The Phenomenon of Conglomerate Crystallization.
IV. The Structure and Absolute Configuration of $[\Lambda(\delta\lambda)(-)_{589}$-*cis*-$Co(en)_2(NO_2)_2]$-$[$*trans*-$Co(NH_3)_2(NO_2)_4]$ a Substance Containing *Clavic* Dyssymmetric Cations and Anions

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Abstract

The crystal structure and the absolute configurations of the species present in the title compound were established by X-ray crystallographic methods. The substance crystallizes in the orthorhombic space group $P2_12_12_1$, with lattice constants of a = 6.521(2), b = 10.735(2), c = 26.085(5) Å and V = 1825.93 Å^3. The calculated density (z = 4) is 1.994 gm·cm^{-3}, given the molecular weight of 548.1574 gm·mol^{-1}. The data were collected with MoKα radiation (λ = 0.71069 Å) and the reduced set consisted of 3680 data for which $I \geqslant 3\sigma$ (I). After refinement of the trial structure was complete, comparison was made with the results of refining its enantiomorph. The values of (R, Rw) for the trial solution and for the enantiomorph were, respectively, (0.0375, 0.0389) and (0.0476, 0.0468) which indicates that the initially chosen coordinates were the correct ones for the diastereoisomeric pair present in the crystal selected for data collection. The above choice of absolute configuration was also confirmed by the measurement of Bijvoet differences between 28 reflections.

The configuration of the cation is the same as that recently found in $\Lambda(\delta\lambda)[(-)_{589}$-*cis*-bisethylenediamine$Co(NO_2)_2]Cl$, with which it shares the interesting property of having one *lel* and one *ob* conformated ethylenediamine ring. The anion, surprisingly, has almost the identical conformation and configuration found in optically active crystals of $K[$*trans*-$Co(NH_3)_2(NO_2)_4]$ recently studied at this laboratory. Both the cation and the anion of this salt share the common feature of displaying *Clavic* dyssymmetry, a newly recognized form of atropisomerism leading to an unusually high ratio of spontaneous resolutions of potentially optically active species.

Differences in the Co–N(NH$_2$) distances in the cation between those *cis* and those *trans* to the $-NO_2$ ligands (av. *cis* = 1.956 Å; av. *trans* = 1.985 Å) clearly document the existence of a *trans* effect. In the anion, the Co–N(NH$_3$) distances average to 1.948 Å, in good agreement with the results for the *cis* pair of the cation, as expected. The results obtained here are in full accord with our previous work on these ions and the importance of this study lies not on the geometrical details of the ions in question; rather, they contribute to an understanding of the phenomenon of conglomerate crystallization, spontaneous resolution of enantiomeric pairs into a mechanical mixture of pure, antipodal, crystals.

Introduction

A conglomerate is a mechanical mixture of optically active crystals obtained when a racemic solution, consisting of a pair of enantiomers or of an enantiomeric mixture of diastereoisomers, spontaneously resolves into antipodal crystals, as opposed to collection of crystals of a single handedness. The classical case of conglomerate formation was, of course, Pasteur's resolution of the antipodes of tartaric acid, a diastereoisomeric substance having two chiral centers. The interested reader is referred to the recent treatise by Jacques, Collet and Wilen [1] for an in-depth discussion of this topic.

In a recent paper, Bernal [2] showed that three substances, sharing the common property of having a pair of *cis* $-NO_2$ ligands binding a central Co(III) ion containing axial $-NH_3$ or $-NH_2$ (as in ethylenediamine, etc...) ligands underwent spontaneous resolution into crystalline conglomerates. The substances in question were $[$*cis*-α-(triethylenetetramine)-$Co(NO_2)_2]Cl\cdot H_2O$ (hereafter **I**), $[$*cis*-bisethylenediamine$Co(NO_2)_2]Cl$ (hereafter **II**) and $K[$*trans*-$(NH_3)_2$-$Co(NO_2)_4]$ (hereafter **III**). In that paper, examples were cited from the inorganic, organic, etc. realm which clearly show that whenever paddle-shaped ligands or substituents can be held by intra or intermolecular forces in fixed, dyssymmetric, conformations the resulting species have an unusual tendency to undergo spontaneous resolution into chiral conglomerates. The reader is referred to the compila-

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TABLE I. Summary of Data Collection and Processing Parameters.

Space Group	$P2_12_12_1$
Cell Constants	$a = 6.521(1)$ Å $b = 10.735(2)$ $c = 26.085(5)$
Cell Volume	$V = 1825.93$ Å^3
Crystal Aligned Approximately Along	$[\bar{1}, 1, 0]$
Asymmetric Unit Formula	$C_4H_{22}N_{12}O_{12}Co_2$
Asymmetric Unit Weight	548.1574 g mol^{-1}
Density (calcd.; $z = 4$)	1.994 g cm^{-3}
Radiation	MoKα ($\lambda = 0.71069$ Å)
Absorption Coefficient	$\mu = 18.12$ cm^{-1}
Data Collection Range	$4.0° \leqslant 2\theta \leqslant 70.0°$
Scan Width	$\Delta\theta = (1.0 + 0.35 \tan\theta)$
Maximum Scan Time	180 sec
Scan Speed Range	0.50 to 4.03 deg min^{-1}
Total Data Collected	4908
Data With $(I) \geqslant 3\sigma(I)$[a]	3680
Total Variables	274
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.0336
$Rw = [\Sigma w^2(\|F_o\| - \|F_c\|)^2/\Sigma w^2\|F_o\|^2]^{1/2}$	0.0337
Weights	$w = [\sigma(F_o)]^{-2}$
Goodness of Fit	2.14

