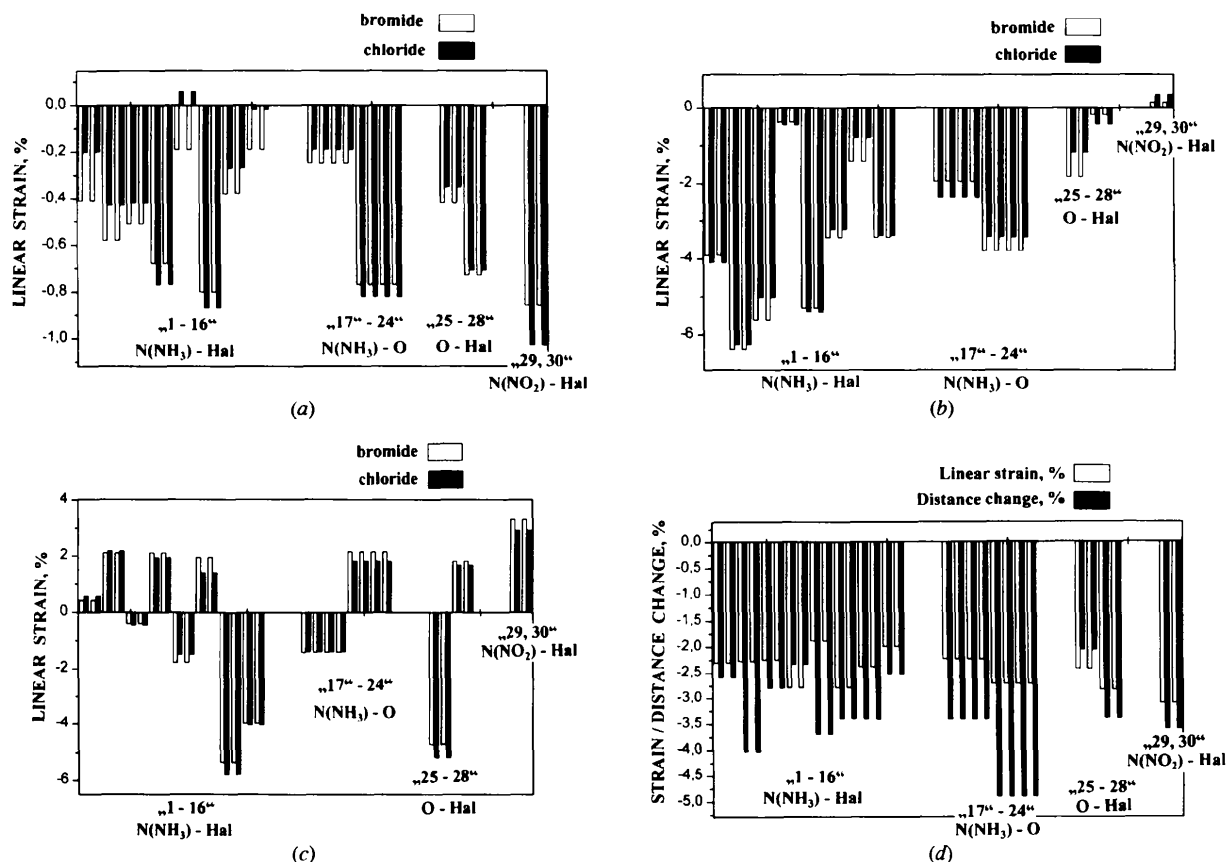


Fig. 6. Linear strain in the directions of the shortest intermolecular contacts of a complex cation with the neighbouring atoms in the structures of $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Br}_2$ with (a) decreasing temperature, (b) increasing pressure, (c) nitro \rightarrow nitrito linkage isomerization or (d) as a result of isomorphous substitution of Br^- for Cl^- in the structure of $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Br}_2$. Symmetry operations for the generation of symmetry-equivalent atoms, numbering of contacts and the lengths of the contacts in the 'starting structures' (290 K, ambient pressure) are given in Tables 2 and 3.

