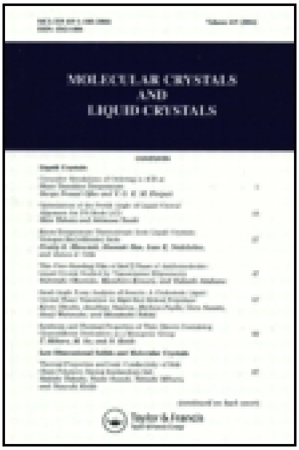

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Intramolecular Linkage Isomerization in the Crystals of Some Co(III) - Ammine Complexes - A Link Between Inorganic and Organic Solid State Chemistry

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INTRAMOLECULAR LINKAGE ISOMERIZATION IN THE CRYSTALS OF SOME Co(III) - AMMINE COMPLEXES - A LINK BETWEEN INORGANIC AND ORGANIC SOLID STATE CHEMISTRY

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Abstract Linkage isomerization in the crystals of some Co(III)-ammine complexes is chosen as an example to illustrate the effect of the crystalline surroundings on an intramolecular process, and vice versa.

INTRODUCTION

One of the central problems of solid state chemistry is the interrelation between the "individual" and "collective": to what extent the behaviour of individual species (atoms, ions, molecules) in solid state reactions is affected by the way in which these species are organized in a solid (i.e. by crystal structure in a very general sense).

In human society, there exist both groups in which the behaviour of the individual is drastically changed (a military detachment or a crowd), and also those in which the behaviour is only slightly modulated (an ideal research team). The extent to which the individuality can be influenced by the surroundings depends on the complexity of the individual and on the type and the intensity of the external action. Among crystals one can also find extremes. At the one extreme, there are molecular crystals with relatively weak short-ranged intermolecular interactions and the complex molecules, forming the crystal, which preserve their "individuality" to a large extent. At the other extreme there are ionic crystals of halides or oxides, in which strong long-range interactions between ions make it impossible to distinguish separate "molecules"; rather the whole crystal is to be considered as a "giant molecule". The difference between these two classes of solids seems to be so large that, traditionally, they are studied by two branches of solid state chemistry, which are being developed so independently that scientists working in one field are usually unaware of the results obtained and the concepts worked out in another.

Solid coordination compounds represent "the golden middle" in the world of crystals: they exhibit long-range interactions between ions, whilst the individuality of complex ions is preserved to a large extent. This makes them very promising for fundamental solid state research. The study of solid coordination compounds can benefit from the application of methods and concepts of both inorganic and organic solid state chemistry. To illustrate this point, the intrasphere nitro - nitrito isomerization of the Co(III)-ammine complexes of general formula $[Co(NH_3)_5NO_2]XY$ and $[Co(NH_3)_5ONO]XY$ ($XY=Cl_2$, Br_2, I_2, $Cl(NO_3)$, $(NO_3)_2$) will be discussed. The example of this linkage isomerization may serve to show that a link can be built between two seemingly independent branches of solid state chemistry.

GENERAL PROBLEM TO BE SOLVED

It has long been known that the NO_2-ligand in Co(III)-ammine complexes can be coordinated to cobalt either via nitrogen ("nitro"-coordination), or via oxygen ("nitrito"-coordination). In fact, this year we may celebrate a 100-year anniversary since the time these linkage isomers were first described by Jorgensen[1]. Nitrito-isomers are less favourable thermodynamically[2], and, when stored, convert into nitro-isomers (heating accelerates the reaction)[3]. Irradiation of the samples with visible (blue) or UV-light results in the reverse process: nitro-isomers convert into nitrito-isomers[3]. The isomerization was shown to be intramolecular, both in solution[4] and in the solid state[5], i.e. coordination of the NO_2-ligand is changed, but the ligand is bound to the same central atom as before the reaction, so that there is no exchange of the ligands between different complex cations.

The problem that I would like to consider can be formulated as the following question:

TO WHAT EXTENT IS THIS INTRAMOLECULAR REACTION REALLY INTRAMOLECULAR, WHEN PROCEEDING IN THE SOLID STATE?

Or, to put it in a less provocative way,

1. Does the intramolecular isomerization in a complex ion influence the surroundings?
2. Do the surroundings of a complex ion in the crystal influence the intramolecular isomerization?

THE EFFECT OF THE INTRAMOLECULAR ISOMERIZATION IN A COMPLEX ION ON THE SURROUNDINGS

Macrodeformation and fragmentation of the crystals

Observation of a crystal during the linkage isomerization provides a clear evidence that the crystal does feel that the NO_2-ligands within the complex cations change their coordination, although this reaction proceeds intramolecularly. Mechanical stresses, generated as a result of the reorganization within the cations, are large enough to cause a violent fragmentation of the crystals (Fig.1a), or, under special experimental conditions, their elastic deformation (Fig.1b)[6]. Fragmentation, of course, is not reversible, that is, a crystal cannot be restored from the fragments by a reverse isomerization. Deformation, however, IS reversible, and a crystal, bent in the course of the nitro-nitrito isomerization, restores its shape after storage at room temperature or after heating, as a reverse nitrito-nitro isomerization proceeds (Fig.1c). Moreover, the properties of a crystal do not change even after a large number of cycles "irradiation - heating"[7,8].

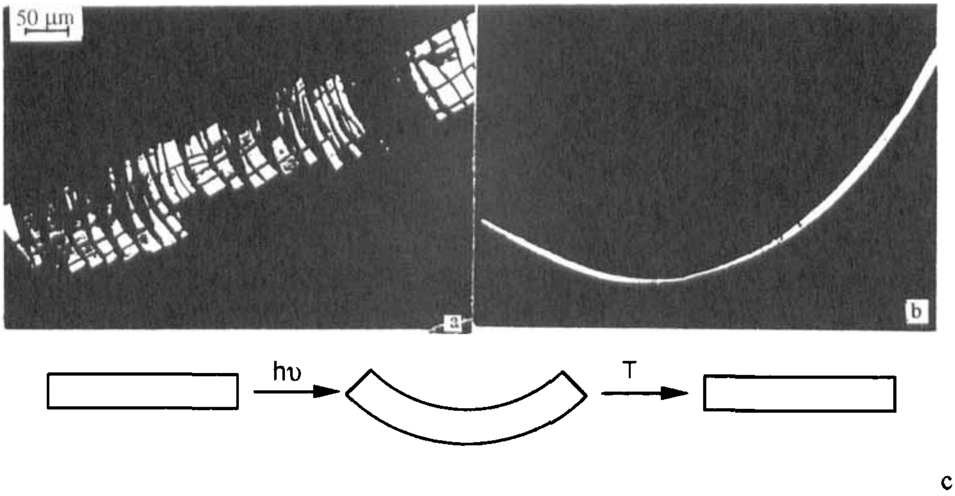


Fig.1 Fragmentation (a) and bending (b) of single crystals of $[Co(NH_3)_5NO_2]Cl(NO_3)$ in the course of photoisomerization. Reversibility of the deformation (c).

Lattice distortion

Obviously, some deformation of crystal structure must correspond to the macrodeformation of the crystals, observed visually. This structural deformation can be followed by X-ray diffraction. Single crystal techniques are difficult to apply for this purpose because of the fragmentation of the crystals in the course of the isomerization. Two attempts known from the literature may be cited[5,9], but the second one[9] was hardly successful (not even changes in lattice parameters were detected), and the first one has also met with some difficulties related to the deterioration of the quality of the crystals as the isomerization proceeded[5]. Luckily, powder diffraction turned out to be quite successful in solving the problem. Grenthe and Nordin were the first to use the technique to follow structural changes in the solid $[Co(NH_3)_5ONO]Cl_2$, precipitated from aqueous solution, in the course of nitrito-nitro-isomerization at ambient temperature[5]. Their study has shown that the reaction proceeds via formation of solid solutions of nitro-isomer in the original nitrito-isomer, and at all times the system remains monophase[5]. Recently, the same was shown to be true not only for $[Co(NH_3)_5ONO]Cl_2$, but for the whole series of complexes $[Co(NH_3)_5ONO]XY$ ($XY=Cl_2$, Br_2, I_2, $Cl(NO_3)$, $(NO_3)_2$)[10].

We have measured the changes in the lattice parameters during the nitro-nitrito photo- and the reverse nitrito-nitro thermoisomerization (Table 1)[10]. Intramolecular linkage isomerization within the complex cations was shown to induce a continuous distortion of the whole crystal structure, forcing both the cations and the anions to change their positions slightly[10]. The structural transformation is topotactical, i.e. at all times during the isomerization the system remains a monophase one, and the main structural framework is preserved, being only continuously distorted. Distortion is reversible: as the reverse isomerization proceeds, the original lattice is restored. As an example, see the sequence of schematically presented powder X-ray diagramms for nitro-nitrito-nitro isomerization in the crystals of bromide (Fig.2). Similar results were obtained for all other compounds of the series studied[10].

In all the complexes $[Co(NH_3)_5NO_2]XY$, the lattice distortion resulting from solid state nitro-nitrito photoisomerization proceeds in such a way that the lattice symmetry either remains unchanged ($XY=I_2$ $Cl(NO_3)$, $(NO_3)_2$), or becomes higher ($XY=Cl_2$, Br_2)[10]. This is remarkable, since the symmetry of the $[Co(NH_3)_5ONO]^{+2}$-cation, formed during photoisomerization, is lower, than that of the $[Co(NH_3)_5NO_2]^{+2}$-cation. The structures of nitro-complexes are known to be determined by the optimal close packing of the complex cations[11]. Analysis of the

COMPOUND	a, Å	b, Å	c, Å	β,°
NO_2	10.351(2)	8.681(2)	10.731(3)	94.78(2)
$[Co(NH_3)_5$] Cl_2				
ONO	10.364(2)	8.854(6)	10.364(2)	90.00
NO_2	10.698(4)	8.853(2)	10.980(3)	94.52(3)
$[Co(NH_3)_5$] Br_2				
ONO	10.799(3)	8.974(2)	10.599(3)	90.00
NO_2	14.558(7)	7.588(4)	10.992(4)	90.00
$[Co(NH_3)_5$] I_2				
ONO	14.557(5)	7.496(4)	10.891(5)	90.00
NO_2	14.848(2)	9.626(4)	7.302(2)	90.00
$[Co(NH_3)_5$]$Cl(NO_3)$				
ONO	14.500(5)	9.451(8)	7.558(3)	90.00
NO_2	7.591(1)	7.591(1)	10.246(1)	90.00
$[Co(NH_3)_5$] $(NO_3)_2$				
ONO	7.479(6)	7.479(6)	10.508(4)	90.00

Table 1 The changes in the lattice parameters in the course of the solid state nitro-nitrito isomerization.