[a] The difference between total data collected and this number is due to subtraction of standards, redundant data and those which do not meet the criterion of having $(I) \geqslant 3\sigma(I)$.

tion of Jacques, Collet and Wilen [1] for statistics on the incidence of conglomerate formation (they quote only 248 cases thus far recorded in all of chemistry's annals). Given that apparently minute incidence, it appeared worth investigating a class of compounds in which such a high proportion undergo conglomerate crystallization, particularly once it was noted that a feature common to all was the presence of dyssymmetry induced by *Clavic* (from the Latin for paddles or tillers) groups or ligands. Thus, it seemed interesting to crystallize salts derived from the cations of (**I**) and of (**II**) with the anion of (**III**) which we have now succeeded in doing. The crystals of both [*cis*-α-triethylenetetramineCo$(NO_2)_2$][*trans*-Co$(NH_3)_2(NO_2)_4$] (hereafter (**IV**)) and of [*cis*-$(en)_2$Co$(NO_2)_2$][*trans*-Co$(NH_3)_2(NO_2)_4$] (hereafter (**V**)) crystallize in the space group $P2_12_12_1$; however, crystals of (**IV**), thus far obtained, are too small to collect a meaningful data set. Larger crystals of (**V**) are readily obtained and, in this manuscript we discuss the structure and absolute configuration of that salt.

Experimental

A. Synthesis and Crystal Growth for (V)

The substance was prepared by weighting 0.05 mol each of (**II**) and of (**III**), prepared as given before [2] and dissolving the mixture of solid enantiomers in the minimal amount of hot water (60 °C) necessary. The resulting racemic solution was cooled to room temperature, filtered and allowed to evaporate slowly whereupon large crystals of the compound were obtained which were ground into spheres suitable for single crystal X-ray diffraction studies. The one selected had an approximate diameter of 0.5 mm.

B. X-Ray Data Collection and Processing

Data were collected with an Enraf-Nonius diffractometer using standard procedures and the significant data employed for the collection of structure amplitudes, as well as those used in processing such information are summarized in Table I. The Patterson function provided the coordinates of the two cobalt atoms and the rest were simply found in difference electron density maps. The hydrogen atoms for the cation were found at reasonable positions but refined only with moderate success. Therefore, they were calculated at ideal positions (C–H, N–H = 1.00 Å) following every cycle of refinement. In the early stages of refinement, the hydrogens of the anion were less well defined on difference maps and refined poorly. Since it is impossible to be certain where to place them in a calculation of idealized positions (*i.e.* are they staggered, eclipsed or at an arbitrary orientation with respect to a marker point?) they were left out momentarily.

When the refinement was complete for this set of coordinates, the enantiomeric coordinates were refined till convergence, at which point the (R, Rw)

factors for the initial and enantiomeric solutions were respectively (0.0375, 0.0389) and (0.0476, 0.0468). The structure factors calculated from the two models were compared and a few suitable pairs, differing significantly, were selected for the Bijvoet test [3], which was implemented in the manner described elsewhere [4]. Both tests selected the initial set of coordinates as the correct model for this particular crystal. However, random selection of another crystal would probably give the reverse result since we are dealing with a conglomerate.

The rather large difference in *R* and *Rw* factors between the two refinements is common for this type of compound even while using MoKα radiation. For example, in the case of compound (**III**) the values of the *R* indices for the two absolute configurations were, respectively, 0.0367 and 0.0475. These large effects may better be understood when the data on Table III are examined. Here, twenty eight reflections are listed whose Bijvoet pairs differ by 5% or more; some (*i.e.*, 1, 9, 8; 1, 8, 3; 1, 5, 7; 1, 1, 7; 2, 1, 5; 3, 5, 11) differ by 10% or more, while one (2, 6, 5) differs by 20%. The last reflection alone would suffice to identify the correct enantiomer. It must be emphasized that no effort was made to find all of the reflections suitable for the Bijvoet test and only some of the most obvious, low angle, ones were selected.

After the absolute configuration was determined, refinement was continued till convergence, whereupon a difference Fourier map showed the missing hydrogens of the $-NH_3$ ligands of the anion at more attractive locations; however, attempts to refine them failed since they drift into unreasonable positions giving either poor N–H distances, poor H–N–H angles or both. Therefore, they were fixed at the initial positions and only an overall thermal parameter was refined for each of them (see Table IIB). The correct absolute coordinates are given in Table II and were used for all further work on this paper.

All calculations associated with the solution and refinement were carried out with SHELX-76 [5]. Long distances associated with hydrogen bonds were calculated with ORFFE [6], torsional angle with a local program and the double stereo plots with BMFIT [7]. The hydrogen atoms were left out of the stereo plots of the anion since they are considered

TABLE IIA. Atomic Coordinates and Thermal Parameters (×1000; Co × 10000).