with any of the crystallographic axes. The direction of the 'bands' linked by hydrogen bonds does not coincide with any of the principal axes of the strain tensors, but it is closer to the more rigid directions when the structures of the chloride and bromide are contracted due to a decrease in temperature or an increase in pressure or when one considers strain induced in the structure of the bromide by substituting Br^- for Cl^- . In Fig. 8, one can also see chains ' $\text{trans-NH}_3-\text{O}(\text{NO}_2)-\text{trans-NH}_3$ ' with long [4.409 (chloride) and 4.572 Å (bromide)] distances between N and O, which are ~ 1.5 Å longer than the characteristic distance for an ' $\text{N}(\text{H})\cdots\text{O}$ ' bond. However, some weak attractive interaction between NH_3 and NO_2 groups can still exist even at such long distances, with electrostatic interactions known to be

very long range. The direction of these chains is very close to the directions of maximum thermal strain in the chloride and bromide, and of maximum strain resulting from substituting Br^- for Cl^- in the structure of bromide, as well as to the direction of maximum expansion (axis 1') under pressure in the chloride. One should mention, of course, that the same directions are also very close to the direction of the ' $\text{N}(\text{NO}_2)-\text{Hal}^-$ ' contacts in the structures of $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Br}_2$. There are also ' $\text{cis-NH}_3-\text{Hal}^-$ ' and ' $\text{cis-NH}_3-\text{O}(\text{NO}_2)$ ' contacts in the directions not coinciding with, but relatively close to, the directions of maximum temperature-induced strain (principal axes 3 and 3') of strain tensors of the chloride and bromide. There seem to be no non-covalent contacts which could be described as a hydrogen bond in the directions close to the crystallographic axis **b** (coinciding with the direction of maximum compression under pressure in the chloride and bromide and with the direction of a small negative thermal expansion in chloride), the smallest value of the angle between the direction of an intermolecular contact and the **b** axis being 54° (for a ' $\text{cis-NH}_3-\text{Hal}^-$ ' contact).

We have also calculated the changes in contact distances for some of the non-covalent contacts in the **ac** plane in the structures of chloride and bromide, the directions of which were close to the principal axes of the strain tensors. In both the chloride and bromide, the long ' $\text{NH}_3-\text{O}(\text{NO}_2)$ ' distances contracted at -0.06 Å (-1.3% , that is equal to the maximum linear strain measured in the structure of the chloride and more than the value of the maximum linear strain in the structure of the bromide), whilst the changes in the distances ' $\text{N}(\text{trans-NH}_3)-\text{Hal}^-$ ' were noticeably smaller

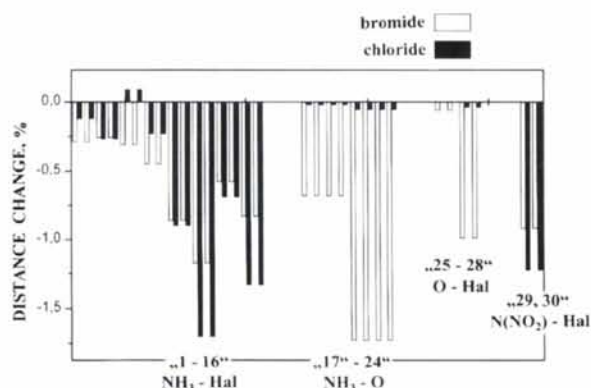


Fig. 7. Changes in the contact distances of complex cations with the nearest neighbours in the structures of $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Br}_2$ resulting from the decrease in temperature from 290 to 150 K. Numbering of the contacts is the same as in Fig. 6.

