Distortion of Crystal Structures of Some Co^{III} Ammine Complexes. I. Distortion of Crystal Structure of [Co(NH$_3$)$_5$NO$_2$]Cl(NO$_3$) on Cooling

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Abstract

The anisotropy of the structural distortion of [Co-(NH$_3$)$_5$NO$_2$]Cl(NO$_3$), pentaamminenitrocobalt(III) chloride nitrate, on cooling 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 distortion in various crystallographic directions. The changes of different intra- and intermolecular distances in the structure were followed. Lattice strain induced by low temperature was compared with lattice strain in the same structure under high hydrostatic pressure and with lattice strain induced by homogeneous nitro–nitrito linkage isomerization.

1. Introduction

It is important to understand the interrelation between the structure of a crystal and the strain resulting from a particular action (temperature, pressure or radiation) in order to be able to predict the behaviour of solids in devices and to design materials that best respond to practical requirements.

Additionally, any chemical reaction in a solid results in the generation of mechanical stresses. The rate (and, sometimes, the very possibility) of the reaction are often determined by the ability of these stresses to relax (see, for example, Ramamurthy & Venkatesan, 1987; Chupakhin, Sidel'nikov & Boldyrev, 1987; Hollingsworth & McBride, 1990). Structural strain is a result of this relaxation. Structural strain induced by a solid-state reaction can affect the further course of the reaction and in this way a feedback arises (Chupakhin *et al.*, 1987; Boldyreva, 1990, 1992). Therefore, it is often important to be able to understand the factors responsible for the absolute value and the anisotropy of structural strain in a crystal, in order to predict solid-state chemical reactivity.

Finally, a structural distortion is a complex result of various interactions between the different units forming a crystal structure. Therefore, studies of structural distortion may throw some light on the nature of these interactions, especially if one compares the structural distortion of related structures or the structural distortions of the same structure resulting from different actions (changes in temperature, changes in pressure and isomorphous substitution of atoms). Studies of intermolecular interactions, in turn, are important for predicting crystal structures and the existence of polymorphs, the design of materials, controlling the course of chemical reactions in crystals and many other applications.

Distortion of a crystal structure can be characterized by the overall change in molar volume or, in other terms, by a mean volume expansion (contraction) coefficient, calculated as

$$\alpha_T = \Delta V(T)/[V_0(T_0)\Delta T].$$

This is, however, not a sufficient characteristic, since distortion of a crystal structure is anisotropic, that is, linear strain (expansion or contraction) depends on the direction (Nye, 1994). Being anisotropic, strain must be characterized by a corresponding strain tensor, which can be defined by the values of its principal components and the orientation of principal axes with respect to crystallographic axes. The principal axes are the three mutually orthogonal directions in the structure which remain orthogonal during deformation. The principal components give the values of linear strain along the directions of principal axes (Nye, 1994). Knowing the strain tensor, one can calculate the changes in linear dimensions (linear strain) of the solid in any direction (Nye, 1994).

The volume expansion (contraction) coefficient and strain tensor can be calculated from the measured changes in lattice parameters. Various algorithms used for these calculations have been described in the literature (Chanh, Clastre, Gaultier, Haget & Meresse, 1988; Jessen & Küppers, 1991; Hazen & Finger, 1982; Nye, 1994; Zotov, 1990; Zotov & Petrov, 1991). Thus, much can be learned of the anisotropy of structural distortion, even from measuring the lattice strain only. Indeed, conclusions on the relationship between the crystal structure and the anisotropy of thermal expan-

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sion in the early publications (for example, Gallagher, Ubbelohde & Woodward, 1955; Pirenne, 1955; Robertson & Ubbelohde, 1939; Ubbelohde & Woodward, 1946) were based on measurements of lattice strain only. However, linear strain in a particular direction is neither equal nor proportional to the actual change in the distances between the atoms which are joined in the starting structure by a vector pointing in this direction.* Therefore, to obtain a better idea of what is happening to a structure in the course of its distortion, it is always advantageous to consider not only the changes in lattice parameters but also the changes in atomic coordinates.

A study of the structural distortion in crystals of $[Co(NH_3)_5NO_2]Cl(NO_3)$ induced by various means is interesting, first of all, with respect to the solid-state reactivity of this compound:

$[Co(NH_3)_5NO_2]Cl(NO_3)$ is known to undergo linkage isomerization (nitro→nitrito when irradiated and reverse nitrito→nitro when stored or heated). This reaction is known to be sensitive to pressure. The effective quantum yield of the photoisomerization in the solid state was shown to be lower in elastically compressed crystals (Boldyreva, 1994; Boldyreva & Sidel'nikov, 1987; Boldyrev, Lyakhov, Pavlyukhin, Boldyreva, Ivanov & Avvakumov, 1990). The reverse thermal nitrito→nitro isomerization is known to be accelerated by high pressure in solutions (Mares, Palmer & Kelm, 1978) and, according to preliminary measurements, also in the solid state (Boldyreva, 1994; Boldyreva & Ahsbahs, 1996).

On the other hand, the reaction itself induces large mechanical stresses in the crystals and this manifests itself in macroscopic elastic deformation and fragmentation of single crystals in the course of the isomerization (Boldyreva, 1994; Boldyreva, Sidel'nikov, Chupakhin, Lyakov & Boldyrev, 1984; Boldyreva & Sidel'nikov, 1987; Boldyrev et al., 1990). A powder X-ray diffraction study (Boldyreva, Virovets, Burleva, Dulepov & Podberezskaya, 1993) has shown the solid-state linkage isomerization of the title compound to result in a continuous and highly anisotropic lattice distortion, the molar volume of the solid nitrito isomer being smaller than that of the solid nitro isomer. Structural distortion during nitrito→nitro isomerization

manifests itself also in frequency shifts in the IR spectra (Dulepov & Boldyreva, 1994), which could be interpreted in terms of 'changes in the internal pressure' (as is often done in the literature, see as examples Chukanov, Golovanova & Korsunski, 1986; Hollingsworth & McBride, 1990; McBride, 1983; McBride, Segmuller, Hollingsworth, Mills & Weber, 1986). The measurements of the frequency shifts in the IR spectra of $[Co(NH_3)_5NO_2]Cl(NO_3)$ with an increase in hydrostatic pressure (Boldyreva, Burgina, Baltakhinov, Ahsbahs, Burleva, Uchtmann & Dulepov, 1992) seem to be in agreement with such a simplified interpretation. However, powder X-ray diffraction studies of the lattice distortion of the same compound under hydrostatic pressure (Boldyreva, Ahsbahs & Uchtmann, 1994) show that the real situation is much more complicated. Compression of the crystals of nitro isomers resulting from hydrostatic pressure was shown to be anisotropic, the anisotropy of the lattice strain being qualitatively different to that resulting from linkage isomerization. The qualitative difference in the anisotropy of contraction of the crystal structure of $[Co(NH_3)_5NO_2]Cl(NO_3)$ (i) in the course of the nitro→nitrito isomerization and (ii) under pressure must also account for the fact that, despite the molar volume of the solid nitro isomer being larger than that of the nitrito isomer, compressing the crystals of $[Co(NH_3)_5NO_2]Cl(NO_3)$ results in a decrease in the effective quantum yield of the nitro→nitrito isomerization (Boldyreva & Sidel'nikov, 1987).