Atom	*x/a*	*y/b*	*z/c*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co1	0.19647(8)	0.21210(5)	0.35280(2)	127(2)	166(2)	238(3)	−12(3)	−2(2)	−3(2)
O1	−0.1006(5)	0.2329(3)	0.4291(1)	27(2)	61(2)	43(2)	−4(2)	14(2)	−16(2)
O2	−0.1890(5)	0.1128(3)	0.3679(1)	17(1)	46(2)	42(2)	−10(2)	−1(2)	4(2)
O3	−0.0888(5)	0.2692(3)	0.2765(1)	28(2)	39(2)	48(2)	−3(2)	−17(2)	3(2)
O4	0.1049(5)	0.4231(3)	0.2969(1)	32(2)	23(2)	46(2)	2(1)	1(2)	9(1)
N1	0.2484(5)	0.3567(3)	0.3963(1)	24(2)	20(2)	25(2)	−1(1)	−1(1)	−3(1)
N2	0.3503(5)	0.1184(3)	0.4060(1)	16(2)	18(2)	27(2)	−1(1)	−1(1)	1(1)
N3	0.4465(5)	0.2409(3)	0.3112(1)	17(2)	26(2)	29(2)	−1(1)	2(1)	2(2)
N4	0.1635(5)	0.0626(3)	0.3106(1)	20(2)	23(2)	26(2)	−2(1)	0(1)	−1(1)
N5	−0.0623(5)	0.1828(3)	0.3889(1)	15(2)	28(2)	30(2)	1(1)	−2(1)	3(2)
N6	0.0504(5)	0.3119(3)	0.3033(1)	18(2)	26(2)	32(2)	4(1)	3(2)	2(2)
C1	0.3998(7)	0.3281(4)	0.4369(2)	30(2)	26(2)	28(2)	−3(2)	−4(2)	−4(2)
C2	0.3683(7)	0.1941(4)	0.4539(2)	28(2)	28(2)	25(2)	−2(2)	−3(2)	3(2)
C3	0.4906(6)	0.1294(4)	0.2783(2)	22(2)	34(2)	41(3)	2(2)	3(2)	−7(2)
C4	0.2919(7)	0.0716(4)	0.2635(2)	26(2)	31(2)	30(2)	−2(2)	−1(2)	−7(2)
H1	0.1168(5)	0.3830(3)	0.4128(1)	48(4)					
H2	0.3023(5)	0.4262(3)	0.3746(1)	48(4)					
H3	0.5419(7)	0.3386(4)	0.4231(2)	48(4)					
H4	0.3794(7)	0.3855(4)	0.4666(2)	48(4)					
H5	0.2401(7)	0.1868(4)	0.4747(2)	48(4)					
H6	0.4880(7)	0.1652(4)	0.4747(2)	48(4)					
H7	0.4906(5)	0.0988(3)	0.3929(1)	48(4)					
H8	0.2761(5)	0.0392(3)	0.4139(1)	48(4)					
H9	0.5656(5)	0.2563(3)	0.3345(1)	48(4)					
H10	0.4250(5)	0.3153(3)	0.2887(1)	48(4)					
H11	0.5749(6)	0.0680(4)	0.2980(2)	48(4)					
H12	0.5669(6)	0.1557(4)	0.2469(2)	48(4)					
H13	0.2214(7)	0.1246(4)	0.2373(2)	48(4)					
H14	0.3161(7)	−0.0134(4)	0.2490(2)	48(4)					
H15	0.0162(5)	0.0539(3)	0.3006(1)	48(4)					
H16	0.2067(5)	−0.0121(3)	0.3309(1)	48(4)					

TABLE IIB. Atomic Coordinates and Thermal Parameters (× 1000, Co × 10000).

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co2	0.20923(8)	0.21623(5)	0.10533(2)	159(2)	170(2)	223(3)	11(3)	16(2)	−6(2)
AO1	0.2617(5)	−0.0273(3)	0.1394(1)	37(2)	22(2)	60(2)	2(1)	12(2)	9(2)
AO2	0.5369(5)	0.0802(3)	0.1431(2)	24(2)	39(2)	75(3)	13(2)	−17(2)	−8(2)
AO3	0.1697(7)	0.0565(4)	0.0223(1)	62(3)	63(3)	63(3)	4(2)	1(2)	−40(2)
AO4	−0.1162(6)	0.1042(3)	0.0550(1)	36(2)	55(2)	59(3)	−15(2)	−11(2)	−6(2)
AO5	0.1368(6)	0.4229(3)	0.0429(1)	64(3)	49(2)	55(3)	18(2)	25(2)	31(2)
AO6	−0.1054(5)	0.3880(3)	0.0950(2)	34(2)	36(2)	80(3)	15(2)	15(2)	8(2)
AO7	0.2738(6)	0.3426(3)	0.1973(1)	64(3)	57(2)	29(2)	−29(2)	15(2)	−14(2)
AO8	0.5129(5)	0.3729(3)	0.1440(2)	28(2)	63(2)	74(3)	−21(2)	13(2)	−24(2)
AN1	0.4318(6)	0.2426(3)	0.0570(1)	27(2)	33(2)	33(2)	3(2)	11(2)	−3(2)
AN2	−0.0148(5)	0.1864(3)	0.1532(1)	17(2)	28(2)	29(2)	−1(1)	1(1)	1(2)
AN3	0.3498(6)	0.0717(3)	0.1323(1)	32(2)	22(2)	26(2)	8(2)	2(2)	−1(1)
AN4	0.0728(7)	0.1117(4)	0.0549(2)	38(2)	28(2)	30(2)	−2(2)	−8(2)	0(2)
AN5	0.0657(6)	0.3613(3)	0.0771(1)	28(2)	22(2)	28(2)	7(2)	−3(2)	−4(2)
AN6	0.3474(6)	0.3241(3)	0.1559(2)	25(2)	21(2)	37(2)	−1(1)	−1(2)	0(2)
AH1	−0.0235(0)	0.2156(0)	0.1875(0)	9(1)					
AH2	0.0019(0)	0.1100(0)	0.1658(0)	9(1)					
AH3	−0.1718(0)	0.2096(0)	0.1323(0)	9(1)					
AH4	0.4180(0)	0.1895(0)	0.0258(0)	15(2)					
AH5	0.5630(0)	0.2230(0)	0.0756(0)	15(2)					
AH6	0.4319(0)	0.3328(0)	0.0472(0)	15(2)					

somewhat unreliable due to potential disorder observed elsewhere [2, 8] and briefly discussed here, again, for the convenience of the reader.

