Monatshefte für Chemie 114, 267—272 (1983)

Monatshefte für Chemie
Chemical Monthly

On the Aplanarity of the Nitrate Group in Inorganic Crystals

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(Received 24 November 1982. Accepted 9 Dezember 1982)

Geometric analysis of carefully refined inorganic nitrate crystal structures shows that weak aplanarities of the NO_3-group, i.e. with a distance d of the nitrogen atom from the plane defined by the three oxygen atoms up to $d \sim 0.02$ Å, are by no means rare exceptions. Much larger aplanarities have been reported to occur in some crystal structures or follow from the published structure data, but all examples with $d > 0.05$ Å seem to need confirmation.

(Keywords: Nitrate group; Crystal chemistry)

Über die Aplanarität der Nitratgruppe in anorganischen Kristallen

Die geometrische Analyse sorgfältig verfeinerter Kristallstrukturen anorganischer Nitrate zeigt, daß schwache Aplanaritäten dieser Gruppe — d. h. solche mit einem Abstand d des Stickstoffs von der Ebene der drei Sauerstoffe bis $d \sim 0,02$ Å — keineswegs seltene Ausnahmen sind. Viel größere Aplanaritäten wurden zwar beschrieben oder ergeben sich aus den veröffentlichten Strukturdaten; alle Beispiele mit $d > 0,05$ Å scheinen jedoch einer Bestätigung zu bedürfen.

Introduction

Modern crystal structure analysis by diffraction methods often allows to locate the vibration centers of the atoms with a standard deviation of ≤ 0.005 Å. Therefore, much smaller stereochemical effects can be investigated than some few decades ago. One of them is the aplanarity of zO_3-groups (z = B, C, N). Survey articles on the stereochemistry of carbonates[1] and of borates[2] paying attention to this topic have been published recently. They will be supplemented here as to the aplanarity of the nitrate group.

In the modern literature, stongly aplanar nitrate groups—i.e. with a distance, d, of the nitrogen atom from the plane defined by the three

0026-9247/83/0114/0267/$ 01.20

oxygen atoms of $d \geq 0.10$ Å—have been reported to occur in barium nitrate[3] and in sodium nitrate[4–6]. Such large d-values result also for the structures of β- and γ-potassium nitrate as given in [7], although this feature is not explicitely mentioned in the paper.

The details of none of these structure determinations seem, however, to be well proved. As to barium nitrate, a very careful reinvestigation[8, 9] could not confirm the earlier result[3]. In sodium nitrate, the large aplanarity of the nitrate group is reported to occur coupled with local disorder and with an only slight and local deviation from an ordered centrosymmetric structure (calcite type). Such cases are extremely difficult to prove unambiguously, and even in their most recent publication, the authors do not claim to have solved all details[6]. It is further to be borne in mind that the reported value of $d = 0.15$ Å[6] can be reduced to $d \sim 0.05$ Å if a tilting of the nitrate group with respect to (00.1) is assumed. The crystal structures of β- and γ-potassium nitrate were determined only from a somewhat limited set of X-ray powder diffraction data[7]; their details need, therefore, in the present authors' opinion careful confirmation.

Much smaller aplanarities ($d \leq 0.03$ Å) were recognized to occur and were well documented in α-potassium nitrate[10] (= potassium nitrate II, aragonite type), in nitric acid trihydrate[11], and in strontium and barium nitrate[8, 9].

In survey articles, the aplanarity of the nitrate group has found little attention as yet: *Baur*[12] reported the results for barium nitrate as given in [3] and for α-potassium nitrate[10] without further comments, *Leclair*[13] in his extensive and in many respects very informative article mentioned β- and γ-potassium nitrate to be the only examples for aplanar nitrate groups, and *Zemann*[1] in his review article on carbonates just mentioned that the aplanarities of the nitrate group have similar values as those of the carbonate groups (i.e. with d-values up to $d \sim 0.03$ Å).

As it was experienced in[1] and[2] that in a number of cases the authors of crystal structure papers did not pay attention to or did not recognize weak aplanarities of zO_3-groups, it seemed worthwhile to start a search for this effect in the literature on nitrate structures.

Examples for Aplanar Nitrate Groups in Inorganic Structures as Derived from the Modern Literature

As the number of very accurate structure determinations and refinements, as indispensable as basis for our discussion, has greatly increased during the last few years, the literature on crystal structures of inorganic nitrates of essentially only the last decade was considered. As main guide to the original publications served the abstracts in "Structure Reports"[14] for the period covered.