The difference in the anisotropy of the structural distortion of $[Co(NH_3)_5NO_2]Cl(NO_3)$ during linkage isomerization and under hydrostatic pressure can be due to the different anisotropy of the 'contracting force field' in the crystal. Therefore, we decided to compare the anisotropy of structural distortion of the same structure resulting from two different scalar actions, such as increasing pressure and decreasing temperature. Although it is sometimes claimed in the literature that structural distortion during thermal and hydrostatic compression of the same compound must be similar,* this hypothesis may be only justified for isotropic distortion. For cubic structures, parameters characterizing the overall volume thermal expansion and those describing compressibility under hydrostatic pressure are interrelated (Hazen & Finger, 1982; Krishnan, Srinivasan & Devanarayanan, 1979; Ledbetter, 1991; Novikova, 1947). However, for any solid with symmetry lower than cubic, the distortion is, in general, anisotropic and one should compare not only the absolute values of volume changes but also the

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* There are two main reasons for this discrepancy. First, the distances between different pairs of atoms in heterodesmic [with different types of chemical bonds and interatomic interactions (Hassel, 1934)] structures can change differently, even if the vectors joining the atoms in these pairs are collinear (for example, obviously enough, intramolecular bonds and intermolecular distances may be expected to be changed to a different extent). Second, the orientation of a vector joining two atoms in a structure with respect to the crystallographic axes (and, correspondingly, to the principal axes of the strain tensor) is usually changed as a result of structural distortion. In this cases the value of linear strain in the direction of the vector in the starting structure also does not give the actual value of the change in the interatomic distance.

* There are also examples of papers with even more general statements. For example, Batsanov (1981) wrote that the changes in the properties of a solid with a decrease in the volume of the solid must be expected to be the same, independently of the method of decreasing the volume, including 'chemical compression' (due to isomorphous substitution and formation of solid solutions).

anisotropy of distortion induced by low temperature and high pressure in the same structure, especially if there are different types of interatomic interactions in the crystal. Some examples of such studies are known. For example, high-pressure and low-temperature compressions were shown to have similar effects on the structure of an organic superconductor di(2,3,6,7-tetramethyl-1,4,5,8-tetraselenafulvalenium) hexafluorophosphate (Gallois, Gaultier, Hauw, Lamcharfi & Filhol, 1986). However, in general, comparative studies of anisotropic strain induced in the same structure by different actions are still rare.

The aim of the present contribution was to study structural distortion induced by a decrease in temperature in $[Co(NH_3)_5NO_2]Cl(NO_3)$ and to compare this distortion with the distortions of the same structure induced by hydrostatic pressure (another isotropic influence) and in the course of nitro–nitrito linkage isomerization (an anisotropic influence).

2. Experimental

X-ray diffraction data were collected on a Rigaku AFC-6S four-circle diffractometer (Mo $K\alpha$ radiation) with a Cryostream (Oxford Cryosystems) open-flow N_2 gas cryostat (Cosier & Glazer, 1986). Since lattice parameters of Co^{III} nitroammine complexes are known to vary slightly from crystal to crystal of the same compound, comparative structural studies at different temperatures were carried out for the same crystal, without removing the crystal from the diffractometer. Full data collection was carried out at 290 (0.1) K, then the temperature was lowered in 20 K steps down to 150 (0.1) K and at every temperature the high-angle cell* was refined, using the reflection centring and cell refinement routines of the diffractometer. At 150 K, a new data collection was carried out, after which the temperature was increased again in 20 K steps, and the high-angle cell was refined at each intermediate temperature. All experiments were carried out in the dark to prevent possible photochemical linkage isomerization.

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

SHELXTL-Plus (Sheldrick, 1991) and JACKAL (Cockroft, 1992) molecular graphics programs were used for plotting the fragments of the structures. Strain tensors were calculated by the program of Ohashi published in the book of Hazen & Finger (1982). Linear strain in various directions was calculated using unpublished programs of the Novosibirsk Institute of

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* Cell parameters were calculated from the refined positions of reflections with relatively high (40–50) values of 2θ.

Solid State Chemistry based on the formula given in Nye (1994). The changes in interatomic distances and angles in the structures were calculated using CRYSTALS (Watkin, Carruthers & Betteridge, 1993).

3. Results

In the present publication, we concentrate our attention on a detailed comparison of the two structures measured at 290 and 150 K, referring to the original data reported elsewhere (Boldyreva et al., 1997).
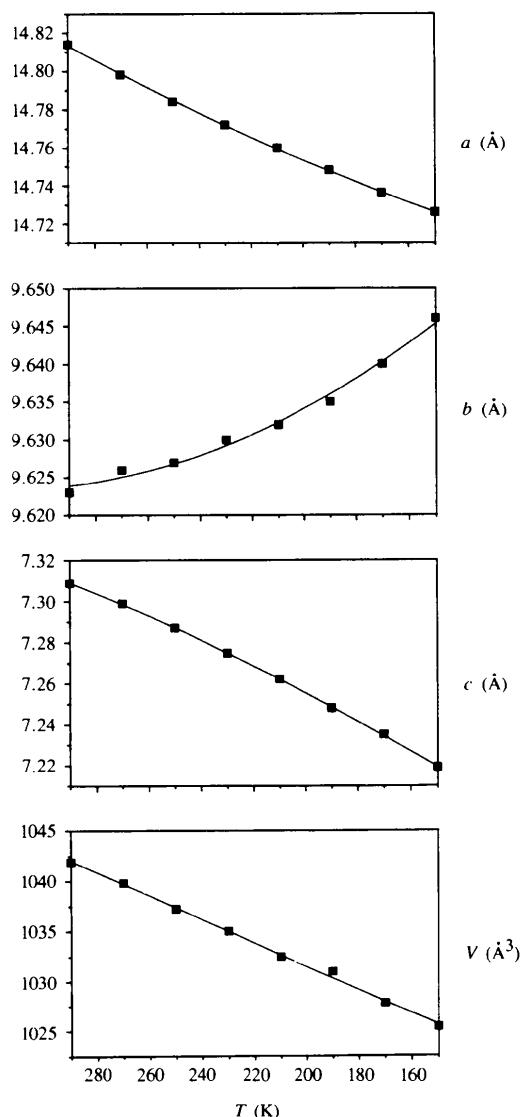

Fig. 1. Changes in lattice parameters and elementary cell volume with decreasing temperature for $[Co(NH_3)_5NO_2]Cl(NO_3)$: (a) a (Å); (b) b (Å); (c) c (Å); (d) V (Å^3). Approximating relationships:
$a = 14.630 + 6.2262 \times 10^{-4}T$ ($R^2 = 0.996$);
$b = 9.7025 - 5.0000 \times 10^{-4}T + 7.8869 \times 10^{-7}T^2$ ($R^2 = 0.990$);
$c = 7.0840 + 1.0357 \times 10^{-3}T - 8.9286 \times 10^{-7}T^2$ ($R^2 = 1.000$);
$V = 1008.080 + 0.117T$ ($R^2 = 1.000$).