TABLE III. Bijvoet Pairs Used in the Determination of the Absolute Configuration of Compound (V).

Reflection			Theory[a]	Experiment[b]
1	9	8	1.14	1.13
1	8	11	1.05	1.06
1	8	4	1.05	1.05
1	8	3	0.86	0.89
1	7	10	0.92	0.90
1	5	7	1.17	1.15
1	5	8	0.95	0.93
1	6	12	0.92	0.94
1	6	8	1.09	1.11
1	6	5	1.05	1.06
1	3	8	0.93	0.92
1	1	5	1.07	1.05
1	1	7	0.90	0.91
2	1	5	1.11	1.12
2	1	4	1.05	1.07
2	1	3	0.93	0.92
2	3	3	1.06	1.05
2	4	5	0.96	0.93
2	4	8	1.05	1.07
2	6	5	0.80	0.83
2	6	8	1.07	1.09
2	7	3	1.05	1.06
2	7	1	1.07	1.06
2	8	3	1.08	1.08
3	6	7	1.09	1.07
3	6	5	0.94	0.95
3	5	5	0.94	0.93
3	5	11	0.89	0.88

[a] Obtained as the calculated ratio F (+++)/F(− − −). [b] Obtained as the measured ratio F (+++)/F (− − −).

Previous Stereochemical Results for the Cation and Anion of (V)

In order to facilitate the discussion which follows, a brief description of the stereochemistry of the cation, as found in ((**II**); X-ray study [2]) and of the stereochemistry of the anion as found in ((**III**); both X-ray [2] and neutron [8] studies) will be reviewed here:

Cation

Our previous results showed the cation of (**II**) to be Λ(δλ), a result which was considered unusual since this conformation is not an energy minimum for this species [10]. However, *en* rings in the *ob* conformation, while relatively rare, are well documented and Saito has discussed the energy barriers for the *lel* $\longleftrightarrow$ *ob* equilibrium [10]. The refinement of (**II**) gave excellent results and thermal parameters of the hydrogens had values of $\langle U \rangle$ *ca.* 0.04 Å^2. Typical errors in bond lengths were $\times 10^{-3}$ and angles $\times 10^{-1}$.

Anion

Studies of the anion in the form of the potassium salt (*i.e.* (**III**)) by X-ray methods [2] gave excellent results for the heavy atoms but poor results for the hydrogens of the two *trans* $-NH_3$ ligands, one much better than the other one. A neutron diffraction [8] study of the same salt shows the reasons for this behavior: (a) one $-NH_3$ ligand is hydrogen bonded to

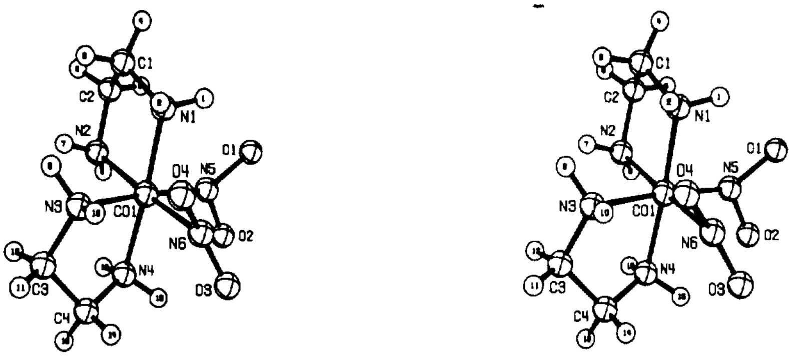

Fig. 1. Stereo view of the cation with the numeric labels used in the crystallographic study. Note the *lel* conformation of the upper *en* ring and the *ob* conformation of the lower one.

two *cis* $-NO_2$ oxygens (b) once the conformation of these pair of *cis* $-NO_2$ ligands is fixed, the other pair of $-NO_2$ ligands forms even weaker hydrogen bonds to the available amine hydrogens (c) however, neither is firmly fixed by these weak hydrogen bonds and while one has relatively lower amplitude of vibrational and librational motion, the other occupies two distinct positions readily observed on difference density maps [8]. The thermal motion of this latter amine has *ca.* double the value of the previous one but the occupancy of the two minima is not 50–50%.

The valuable result derived from the neutron study [8] was to show that the X-ray data, while incapable of allowing quality of refinement of the individual hydrogens, was approximately correct all along, particularly with respect to the better-behaved amino ligand. Therefore, when the exact same behavior was found for the anion of (V), we feel confident that the results to be presented below are reasonable and tempered by the previous experience; *i.e.*, the amino group with better thermal motion is reasonably reliably placed, the other one is as chancy as its analog in (**III**). Yet, for all the problems they may have with precision of location, the pattern of stereochemistry that emerges and the changes observed, when compared with the results of (**II**) and (**III**) make excellent chemical sense, as the reader shall see.

Description of the Structure

The packing diagram (Fig. 3) shows that the cations and anions are so arranged as to form a rich network of inter and intramolecular hydrogen bonds. Some of the former are a little weaker (shortest are *ca.* 2.3 Å) than the latter, the shortest of which (H1···O1) is only *ca.* 2.2 Å. These values of the intramolecular NH···O hydrogen bonds are in good agreement with our previous X-ray studies [2] of both these ions as well as with our neutron diffraction [8] study of (**III**).

