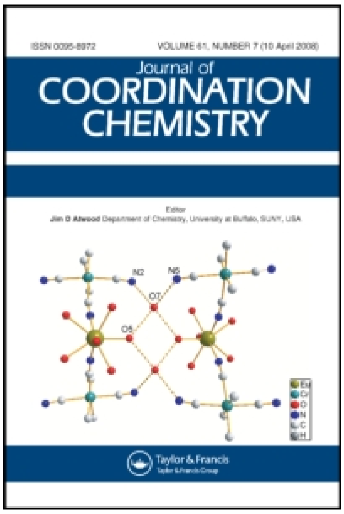

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THE PHENOMENON OF CONGLOMERATE CRYSTALLIZATION. XVII. CLAVIC DISSYMMETRY IN COORDINATION COMPOUNDS. XV. THE EFFECT OF THE CHARGE COMPENSATING IONS ON THE PHENOMENON OF CONGLOMERATE CRYSTALLIZATION

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In this report, we discuss the effect of the counter ion on the crystallization behaviour of chiral ions which may produce racemic or conglomerate crystals. We demonstrate that the counter ion is often capable of influencing the crystallization pathway and provide examples of substances in which the same chiral ion produces enantiomorphic crystals or racemic crystals depending on the nature of the counter ion. Moreover, we demonstrate that the crystal structures of such species amply demonstrate the reasons for such differences in crystallization pathway. In the species selected for the illustrations, the underlying phenomenon being influenced by the choice of counter ion is hydrogen bonding. This summary provides examples of counter ion pairs as varied as halides *vs* NO_3^-, halides *vs* NO_2^-,K^{+1} *vs* Ag^+, *etc.*, influencing the choice of crystallization pathway. Also, we illustrate the fact that the same ion (*i.e.*, NO_3^-) can play either a positive or a negative role in such a selection.

Keywords: Conglomerates, racemates, crystallization, hydrogen bonding, counter ions

INTRODUCTION

The first example we reported[1] of conglomerate crystallization in coordination compounds was the case of $[Ni(en)_3](NO_3)_2$, which was found to form massive crystals (space group $P6_322$). Subsequently, we reported[2] that a number of divalent cations with formula $[M(en)_3](NO_3)_2$ were isomorphous with the Ni salt, particularly the Zn derivative which, being transparent, made an ideal matrix to study axial rotational strengths in oriented single crystals.

We stated in that report[1] that "extensive and complex hydrogen bonding exists between the $-NH_2$ hydrogen atoms of the ethylenediamine and the oxygen atoms of the nitrate anions. Although formally there are only two nitrate anions per $[Ni(en)_3]^{2+}$ ion, the packing of the lattice is such that eight nitrates are arranged about the cations and each amine hydrogen is shared in an unusual, bifurcated manner by two oxygen atoms". Both those oxygens belong to the same nitrate anion; therefore we can visualize the NO_3^- anions as bidentate ligands to amine hydrogens. Moreover, "each oxygen has five close approaches by hydrogen atoms—two from amine hydrogen atoms lying almost exactly in the plane of the anion, two from amine

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hydrogen atoms lying above or below the plane of the anion, and one contact from a methylene hydrogen located 2.43 Å away. This last contact, probably not a true hydrogen bond, has a geometry such that the N–O...H angle is nearly 180° which would make no sense from a molecular orbital argument".

The important fact about the above observations is that, as a result of this extensive hydrogen bonding, the three $-NH_2$ groups at the trigonal faces of the $[M(en)_3]^{2+}$ cations are firmly locked, in the solid state, in a rigid fashion unlike the well-known labile solution behaviour of these species.