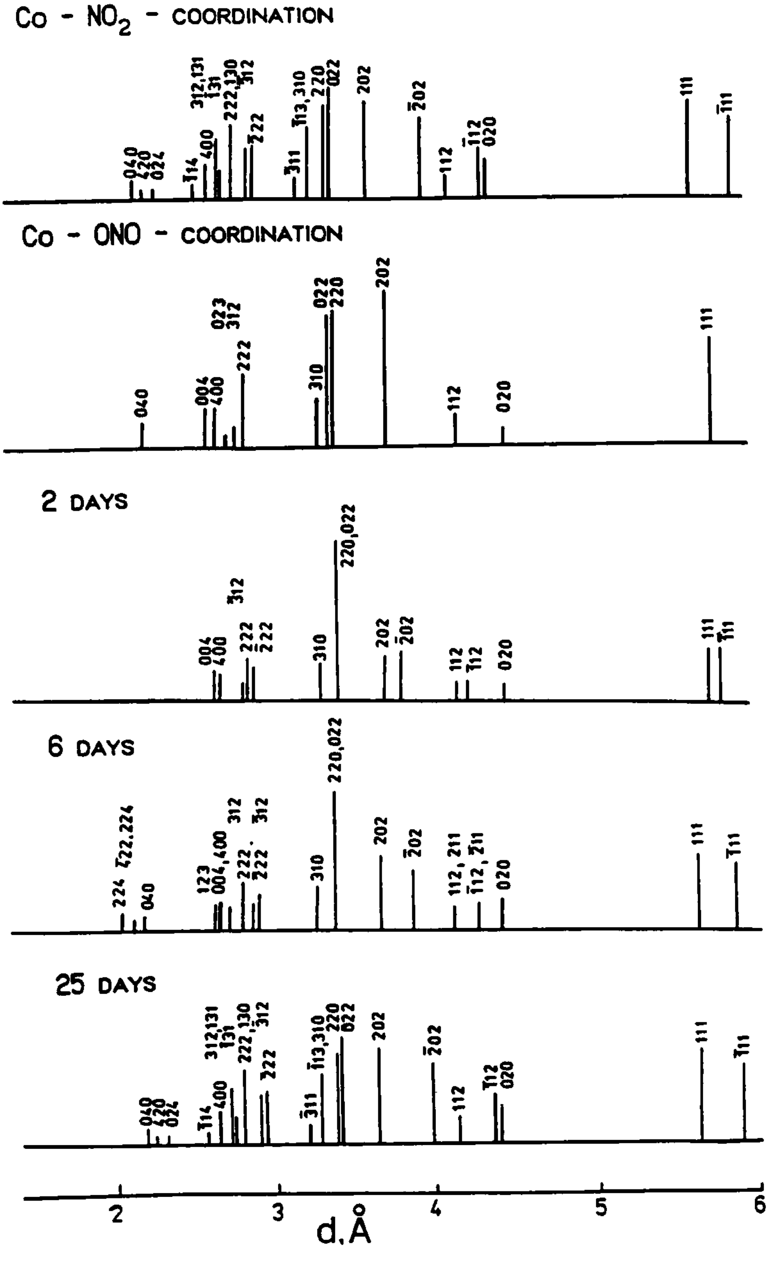


Fig.2 Powder X-ray diagramms for nitro-nitrito-nitro isomerization in $[Co(NH_3)_5NO_2]Br_2$.

symmetry of the cation sublattice in the starting nitro-structures, and of the possible changes of symmetry resulting from the changes in the lattice parameters[12], allowed us to suppose that the space groups of the crystal structures of the nitrito-isomers $[Co(NH_3)_5ONO]XY$ ($XY=I_2$, $Cl(NO_3)$, $(NO_3)_2$), formed in the course of the linkage photoisomerization, must be the same as the space groups of the starting nitro-isomers (Pnma, $Pna2_1$, I4mm, correspondingly), and are to be changed from C2/c to Cmcm in the case of nitro-nitrito isomerization in $[Co(NH_3)_5NO_2]Cl_2$ and $[Co(NH_3)_5NO_2]Br_2$ (Table 2). The systematic absences did not contradict this hypothesis[10], and recently a more direct confirmation for the $[Co(NH_3)_5NO_2]Br_2$ - $[Co(NH_3)_5ONO]Br_2$ isomerization was obtained using a Rietveld refinement technique[13].

XY	Metric symmetry		Space group	
	Coordination		Coordination	
	NO_2^-	ONO^-	NO_2^-	ONO^-
Br_2	monoclinic	orthorhombic	C2/c	Cmcm*
Cl_2	monoclinic	tetragonal	C2/c	Cmcm
I_2	orthorhombic	orthorhombic	Pnma	Pnma
$Cl(NO_3)$	orthorhombic	orthorhombic	$Pna2_1$	$Pna2_1$
$(NO_3)_2$	tetragonal	tetragonal	I4mm	I4mm

* - confirmed by Rietveld refinement

Table 2 Metric and space symmetry of the structures of $[Co(NH_3)_5NO_2]XY$ complexes and of the corresponding nitrito-complexes, obtained in the course of the solid state nitro-nitrito photoisomerization

In the crystals of the nitro-series, only in the $[Co(NH_3)_5NO_2]I_2$ and in the $[Co(NH_3)_5NO_2](NO_3)_2$ site symmetry of the positions occupied by complex cations is higher than the symmetry of individual cations themselves, and this requires a disordered orientation of NO_2-groups[14-18]. Site symmetry of the positions occupied by complex cations, $[Co(NH_3)_5ONO]^{+2}$, in the structures of $[Co(NH_3)_5ONO]XY$, formed in the course of nitro-nitrito photoisomerization, requires disordered orientations of the ONO-ligand in almost all the complexes of the series. The only exception seems to be $[Co(NH_3)_5ONO]Cl(NO_3)$, in which cations are in general positions, and disordered orientation of ONO-ligands is not unavoidably necessary. In fact, disordered orientation of ONO-ligands in the structures of photochemically synthesized $[Co(NH_3)_5ONO]Br_2$ and $[Co(NH_3)_5ONO]Cl_2$ was confirmed by Rietveld refinement[13]. The study of $[Co(NH_3)_5ONO]Cl(NO_3)$ is in progress[19].

Fourier difference maps, obtained for the structures of $[Co(NH_3)_5ONO]Br_2$ and $[Co(NH_3)_5ONO]Cl_2$, formed in the course of nitro-nitrito isomerization, suggest also that, besides an orientational disorder, $[Co(NH_3)_5ONO]^{+2}$ - cations with different geometries of ONO-ligand may coexist within the structure, the ratio of different geometries being possibly dependent upon the ratio of nitro- and nitrito-cations in the crystal (i. e. upon the degree of isomerization, α)[13].

The integral change in the molar volume as a result of nitro-nitrito linkage isomerization is negative (Table 3)[10]. This may seem to contradict the data, obtained previously by M. Mares et al, who have estimated the effective volume of the nitrito-cation to be approximately 1.2 times larger than that of the nitro-isomer[20]. However this contradiction is only apparent. First, the effective volumes reported in [20] refer to the ions in solution. The molar volumes, calculated from X-ray powder experiments for solids, include not only the volumes of the ions, but also the free volume, which is always present in any crystal structure. If the free volume in the crystal decreases, the integral molar volume of the solid may also decrease, even if the effective volumes of cations increase. Second, lattice distortion during the isomerization is anisotropic[10]. In the crystals, despite an integral decrease in the molar volume as a result of nitro-nitrito isomerization, there are directions which expand rather than contract. This can be seen simply from a summary of lattice parameter changes (Tables 1 and 4)[10]. However, a better way to visualize the anisotropic deformation of a lattice is to use the experimental data on the changes of the parameters to calculate the corresponding strain tensor and to plot the strain ellipsoid with respect to the crystallographic axes[21]. As an example, a strain ellipsoid for the nitro - nitrito photoisomerization in the bromide is shown in Fig.3 (a). Fig.3 (b, c) is to give an impression of how the principal axes of the ellipsoid are oriented with respect to the

COMPOUND	VOLUME, Å^3
NO_2	960.9(4)
$[Co(NH_3)_5$ $]Cl_2$	
ONO	951.0(7)
NO_2	1036.7(5)
$[Co(NH_3)_5$ $]Br_2$	
ONO	1027.2(5)
NO_2	1214.(1)
$[Co(NH_3)_5$ $]I_2$	
ONO	1188.(1)
NO_2	1043.7(5)
$[Co(NH_3)_5$ $]Cl(NO_3)$	
ONO	1036.(1)
NO_2	1180.8(2)
$[Co(NH_3)_5$ $](NO_3)_2$	
ONO	1175.6(7)

Table 3 The change in the volume of elementary cell (per 4 formula units in all the compounds) as a result of solid state nitro-nitrito linkage isomerization

COMPOUND	$\frac{\Delta V}{V}$, %	$\frac{\Delta a_1}{a_1}$, %	$\frac{\Delta a_2}{a_2}$, %	$\frac{\Delta a_3}{a_3}$, %
$[Co(NH_3)_5NO_2]Cl_2$	-1.0(1)	-3.42(5)	0.13(4)	2.0(1)
$[Co(NH_3)_5NO_2]Br_2$	-0.9(1)	-1.65(5)	-0.93(7)	1.37(5)
$[Co(NH_3)_5NO_2]I_2$	-2.1(2)	0.0(1)	-0.92(8)	-1.2(1)
$[Co(NH_3)_5NO_2]Cl(NO_3)$	-0.7(1)	-2.34(5)	-1.8(1)	3.51(7)
$[Co(NH_3)_5NO_2](NO_3)_2$	-0.4(1)	2.56(5)	-1.48(8)	-1.48(8)