Individual stereo plots of the cation and anion are given in Figs. 1 and 2. The numbering system employed in the crystallographic study is given in these Figs., which are correlated with the numbering system used previously [2, 8]. The following observations can now be made about the individual ions:

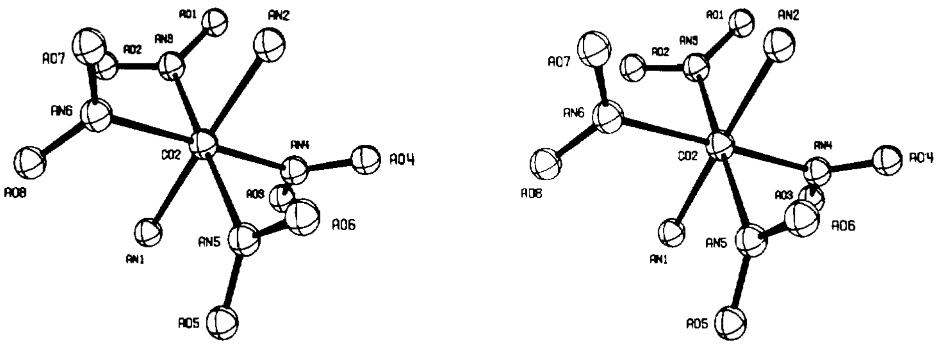

Fig. 2. Stereo view of the anion.

Fig. 3. Packing of the ions in the lattice. A full unit cell is shown. Note that the $-NO_2$ ligands of both ions are suitably oriented to form hydrogen bonds with those on either $-NH_2$ or $-NH_3$ neighbors.

(a) Cation

The absolute configuration of this species is shown (Fig. 1) to be Λ(δλ), which means that one of the ethylenediamine rings is *lel* (the upper one) while the other one is *ob*. This was something of a surprise since, as mentioned earlier, the frequency of occurrence [10] for the *ob* conformation is quite low. The line of sight chosen emphasizes that conformational aspect of this cation. It is also clear from Fig. 1 that O4 makes hydrogen bonds with H2 (2.405 Å) and H10 (2.405 Å) while O3 interacts with H15 (2.493 Å). The other $-NO_2$ ligand has contacts between O1 and H1 and between O2 and H15 of 2.193 and 2.300 Å, respectively. These are the shortest intramolecular NH···O hydrogen bonds present in the cation. It would appear, however, that in most cases the conformation of $-NO_2$ ligands are dictated by intramolecular hydrogen bonds; otherwise, the remarkable uniformity in conformations noted ealier [2] and here (see Figs. 4 and 5) could not be accounted for. After all, there are significant changes in space groups and in the nature of charge compensating ions between (**I**), (**II**), (**III**), (**V**) and other species discussed earlier [2]; yet, the largest deviation in conformation observed thus far is in the torsional angle of one $-NO_2$ ligand of (**V**) when compared with (**II**). See Fig. 4 and Tables V and VI for details. This single, largest, change in torsional angle (*ca.* 60°) is probably due to a combination of factors such as the conformational changes in the en rings of the cation and of favorable intermolecular hydrogen bonds. What is most remarkable here is not that this torsional angle change occurred at an $-NO_2$ group of the cation but how little overall change occurred in both the cation and the anion going from one compound to another. These observations are all the more interesting in view of the fact that even the two shortest hydrogen bonds observed in all of these cases are relatively weak. For example, in the current case, the shortest intramolecular bond for the cation (O1···H1 = 2.19 Å) is a weak bond since, as shown previously [9], strong NH···O bonds are in the 1.86 Å range.

(b) Anion

As is clear from the Figs. 2, 3 and 5 as well as from the data on Table IV, the anion is also intra- and inter-molecularly hydrogen bonded. The former bonds are somewhat shorter than the latter (four intramolecular bonds are *ca.* 2.15 Å, while the two shortest intermolecular bonds are *ca.* 2.38 Å). This

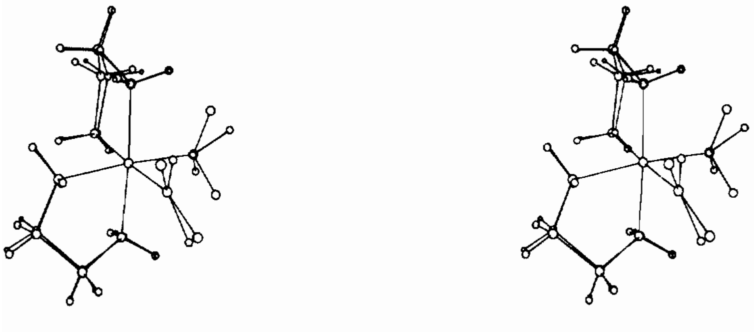

Fig. 4. BMFIT comparison of the conformation and configuration of the cations of ((**V**); larger circles for its atoms) and ((**II**); smaller circles). The orientation of the Figure is identical with that for cation (**V**) in Fig. 1.

TABLE IV. Bond Lengths (Å) and Angles (°) with e.s.d.s in Parentheses.