At the time,[1] we were not aware of the fact that an unnoticed and closely related set of examples was in fact already in the literature. In 1969, Stephens[3,4] reported the structures of [*mer*-Cu(dien)$_2$]X$_2$ (X = Cl and Br[3] (isomorphous, $P2_1/c$) racemic; NO_3, crystallizes[4] in $P2_12_12_1$, a conglomerate). In the latter species, the nitrate anions bind a terminal $-NH_2$ hydrogen of a dien with one oxygen and bind a secondary –NH hydrogen of the second dien of the same cation with another oxygen. This latter oxygen also binds a hydrogen of a terminal $-NH_2$ on an adjacent cation, *etc.* Thus, it locks this species into a more rigid, dissymmetric arrangement. That the effect of the nitrate anion on cation stereochemistry is not trivial is best illustrated by the fact that, as a result of the Jahn–Teller effect, the halo species contain an axially elongated Co–N_6 geometry (four co-planar nitrogens at distances of 2.03–2.13 Å and two axial ones at 2.35 and 2.46 Å). On the other hand, the nitrate is axially compressed, with the basal plane Cu–N $\simeq$2.22 Å and the shorter, axial Cu–N $\simeq$ 2.01 Å.

In a third paper dealing with conglomerate crystallization[4] we pointed out that whereas [*cis*–Co(en)$_2$(NO$_2$)$_2$]X (X = Cl and Br) form conglomerates, when X = NO_3^-, the substance crystallizes as a racemate. At that time, we suggested[3,4] that the change in crystallization mode was to be attributed to hydrogen bonding differences. In the halide salts, the strongest hydrogen bonds formed are between the amine hydrogens of ethylenediamine and the oxygens of an $-NO_2$ ligand on an adjacent cation. There also exists some intramolecular hydrogen bonding between $-NO_2$ oxygens and the axial $-NH_2$ hydrogen atoms, while the halide anions interact with the basal plane $-NH_2$ hydrogen atoms located *trans* to the $-NO_2$'s. With nitrates as compensating anions, the strongest hydrogen bonds are between the axial $-NH_2$ hydrogens and the nitrate oxygens.[7] Finally, we have recently refined the structure of [*cis*-Co(en)$_2$(NO$_2$)$_2$]NO$_2$ which crystallizes in the polar (non-enantiomorphic) space group *Cc*.[8] The hydrogen bonds between the axial $-NH_2$ hydrogens and the nitrite anion are even stronger than those found by Börtin[5] in the case of the nitrate derivative. We have also demonstrated[3,9] that [*cis*-α-Co(trien)(NO$_2$)$_2$]X (X = Cl, I) crystallize as conglomerates whereas the nitrate[7] forms racemic crystals, space group $P2_1/c$. The strongest hydrogen bonds formed in these halide salts are intramolecular interactions between the axial $-NH_2$ hydrogen atoms and nitro group oxygens. The same hydrogen bonding pattern of the nitrate salt prevails for this compound as with [*cis*-Co(en)$_2$(NO$_2$)$_2$]NO$_3$.

Thus, the pattern of results is completely consistent. For the [Me(en)$_3$](NO$_3$)$_2$ series the nitrate anions lock the labile cations into more robust, dissymmetric species (positive interaction). However, in the case of the [*cis*-Co(en)$_2$(NO$_2$)$_2$]$^+$ and [*cis*-α-Co(trien)(NO$_2$)$_2$]$^+$ cations, strong hydrogen bonding anions such as NO_3^- and NO_2^- disrupt an effective intramolecular and/or intercationic hydrogen bonded system which with poor hydrogen bonding counterions (such as halides) form conglomerates (negative interaction).

Finally, mention was made[3,11] that certain $-NO_2^-$ derivatives of Co(III) amines

(Co–NH_3) also formed conglomerates. That information, together with additional data acquired since, is indicated below

Compound	*Space Group*	*Ref.*
$[Co(NH_3)_5(NO_2)]Cl_2$	$C2/c$	12
$[Co(NH_3)_5(NO_2)]Br_2$	$C2/c$	13
$[Co(NH_3)_5(NO_2)]Cl_2$	$P2_1nb$	14*
[*cis*-$Co(NH_3)_4(NO_2)_2]NO_3$	$P2_12_12_1$	15
[*trans*-$Co(NH_3)_4(NO_2)_2]NO_3$	$P2_12_12_1$	16
[*trans*-$Co(NH_3)_4(NO_2)_2$]acetate	$Cmcm$	17
$[Co(NH_3)_3(NO_2)_2Br]$(*cis*-$(NO_2)_2$	$P2_1/n$	18**
$[Co(NH_3)_3(NO_2)_2Cl]$(*trans*-$(NO_2)_2$	$I4_1/a$	19**
[*mer*-$Co(NH_3)_3(NO_2)_3$]	$P2_12_12_1$	20
[*fac*-$Co(NH_3)_3(NO_2)_3$]	$P2_12_12_1$	21
K[*trans*-$Co(NH_3)_2(NO_2)_4$]	$P2_12_12_1$	5,22
Ag[*trans*-$Co(NH_3)_2(NO_2)_4$]	$P4/nnc$	23
$[Co(NH_3)_4(ox)]I.H_2O$	$P2_1/n$	24
$[Co(NH_3)_4(ox)](NO_3).H_2O$	$P2_12_12_1$	24