Table 4 Relative changes in the molar volume and of the linear lattice parameters in the case of nitro-nitrito solid state photoisomerization ($a_1>a_2>a_3$)

various groups of atoms forming the crystal structure of the starting nitro-isomer. This helps to understand the forces that act in the crystal as the isomerization proceeds, and what sort of movement of atoms may be supposed to take place. Thus, e.g., the strain ellipsoid for NO_2-ONO isomerization in the bromide (and the same, with only slight quantitative differences, for the isostructural chloride) shows (Fig.3) that during the reaction the lattice expands slightly in the direction of the Co-NO_2 bond (axis **b**, coinciding with the principal axis **2** of the strain ellipsoid). The directions of major expansion (principal axis **1**) and major contraction (principal axis **3**) do not coincide with the direction of any crystallographic axis. It is possible to notice, however, that the direction of maximal expansion is perpendicular to the plane of the NO_2-group, and the lattice is compressed in the direction close to the perpendicular to the bisector of the O-N-O-angle. This seems to indicate that, in the crystal, the NO_2-group leaves the original plane as the coordination of this group to cobalt is changed from nitro- to nitrito. In fact, this is in agreement with the location of maxima at the Fourier difference map, obtained from powder diffraction experiments[13]. The result contradicts the statement of Kubota and Ohba that nitro-nitrito photoisomerization in the crystals of $[Co(NH_3)_5NO_2]Cl_2$ takes place nearly in the nitro-plane[9], but, nevertherless, seems to be quite reasonable.

Fig.3, a

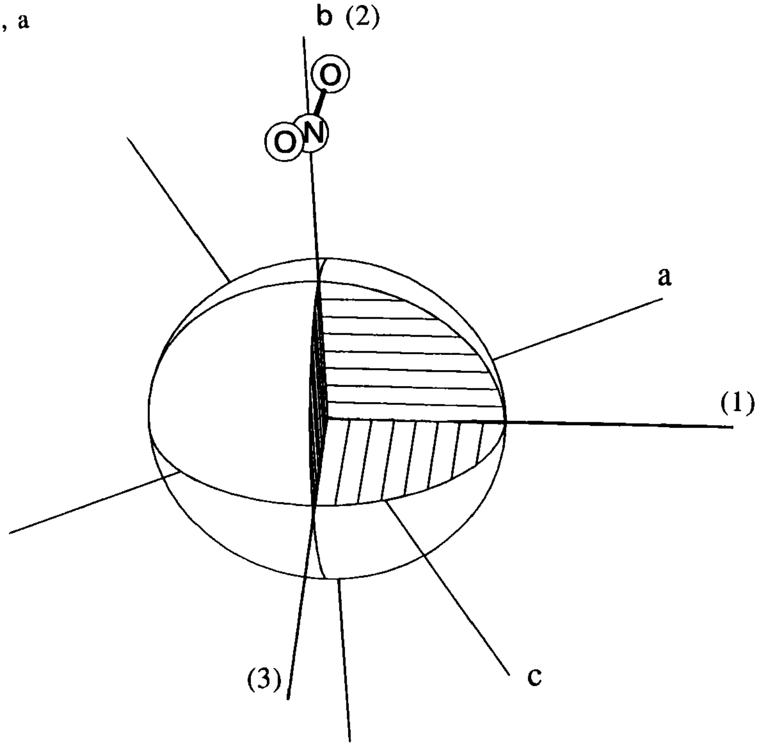
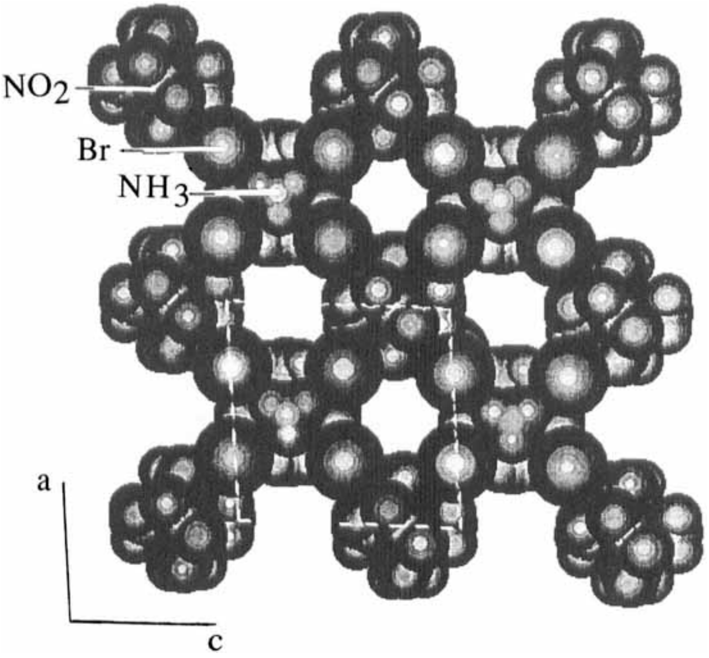


Fig.3 Strain ellipsoid for the lattice distortion in the course of solid state nitro-nitrito photoisomerization in $[Co(NH_3)_5NO_2]Br_2$. Deformation is exaggerated.
a, b, c, - crystallographic axes; **1, 2, 3** - principal axes of the ellipsoid.

a: Orientation of the strain ellipsoid with respect to the crystallographic axes. NO_2-group in the parent structure of the nitro-isomer is also plotted in the same coordinate system.

b, c: Orientation of strain ellipsoid with respect to various groups of atoms in the crystal:
Above: structure of the parent nitro-isomer (different projections). Only one layer of complex cations and anions in the unit cell is plotted. White dashed lines show a unit cell.
Below: Projections of the strain ellipsoid on the same planes. Dashed line plots a reference sphere.



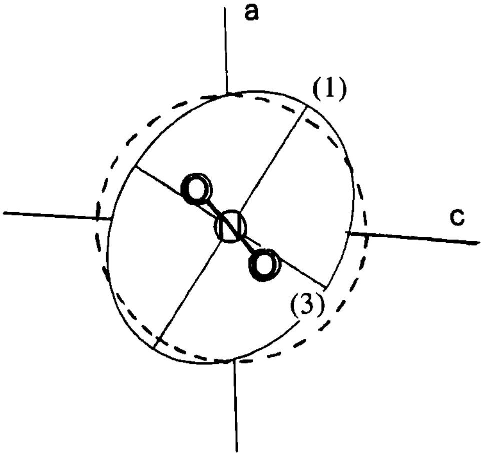
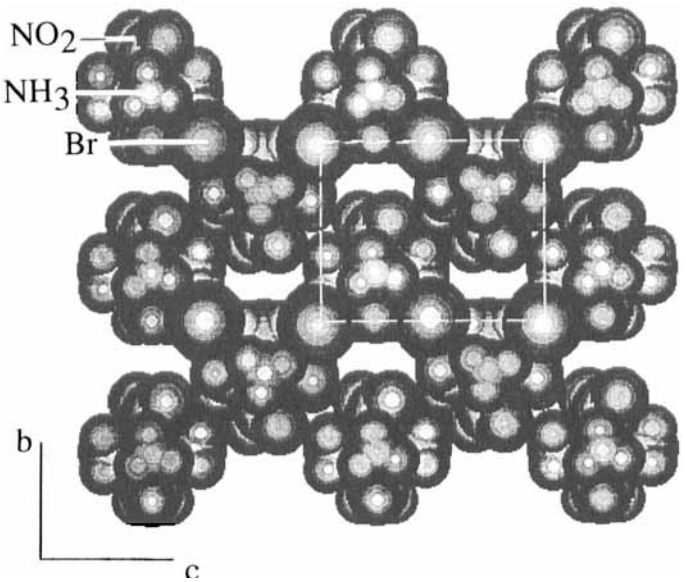


Fig.3, b



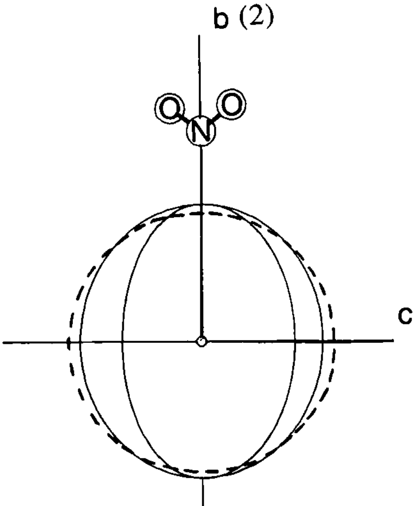


Fig.3, c

Earlier Grenthe and Nordin have supposed, based on the Van-der-Waals contact distances, that nitrito-nitro isomerization in solid $[Co(NH_3)_5ONO]Cl_2$ cannot take place in the original plane of the nitro-group[5]. A similar conclusion was made when intermolecular contacts were analyzed in crystals of $[Co(NH_3)_5NO_2]Cl(NO_3)$[22]. In fact, this is in good agreement with the orientation of the strain ellipsoid with respect to the direction of NO_2-plane in $[Co(NH_3)_5NO_2]Cl(NO_3)$: the direction of major expansion is perpendicular to the plane, whereas along the Co-NO_2 bond the lattice actually contracts (Fig.4).

Taking into account the anisotropy of the crystal structure distortion during the isomerization helps to explain one more apparent contradiction in the experimental observations. When irradiated only from one side, the crystals of $[Co(NH_3)_5NO_2]Cl(NO_3)$ bend in the course of the nitro-nitrito isomerization (Fig.1b)[6]. The reason is that light is strongly absorbed by the surface layers of the crystal and, hence, the reaction proceeds inhomogeneously within the volume, but mainly in these surface layers[23]. The crystal bends in such a way that its convex side faces the incident light flux. In the case of an isotropic deformation, this would indicate that the increase of molar volume results from nitro-nitrito isomerization. The experimentally measured decrease in the volume (Table 3)[10] does not contradict, however, the visual observations of the macrodeformation of the single crystals (Fig.1b)[6], since the distortion is anisotropic[10], and it is the direction along the axis of the needle-shaped $[Co(NH_3)_5NO_2]Cl(NO_3)$ single crystal which expands by about 3.5%, whereas the perpendicular directions contract[10]. This example clearly shows how careful one should be when estimating the values of the internal stresses induced in the crystal in the course of a solid state reaction. Estimates based on measurements of macrodeformations can give an erroneous sign, if a crystal is approximated by an isotropic medium[23].

