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The Phenomenon of Conglomerate Crystallization. V. *Clavic* Dissymmetry in Coordination Compounds. IV. A Neutron Diffraction Study of K[*trans*-$Co(NH_3)_2(NO_2)_4$]

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Abstract

The structure of K[*trans*-$Co(NH_3)_2(NO_2)_4$] has been determined by neutron diffraction data collected at room temperature (*ca.* 21 °C). The substance crystallizes as a conglomerate of antipodal crystals, many large enough for neutron diffraction work. The space group and cell constants are: $P2_12_12_1$; $a = 11.275(3)$, $b = 12.806(5)$ and $c = 6.696(3)$ Å. The cell volume is 966.82 Å^3 and given the M_r of 316.12 g mol^{-1}, the D(calc; $Z = 4$) is 2.170 g cm^{-3}. The data (1553 unique reflections) were corrected for absorption ($\mu = 79.533$ cm^{-1}) and there was no decay during data collection, as expected from the X-ray study. All heavy atoms were initially placed at the positions found with X-rays, refined isotropically and, after locating the hydrogens in a difference map, all atoms were refined isotropically. Conversion to anisotropic motion was followed by 12 cycles of least-squares fitting (200 variables), at which point the structural refinement converged to its final R and R_w factors of 0.056 and 0.056, respectively. The goodness of fit was 1.133.

The positional parameters of the two studies are in close agreement, as expected. For example, the average value of the Co–$N(NH_3)$ bonds in the X-ray and neutron studies are, respectively, 1.958(3) Å and 1.949(9) Å. The average value of the Co–$N(NO_2)$ distances for the X-ray and neutron studies are 1.956(3) Å and 1.948(9) Å, while the average N–O distances are 1.230(4) and 1.222(6) Å for the former and latter, respectively.

The most important result derived from this study is the accurate location of the hydrogens of the $-NH_3$ ligands which had caused problems in two previous X-ray studies of salts of this anion. In this analysis, we found that $-N1(NH_3)$ is well behaved thermally while $-N2(NH_3)$ is much less so, the reason being that the three hydrogens of the amines attempt to form hydrogen bonds with the adjacent oxygens of the basal plane $-NO_2$ ligands – which is impossible while satisfying all of them equally well. One of the two amino ligands manages better than the other one, as we shall demonstrate below.

Introduction

A short time ago, one of us [1, 2] discovered that a large number of substances, regardless of nature (*i.e.*, organic, inorganic, etc.) appeared to be particularly prone to undergo spontaneous resolution into conglomerates of antipodal crystals. For the concept of conglomerate crystallization, the reader is referred to the book by Jacques, Collet and Wilen [3]; now, we will merely point out that Pasteur's resolution of the antipodes of $Na(NH_4)$ tartrate·$4H_2O$ was the first observation of conglomerate crystallization. Here, we are dealing with an achiral K cation and with an anion which is potentially optically active when hydrogen bonding links the paddle-shaped $-NO_2$ anions into fixed dissymmetric configurations. In earlier studies, these atropisomers were recognized by Bernal [1, 2] as belonging to a new class labelled *clavic* (from the Latin for paddles or tillers) in order to emphasize the source of dissymmetry. This anion, [*trans*-$Co(NH_3)_2(NO_2)_4$]$^-$, has been found to crystallize in a number of salts [1, 2] all of which spontaneously undergo resolution into mechanical mixtures of pure antipodal crystals (conglomerates, in the definition of Jacques, Collet and Wilen [3]). Since the diffraction experiments we engage in require only one crystal, we are able to carry out the conformation and configurational analysis necessary. The Bijvoet test [4] provides the absolute configuration of the anion present in a specific crystal, which can then be correlated to previous studies in which these species were charac-

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terized by structural and optical measurements (see refs. 1 and 2 for details).

Since two previous X-ray studies of this key anion [1, 2] did not produce the desired precision in the geometry of the $-NH_3$ ligands, we resorted to a neutron diffraction investigation of the problem. The room temperature study is presented below.