DISCUSSION

The above results indicate that the halides of the pentaaminenitro series do not conglomerate. The structures of the nitrate and nitrite derivatives are not available at the moment. In the tetraamine series both the *cis*- and the *trans*-dinitro nitrates conglomerate; however, the acetate does not and neither do the two neutral halo salts derived from *cis* and *trans*-dinitrotriamineCo(III) species. These results suggest that the presence of two nitro ligands, either *cis* or *trans*, provides insufficient anchoring of their oxygens to the amines to influence their crystallization behaviour towards conglomeration. Both *mer*- and *fac*-trinitrotriamine complexes form conglomerates, and in the *trans*-diaminetetranitro series the K salt is a conglomerate, whereas the Ag salt is a racemate. Finally, in the tetraamine-oxalato series, the nitrate is a conglomerate while the iodide is a racemate.

It was pointed out by Oonishi *et al.*[15,16] that for both the *cis*- and *trans*-dinitrotetraamine nitrates, the nitrate anions provided a rich network of hydrogen bonding to the amines and that these bonds were very substantial. Thus in both these cases the nitrates are playing a role analogous to that we[1] described for the $[M(en)_3](NO_3)_2$ salts. Because of its mode of binding, the acetate,[17] obviously, cannot provide the additional dissymmetric anchoring supplied by the nitrate anions. Examination of its structure[17] shows each of the two acetate oxygens binding, in identical fashion, a pair of *cis*-NH_3 ligands which are related by a mirror plane. Thus the resulting ion pair is achiral—the cation sits at a 2*mm* site in which the two-fold axis passes along the O_2N–Co–NO_2 N–Co–N direction.

The nitrate anions contribute to the dissymmetry of the *cis*- or *trans*-$[Co(NH_3)_4(NO_2)_2]^+$ cation by aiding –NO_2 in locking the amines in positions such that, in the solid, the cation becomes dissymmetric. In other words, there is a synergistic

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* Obtained from solid state rearrangement of the nitrito compound.

** The three NH_3 ligands exhibit the *mer* geometry.

collaboration between the intramolecular hydrogen bonds of the $-NO_2$ ligands and the interionic ones due to the nitrates. This observation is in accord with an interesting experiment carried out by Bosnich and Harrowfield,[25] who studied the solution and solid state CD spectra of $[Co(NH_3)_6]^{3+}$ in the presence of bromcamphorsulfonate. As expected, solutions produced no CD absorption in the region of the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition. However, in the solid (KBr pellets) there was significant rotational strength in the region associated with that metal d–d transition, implying that the $-SO_3^-$ fragment of the anion locked the amines, by hydrogen bonds, in a dissymmetric conformation capable of producing a net CD rotation in the region of the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition. A similarly dissymmetric ion pair is formed by the nitrate anions in the above cases.

The only comment that needs to be made concerning the trinitro series is that in both cases the three nitro groups must be capable of providing the necessary anchoring to render the species chiral. Previously[3,6,22,27] we pointed out that when nitro groups are *cis* to one another, they must maintain an O–O distance of about 3.1–3.2 Å which limits their freedom to orient themselves in ways so as to improve hydrogen bonding interactions. In the case of the *mer* and *fac*-trinitro cations, this constraint seems to aid the locking of the amines into a dissymmetric conformation. Each pair of adjacent nitro groups has to maintain that distance and resist attempts by the third $-NO_2$ ligand to twist freely. On the other hand, all three try to form as strong a set of hydrogen bonds as possible. The final, compromise conformation of the complex is a chiral entity frozen in the solid state, even if achiral in solution due to rotation of the ligands. Thus, the presence of three nitro groups with their repulsive O–O interactions on the one hand, and their attractive O–H bonds on the other, seems to be necessary and sufficient to induce *mer*- and *fac*- trinitrotriamine complexes into conglomerate crystallization.