Shifts of vibrational frequences

We have already discussed two ways in which the influence of the intramolecular linkage isomerization on the surroundings of the crystal manifests itself. The first was the visually observed macrodeformation and/or fragmentation of single crystals during the isomerization. The second was the distortion of crystal structure, observed in the X-ray powder diffraction experiments. This is already a "more microscopic level" of studying the influence, since it shows clearly that "intermolecular properties", namely the juxtapositions of cations and anions, are being changed. IR-vibrational spectroscopy provides evidence that, also, the "intramolecular properties"

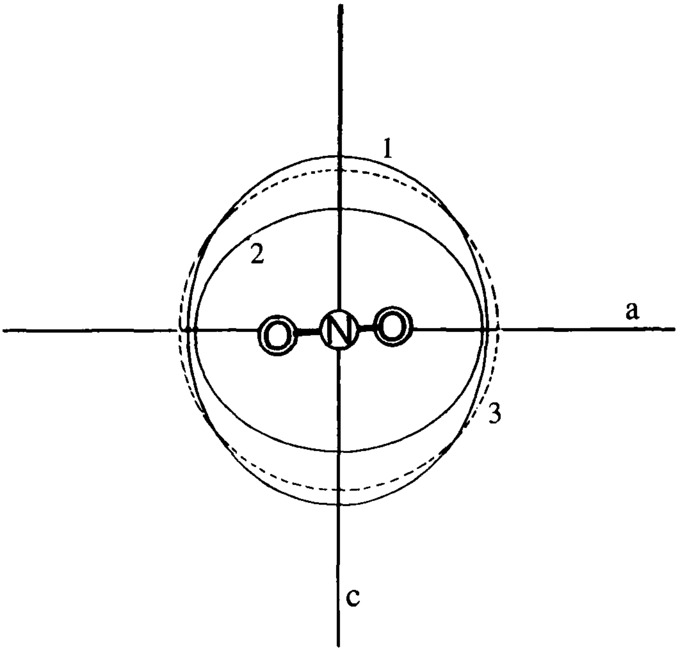


Fig.4 Projections of strain ellipsoids for the distortion of crystal structure of $[Co(NH_3)_5NO_2]Cl(NO_3)$:
1 - nitro-nitrito isomerization;
2 - hydrostatic pressure;
3 - reference sphere (dashed line)

of the cations are affected by the isomerization proceeding in this crystal. Thus, a large shift of the vibrational frequencies of the nitrito-group was measured as the crystals were undergoing the nitrito-nitro isomerization (Fig.5)[24]. It is important to stress that this is not the frequency shift related to the change in the coordination type from nitrito- to nitro-, but the shift of the vibrational frequencies of the oxygen-coordinated ligands, observed as the ratio of nitrito-isomers to nitro-isomers in the crystal decreased. Similar frequency shifts were observed earlier when studying various solid state decomposition reactions, and were interpreted in terms of local stresses induced in the crystals[25-29]. Even some quantitative estimates of stress values (neglecting the anisotropy of stresses) were made, based on a comparison of the frequency shifts, observed in the course of reactions, with the corresponding pressure induced frequency shifts[25-29]. More generally, one could speak of some inter- and intramolecular distortions, induced in the crystals by solid state reactions, that manifest themselves in the IR-vibrational spectra. Whatever terms be used to describe

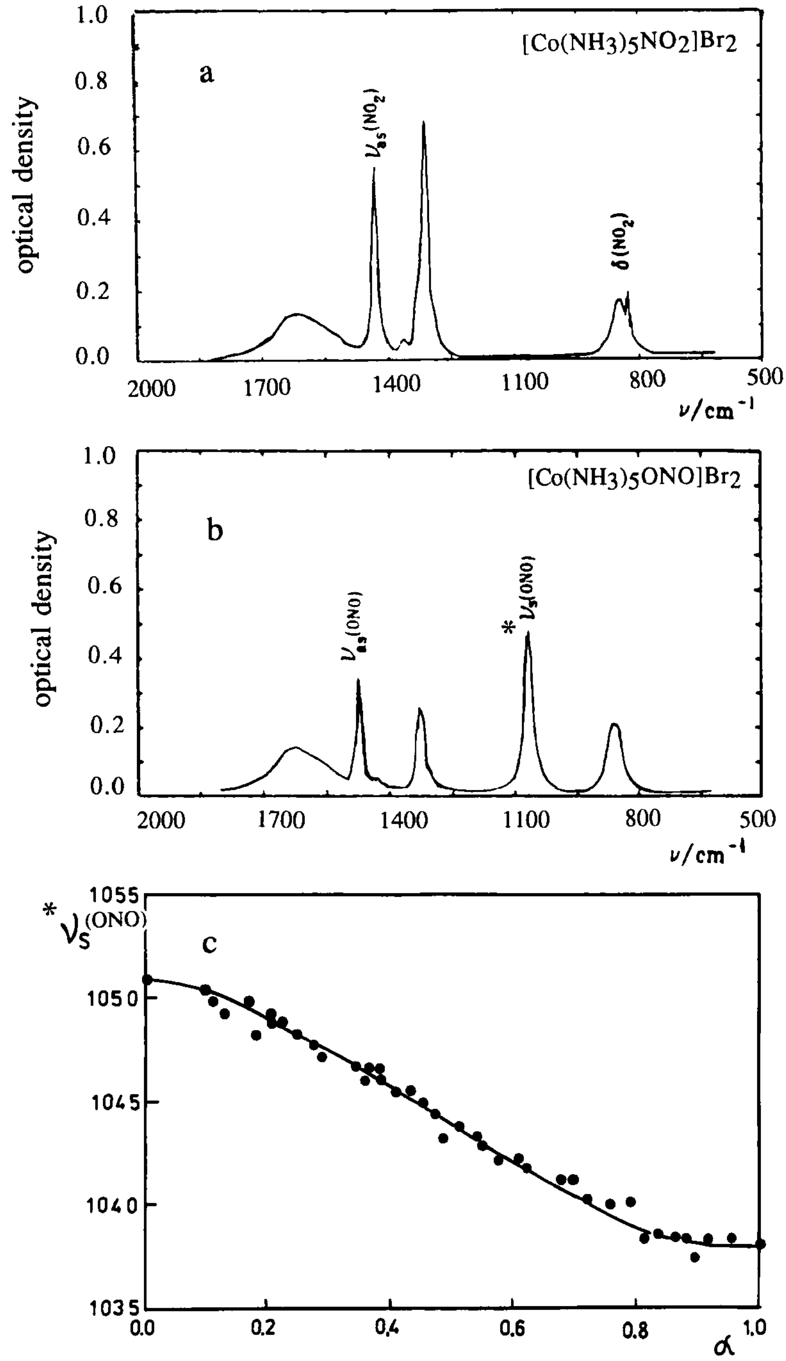


Fig.5 IR-absorbtion spectra of solid $[Co(NH_3)_5NO_2]Br_2$ (a) and $[Co(NH_3)_5ONO]Br_2$ (b); (c) - the shift of $\nu_s^{(ONO)}$ (marked * in Fig.6b) in the course of nitro-nitrito isomerization (α - degree of transformation).

the effect, vibrational frequency shifts mean that isomerization in complex cations, which have reacted first, influences vibrations, and, hence, most probably, also the reactivity with respect to linkage isomerization, in the neighbouring cations. Hence, a feed-back may be expected to arise in this solid state reaction[30-33].

Intermediate summary

Summing up the first part of the discussion, we can make the following conclusion: The changes induced in the complex cations as a result of the intramolecular linkage isomerization are large enough to influence the other cations and anions in the crystal. They induce anisotropic distortion of the crystal structure, resulting in the macroscopic deformation and/or the fragmentation of the crystals, and in shifts of the vibrational frequencies of the cations which have not yet participated in the reaction directly. These intra- and intermolecular changes in the crystal may influence the further course of solid state linkage isomerization, and, thus, feed-back may arise in this solid state reaction.

THE EFFECT OF THE SURROUNDINGS ON THE INTRAMOLECULAR ISOMERIZATION

Three main methods of changing the surroundings of a complex cation in the crystal can be suggested:

1. A "chemical" method - changing the anions XY in the series $[Co(NH_3)_5ONO]XY$ and $[Co(NH_3)_5NO_2]XY$.
2. Changing the polymorphic modification of the same compound.
3. Deformation of crystal structure by some external action (e.g. by applying hydrostatic pressure).

Each of the three methods modifies the surroundings in a different way and has its advantages and disadvantages. Thus, the "chemical" method is probably the most effective one to induce an essential redistribution of the electron density in the cation. At the same time, the method changes many parameters of the system simultaneously, since a change in the chemical composition usually results also in a change in the crystal structure[14-18]. The study of different polymorphic modifications allows one to keep chemical composition constant, modifying the crystal structure. The problem, however, is that one is too dependent upon Nature and its willingness to provide us with several polymorphs of the same compound. Even if it is possible to find ways of preparing several polymorphs, one is not free in chosing the way in which the juxtaposition of the cations and anions differs in different structures. Applying some external action has an important advantage as compared with changing chemical composition or preparing different polymorphs, since it allows one to modify the surroundings of a complex cation in the same crystal structure of the same chemical compound in a continuous way. Besides, the same action can be applied to different complexes of the series $[Co(NH_3)_5ONO]XY$ and $[Co(NH_3)_5NO_2]XY$, making generalizations easier.