Thus, we found approximately 60 nitrate groups with a given standard deviation $\sigma(\text{N—O}) \leq \sim 0.005$ Å for the N—O bond length(s) and with a point symmetry allowing aplanarity. They were closer inspected, and the distance d of the nitrogen atom from the plane through the three oxygen atoms was computed with program "Kristallchemie"[15]. As for both X-rays and neutrons the scattering powers of N and O are not very much different, $\sigma(d) = 1.5\,\sigma(\text{N})$ was considered to be a fair approximation for the standard deviation of d, where $\sigma(\text{N})$ is the standard deviation of the localization of the nitrogen atom.

The nitrate groups with $d \geq 2\,\sigma(d)$ are listed in Table 1. This compilation is not claimed to be exhaustive, but it is hoped that the majority of characteristic cases have come to our attention.

Deliberately omitted from Table 1 were in addition to the examples mentioned already in the introduction ($BaNO_3$ according to[3], $NaNO_3$

Table 1. *Examples of aplanar nitrate groups* [$d > 2\,\sigma(d)$] *in inorganic crystal structures.* d: distance of the N-atom from the plane of the three O-atoms, with standard deviation in units of last digit in brackets. The numbering of the N-atoms is that of the paper referred to

Substance	d (Å)	References
KNO_3 II (= α KNO_3)	0.018 (2)[a]	10, 16
$(NH_4,K)NO_3$ III	0.012 (2)[b]	16, 17
$SrNO_3$ [$BaNO_3$]	0.005 (1) [0.006 (1)]	8, 9
$KAg(NO_3)_2$ [$RbAg(NO_3)_2$]	0.018 (6) [0.015 (6)][c]	18
$K_3Pr_2(NO_3)_9$	0.031 (8) [N(2)]	19
$Hg(OH)NO_3$	0.016 (5)	20
$H_3O(NO_3) \cdot 2H_2O$	0.007 (1)	11
$Ca(NO_3)_2 \cdot 21/17\,H_2O$	0.012 (4) [N(3)]	21
	0.019 (8) [N(8)]	21
$[Y(NO_3)_3(H_2O)_4] \cdot 2H_2O$	0.021 (8) [N(2)]	22
$[Ce(NO_3)_3(H_2O)_5] \cdot H_2O$	0.019 (7) [N(1)]	23
$Cs[HN_2O_6]$	0.037 (14)[d]	24

[a] Average of four determinations: 0.010 (1) [25 °C][10], 0.018 (2) [100 °C][10], 0.024 (4)[16], and 0.019 (3) [containing NH_4NO_3 with atomic fraction K^+ 0.952 (6)][16].

[b] Mean of seven determinations of crystals with KNO_3 contents varying from 4 to 40 weight % and d-values varying from 0.009 (2) to 0.014 (3).

[c] In both phases for N (2).

[d] Error possibly larger because of disorder in the (HN_2O_6)-group.

according to[4–6], β- and γ-KNO_3[7]) also the nitrate groups in $RbNO_3$. From very recent neutron diffraction work on this phase[25] the results for the three crystallographically different kinds of nitrate groups are at 25 °C $d[N(1)] = 0.048(7)$, $d[N(2)] = 0.039(5)$ and $d[N(3)] = 0.010(6)$ Å, at 130 °C, however, $d[N(1)] = 0.009(17)$, $d[N(2)] = 0.003(14)$ and $d[N(3)] = 0.053(14)$ Å; further, the two deviations for N(1) point into opposite directions as compared with the rest of the atomic arrangement. This somewhat large difference between the structures determined at the two temperatures given indicates that the standard deviations for the localization of the atoms are probably too small—possibly a consequence of the polar space group—, and that the minor details of the structure should be considered with some caution.

Discussion

Inspection of Table 1 shows that weak aplanarities of the nitrate group, i.e. up to $d \sim 0.02$ Å are by no means very rare exceptions in crystal structures.

In this connection it seems worth mentioning that in all structure determinations of KNO_3 II and of $(NH_4, K)NO_3$ III considered in this paper, as well as in the pairs $SrNO_3$—$BaNO_3$ and $KAg(NO_3)_2$—$RbAg(NO_3)_2$ the direction of the deviation of the nitrogen atom from the plane of the oxygen atoms is constant with respect to the rest of the structure. This is, of course, further evidence for the qualitative correctness of the aplanarities in the four structure types. It should further be remarked that in KNO_3 II the aplanarity is analogous to that of the carbonate group in the isotypic $CaCO_3$ modification aragonite[1, 26, 27].