Of the two examples of the M[*trans*-$Co(NH_3)_2(NO_2)_4$] series, the NH_4^+ and the K^+ salt are conglomerates while the silver salt is a racemate. The former are isomorphous and isostructural. The original reports[3,22,18] do not contain suitable diagrams to observe the environment of these cations in their respective salts; therefore, we present here Figs. 1 and 2 which show the details of the environment around the K and Ag cations. The sphere of enclosure about K (drawn to 3.0 Å) shows it to be coordinated by oxygens of each of the four $-NO_2$ ligands. The three shortest K–O contacts are 2.81, 2.83 and 2.87 Å, very similar to the results obtained for the $K_3[Cu(NO_2)_5]$ salt.[26] Therefore, the K–O distances in the K[*trans*-Co-$(NH_3)_2(NO_2)_4$] salt are quite long, as they normally are in salts of this type. This subject was discussed in some detail by Klanderman, Hamilton and Bernal[26] who described the structure of $K_3[Cu(NO_2)_5]$ in which there are eight independent K cations in the asymmetric unit. In this salt, the shortest K–O distance is 2.82 Å. Thus, the K cation of K[*trans*-$Co(NH_3)_2(NO_2)_4$] does not disturb the hydrogen bonding interactions between NO_2 oxygens and the NH_3 hydrogens which are known from a neutron diffraction structure[22] to help render the anion a highly dissymmetric propeller.[27]

Pertinent to these observations on the K–O contacts in K[*trans*-$Co(NH_3)_2(NO_2)_4$] are the comments made by Lenhert and Joesten[28] on similar contacts present in $KPb[Co(NO_2)_6]$ and in $KBa[Co(NO_2)_6]$ (the structure of the latter was determined earlier by J.A. Bertrand and D.A. Carpenter[29]) and their Rb analogues. Lenhert and Joesten pointed out that the difference in ionic radius between Rb and K is 0.15 Å; yet, the K–O contacts were only 0.042 Å shorter. Moreover, the distances ranged from 3.054 Å[28] to 3.13 Å,[29] which are quite long, and even longer than those described by Klanderman, Hamilton and Bernal.[26] Thus, potassium cations merely fill lattice cages with which they interact only coulombically.

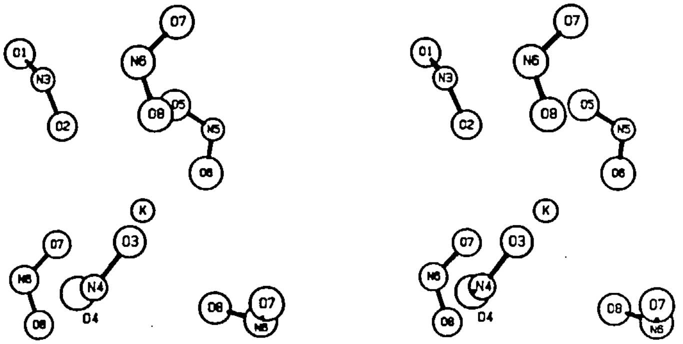

FIGURE 1 Stereo view of the environment of the K cations in the chiral lattice of K[*trans*-Co$(NH_3)_2(NO_2)_4$]. Note that unlike the Ag salt (see Fig. 2) this derivative contains the cation in a highly unsymmetrical environment which markedly resembles the environments of the K cations found[25] in $K_3[Cu(NO_2)_5]$. Since the latter is a racemic salt, it is obvious that the environment of the K cations in the former are not being determined by its crystallizing in an enantiomorphic space group.