Experimental evidence of the existence of the effect

There is experimental evidence that nitro - nitrito linkage isomerization in crystals of Co(III)-ammine complexes is affected by changes in the surroundings of complex cations by any of the three methods mentioned above. Adell has already noticed the rate of solid state nitrito-nitro isomerization at ambient temperature to be lower in $[Co(NH_3)_5ONO]I_2$ than that in chloride or nitrate[34]. Recently we have confirmed the results of Adell and have also shown that the substitution of the anion in the series $[Co(NH_3)_5ONO]XY$ ($XY = Cl_2, Br_2, I_2, Cl(NO_3), (NO_3)_2, C_2O_4, Cr_2O_7$) noticeably affects the kinetics of the solid state isomerization[24, 35]. We have also compared the kinetics of nitrito - nitro-isomerization in different polymorphs of $[Co(NH_3)_5ONO]Cl_2$, $[Co(NH_3)_5ONO]Br_2$, $[Co(NH_3)_5ONO]I_2$ and have shown the reaction rate to be noticeably affected by crystal structure, even if the chemical composition of the solid is the same[35]. Finally, we have used the third method and have applied hydrostatic pressure to the sample to induce a continuous distortion of the same polymorph of the same compound. High pressure was shown to influence both the equillibrious ratio of nitrito- to nitro-coordinated cations in the crystals achieved by the irradiation of solid nitro-isomer and the rate of the nitrito-nitro solid state isomerization (Fig.6)[36]. Similar results were obtained when nitro-nitrito photoisomerization in single crystals of $[Co(NH_3)_5NO_2]Cl(NO_3)$ was studied[7,8]. The effective quantum yield of the photoisomerization was shown to decrease in elastically compressed crystals (Fig.7)[7,8].

The reasons of the effect of the surroundings on the solid state intramolecular isomerization (general consideration)

As was shown above, the surroundings of the cations in the crystal, i.e. the atoms not participating directly in the intramolecular isomerization, do affect the reaction

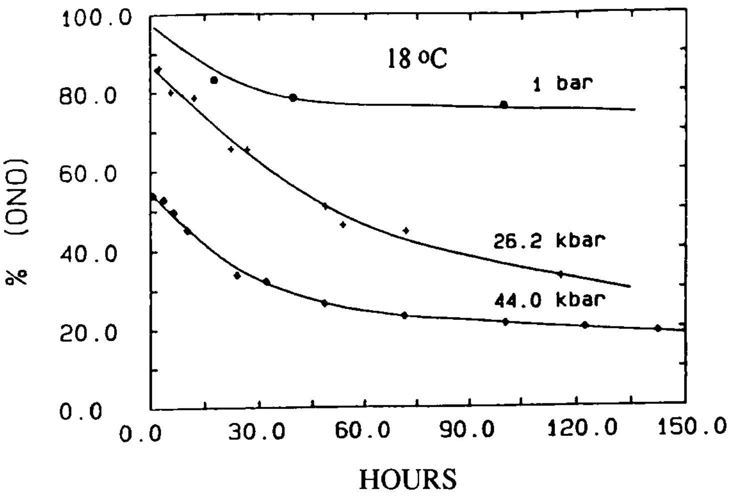


Fig. 6 Effect of hydrostatic pressure on the solid state nitrito-nitro linkage isomerization $[Co(NH_3)_5ONO]Br_2$ - $[Co(NH_3)_5NO_2]Br_2$. Starting $[Co(NH_3)_5ONO]Br_2$ was obtained by irradiation of solid $[Co(NH_3)_5NO_2]Br_2$. The ratio of ONO-coordinated cations to the NO_2-coordinated cations was calculated from the integral intensities of $\nu_s^{(ONO)}$-bands in the IR-vibrational spectra.

course. This phenomenon finds its proper place among similar phenomena known in other fields of chemistry: the inductive effect of substitutes (coordination chemistry,[37, 38] organic chemistry[39]); the effect of crystal structure on the conformations of organic molecules[40] (organic solid state chemistry); the effect of solvent, other ions, ionic force of the solution on the intramolecular reactions[41] (solution coordination chemistry); the effect of crystal structure on the electronic transitions in the individual species within the solid (crystal physics[42], materials science[43]), etc. The concepts developed in different areas, such as "the formation of outer-sphere complexes"[38, 44] (solution coordination chemistry), the concepts of the "reaction cavity", "cage", or "microreactor" (organic solid state chemistry[45-47], radiation inorganic solid state chemistry[48, 49], radical chemistry in condensed medium[50.51], chemistry in the channels of solids[52], polymer chemistry[53, 54], or chemistry of organized liquid media[55]), can be successfully applied when discussing possible mechanisms of the effect of the surroundings on the intramolecular isomerization in crystals of coordination compounds.

The effect of the surroundings on the reaction can be considered in various aspects and in different approximations (see Fig.8).

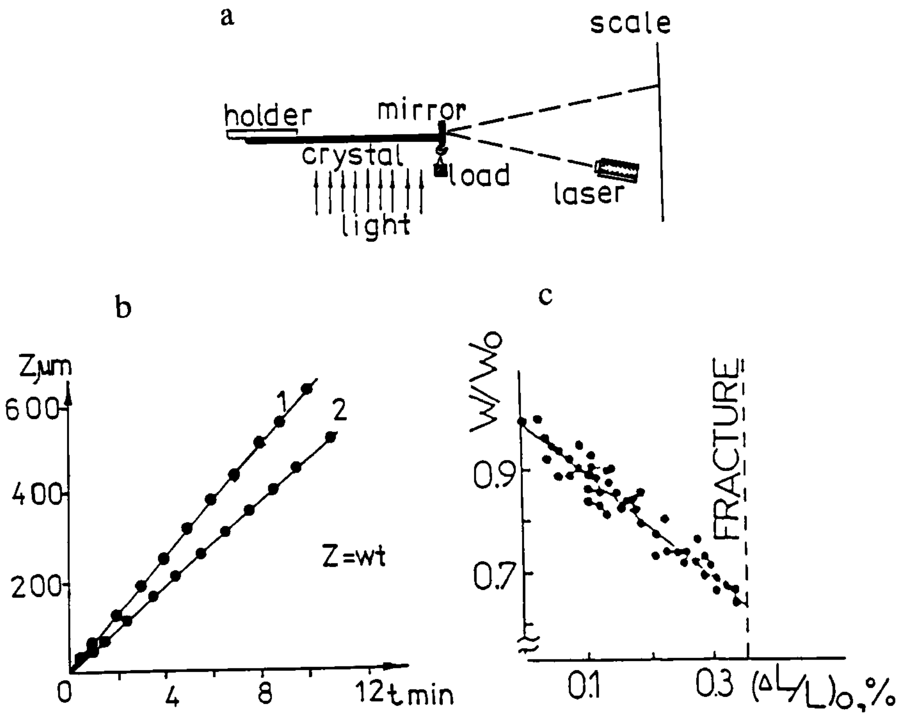
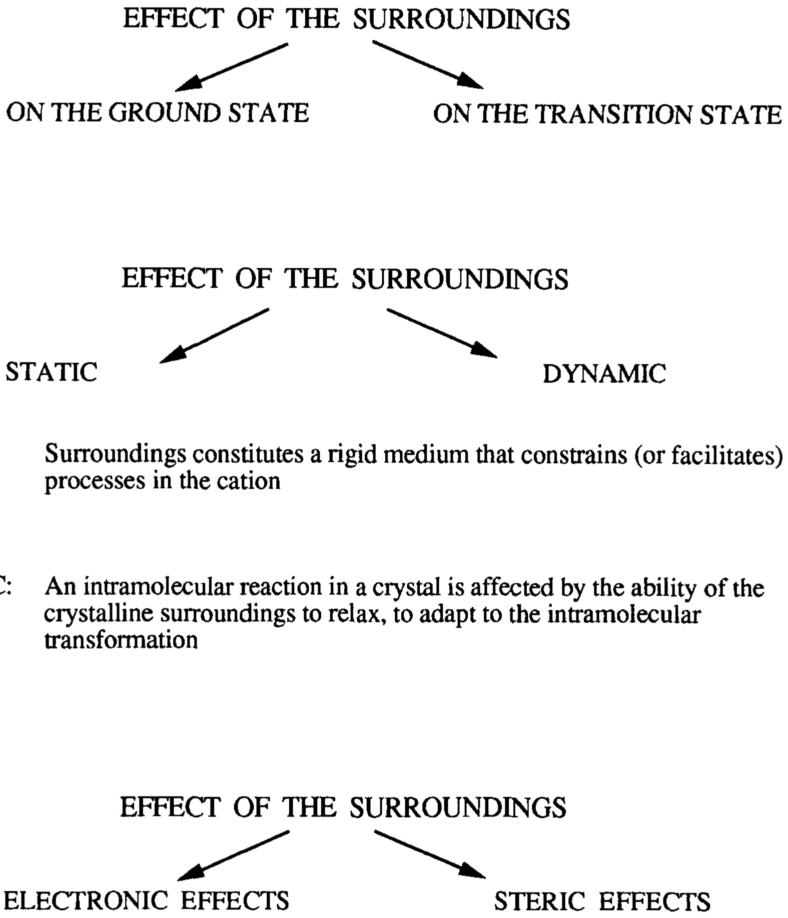


Fig.7 Effect of elastic loading on the nitro-nitrito photoisomerization in the crystals of $[Co(NH_3)_5NO_2]Cl(NO_3)$.

a) scheme of the experiments;

b) primary experimental data: deviation of the free end of the crystal from the initial position as a result of photoisomerization versus time of irradiation with constant light flux; 1 - no loading, 2 - crystal elastically loaded during irradiation;

c) estimates of relative quantum yield of photoisomerization in the elastically compressed crystals as compared with unloaded crystals. $(\Delta l/l)_0$ - change in the length of the middle line of the crystal under the load, correlates with the value of mechanical stresses in the crystal, allows to compare different crystals.