Fig. 1 shows the changes with temperature in lattice parameters and the unit-cell volume measured for $[Co(NH_3)_5NO_2]Cl(NO_3)$. The molar volume decreased linearly with decreasing temperature (the mean volume coefficient of thermal expansion from 150 to 290 K is equal to $113 \times 10^{-6} \deg^{-1}$). The value is comparable with the mean volume coefficients of thermal expansion for ionic crystals of inorganic compounds (Krishnan *et al.*, 1979), for example, $114 \times 10^{-6} \deg^{-1}$ for NaCl or $115 \times 10^{-6} \deg^{-1}$ for $NaNO_2$; and is smaller than the corresponding values characterizing molecular organic crystals ($178 \times 10^{-6} \deg^{-1}$ for *p*-dinitrobenzene, $182 \times 10^{-6} \deg^{-1}$ for *p*-nitroaniline, $194 \times 10^{-6} \deg^{-1}$ for thiourea and $209 \times 10^{-6} \deg^{-1}$ for oxalic acid).

Lattice strain on cooling from 290 to 150 K was clearly anisotropic (Fig. 2a). In accordance with Neumann's principle (Nye, 1994), the directions of all the three principal axes of strain tensor for ortho-rhombic $[Co(NH_3)_5NO_2]Cl(NO_3)$ coincide with the directions of the crystallographic axes. At the same time, although the orientation of the principal axes is fixed, Neumann's principle imposes no restrictions on the absolute values of the principal components of strain tensor and on their ratio. Nature was still free to choose which of the three principal directions was to be the 'softest' and which the most 'rigid', and how large the difference between linear strain in different directions actually would be. Comparing Figs. 2(a)–(c), one can see that for lattice contraction induced in $[Co(NH_3)_5-NO_2]Cl(NO_3)$ by (a) a decrease in temperature, (b) an increase in pressure or (c) by homogeneous linkage isomerization (isomorphous substitution of $[Co(NH_3)_5-$

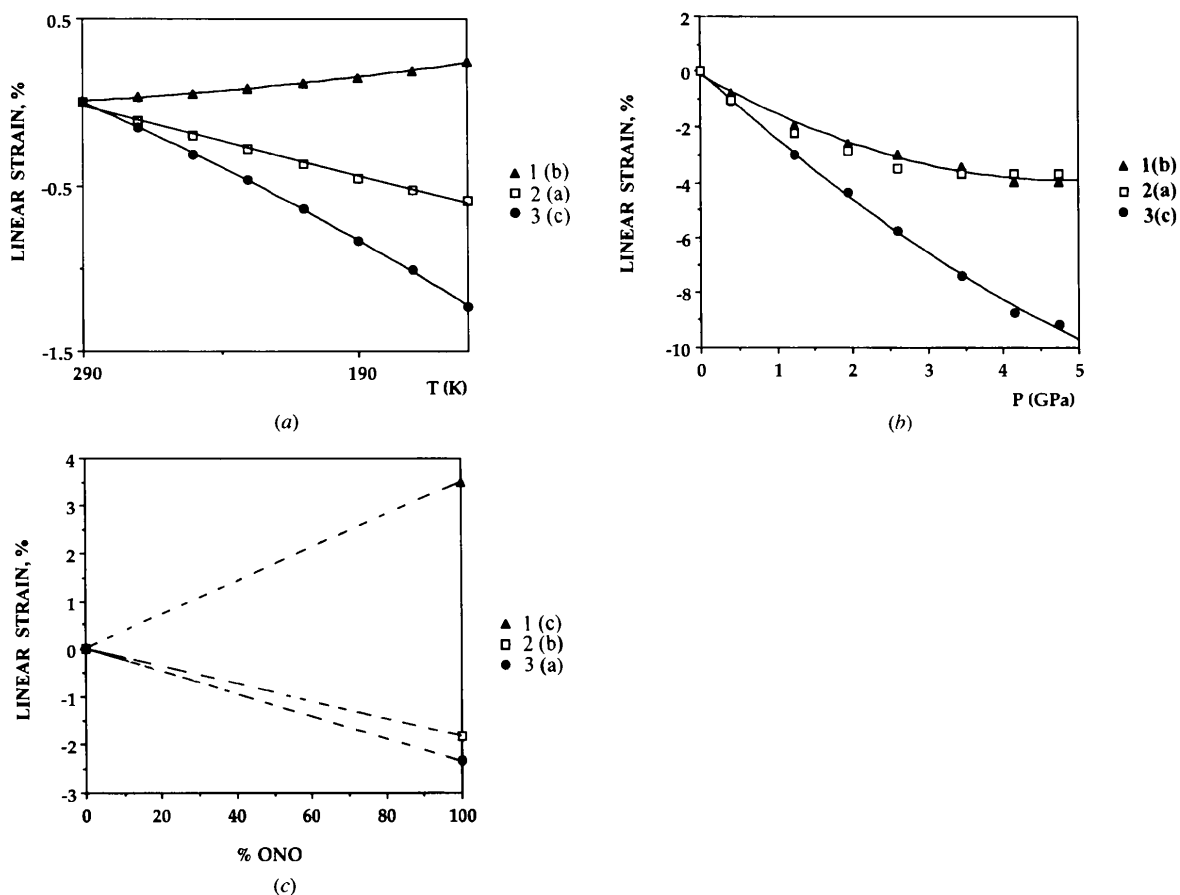Fig. 2. Linear strain in the directions of three principal axes of strain tensors for $[Co(NH_3)_5NO_2]Cl(NO_3)$; compression of the structure resulting from: (a) a decrease in temperature from 290 to 150 K; (b) an increase in pressure from ambient to 5.0 GPa; (c) nitro→nitrito linkage isomerization. Approximating relationships: (a) temperature-induced strain: $\Delta l_1/l_1(\Delta b/b) = 0.68523 - 3.7071 \times 10^{-3}T + 4.6875 \times 10^{-6}T^2$ ($R^2 = 0.998$); $\Delta l_2/l_2(\Delta a/a) = -1.2458 + 4.2315 \times 10^{-3}T$ ($R^2 = 0.997$); $\Delta l_3/l_3(\Delta c/c) = -2.5018 + 8.7292 \times 10^{-3}T$ ($R^2 = 0.997$); (b) pressure-induced strain: $\Delta l_1/l_1(\Delta a/a) = \Delta l_2/l_2(\Delta b/b) = -2.6129 \times 10^{-2} - 2.5347P + 0.11883P^2$ ($R^2 = 0.998$); $\Delta l_3/l_3(\Delta c/c) = -0.13128 - 1.5569P + 0.15904P^2$ ($R^2 = 0.993$); (c) strain induced by nitro–nitrito isomerization. Only extremes (100% NO_2 isomer and 100% ONO isomer) were studied. The dashed lines connecting the experimentally measured points are guides to the eye. 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 strain *quadric!*) has maximum, medium and minimum linear dimensions. $\Delta l_i/l_i$ linear strain in the direction of the principal axis i ($i = 1, 2, 3$).