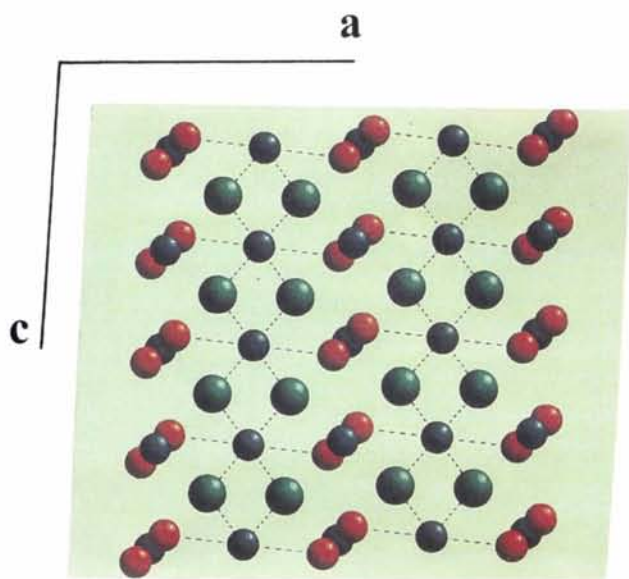


Fig. 8. A fragment of the structures of $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Br}_2$. Plane (**ac**), atoms in a layer centred at the level $y = 0$. Dotted lines show hydrogen bonds $\text{trans-NH}_3-\text{Cl}$ ($\text{trans-NH}_3-\text{Br}$); dashed lines show long contacts between NO_2 groups and NH_3 ligands (4.409 Å at 290 K and 4.351 Å at 150 K in the chloride; 4.572 Å at 290 K and 4.511 Å at 150 K in the bromide). Red = O; blue, small = N; green, large = Hal^- (Cl^- or Br^-). Distances from the plane: $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$. Cl^- : ± 0.140 Å; trans-NH_3 : ± 0.492 Å; $\text{O}(\text{NO}_2)$: ± 0.681 Å; $\text{N}(\text{NO}_2)$: ± 0.062 Å. Below and above the slice (at levels $ca \pm 2$ Å, namely ± 1.84 , ± 1.85 and ± 2.50 Å) there are cis-NH_3 ligands also forming hydrogen bonds with Cl^- anions. $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Br}_2$. Br^- : ± 0.136 Å; trans-NH_3 : ± 0.559 Å; $\text{O}(\text{NO}_2)$: ± 0.671 Å; $\text{N}(\text{NO}_2)$: ± 0.059 Å. Below and above the slice (at levels $ca \pm 2$ Å, namely ± 1.83 , ± 1.87 , ± 2.54 and ± 2.59 Å) there are cis-NH_3 ligands also forming hydrogen bonds with Br^- anions.

[-0.01 \AA (-0.2%) in the chloride and -0.02 \AA (-0.4%) in the bromide].

4. Conclusions

The present study demonstrates on two more examples, in addition to the data reported for structural distortion in $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}(\text{NO}_3)$ in our previous contribution (Boldyreva *et al.*, 1997a), that, contrary to an existing view, structural distortion of the same structure may be qualitatively and quantitatively different, even if the symmetry of the compressing action is the same, as in the cases of (i) cooling and (ii) increasing pressure.

Anisotropy of structural strain under some scalar action is a result of the anisotropy of the interatomic forces acting in the crystal. Despite many efforts (see some references in Boldyreva *et al.*, 1997a), it still remains problematic not only to *predict* the anisotropy of structural strain in a known structure under a particular action, but even simply to *explain* the anisotropy measured experimentally. The problem of explaining the observed anisotropy of strain is the problem of finding the type(s) of intermolecular interactions in the crystal predominantly responsible for each type of structural distortion.

The anisotropy of the structural strain of the chloride and bromide on cooling can be correlated with the directions of hydrogen bonds and hydrogen-bonded chains in the structures. At the same time, it seems to be even more difficult to give the full interpretation of the anisotropy of strain on cooling, under pressure and especially in the course of linkage nitro–nitrito isomerization than it was for the chloride–nitrate (Boldyreva *et al.*, 1997a). Relative strengths of different types of hydrogen bonds ($\text{N}-\text{H}\cdots\text{O}$, $\text{N}-\text{H}\cdots\text{Cl}$ and $\text{N}-\text{H}\cdots\text{Br}$), as well as other non-covalent interactions in the structures, namely those between the NO_2 ligands and Hal^- (Cl^- or Br^-) anions, should also be taken into account.

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