EFFECT OF THE SURROUNDINGS

ON THE GROUND STATE

ON THE TRANSITION STATE

EFFECT OF THE SURROUNDINGS

STATIC

DYNAMIC

STATIC: Surroundings constitutes a rigid medium that constrains (or facilitates) processes in the cation

DYNAMIC: An intramolecular reaction in a crystal is affected by the ability of the crystalline surroundings to relax, to adapt to the intramolecular transformation

EFFECT OF THE SURROUNDINGS

ELECTRONIC EFFECTS

STERIC EFFECTS

Fig.8 Various aspects and approximations of considering the effect of the surroundings on an intramolecular reaction in a solid

When changing the surroundings, some changes in the complex cation (redistribution of the electron density, distortion of the geometry, changes in the vibrational frequencies) can be induced before any reaction starts. Interrelations between the distortions of the molecules in their ground state and the parameters characterizing the reaction course (e. g. activation energy) are known to exist, and were analyzed for a number of organic solid state reactions[56]. One can expect that similar interrelations may exist also between distortions of complex cations and the linkage isomerization: the geometry of the NO_2-group is known to be "flexible" both in the NO_2-ion[57], and in the ligand, coordinated to a metal in various nitro- and nitrito-complex cations[3]. The changes in the geometry are closely interrelated with electronic structure and vibrational frequencies[3, 57, 58].

The changes of the surroundings can affect not only the state of a complex ion prior to the reaction, but also the transition from one isomeric form into another. A first approximation would be to consider the crystalline surroundings as a static rigid medium that surrounds the reacting cation. It could be possible, e. g., to estimate the space available for possible transition and final states of a complex cation in the crystal, that is the space known in organic solid state chemistry as a “reaction cavity”. A similar level of consideration would be to include the surrounding atoms at their fixed “prereactional” sites in the model, when optimizing the reaction route and the structure of the transition state. Examples of such studies are known for the reactions of solid organic and organometallic compounds[59-67].

The next level would be to consider "dynamic effects", i.e. to take into account that the crystalline surroundings must respond to a process within a complex cation. Pure mechanical properties (e. g. plasticity), and their anisotropy, can determine the ease of relaxation of mechanical stress, induced by the reaction, and thus influence the reaction course. Such effects are well-known in inorganic solid state chemistry and are used to control the kinetics and spatial propagation of solid state reactions[68]. In organic solid state photochemistry the concepts of “dynamical preformation” and “dynamic reaction cavity” were worked out to deal with the relaxation of the crystalline surroundings after absorbtion of light by a molecule, and/or further photochemical transformations[69]. It was shown in a number of careful and impressive studies[25-27, 69-72] that the "dynamic effects", the ability of the surroundings to relax, can be responsible for the formation of products, which would not be expected if only the "frozen", static, structures of parent crystals were considered. As far as solid state linkage isomerization is concerned, it is also possible that not only a “prereactional” state of the crystal, but, to a larger extent, the flexibility of the surroundings, the ability to follow intramolecular reorganization, can be responsible for the different rates of intramolecular isomerization and different equillibrium ratio of two isomeric forms, achieved in different crystalline surroundings.

A detailed study of all the aspects of the effect of the surroundings on the intramolecular isomerization in complex cations is a life-consuming problem, and we are far from having solved it. In the present contribution, discussion will be limited only by how high pressure studies can contribute to the understanding of static and dynamic aspects of the effect of the environment on the intramolecular processes in solids. The preference to the pressure among other methods of changing the surroundings was given for two main reasons. First, because, as it was already mentioned above, this is a method allowing one to distort the same structure of the same complex in a continuous way and to compare the results obtained for different complexes. Second, because, as was also already discussed above, reaction itself induces mechanical stresses and continuous lattice distortion. Comparison of the lattice distortion, induced by high pressure and by isomerization, must be helpful to understand the forces that act during the reaction. The study of the effect of high pressure on the crystals and on the intramolecular isomerization in them must be important also for the problem of possible feed-back in intramolecular solid state reactions. It can help to understand how and why the crystalline surroundings relax as intramolecular isomerization proceeds, and what effect this relaxation may have on the reaction in the neighbouring complex cations.

Pressure induced lattice distortion

A series of nitro-isomers $[Co(NH_3)_5NO_2]XY$ were studied by the X-ray powder diffraction technique at pressures up to 40 kbar using a diamond anvil cell[36]. No phase transitions were observed, but a continuous pressure induced lattice distortion was measured. As a typical example, the changes in the lattice parameters of $[Co(NH_3)_5NO_2]Br_2$ with pressure are shown in Fig.9. The lattice is remarkably soft, the changes are comparable in the order of magnitude with the pressure induced parameter changes in such plastic crystals as halides of alkaline metals[21].

The lattice distortion is anisotropic. Moreover, in the monoclinic $[Co(NH_3)_5NO_2]Br_2$ and $[Co(NH_3)_5NO_2]Cl_2$ there are directions which expand under pressure, despite the natural integral decrease in the molar volume (Fig.10)[36]. Again, the anisotropy of lattice deformation can be most easily visualized by calculating the stress tensor and plotting the strain ellipsoid with respect to crystallographic axes. Fig.10 shows the strain ellipsoid for $[Co(NH_3)_5NO_2]Br_2$ under 35 kbar.

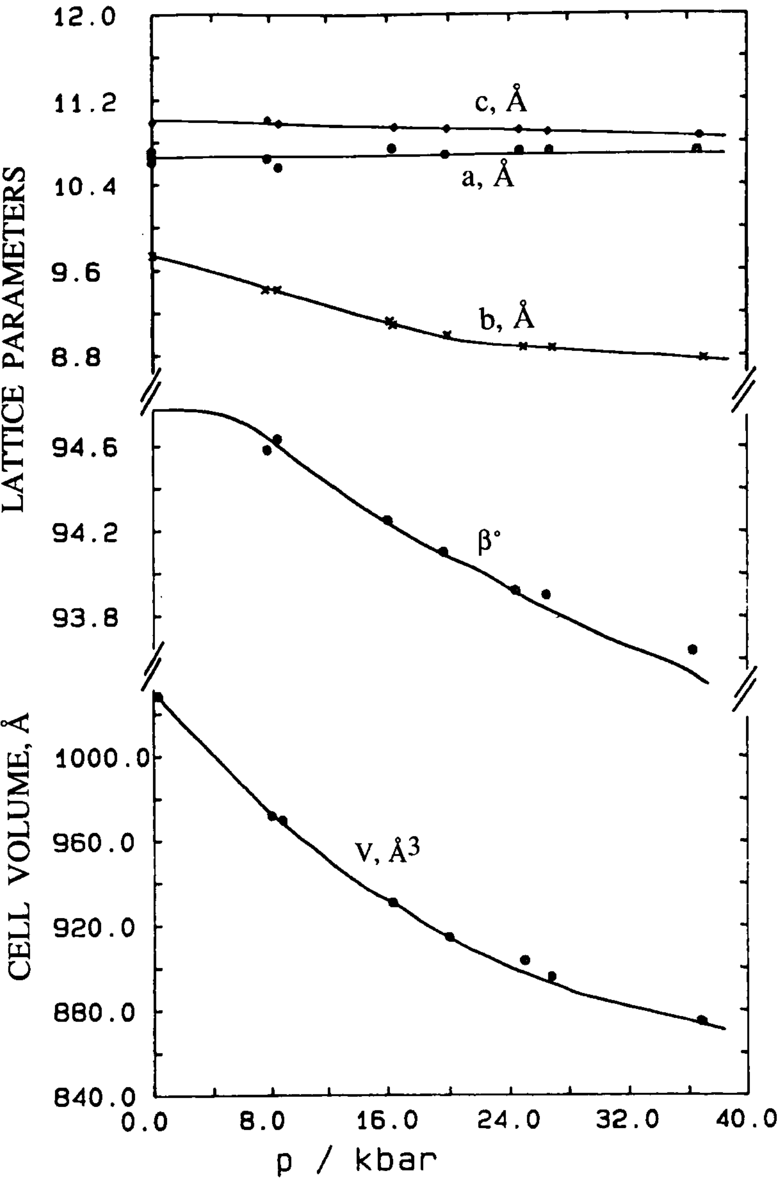


Fig.9 The changes in the lattice parameters and cell volume of $[Co(NH_3)_5NO_2]Br_2$ with pressure.

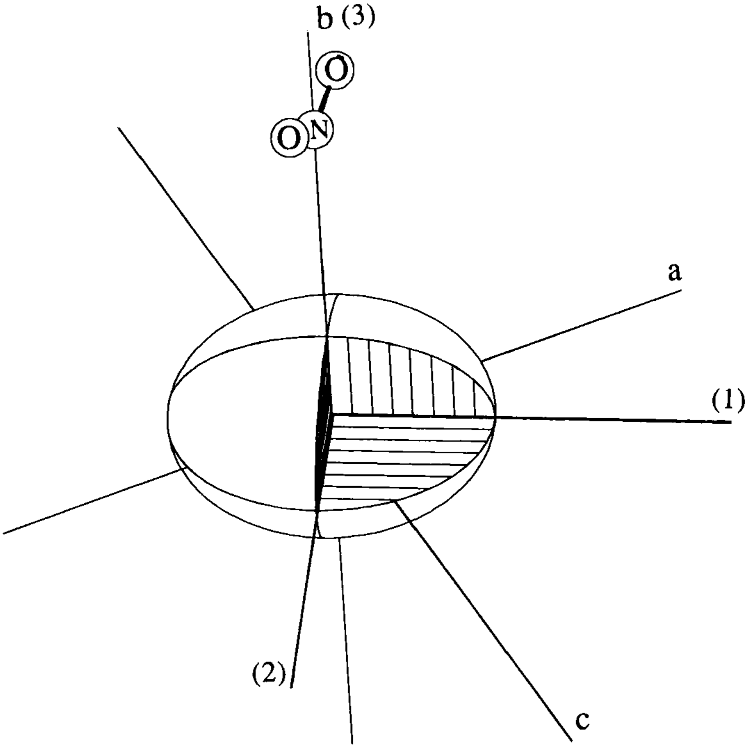


Fig. 10 Strain ellipsoid for $[Co(NH_3)_5NO_2]Br_2$ under pressure (p = 35 kbar). **a**, **b**, **c**, - crystallographic axes; **1**, **2**, **3** - principal axes of the ellipsoid. Deformation is exaggerated. Compare with Fig.3, a (scale is the same as in Fig.3, a).