$NO_2]^{+2}$ to $[Co(NH_3)_5ONO]^{+2})$ nature did choose different 'soft' and 'rigid', expanding and contracting directions. During thermal contraction (a) and during contraction resulting from linkage isomerization (c), despite the overall decrease in molar volume, the structure expanded in some directions. Contraction under hydrostatic pressure (b) was in some sense 'inverse' compared with contraction resulting from linkage isomerization (c). Finally, one can see qualitative differences in the anisotropy of lattice contraction resulting from two different isotropic influences: a decrease in temperature (a) and an increase in pressure (b).

We would also like to comment on the differences in 'scaling effects' (i) when overall volume changes or (ii) when linear strain is compared. Cooling from 290 to 150 K results in the -1.6% relative change in the molar volume, which is more than twice as large as the -0.7% change in the volume resulting from nitro→nitrito isomerization (Boldyreva et al., 1993). At the same time, if one compares linear strain one can see that the maximum values of linear strain in a particular direction are comparable for strain resulting from linkage isomerization and for strain induced by hydrostatic pressure as high as 2.0 GPa (with an order of magnitude larger overall volume changes!), whilst the values for thermal linear contraction are smaller. Thus, one can see once again how problematic and ambiguous it would be to interpret the anisotropic contraction of the crystal structure resulting from the isomerization in terms of 'internal pressure'.
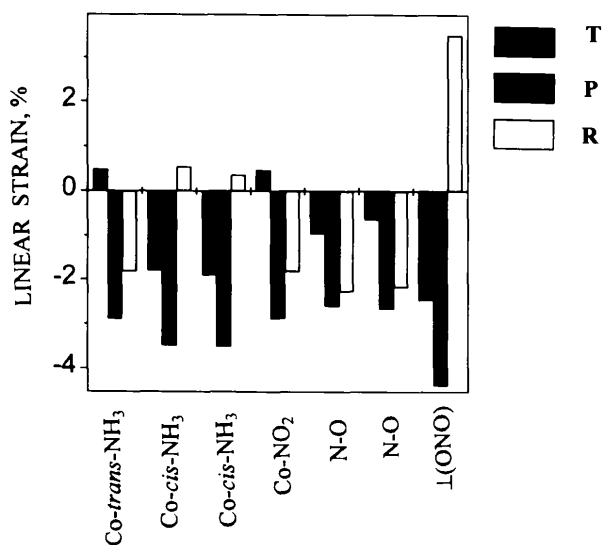
Table 1. *Selected intramolecular distances (Å) and angles (°) in [Co(NH$_3$)$_5$NO$_2$]Cl(NO$_3$) at 290 and 150 K*

	290 K	150 K
Co(1)—N(1) (trans-NH$_3$)	1.988 (2)	1.988 (2)
Co(1)—N(2) (cis-NH$_3$)	1.971 (2)	1.969 (1)
Co(1)—N(3) (cis-NH$_3$)	1.959 (2)	1.958 (1)
Co(1)—N(4) (NO$_2$ ligand)	1.961 (2)	1.961 (2)
N(4)—O(1)	1.221 (3)	1.222 (2)
N(4)—O(2)	1.206 (3)	1.219 (2)
Co(1)—N(4)—O(1)	118.0 (2)	117.8 (1)
Co(1)—N(4)—O(2)	119.1 (2)	118.9 (1)
O(1)—N(4)—O(2)	122.9 (2)	123.3 (2)

Differences and similarities in the anisotropy of contraction of crystal structure of $[Co(NH_3)_5NO_2]Cl(NO_3)$ on cooling, with increasing pressure, or in the course of nitro→nitrito linkage isomerization can be also seen if linear strain is calculated in the directions collinear with vectors linking different atoms in complex cations $[Co(NH_3)_5NO_2]^{2+}$ (Fig. 3). The orientation of complex cations with respect to the directions of contraction and expansion in the structures is different for different methods of decreasing the molar volume (low-temperature, high-pressure, homogeneous linkage isomerization). Most striking differences in the anisotropy of contraction can be observed in the direction perpendicular to the O—N—O plane, which is close to the direction of maximum contraction with decreasing temperature or increasing pressure and to the direction of maximum expansion during linkage isomerization.

The changes in the 'intramolecular' bond lengths in a complex cation on cooling from 290 to 150 K were within experimental error, that is smaller than 0.003 Å, if observed at all (Table 1).* The observed distortion of crystal structure on cooling was due almost entirely to the changes in the 'intermolecular' distances in the structure, that is in the non-covalent contacts of complex cations with anions and with other cations.

Fig. 4 shows the nearest environment of a complex cation in the structure.† Negatively charged halide anions are located directly below and above the N atoms of the NO$_2$ ligands; O atoms of the NO$_2$ ligands form weak hydrogen bonds with cis-NH$_3$ ligands of the neighbouring cations and trans-NH$_3$ ligands form hydrogen bonds with the anions. The environment of the NO$_2$ fragment is qualitatively similar to the 'generalized crystalline environment' reported for the NO$_2$ fragment in organic crystals: negatively charged species below and above the NO$_2$ group and bent

Fig. 3. Linear strain in the directions collinear with vectors linking different atoms in complex cations in the structure of [Co(NH$_3$)$_5$-NO$_2$]Cl(NO$_3$). T: Lattice distortion induced by a decrease in temperature from 290 to 150 K; P: lattice strain at hydrostatic pressure 2 GPa; R: lattice strain resulting from nitro→nitrito linkage isomerization.

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* Compare this result with the data on the noticeable (Δl in the range from -0.016 to -0.018Å or $\Delta l/l$ in the range from -1.26 to -1.45%) contraction of the N—O bonds in the [Co(NO$_2$)$_6$]$^{3-}$ ion in the structure of Li[N(CH$_3$)$_4$]$_2$[Co(NO$_2$)$_6$], on cooling from 293 to 113 K [relative volume change $\Delta V/V \simeq -3.21\%$, i.e. ca twice as large as the volume change in [Co(NH$_3$)$_5$NO$_2$]Cl(NO$_3$) on cooling from 290 to 150 K (Adovasio, Lina, Nardelli & Pelizzi, 1994)].