A. Bond Lengths for the Cation[a]

Co1–N1	1.953(3)	C2–N2	1.494(5)
Co1–N2	1.986(3)	N3–C3	1.501(5)
Co1–N3	1.984(3)	C3–C4	1.487(6)
Co1–N4	1.958(3)	C4–N4	1.492(5)
Co1–N5	1.957(3)	N5–O1	1.207(4)
Co1–N6	1.929(3)	N5–O2	1.243(4)
N1–C1	1.479(5)	N6–O3	1.234(4)
C1–C2	1.520(6)	N6–O4	1.257(4)

B. Bond Lengths for the Anion[b]

Co2–AN1	1.944(3)	AN5–AO5	1.205(4)
Co2–AN2	1.952(3)	AN5–AO6	1.242(5)
Co2–AN3	1.935(3)	AN6–AO7	1.200(4)
Co2–AN4	1.945(4)	AN6–AO8	1.240(4)
Co2–AN5	1.961(4)	AN1–AH1	1.01
Co2–AN6	1.972(4)	AN1–AH2	1.00
AN3–AO1	1.223(4)	AN1–AH3	0.97
AN3–AO2	1.255(5)	AN2–AH4	1.19
AN4–AO3	1.216(5)	AN2–AH5	0.95
AN4–AO4	1.234(5)	AN2–AH6	1.00

C. Intramolecular Contacts Less than 2.40 Å

a. For the Cation

O1–H1	2.19	O2–H15	2.30

b. For the Anion

AO1–AH6	2.15	AO4–AH4	2.34
AO2–AH1	2.34	AO5–AH2	2.17
AO2–AH4	2.38	AO6–AH4	2.19
AO3–AH3	2.17	AO7–AH5	2.39

D. Intermolecular Contacts Less Than 2.50 Å

O3–AH5	2.43	O4–AH6	2.32

E. Bond Angles for the Cation

N1–Co1–N2	84.8(1)	Co1–N1–C1	111.5(2)
N1–Co1–N3	93.0(1)	N1–C1–C2	108.4(3)
N1–Co1–N4	175.9(1)	C1–C2–N2	106.3(3)
N1–Co1–N5	89.9(1)	C2–N2–Co1	110.4(2)
N1–Co1–N6	91.9(1)	Co1–N3–C3	110.2(2)
N2–Co1–N3	92.7(1)	N3–C3–C4	108.4(3)
N2–Co1–N4	91.9(1)	C3–C4–N4	107.5(3)
N2–Co1–N5	91.0(1)	C4–N4–Co1	110.4(2)
N2–Co1–N6	176.6(1)	Co1–N5–O1	121.7(3)
N3–Co1–N4	84.9(1)	Co1–N5–O2	117.3(3)
N3–Co1–N5	175.5(2)	O1–N5–O2	120.9(4)
N3–Co1–N6	87.3(1)	Co1–N6–O3	122.3(3)
N4–Co1–N5	92.5(1)	Co1–N6–O4	118.5(3)
N4–Co1–N6	91.5(1)	O3–N6–O4	119.0(4)
N5–Co1–N6	89.1(1)		

F. Bond Angles for the Anion

AN1–Co2–AN2	178.7(1)	AO5–AN5–AO6	119.9(4)
AN1–Co2–AN3	89.9(2)	AO7–AN7–AO8	120.3(4)

TABLE IV. *(Continued)*

AN1–Co2–AN4	89.2(2)	Co2–AN3–AO1	122.0(3)
AN1–Co2–AN5	89.9(2)	Co2–AN3–AO2	118.9(3)
AN1–Co2–AN6	90.5(2)	Co2–AN4–AO3	121.0(3)
AN2–Co2–AN3	89.4(1)	Co2–AN4–AO4	119.6(4)
AN2–Co2–AN4	89.7(2)	Co2–AN5–AO5	122.1(3)
AN2–Co2–AN5	90.8(2)	Co2–AN5–AO6	118.1(3)
AN2–Co2–AN6	90.6(2)	Co2–AN6–AO7	121.1(3)
AN3–Co2–AN4	90.0(2)	Co2–AN6–AO8	118.6(3)
AN3–Co2–AN5	179.1(2)	AH1–AN1–AH2	108.8
AN4–Co2–AN5	89.1(2)	AH1–AN1–AH3	110.6
AN4–Co2–AN6	179.2(2)	AH2–AN1–AH3	110.3
AN5–Co2–AN6	90.2(1)	AH4–AN2–AH5	108.4
AO1–AN3–AO2	119.1(4)	AH4–AN2–AH6	110.6
AO3–AN4–AO4	119.4(4)	AH5–AN2–AH6	110.3

[a] All C–H and N–H distances and angles were fixed at ideal positions, as described in the section on refinement. [b] Only an overall thermal parameter was refined for the –NH hydrogens, see refinement.

TABLE V. Distances (Å) Between Stereochemically Related Atoms as Calculated by Program BMFIT.

Atom	Distance	Atom	Distance
A. Cation of (V) *vs.* Cation of (II)			
Co	0.006[a]	H1	0.14
N5	0.026[a]	H2	0.08
N6	0.022[a]	H3	0.08
N1	0.07	H4	0.08
N2	0.08	H5	0.30
N3	0.08	H6	0.30
N4	0.06	H7	0.10
C1	0.07	H8	0.08
C2	0.20	H9	0.07
C3	0.20	H10	0.11
C4	0.12	H11	0.30
O1	N.M.[b]	H12	0.28
O2	N.M.[b]	H13	0.16
O3	0.24	H14	0.13
O4	0.31	H15	0.07
		H16	0.16
B. Anion of (V) *vs.* Anion of (III)			
Co2	0.006[a]	AO6	0.107
AN1	0.010[a]	AO7	0.290
AN2	0.107[a]	AO8	0.175
AN3	0.012[a]	AN6	0.055
AN4	0.027[a]	AH1	0.852
AN5	0.024[a]	AH2	0.877
AO1	0.093	AH3	0.861
AO2	0.107	AH4	0.709
AO3	0.213	AH5	0.541
AO4	0.239	AH6	0.739
AO5	0.261		

[a] Atoms used for the least-squares fit. [b] N.M. = no match less than 1.00 Å.