TABLE I. Summary of Data Collection and Processing Parameters

Space group	$P2_12_12_1$
Cell constants	$a = 11.275(3)$ Å $b = 12.806(5)$ Å $c = 6.696(3)$ Å
Cell volume	$V = 966.76$ Å^3
Asymmetric unit formula	$KCoN_6H_6O_8$
Asymmetric unit weight	316.178 g mol^{-1}
Density (calc; $Z = 4$)	2.170 g cm^{-3}
Radiation wavelength	$\lambda = 1.058(3)$ Å
Absorption coefficient	$\mu = 79.533$ cm^{-1}
Data collection range	$4° \leqslant 2\theta \leqslant 55°$
Scan width	1.95° (fixed)
Total data collected	3106
Data with $I = 3\sigma(I)$[a]	2573
Data used in refinement	1553
Total variables	200
$R = \Sigma \lvert\lvert F_o\rvert - \lvert F\rvert\rvert / \lvert F_o\rvert$	0.056
$R_w = [\Sigma w^2(\lvert F_o\rvert - \lvert F_c\rvert)^2 / \Sigma w^2 \lvert F_o\rvert^2]^{1/2}$	0.056
Weights	$w = [\sigma^2(F_o) + 0.05 F_o^2]^{-1}$
Goodness of fit	1.133

[a]The difference between total data collected and this number is due to subtraction of standards and those which do not meet the criterion of having $F_0^2 > 3\sigma(F_0^2)$. The difference between this number and the next one is due to the fact that nearly two complete symmetry related sets were collected and averaged.

TABLE II. Positional Parameters and their Estimated Standard Deviations[a]

Atom	x	y	z	B_{A2}
Co	−0.0829(8)	−0.3106(6)	−0.255(1)	1.5(1)
K	−0.3648(5)	0.0236(4)	−0.1873(9)	2.3(1)
O1	−0.2569(4)	−0.3957(4)	−0.0201(8)	3.93(9)
O2	−0.0839(4)	−0.4305(4)	0.0873(7)	3.70(9)
O3	−0.2042(4)	−0.1596(3)	−0.0375(6)	3.28(8)
O4	−0.2502(4)	−0.1582(4)	−0.3444(8)	4.24(9)
O5	0.0469(5)	−0.1550(4)	−0.4484(8)	4.8(1)
O6	−0.0571(6)	−0.2408(5)	−0.6463(7)	5.9(1)
O7	0.0103(4)	−0.4806(3)	−0.4604(7)	3.90(9)
O8	0.1197(4)	−0.4332(4)	−0.2236(8)	4.11(9)
N1	0.0308(2)	−0.2454(2)	−0.0761(3)	2.28(4)
N2	−0.1989(2)	−0.3742(2)	−0.4347(4)	2.80(4)
N3	−0.1493(2)	−0.3890(2)	−0.0359(4)	2.31(4)
N4	−0.1923(2)	−0.1960(2)	−0.2048(4)	2.20(4)
N5	−0.0199(2)	−0.2278(2)	−0.4777(3)	2.55(4)
N6	0.0292(2)	−0.4220(2)	−0.3207(3)	2.07(3)
H1	0.0008(7)	−0.2398(8)	0.063(1)	5.4(2)
H2	0.0507(9)	−0.1752(7)	−0.118(1)	6.3(2)
H3	0.1039(7)	−0.2881(8)	−0.069(2)	6.2(2)
H4	−0.2718(9)	−0.355(1)	−0.414(2)	12.3(3)
H5	−0.199(1)	−0.4458(8)	−0.435(2)	10.3(3)
H6	−0.182(1)	−0.362(1)	−0.559(2)	11.5(3)

[a]Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)$-$[a_2b_{(1,1)} + a_2b_{(2,2)} + c_2b_{(3,3)} + ab(\cos\gamma)b_{(1,2)} + ac(\cos\beta)$-$b_{(1,3)} + bc(\cos\alpha)_{(2,3)}]$.

Data Collection and Refinement

Data were collected at room temperature (*ca.* 21 °C) at the University of Missouri (Columbia) Reactor UMRR under conditions nearly identical with those described in detail elsewhere [5]. The parameters which are specific to this experiment are listed on Table I, which also give a summary of the results of the data processing and refining.