† Symmetry codes for generating the atoms in Fig. 4 are given in Table 2.

hydrogen bonds of the NO_2 fragment with amine fragments of the neighbouring molecules (Taylor, Mullaley & Mullier, 1990).

The absolute values of the contact distances in the starting structure of the nitro isomer at 290 K and ambient pressure are summarized in Table 3 and their relative changes with decreasing temperature, increasing pressure or nitro→nitrito isomerization are plotted in Figs. 5(a)–(c). Apart from a different 'scaling factor', the relative strain in the directions of various non-covalent contacts is rather similar for contraction resulting from changes in temperature and pressure (Figs. 5a and b), and is qualitatively different for contraction resulting from isomerization. For lattice contraction resulting from cooling, or from an increase in pressure, linear strain in the directions of all the intermolecular contacts was negative. In contrast to this, the structure 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 the directions of different contacts were noticeably different. The largest
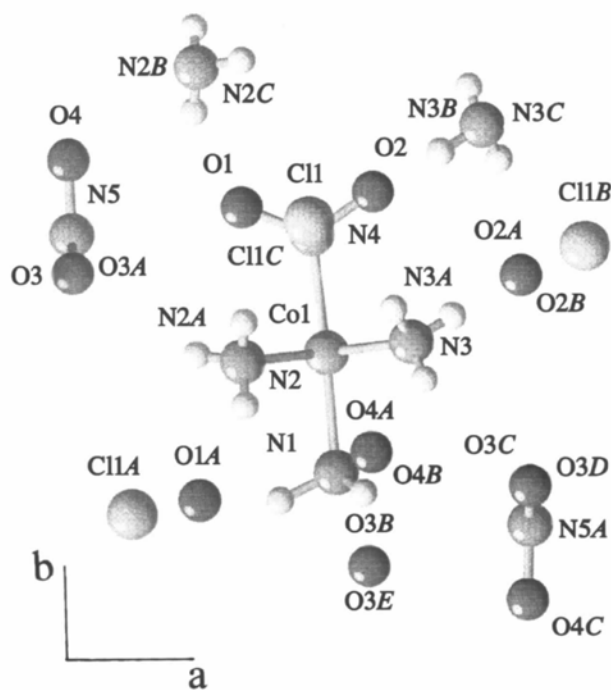

Fig. 4. The nearest environment of a complex cation in the structure of $[Co(NH_3)_5NO_2]Cl(NO_3)$. Projection on the plane of the NO_2 group is shown. The generation of symmetry-equivalent atoms is explained in Table 2. Distances of atoms from the projection plane are also given in Table 2. The contact distances between the atoms of a complex cation and the atoms in the nearest environment are summarized in Table 3. N(1) = nitrogen of trans-NH_3, N(2) and N(3) = nitrogens of cis-NH_3, N(4) = nitrogen of NO_2 ligand, N(5) = nitrogen of NO_3 anion; O(1) and O(2) = oxygens of NO_2 ligand, O(3) and O(4) = oxygens of NO_3 anion.

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. 4 at 290 K and ambient pressure*

Atom	Symmetry code	Distance (Å)
Atoms in the environment		
Nitrogens of cis-NH_3		
N(2B)	$\frac{1}{2}-x, y-\frac{1}{2}, -z$	2.247 (2)
N(3B)	$-x, -y, -z$	2.283 (2)
N(2C)	$\frac{1}{2}-x, y-\frac{1}{2}, z-\frac{1}{2}$	−2.247 (2)
N(3C)	$-x, -y, z-\frac{1}{2}$	−2.283 (2)
Nitrogen of NO_3 anion		
N(5A)	$x-\frac{1}{2}, \frac{1}{2}-y, z$	0.0
Oxygens of NO_2 ligand		
O(1A)	$\frac{1}{2}-x, \frac{1}{2}+y, -z$	3.655 (2)
O(1B)	$\frac{1}{2}-x, \frac{1}{2}+y, -1-z$	−3.655 (2)
O(2A)	$-x, -y, -z$	3.655 (2)
O(2B)	$-x, -y, z-\frac{1}{2}$	−3.655 (2)
Oxygens of NO_3 anion		
O(3)	x, y, z	1.080 (2)
O(3A)	$x, y, -\frac{1}{2}-z$	−1.080 (2)
O(3B)	$\frac{1}{2}-x, \frac{1}{2}+y, -z$	2.574 (2)
O(3C)	$x-\frac{1}{2}, \frac{1}{2}-y, z$	1.080 (2)
O(3D)	$x-\frac{1}{2}, \frac{1}{2}-y, -\frac{1}{2}-z$	−1.080 (2)
O(3E)	$\frac{1}{2}-x, \frac{1}{2}+y, z-\frac{1}{2}$	−2.574 (2)
O(4A)	$\frac{1}{2}-x, \frac{1}{2}+y, -z$	3.655 (2)
O(4B)	$\frac{1}{2}-x, \frac{1}{2}+y, -1-z$	−3.655 (2)
Chlorine anions		
Cl(1)	x, y, z	3.655 (2)
Cl(1A)	$\frac{1}{2}-x, \frac{1}{2}+y, -z$	0.0
Cl(1B)	$-x, -y, -z$	0.0
Cl(1C)	$x, y, z-1$	−3.655 (2)
Atoms of a complex cation		
Nitrogens of cis-NH_3		
N(2)	x, y, z	1.408 (2)
N(3)	x, y, z	1.372 (2)
N(2A)	$x, y, -\frac{1}{2}-z$	−1.408 (2)
N(3A)	$x, y, -\frac{1}{2}-z$	−1.372 (2)
Nitrogen of trans-NH_3		
N(1)	x, y, z	0.0
Nitrogen of NO_2 ligand		
N(4)	x, y, z	0.0
Oxygens of NO_2 ligand		
O(1)	x, y, z	0.0
O(2)	x, y, z	0.0
Cobalt		
Co(1)	x, y, z	0.0

strain was measured: (i) in the directions of contacts between the nitrogen of the NO_2 ligand and the Cl^- anion; (ii) in the directions of some of the contacts between NH_3 ligands and oxygens of either the NO_2 ligands of the neighbouring cations or of the NO_3^- anions; (iii) in the directions of some of the contacts NH_3—Cl^-. The largest *positive* strain resulting from isomerization was observed for many of the contacts, for which the largest *negative* strain was measured at low temperature and at high pressure.