TABLE VI. Selected Torsional Angles (°).

A. Comparison of the Cation of **(V)** with the Cation of **(II)**

Angle	**(V)**	**(II)**[a]
N1–Co1–N5–O1	–14.57	39.93
N1–Co1–N5–O2	163.52	–137.29
N4–Co1–N5–O1	162.14	–141.15
N4–Co1–N5–O2	–19.78	41.63
N1–Co1–N6–O3	–150.57	–165.45
N1–Co1–N6–O4	32.32	15.86
N4–Co1–N6–O3	31.77	16.41
N4–Co1–N6–O4	–145.34	–162.28
N1–C1–C2–N2	46.59	50.21
N3–C3–C4–N4	–46.60	–48.09
N5–Co1–N1–H1	–17.92	–22.05
N5–Co1–N1–H2	–137.32	–141.83
N6–Co1–N1–H1	71.21	66.56
N6–Co1–N1–H2	–48.18	–53.22
N5–Co1–N4–H15	39.12	44.44
N5–Co1–N4–H16	–80.60	–75.39
N6–Co1–N4–H15	–50.08	–44.18
N6–Co1–N4–H16	–169.80	–164.01
Co1–N1–C1–C2	–35.17	–34.57
Co1–N4–C4–C3	35.58	36.95
Co1–N3–C3–C4	32.97	36.85

B. Comparison of the Anion of **(V)** with the Anion of **(III)**

Angle	**(V)**	**(III)**
AO1–AN3–Co2–AN1	–132.78	–136.54
AO1–AN3–Co2–AN2	46.13	43.28
AO2–AN3–Co2–AN1	47.69	41.37
AO2–AN3–Co2–AN2	–133.30	–138.81
AO3–AN4–Co2–AN1	26.68	39.71
AO3–AN4–Co2–AN2	–152.68	–139.39
AO4–AN4–Co2–AN1	–151.28	–140.23
AO4–AN4–Co2–AN2	29.36	40.66
AO5–AN4–Co2–AN1	–0.93	12.50
AO5–AN4–Co2–AN2	–179.83	–167.30
AO6–AN5–Co2–AN1	178.15	–174.80
AO6–AN5–Co2–AN2	–0.76	5.39
AO7–AN6–Co2–N1	–179.24	168.35
AO7–AN6–Co2–N2	0.13	–12.53
AO8–AN6–Co2–N1	0.87	–9.91
AO8–AN6–Co2–N2	–179.75	169.20
AH1–AN1–Co2–AN3	–38.91	–88.97
AH1–AN1–Co2–AN4	–128.94	180.00
AH1–AN1–Co2–AN5	141.96	92.16
AH1–AN1–Co2–AN6	51.74	2.67
AH2–AN1–Co2–AN3	–155.65	151.04
AH2–AN1–Co2–AN4	144.32	60.00
AH2–AN1–Co2–AN5	25.22	–27.83
AH2–AN1–Co2–AN6	–65.00	–117.32
AH3–AN1–Co2–AN3	82.61	31.04
AH3–AN1–Co2–AN4	–7.43	–60.00
AH3–AN1–Co2–AN5	–95.62	–147.83
AH3–AN1–Co2–AN6	173.26	122.67
AH4–AN2–Co2–AN3	–142.09	180.00
AH4–AN2–Co2–AN4	–52.05	–88.97
AH4–AN2–Co2–AN5	37.04	–1.13
AH4–AN2–Co2–AN6	127.27	88.35
AH5–AN2–Co2–AN3	87.03	60.00
AH5–AN2–Co2–AN4	177.07	151.04
AH5–AN2–Co2–AN5	–93.85	–121.13
AH5–AN2–Co2–AN6	–3.62	–31.65
AH6–AN2–Co2–AN3	–17.37	–60.00
AH6–AN2–Co2–AN4	72.67	31.03
AH6–AN2–Co2–AN5	161.75	118.87
AH6–AN2–Co2–AN6	–108.02	–151.65

[a] In the original paper (ref. 2) the labels of O1 and O2 are inverted with respect to the current labeling scheme.

is an important observation since, as pointed out earlier [2], when anions such as NO$_3^-$ which are capable of forming stronger hydrogen bonds with the –NH$_2$ or –NH$_3$ ligands than are the –NO$_2$ oxygens, the compounds do not undergo conglomerate crystallization.

Note that two *cis* –NO$_2$ ligands are nearly perpendicular to the basal plane defined by Co, AN3, AN4, AN5 and AN6, as shown by the torsional angles AO6–AN5–Co2–AN1 = 178.15° and AO7–AN6–Co2–AN1 = –179.24°. At the same time, the other two –NO$_2$ ligands are canted at large angles to this plane (AO1–AN3–Co2–AN1 and AO3–AN4–Co2–AN1 are, respectively, –132.78° and 26.68°) in order to minimize Coulomb repulsion between oxygens. The exact same pattern was found for this anion in the case of **(III)**, as shown by comparison of the torsional angles (Table VI).