Pressure induced IR-vibrational frequencies shifts

The lattice distortion that manifests itself in a high pressure X-ray powder diffraction pattern is mainly a change of the juxtapositions of the anions and the complex cations in the structure. To study which "intramolecular" distortions within the complex cations accompany the lattice distortion under pressure, it was necessary to combine high pressure X-ray powder diffraction with high pressure IR-spectroscopy.

The diamond anvil cell technique was applied to study the IR-vibrational absorption spectra of solid $[Co(NH_3)_5NO_2]XY$ and $[Co(NH_3)_5ONO]XY$ complexes at pressures up to 20 kbar[73]. The shifts of symmetric and antisymmetric stretching and deformational vibrations of the NO_2-ligand were measured. The results obtained were qualitatively different for nitro- and for nitrito-complexes. Typical examples are shown in Fig.11 (a, b). At the same time, within the nitro- and within the nitrito-series the difference in the results obtained was only quantitative, the qualitative changes of the spectra with pressure being essentially the same (Fig.11, c, d). This allowed us to interpret the experimental data on the basis of the results of a theoretical simulation of the spectra for the models of individual cations, $[Co(NH_3)_5NO_2]^{+2}$ and $[Co(NH_3)_5ONO]^{+2}$. Normal coordinate analysis was carried out and the vibrational frequencies were calculated as a function of dynamic (force constants) and kinematic (bond lengths and valence angles) parameters[73]. The crystalline surroundings were not taken into consideration directly, but, of course, any changes in the dynamic and kinematic parameters of the cations result from the interactions with the surroundings. The results of the simulation are summarized in Fig.12.

Comparison of the frequency shifts, measured experimentally and calculated theoretically, suggests a model of the high pressure distortion of complex cations in crystals. We have supposed that, under pressure, the valence angle O-N-O slightly increases in nitro-complexes (~1_ at p=10 kbar), and slightly decreases (~1-2_ at p=10 kbar) in nitrito-complexes. Simultaneously, N-O bonds may slightly shorten (~0.02 Å at 10 kbar).

When explaining why the same external action (hydrostatic pressure) results in changing the value of the O-N-O angle in different directions for nitro- and for nitrito-isomers, two main groups of factors are to be taken into account. The first one deals with the properties of individual cations and the differences in energies required to decrease and to increase the O-N-O angle in nitro- and nitrito-isomers. The second group of factors is connected with the orientation of the NO_2-group in the crystal structures of nitro- and nitrito-isomers with respect to the principal axes of strain ellipsoids, describing lattice distortion under pressure. *Ab initio* calculations of the $[Co(NH_3)_5NO_2]^{+2}$ ion have shown that less energy is required to increase the O-N-O angle (as compared with the optimal value) than to decrease the angle at the same value[75]. The orientation of the NO_2-group with respect to the principal axes of the strain ellipsoid in crystals of nitro-complexes also suggests that pressure increases the value of the O-N-O angle. In $[Co(NH_3)_5NO_2]Cl_2$ and in $[Co(NH_3)_5NO_2]Br_2$ the direction of the $Co\text{-}NO_2$ bond coincides with the direction of the maximal contraction

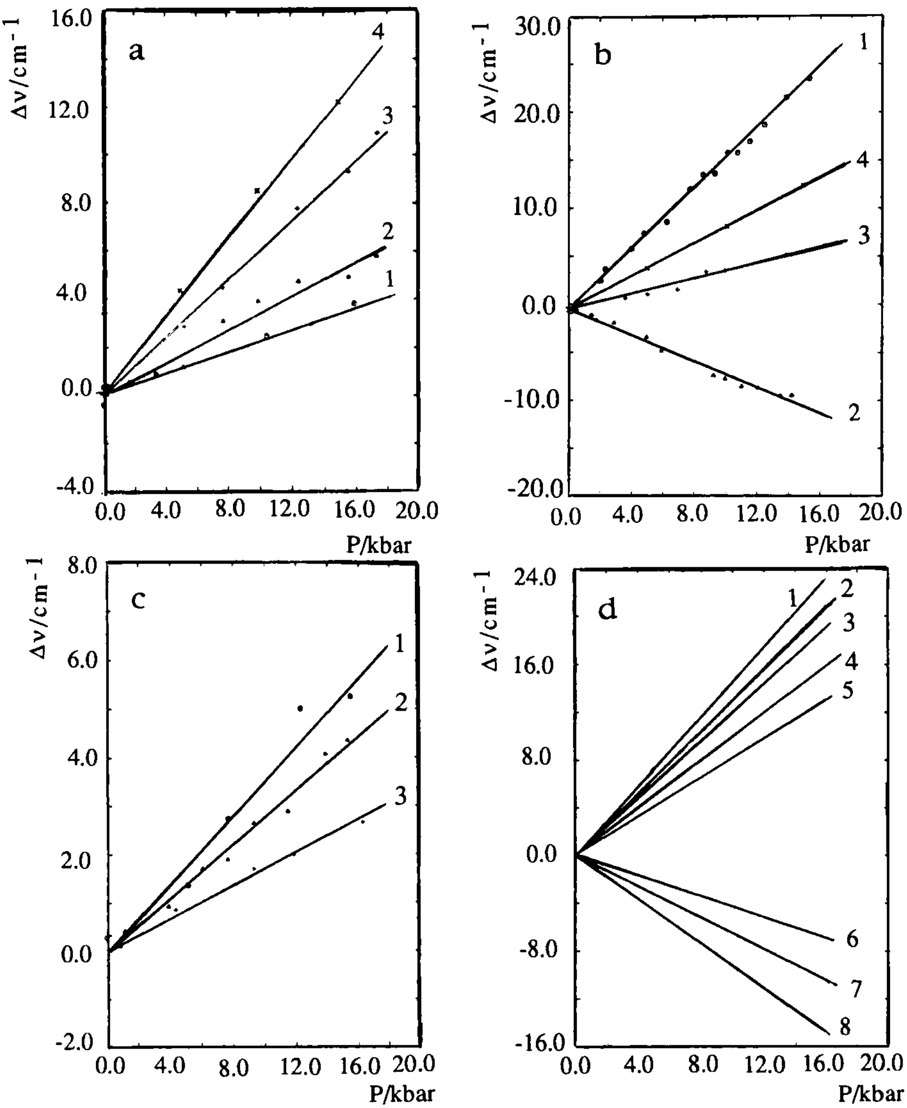


Fig.11 Effect of pressure on the IR-vibrational frequencies in solid $[Co(NH_3)_5NO_2]XY$ and $[Co(NH_3)_5ONO]XY$ complexes ($XY = Cl_2$, Br_2, I_2, $Cl(NO_3)$, $(NO_3)_2$).

a: $\delta(NO_2)$ (1), $\nu_{as}(NO_2)$ (2), $\rho_r(NH_3)$ (3) frequencies in $[Co(NH_3)_5NO_2]Cl_2$; (4) - "nitrite scale" (NO_2^- in KBr-matrix)[74]. $\nu_0 = 827\ cm^{-1}$ (1), $1429\ cm^{-1}$ (2), $854.5\ cm^{-1}$ (3), $1279\ cm^{-1}$ (4).

b: $\nu_s(ONO)$ (1), ν_{as} (ONO) (2), $\rho_r(NH_3)$ (3) frequencies in $[Co(NH_3)_5ONO]Cl_2$; (4) - "nitrite scale". $\nu_0 = 1066\ cm^{-1}$ (1), $1453\ cm^{-1}$ (2), $854\ cm^{-1}$ (3), $1279\ cm^{-1}$ (4).

c: $\delta(NO_2)$ in $[Co(NH_3)_5NO_2]XY$, $XY = Cl_2$ (1), Br_2 (2), $Cl(NO_3)$ (3) ;$\nu_0 = 827\ cm^{-1}$ (1), $824\ cm^{-1}$ (2), $826\ cm^{-1}$ (3)

d: $\nu_s(ONO)$ and $\nu_{as}(ONO)$ in $[Co(NH_3)_5ONO]XY$; $\nu_s(ONO)$ shifts: $XY = Cl_2$ (1), I_2 (2), Br_2 (3), $(NO_3)_2$ (4), $Cl(NO_3)$ (5);$\nu_{as}(ONO)$ shifts: $XY = Br_2$ (6), Cl_2 (7), I_2 (8);$\nu_0 = 1066\ cm^{-1}$ (1), $1016\ cm^{-1}$ (2), $1048\ cm^{-1}$ (3), $1030\ cm^{-1}$ (4), $1042\ cm^{-1}$ (5), $1460\ cm^{-1}$ (6), $1453\ cm^{-1}$ (7), $1478\ cm^{-1}$ (8)