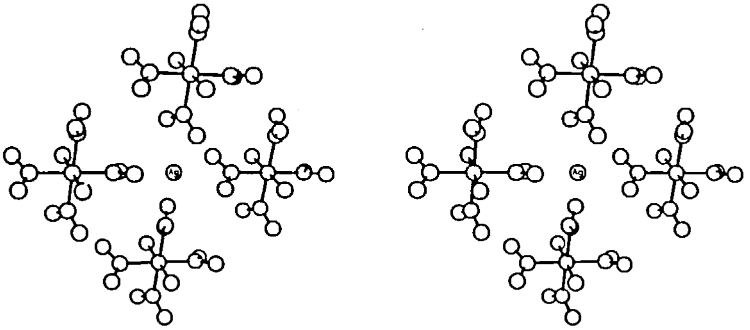

FIGURE 2 The environment about the silver cation in Ag[*trans*-Co$(NH_3)_2(NO_2)_4$]. Ag is symmetrically surrounded by eight oxygens belonging to four different [*trans*-Co$(NH_3)_2(NO_2)_4$] anions. If we consider the small bite of the $-NO_2$ ligands, silver can best be described as being four coordinate.

On the other hand, if we consider the results for the silver salt, Ag[*trans*-Co$(NH_3)_2(NO_2)_4$] (see Fig. 2) the Ag^+ cation is surrounded by four anions whose $-NO_2$ oxygens are symmetrically bidentate to Ag^+. The Ag–O contacts are all 2.56 Å. These are quite strong interactions since the structure of $AgNO_2$ shows[30] three different Ag–O bonds (2.42, 2.47 and 2.73 Å). Thus, despite the fact that the $-NO_2$ ligands are forming Co–N bonds, the Ag–O bonds in Ag[*trans*-Co$(NH_3)_2(NO_2)_4$] are remarkably short and of length comparable with those considered to be **normal covalent bonds** for $AgNO_2$.

The result of forming nearly normal, covalent bonds between Ag and the $-NO_2$ oxygens is that the latter are no longer available for hydrogen bonded interactions with the *trans*-diamine hydrogens. Moreover, Ag^+ apparently likes to form highly symmetrical, bidentate bonds with such nitro ligands,[30] giving rise in this case to an achiral anion which sits at an inversion centre of the tetragonal lattice in which it crystallizes.

Finally, attention should be drawn to the consistency between the results of the oxalatotetramine series and the dinitrotetraamine series, namely whereas the halides do not conglomerate, the nitrates do. As will be shown in a future paper on the oxalates,[24] the nitrate anion is involved in strong bonds with the amine hydrogens, again locking a labile cation into a more robust, dissymmetric conformation which conglomerates.

Earlier, we[1] suggested that an ion, such as nitrate, could play a constructive role in conglomerate crystallization by locking, through hydrogen bonds, its counterion in a dissymmetric conformation which is then frozen in the solid state during conglomerate crystallization. At that time, we only knew of one series of compounds, $[M(en)_3](NO_3)_2$ (M = Ni, Zn, *etc*) for which this could be documented to be a plausible phenomenon. Now we find that the same reasoning can be used to account for the crystallization behaviour of the [*mer*-$Cu(dien)_2]X_2$ series of Stephens[3,6] as well as for the series *cis*- and *trans*-$[Co(NH_3)_4(NO_2)_2]NO_3$ and for the conglomerate crystallization of $[Co(NH_3)_4(oxalato)]NO_3.H_2O$. We also find that the destructive role we ascribed to nitrate[3,6] in the case of [*cis*-$Co(en)_2(NO_2)_2]^+$ and [*cis*-α-$Co(trien)(NO_2)_2]^+$ cations is now found for Ag^+ interacting with [*trans*-$Co(NH_3)_2(NO_2)_4]^-$. Thus, there is an inner consistency to the argument that suitable intra- or intermolecular hydrogen bonded interactions are responsible for the occurrence of conglomerate or racemic crystallization in the systems described. Moreover, the mechanism associated with the phenomenon of conglomerate crystallization of these systems is quite general and devoid of the parochiality of being the exclusive province of selected species, such as nitrate anions, which in fact can play both a constructive and a destructive role in conglomerate crystallization.

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