Cation Bonds

Comparison of the Co–N(NH$_2$) bonds reveal that Co1–N1 and Co1–N4 are shorter (av. = 1.956 Å) than the Co1–N2 and Co1–N3 pair (av. = 1.985 Å), the former corresponds to nitrogens *cis* to –NO$_2$ ligands while the latter pair are *trans* to them. As mentioned above, the –NO$_2$ oxygens interact with the amino(–NH$_2$) hydrogens. A measure of this interaction is the angle Co1–N–O which should be influenced by the hydrogen bonds such that the stronger the hydrogen bond, the smaller this angle should be:

Co1–N5–O1 = 121.7°   Co1–N5–O2 = 117.3°
Co1–N6–O3 = 122.4°   Co1–N6–O4 = 118.5°

and we note that the hydrogen bonds formed by O2 and O4 are shorter than those formed by the other oxygens. It is also noticeable that the N–O distances are affected by the presence of hydrogen bonds:

N5–O1 = 1.207 Å   N5–O2 = 1.243 Å
N6–O3 = 1.234 Å   N6–O4 = 1.257 Å

i.e., O2 and O4, which form the stronger hydrogen bonds, also have the longer N–O distances. Thus, a completely consistent set of geometrical parameters are found for the cation which point at the impor-

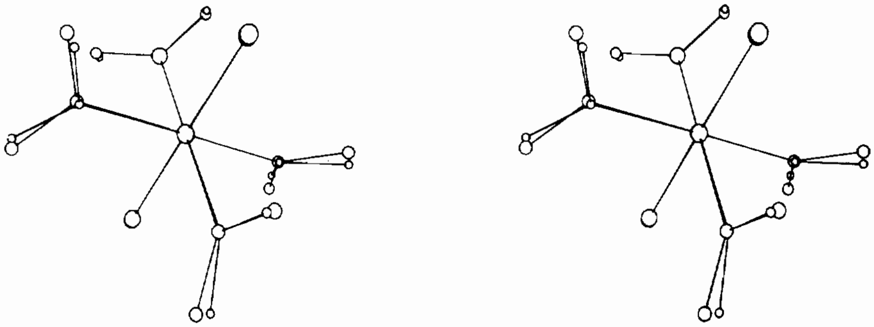

Fig. 5. BMFIT comparison of the anion of ((V); larger circles) with that of (III). Note how remarkably close the torsional angles of the paddle-like (*Clavic*) $-NO_2$ ligands are in this pair. The largest distance between oxygens is *ca.* 0.25 Å (at AO5). For details see Tables V and VI, which list the deviations in Å (Table V) and in degrees (Table VI).

tance of the intramolecular hydrogen bonds within these species.

Anion Bonds

As expected, the two Co2–N(NH_3) bonds are similar and their average value (1.948 Å) is a little shorter than the average of the two mutually *trans* Col–N(NH_2) distance, 1.956 Å, found for the cation, implying that a pair of either $-NH_2$ or $-NH_3$ ligands, located *trans* to one another and *cis* to $-NO_2$ ligands, have approximately the same ligand field strength, inspite the charge difference in the cation and anion under discussion.

As was the case for the cation, the Co2–N–O angles reflect the presence of hydrogen bonds. For example, AO2 forms two hydrogen bonds (*ca.* 2.36 Å) and the Co2–AN3–AO2 angle (118.9°) is smaller than that formed by AO1 (Co2–AN3–AO1 = 122.0°) which forms only one hydrogen bond to AH6 (2.15 Å). Note also that AN5–AO6 is longer (1.242 Å) than AN5–AO5 (1.205 Å), as it should given the above rules. However, for the anion, the quality of the hydrogen positions is a little less secure than in the case of the cation and we will not put so much emphasis on these parameters.

Comparison of Conformations via Torsional Angles

A. Cation of (V) vs. Cation of (II)

Table VI A gives a detailed description of the torsional angles found for these two cations and the stereo BMFIT diagram (Fig. 4) gives a pictorial resume of the comparison. It is clear that the largest deviations are between the $-NO_2$ oxygens which are twisted by *ca.* 15 and 59 deg. This is, no doubt, the result of hydrogen bonding between these cation oxygens with the anion which is impossible in the cation of (**II**) since the compensating anion in that compound is Cl^-. The rest of the atoms of the two cations differ by little, as can be verified by the distances quoted on Table VA.

B. Anion of (V) vs. Anion of (III)

The agreement in conformation between the heavy elements of these two species is quite remarkable since the largest deviation of any atom pair is 0.290 Å (at AO7; see Table V B) and the difference in torsional angle for the two nitro groups in question is *ca.* 13 deg. Note, however, that the hydrogens of each pair of amino ligands are twisted such that they both differ by *ca.* 40 deg. What is interesting is that as one of the $-NH_3$ ligands of these anions is rotated, the other seems to follow it keeping each *trans* pair almost staggered, as is the case in ethane.

Conclusions

As predicted earlier [2], *Clavic* cations such as [*cis*-α-triethylenetetramineCo$(NO_2)_2]^+$ and [*cis*-Co$(en)_2(NO_2)_2]^+$ combine with *Clavic* anions such as [*trans*-Co$(NH_3)_2(NO_2)_4]^-$ to form crystalline conglomerates containing pure optically active cations and anions of a single chirality for each of them, thus behaving as resolving agents for one another just as if we had used tartaric acid to resolve an enantiomeric cation. Furthermore, there is a remarkable similarity in the conformation of this pair of *Clavic* ions as found in this and other lattices, studied here earlier, in which their respective counterions were totally different. These facts point at an unsuspected robustness for the conformations of these species and, again, emphasize the correctness of our earlier conclusions concerning the unusual frequency of spontaneous resolutions in *Clavic* systems.

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