For structural contraction on cooling, *linear strain in the direction of contacts* was compared with the actual *changes in the contact distances* (Fig. 5a). The values did not coincide, but general trends were similar. Large changes in the intermolecular distances were measured

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 (Å)
	N (NH$_3$)—O (NO$_3^-$)	
1, 2	N(3)—O(4A), N(3A)—O(4B)	2.982 (2)
3, 4	N(1)—O(3B), N(1)—O(3E)	3.016 (2)
5	N(3)—O(3C)	3.078 (2)
6, 7	N(2)—O(3), N(2A)—O(3A)	3.132 (2)
8, 9	N(1)—O(3C), N(1)—O(3D)	3.348 (2)
	N (cis-NH$_3$)—O (NO$_2^-$)	
10, 11, 12, 13	N(3)—O(2A), O(2)—N(3B), O(2)—N(3C), N(3A)—O(2B)	3.092 (2)
14, 15, 16, 17	N(2)—O(1A), O(1)—N(2B), O(1)—N(2C), N(2A)—O(1B)	3.279 (2)
	N (NH$_3$)—Cl$^-$	
18, 19	N(2)—Cl(1), N(2A)—Cl(1C)	3.386 (2)
20	N(1)—Cl(1A)	3.391 (2)
21, 22	N(2)—Cl(1A), N(2A)—Cl(1A)	3.414 (2)
23, 24	N(3)—Cl(1), N(3A)—Cl(1C)	3.448 (2)
25, 26	N(3)—Cl(1B), N(3A)—Cl(1B)	3.536 (2)
	N (trans-NH$_3$)—N (NO$_3^-$)	
27	N(1)—N(5A)	3.274 (3)
	O (NO$_2^-$)—N (NO$_3^-$)	
28	O(1)—N(5)	2.811 (3)
	O (NO$_2^-$)—O (NO$_3^-$)	
29	O(1)—O(4)	2.908 (4)
30, 31	O(1)—O(3), O(1)—O(3A)	3.161 (2)
	O (NO$_2^-$)—Cl$^-$	
32	O(2)—Cl(1B)	3.542 (2)
	N (NO$_2^-$)—Cl$^-$	
33, 34	N(4)—Cl(1), N(4)—Cl(2C)	3.661 (0)

for the 'NH$_3$—O(NO$_2$)' contacts (in the range −0.03 to −0.04 Å or from −1.2 to −1.0%), as well as for some of the contacts 'N(NH$_3$)—Cl' (−0.04 Å or −1.0%) or of the contacts 'NH$_3$—O(NO$_3$)' (−0.03 Å or −0.9%). The changes in the distances 'N(NH$_3$)—Cl' were comparable with those measured for the 'N(NH$_4$)—Cl$^-$' distances during thermal expansion of ammonium chloride, NH$_4$Cl* (Boiko, 1969; Pöyhönen, 1960). The largest changes in the intermolecular distances were measured for 'N(NO$_2$)—Hal' contacts and also the lattice strain measured in the directions of these contacts was the largest. Absolute (relative) changes in the 'N—Cl' distances in [Co(NH$_3$)$_5$-NO$_2$]Cl(NO$_3$) were, respectively, −0.05 Å (−1.2%). This is 100% of the maximum linear strain in the structure.

As a result of structural distortion, the vectors linking atoms rotated (not more than 0.5–1°) with respect to the crystallographic axes and to the principal axes of the strain tensor. The angles between various vectors also

*The measurements of thermal expansion of ammonium chloride were carried out in different temperature intervals, therefore, such a comparison could be carried out only 'per one degree of temperature change', and should be treated with caution only as an approximate estimate. Still, we give these values here as a 'reference point', since no relevant literature data which could characterize the contraction of N—H···Cl bonds with decreasing temperature seem to be available.
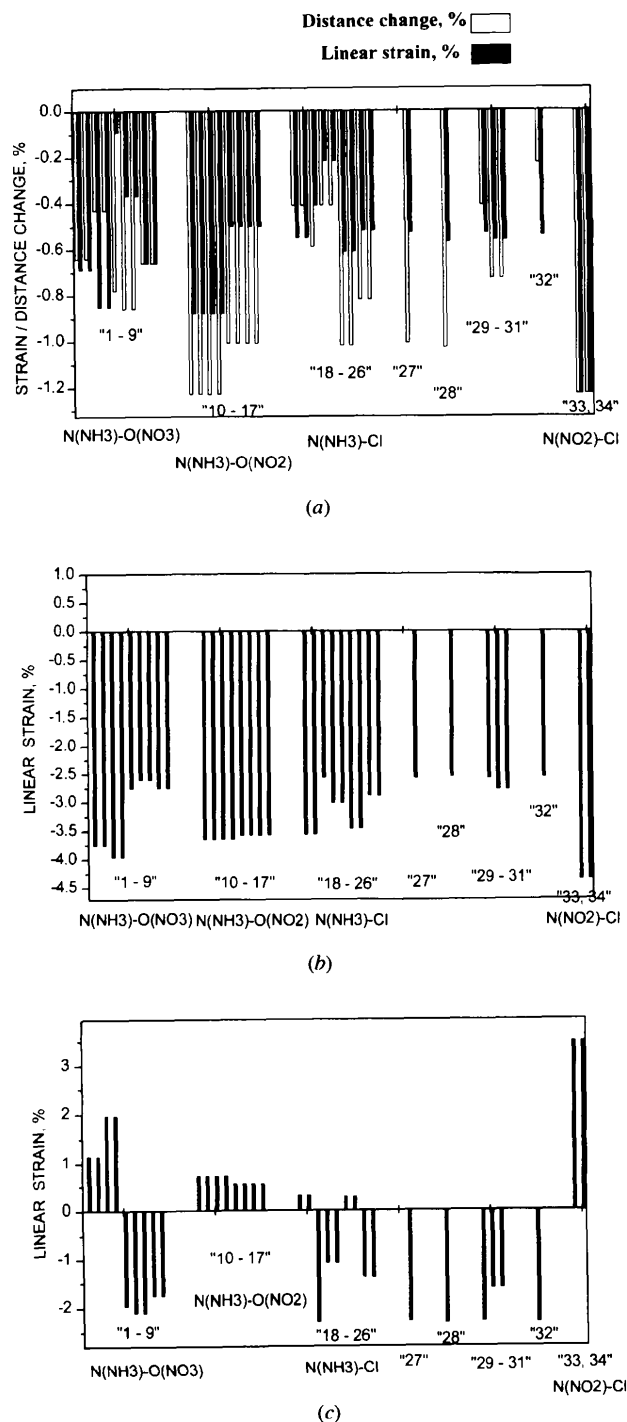

Fig. 5. Linear strain in the directions of the shortest intermolecular contacts of a complex cation with the neighbouring atoms in the structure of [Co(NH$_3$)$_5$NO$_2$]-Cl(NO$_3$) with (a) decreasing temperature, (b) increasing pressure and (c) nitro→nitrito linkage isomerization. Symmetry operations for generation of symmetry-equivalent atoms, numeration of contacts and the contact distances in the 'starting structure' (290 K, ambient pressure) are given in Tables 2 and 3.

changed slightly. As discussed in an early paper of Megaw (1939), an expansion of the lattice can result from a change in bond angles with temperature even if there is no change in bond lengths. Megaw has termed this a 'bond-angle' expansion, in contrast to an 'anharmonicity' or a 'bond-length' expansion. For directional interactions in the crystal, not only the distance changes but also changes in angles (even if they are small) may affect the properties and chemical reactivity to a noticeable extent.