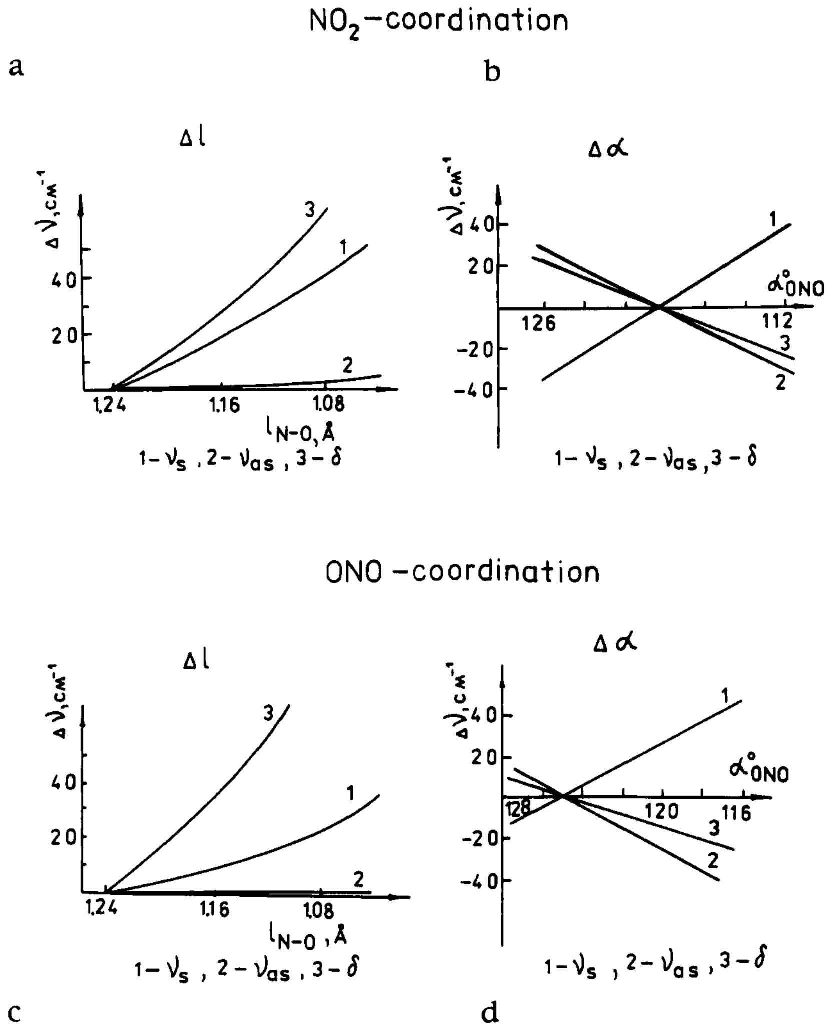


Fig.12 The results of the theoretical simulation of the IR-vibrational spectra of $[Co(NH_3)_5NO_2]^{+2}$(a,b), and $[Co(NH_3)_5ONO]^{+2}$ (c, d). The effect of the distortions of N-O bond lengths, Δl (a,c), and O-N-O bond angle, Δα (b, d), is shown.

of the lattice under pressure. In $[Co(NH_3)_5NO_2]Cl(NO_3)$ the lattice also contracts in the direction of the Co-NO_2 bond, but this contraction is essentially smaller. This seems to be in good agreement with the experimental high pressure spectroscopic data[39]: the shifts of vibrational frequencies measured for $[Co(NH_3)_5NO_2]Cl(NO_3)$ are smaller than the corresponding shifts in $[Co(NH_3)_5NO_2]Br_2$ and $[Co(NH_3)_5NO_2]Cl_2$ (Fig. 11b).

Unfortunately, the same detailed discussion of the factors responsible for the decrease of the O-N-O angle under pressure in solid nitrito-isomers is not yet possible. Neither the results of *ab initio* calculations, nor the X-ray diffraction data on the structural distortion in solid nitrito-isomers under pressure are available. I hope that the situation improves by the next Meeting.

Contribution of high pressure studies to understanding of the effect of the surroundings on the intramolecular isomerization.

High pressure experiments can contribute to the study of static aspects (see above) of the effect of the surroundings on the intramolecular isomerization.

First, high pressure provides a tool for distorting intramolecular geometry, and doing it continuously, without changing the chemical formula of the complex or the main structural framework. Thus, it becomes possible to test theoretical predictions of the existence of correlations between "distortion of the complex cation" and "kinetics of linkage isomerization".

Second, one can study the interrelations between two types of distortions, induced in the crystals by high pressure: intramolecular and intermolecular (lattice) distortions. This helps in the understanding of which types of intramolecular distortions may be expected to be induced by some changes in the crystalline surroundings, not only when pressure is applied but, e. g., when the crystal lattice distorts following initiation of intramolecular isomerization.

If one neglects any relaxation of the surroundings in the course of the isomerization and remains within the limits of the approximation of the "rigid reaction cavity", it is possible to use high pressure experiments to look for correlations between "volume of the reaction cavity" and "reaction kinetics (and/or the equillibrious ratio of the isomeric forms obtained)". The size of the reaction cavity can be calculated from the experimental data, and changes continuously with pressure, the chemical composition and the main structural framework being kept constant. It is worth stressing that the study of the volume of the reaction cavity cannot be substituted adequately by the integral measurements of molar volume. To illustrate this, it is sufficient to recall the experimental facts already mentioned above. Pressure accelerates solid state nitrito-nitro isomerization[36] and decreases the effective quantum yield of nitro-nitrito photoisomerization[7,8], although the nitrito-nitro isomerization proceeds with an increase, and nitro-nitrito isomerization with a decrease in molar volume[10]. The phenomenon is, however, well explained if the anisotropy of lattice distortion under pressure and during the reaction are taken into account. Despite the integral molar volume decrease in the course of nitro-nitrito photoisomerization, the crystal expands in some directions. These directions are related to the orientation of the Co-NO_2 bond. Under pressure, the structure is compressed mostly in these directions, and the effect of this on the reaction course is much more important than that of the integral increase of the molar volume (resulting from appearance of additional free space far from the reacting ligand and thus not very essential for the reaction).

High pressure experiments also provide valuable data required to go beyound the limits of the "approximation of rigid reaction cavity" and to consider relaxation of the surroundings in the course of solid state intramolecular isomerization.

Let us compare distortion of crystal structure of $[Co(NH_3)_5NO_2]Br_2$, resulting from nitro-nitrito isomerization, and distortion under hydrostatic pressure. One can clearly see that the two strain ellipsoids, corresponding to the lattice distortion during reaction (Fig.3) and under pressure (Fig.10) are not identical. In this respect $[Co(NH_3)_5NO_2]Br_2$ is not an exception. One can compare, e.g., the principal sections of strain ellipsoids for $[Co(NH_3)_5NO_2]Cl(NO_3)$, plotted in Fig.4.

The shape of a strain ellipsoid and its orientation with respect to the crystallographic axes are determined by two factors: by the properties of the crystal itself and by the directions and values of the forces which induce the distortion. Hydrostatic pressure is a scalar, and therefore these are purely the properties of the crystal structure that determine the strain ellipsoid plotted for pressure induced lattice distortion[76]. A “reaction” strain ellipsoid reflects not only the anisotropy of the crystal structure, but also the directions in which the forces act, which are induced in the crystal by the intramolecular reorganization within complex cations, and which are responsible for lattice distortion. As a result, e.g. in $[Co(NH_3)_5NO_2]Cl(NO_3)$, the direction of maximal contraction under pressure (coinciding with the crystallographic axis **c**) becomes the direction of maximal expansion during the reaction. In $[Co(NH_3)_5NO_2]Cl_2$, and in $[Co(NH_3)_5NO_2]Br_2$, the direction of maximal expansion during linkage isomerization coincides with the direction of maximal expansion(!) under pressure. The direction of maximal contraction during isomerization corresponds to the direction of medium contraction under pressure, and, vice versa, the direction of maximal contraction under pressure is the same as the direction of medium expansion during reaction. Thus, the real, anisotropic stress field, arising in the crystals in the course of the isomerization, can be analyzed on the basis of the comparison of "pressure" and "reaction" strain ellipsoids.

The comparison of the “pressure” and the “reaction” strain ellipsoids clearly shows once again that one must be very careful when discussing the mechanical stresses arising in the crystals as a result of solid state transformations (phase transitions, chemical reactions) in terms of “internal pressure” (common in the literature). These estimates are based on measurements of the changes in molar volume[68], the curvature of the crystals deformed by the process[23], or the shifts of vibrational frequencies as compared with the corresponding frequency shifts under pressure[25-29]. However, the same value of the change in molar volume as a result of a reaction and under pressure can correspond to different fields of mechanical stresses in the crystal. Estimates of pressure from the measurements of the curvature of bent crystals[23], based on the approximation of an isotropic medium, can give an erroneous sign. Vibrational frequences are affected by pressure, since the juxtaposition of atoms in the crystal is distorted. If the type of this distortion is different during a solid state reaction and under pressure, it is not correct to describe mechanical stresses, arising in the crystals in the course of the reaction, in terms of "internal pressure" and to estimate them quantitatively on the basis of the data of corresponding high pressure spectroscopic experiments, especially if these spectroscopic experiments refer not to solid samples.

Finally, the knowledge of "high pressure" strain ellipsoids helps to understand the intermolecular interactions in the crystal, and provides a tool with which to test if a chosen model intermolecular potential can describe these interactions adequately[77]. And these are the satisfactory intermolecular potentials that are necessary for any theoretical study of the dynamical aspects of the effect of the crystalline surroundings on the intramolecular processes in the solid state[59-66].

Intermediate summary

Summing up the second part of the discussion, we can make the following conclusion. There is experimental evidence that the surroundings of a complex ion in the crystal, modified chemically by substitution of anions, or by preparation of different polymorphs, or by applying high pressure, does influence the intramolecular isomerization. This may be due to some changes that are induced in the crystal before any reaction starts (distortion of the cations, redistribution of the electron density, changes in the vibrational frequencies, changes in the free space around the reacting ligands, etc.). These changes manifest themselves in X-ray diffraction patterns and in IR-vibrational spectra and hence can be studied experimentally. Another possibility is that the intramolecular reaction is affected by the ability of the surroundings to follow the reorganization in a cation, and thus the anisotropy of mechanical properties, the flexibility of the reaction cavity, the plasticity of the crystal, etc., are the parameters to be taken into account.

SUMMARY

The problem to be discussed in the present contribution was formulated as the following two questions:

1. Does the intramolecular isomerization in a complex ion influence the surroundings?
2. Do the surroundings of a complex ion in the crystal influence the intramolecular isomerization?

The answers to both questions were shown to be positive. Experimental data and the results of theoretical simulations giving this evidence were discussed in two parts of the present paper (each corresponding to a question to be answered). The main results were summarized in two "Intermediate summaries". The only thing to add is to stress once more that a solid state reaction is not so "absolutely intramolecular" as one could imagine. The surroundings of a complex cation do influence an intramolecular process, although not participating in it directly. In turn, an intramolecular process influences the surroundings, induces lattice distortion, and this manifests itself in macrodeformation and fragmentation of the crystals, in the shifts of IR-vibrational frequencies and in the changes in X-ray diffraction patterns. "Individuals are not absolutely independent in the crystal and do influence each other". Since both the reaction influences the surroundings, and the surroundings affect the intramolecular reaction, feed-back is not less likely to be expected in these solid state reactions, than in any other solid state transformation.

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