The reader's attention is further drawn to the crystal structures of $NH_4Ag(NO_3)_2$[18] with $d[N(2)] = 0.005(4)$ Å and $[La(NO_3)_3(H_2O)_5] \cdot H_2O$[28] with $d[N(1)] = 0.016(9)$ Å. The structures are isotypic to $KAg(NO_3)_2$ and $RbAg(NO_3)_2$[18], and to $[Ce(NO_3)_3(H_2O)_5] \cdot H_2O$[23], respectively. Although both nitrate groups have not been included into Table 1 because of $d < 2\sigma(d)$, the orientations of their aplanarity are identical with those of the isotypic substances of the Table.

While weak aplanarities of the nitrate group seem now to be well documented for approximately a dozen examples, all cases with $d > 0.05$ Å are not considered to be definitely proved and the corresponding crystal structures seem to need further refinement to settle this detail. From the limited set of data presented in Table 1 one gets the impression that the aplanarities of nitrate groups are on the average somewhat smaller than those of borate groups[2] and possibly also than those of carbonate groups[1, 29, 30].

As to the variation of the *d*-values in nitrates and the orientation of the aplanarity with respect to the rest of the structure very little can be said at present. A prerequisite for the aplanarity seems to be a polar surrounding—some few typical examples are presented in Fig. 1.

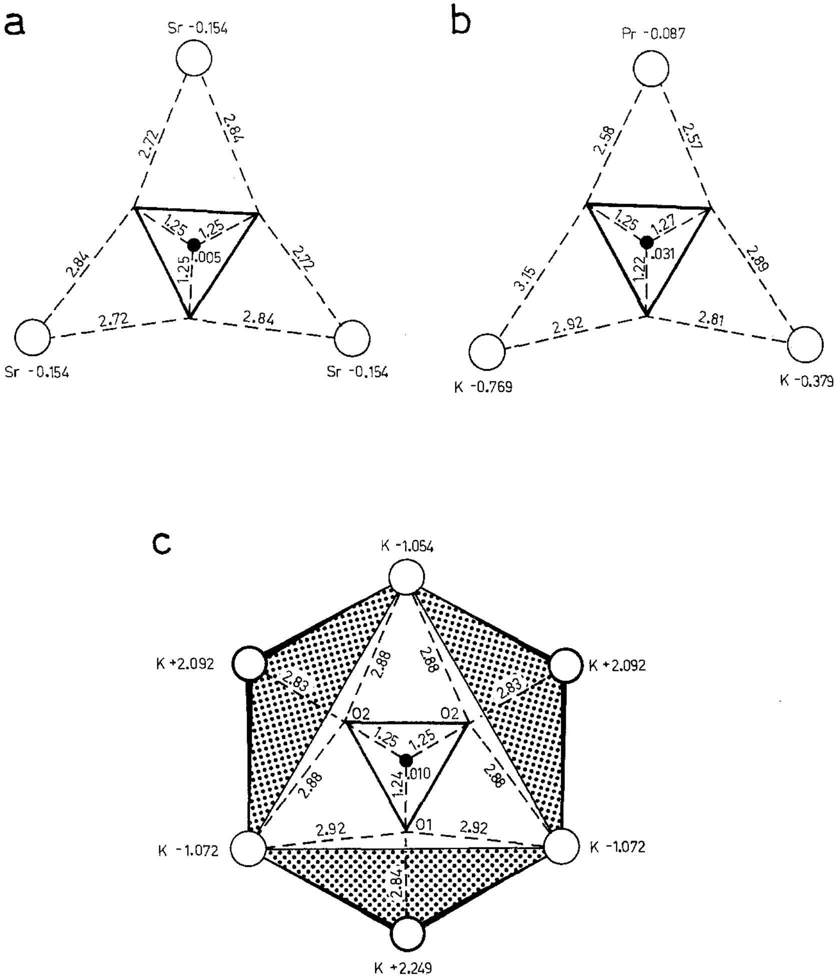

Fig. 1. Three simple examples for the surrounding of an aplanar nitrate group. The oxygen atoms lie in the drawing plane, the nitrogen atoms above of it (+). All distances in Å. For the surrounding cations also the sign of the deviation from the reference plane is given. *a* $Sr(NO_3)_2$[8,9]; *b* N(2) of $K_3Pr_2(NO_3)_9$[19]; *c* KNO_3[10]

Acknowledgements

Computing time was provided by "Interuniversitäres Rechenzentrum Wien".

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