It is hardly possible to discuss the anisotropy of the distortion of a crystal structure without considering the fragments of the structure larger than just a complex cation and its nearest environment. A fragment of the structure of $[Co(NH_3)_5NO_2]Cl(NO_3)$ (atoms in a layer parallel to the mirror plane **ac**, centred at the level $y = 0$) is plotted in Fig. 6. On cooling, the structure of $[Co(NH_3)_5NO_2]Cl(NO_3)$ contracts in the directions of the crystallographic axes **a** (medium contraction) and **c** (maximum contraction), and expands in the direction **b**, perpendicular to the **ac** plane. The maximum compression under pressure and the maximum expansion as a result of linkage isomerization are also along the **c** axis.

The **c** axis in the structure coincides with the direction of hydrogen-bonded chains formed by *trans*-NH_3 ligands of the cations and NO_3 anions* (Fig. 6). The crystallographic axis **a** is close to the directions of hydrogen bonds between *trans*-NH_3 ligands and Cl^- anions [contacts $N(1)-Cl(1A)$ in Table 3]. There are also some longer $N(H)\cdots O$ hydrogen bonds ('N—O' distance 3.132 (2) Å, see Table 3) between NH_3 ligands and O atoms of the NO_3 anion relatively close to the **a** direction. Neither the '*trans*-$NH_3\cdots Cl^-$' nor the '$NH_3\cdots O(NO_3)$' bonds alone form continuous chains

* The hydrogen bonds in these chains are the shortest in the structure. The $N(H)\cdots O$ distances are equal at 290 K to 2.982 (2) and 3.016 (2) Å (Table 3).

in the **a** direction. There seem to be no vectors linking atoms involved in 'intermolecular' non-covalent interactions, which point close to the **b** direction in the structure.

The directions of maximum thermal expansion and of maximum compression under hydrostatic pressure in the structure of $[Co(NH_3)_5NO_2]Cl(NO_3)$ (**c** direction) is parallel to the planes of NO_3 anions. This is very different from the anisotropy of thermal expansion of some simple ionic nitrates, such as, for example, sodium nitrate, in which the thermal expansion in the directions parallel to the planes of NO_3 ions is an order of magnitude *less* than that in the direction perpendicular to the planes (Kantola & Vilhonen, 1960).

4. Discussion

Thermal expansion is often considered to be one of the most important thermodynamic properties of a crystal in relation to its structure (see, for example, Robertson & Ubbelohde, 1939; Krishnan *et al.*, 1979). Anisotropy of thermal expansion is a result of the anisotropy of the intermolecular forces and has its origin in the distribution of the particular types of bonds within the given crystal. To be able to calculate and predict thermal expansion of a solid, one would have to formulate a model for the forces in the crystal. Such attempts are being done, but even for the simplest possible systems with *isotropic* thermal expansion, such as cubic structures of metals, of alkaline metal halides or of hexametallates, the problem is far from being solved (Gupta & Goyal, 1984; Jain & Goyal, 1991; Krishnan *et al.*, 1979; Ledbetter, 1991; Novikova, 1947).

There is much less theoretical work on the thermal expansion of *anisotropic* materials. Thermal expansion of a crystalline solid is a structure-dependent physical property, but attempts to predict the expansion
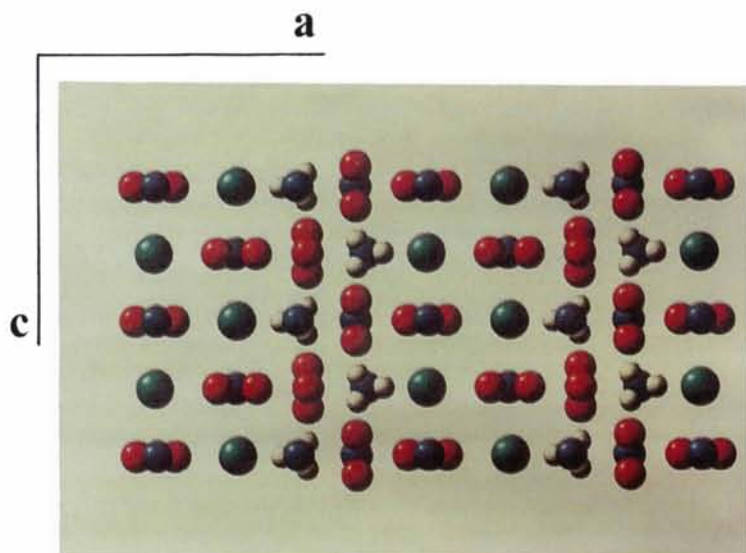

a

c

Fig. 6. The fragment of the structure of $[Co(NH_3)_5NO_2]Cl(NO_3)$: plane **ac**, atoms in a layer centred at the level $y = 0$. Distances from the level $y = 0$ (at 290 K): Cl^-: ±0.183 Å; *trans*-NH_3: ±0.864 Å; $O(NO_2)$: ±0.439 and ±0.678 Å; $N(NO_2)$: ±0.015 Å; $N(NO_3)$: ±0.009 Å; $O(NO_3)$: ±0.620; ±1.241 Å. Red = O; blue, small = N; white = H; green, large = Cl.

behaviour of a known crystal structure have met with limited success. Theoretical evaluation of the coefficient of expansion is possible if the effective potential well in which a particular atom is situated is known (Smyth, 1955; Mitra & Joshi, 1961; Killean, 1974). However, this method is only suitable for calculating the average expansion coefficient of simple metals and ionic crystals where the displacements of atoms are controlled by a single force constant. Among some attempts to predict the anisotropic thermal expansion behaviour, one can cite the paper of Khan (1976) treating some simple ionic solids. The approach is empirical and the method essentially consists of calculating the unit-cell and position parameters of a structure after predicting the expansion of various coordination polyhedra. Another example is a theoretical paper of Lifshits (1952), dealing with the anisotropy of thermal expansion of chain and layer structures. We refer to these relatively old publications, since not too much new seems to have been suggested in this field.

The complexity of crystal structures and the state of incompleteness of the theory of crystal physics make it sometimes feasible to study the connection between crystal structure and physical properties by a descriptive method of correlation rather than by attempting a strict and detailed theory. Therefore, starting from the very early publications on the thermal expansion up until nowadays, attempts were made to correlate empirically the anisotropy of thermal expansion with the orientation of the complex ions/molecules in the crystal (Choi & Prask, 1983; Megaw, 1939; Kitaigorodsky, 1971; Kozhin & Kitaigorodsky, 1953a,b, 1955; Lonsdale, 1959; Ryzhenkov, 1972).

Anisotropy of thermal expansion was often correlated in the literature with the directions of hydrogen bonds in the crystal structure (Filhol & Thomas, 1984; Gallagher et al., 1955; Krishnan et al., 1979; Lonsdale, 1959; Nitta, 1973; Pirenne, 1955; Robertson & Ubbelohde, 1939; Sadanadam & Suryanarayana, 1979; Swaminathan, Craven & McMullan, 1984; Ubbelohde, 1939; Ubbelohde & Woodward, 1946; Wang, Tsai, Liu & Calvert, 1985; Whuler, Spinat & Brouty, 1978).* In several publications, starting with the early measurements of changes in lattice parameters with temperature (Gallagher et al., 1955; Robertson & Ubbelohde, 1939; Ubbelohde & Woodward, 1946) and ending with precise electron-charge-density studies (Wang et al., 1985), short hydrogen bonds were shown to expand with increasing temperature, whilst long hydrogen and hydroxyl bonds contract. At the same time, opposite examples are also known, when there was little or practically no thermal expansion observed in the crystallographic planes of intermolecular hydrogen-

bond networks, whilst maximum thermal expansion was measured in the direction perpendicular to this plane (Nitta, 1973; Ryzhenkov, 1972). The interrelation between the anisotropy of thermal expansion and the directions of hydrogen bonds in the structure (maximum thermal expansion in the direction of the short hydrogen bonds) was claimed to be more pronounced in molecular crystals than in ionic crystals, the hydrogen bond being stronger than van der Waals forces but weaker than the ionic bond (Pirenne, 1955; Ubbelohde, 1939).

Garnier, Calvarin & Weigel (1972) and Weigel, Beguemsi, Garnier & Gerar (1978) have suggested interpreting the principal coefficients of the thermal expansion tensor as those of the weakest and strongest chemical 'repulsive' interactions in the structure. The role of dipole–dipole interactions between the ions, for example, between the NO_2^- ions, or of the molecular vibrations and librations (Gesi, 1969; Krishnan et al., 1979; Lonsdale, 1959), for example, of the librations of such ions as NO_3^- (Choi & Prask, 1983), in determining the anisotropy of thermal expansion was also discussed. Despite so many efforts, it still remains problematic not only to *predict* the anisotropy of thermal expansion of a known structure but even simply to *explain* the anisotropy measured experimentally.

The crystal structure of $[Co(NH_3)_5NO_2]Cl(NO_3)$ is built from complex cations, $[Co(NH_3)_5NO_2]^{2+}$, and anions (Cl^- and NO_3^-). It was supposed to be determined almost entirely by close packing of complex cations, which are substantially larger than the anions (Podberezskaya, Yudanova, Magarill, Ipatova, Romanenko, Pervukhina & Borisov, 1991). At the same time, the complexes of the $[Co(NH_3)_5NO_2]XY$ series with different anions are not isostructural (the only exceptions are the chloride and bromide) and this indicates that interactions between cations and anions are no less important for the choice of crystal structure made by nature for each particular compound. One can expect the same to be also true for the anisotropy of distortion of this structure resulting from a particular influence.

It was difficult to say *a priori* which of the interactions in the heterodesmic* crystal structure of $[Co(NH_3)_5NO_2]Cl(NO_3)$ is most important for structural distortion. The main non-covalent interactions in the crystals are Coulomb interactions between charged anions and cations, as in 'usual' ionic crystals, and van der Waals interactions, as in 'usual' molecular crystals. Several types of hydrogen bonds can be found in the structure, namely (i) the bonds between the NH_3 ligands of the cations and the halide anions, (ii) the bonds between the NH_3 ligands of cations and the O atoms of the NO_2 ligands of the neighbouring cations and (iii) the

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* Moreover, in the early papers on the subject, Ubbelohde and his co-workers were suggesting measuring the thermal expansion of crystals as a method of obtaining information on hydrogen and hydroxyl bonds in the structure.

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* Heterodesmic structures: structures with different types of chemical bonds and interatomic interactions, as first defined by Hassel (1934) or by Evans (1946).

bonds between the NH_3 ligands of the cations and the O atoms of NO_3 anions. One cannot also exclude the existence of specific non-bonded interactions between NO_2 and Cl^- (Desiraju, 1995).

Hydrogen bonds may act as 'joints', which account for large, anisotropic and reversible distortions of the crystal structure. They are known to play a central role in the lattice dynamics and structural transformations in complex ammines of transition metals (Bates, Hughes & Somerford, 1983; Elgsaeter & Svare, 1970; Essmann, Fischer & Vogt, 1996; Hoser, Prandl, Schiebel & Heger, 1990; Janik, Janik & Janik, 1978). At the same time, the anisotropy of structural distortion of the same structure even at two scalar isotropic actions (temperature and pressure) is different. This shows that the real situation with distortion of $[Co(NH_3)_5NO_2]Cl(NO_3)$ is even more complicated and other interactions in the structure (such as, for example, Coulomb interactions between the charged cations and anions, interactions between the NO_2 ligand and Cl^- anion or van der Waals interactions) have also to be taken into account. The relative role of different types of interactions in structural contraction resulting from different actions seems to be different. One can suppose that the main interplay must be between optimizing weak (but cumulative!) non-covalent interactions and the tendency to decrease the 'free space' in the structure.

The present contribution is (to the best of our knowledge) one of the few attempts to compare in detail distortions induced by different actions in the same structure. We aimed to show experimentally that, contrary to an existing view, distortion of the same structure may be not only quantitatively but also qualitatively different, even if the symmetry of the compressing action is the same, and to attract attention to the problem of finding the type(s) of intermolecular interactions in the crystal predominantly responsible for each type of structural distortion.

5. Conclusions

The present study has shown the structural distortion of $[Co(NH_3)_5NO_2]Cl(NO_3)$ on cooling to be highly anisotropic. The anisotropy of distortion of the same structure under another scalar influence, namely hydrostatic pressure, is different from that on cooling. The anisotropy of contraction of the same structure during linkage nitro-nitrito isomerization is even more different. In all three cases, the anisotropy of strain can be correlated with the directions of '$NH_3 \cdots NO_3^-$' chains linked by the shortest '$N-H \cdots O$' hydrogen bonds in the structure. The hydrogen bonds '$N-H \cdots Cl^-$' between $trans$-NH_3 ligands and Cl^- anions, and the non-bonded interactions between the NO_2 ligands and the Cl^- anions also seem to play an important role in determining the anisotropy of strain.

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