Nearly two complete sets of data were collected which were symmetry related (*i.e.*, *h*, *k*, *l*, and *h*, *k*, *l̄*). Details of data processing have been described elsewhere [5]. After standards and symmetry related data were averaged and those having F_0^2 less than $3\sigma(F_0^2)$ removed, a set of 1553 data remained which were used in the structural analysis. The coordinates of the non-hydrogen atoms derived from the X-ray [1] study were used to refine the scale factor and the individual, isotropic thermal parameters. A difference map revealed the positions of the missing hydrogens; those associated with N1 were nearly at the same location as those on the X-ray study while those associated with N2 were found poorly placed by the study [1]. Refinement of the entire set of atoms revealed the reason for the problem with H4, H5 and H6 – they appear to be disordered over two sets of positions which are staggered with respect to one another and their thermal motion was approximately twice as large as that of H1, H2 and H3 (see Table II, bottom of column 5). At this stage, we cannot tell whether this behavior is due to a dynamic phenomenon (extensive freedom of librational motion about the Co–N2 axis) or to static disorder over two well-defined potential minima.

The results of refining the set of 22 atoms anisotropically are given in Tables II–IV which describe the positional, and thermal parameters as well as the bond lengths and angles. As expected from the behavior of the refinement described above, the appearance of the molecule and its packing diagram are sufficiently close to the description given by the X-ray report that we do not repeat the latter. Figure 1 is a view of the anion generated with the coordinates obtained from the present study and it differs from that derived from X-ray data only in the region of the hydrogens (H4, H5, H6) asso-

TABLE III. Bond Distances (Å)[a]

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Co	N1	1.941(9)	N3	O2	1.228(5)	N1	H1	0.993(11)
Co	N2	1.957(9)	N4	O3	1.221(5)	N1	H2	0.969(11)
Co	N3	1.927(9)	N4	O4	1.239(6)	N1	H3	0.990(12)
Co	N4	1.946(9)	N5	O5	1.214(6)	N2	H4	0.87(2)
Co	N5	1.964(9)	N5	O6	1.216(6)	N2	H5	0.917(15)
Co	N6	1.956(9)	N6	O7	1.218(5)	N2	H6	0.87(2)
N3	O1	1.221(5)	N6	O8	1.219(5)			
H1	O6	2.054(11)	H3	O8	2.132(11)	H5	O7	2.41(2)
H2	O5	2.226(12)	H4	O5	2.245(15)	H6	O6	2.17(2)
H3	O3	2.376(11)	H5	O1	2.167(13)			

[a]Numbers in parentheses are estimated standard deviations in the least significant digits.

TABLE IV. Bond Angles (°)[a]

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
N1	Co	N2	179.1(5)	O1	N3	O2	120.6(4)	Co	N2	H5	114.8(8)
N1	Co	N3	90.7(4)	Co	N4	O3	121.0(4)	Co	N2	H6	111.6(9)
N1	Co	N4	89.3(4)	Co	N4	O4	120.0(4)	H4	N2	H5	106(2)
N1	Co	N5	89.9(4)	O3	N4	O4	119.0(4)	H4	N2	H6	108(2)
N1	Co	N6	91.5(4)	Co	N5	O5	121.0(4)	H5	N2	H6	100(2)
N2	Co	N3	89.5(4)	Co	N5	O6	120.5(4)	O7	H5	N2	100(1)
N2	Co	N4	89.8(4)	O5	N5	O6	117.9(4)	O6	H6	N2	122(1)
N2	Co	N5	89.9(4)	Co	N6	O7	120.7(4)				
N2	Co	N6	89.3(4)	Co	N6	O8	120.4(4)				
N3	Co	N4	90.9(4)	O7	N6	O8	118.9(4)				
N3	Co	N5	178.1(5)	Co	N1	H1	112.6(6)				
N3	Co	N6	92.5(4)	Co	N1	H2	111.9(6)				
N4	Co	N5	87.3(4)	Co	N1	H3	109.9(6)				
N4	Co	N6	176.5(5)	H1	N1	H2	107(1)				
N5	Co	N6	89.3(4)	H1	N1	H3	106(1)				
Co	N3	O1	119.2(4)	H2	N1	H3	109(1)				
Co	N3	O2	120.2(4)	Co	N2	H4	114.5(8)				
O6	H1	N1	175(1)	O8	H3	N1	121.9(7)				
O5	H2	N1	113.1(8)	O5	H4	N2	144(1)				
O3	H3	O8	79.9(4)	O1	H5	O7	91.8(7)				
O3	H3	N1	158.1(8)	O1	H5	N2	160(1)				

[a]Numbers in parentheses are estimated standard deviations in the least significant digits.

ciated with the partially disordered –N2(NH_3). Much more interesting are the two contour maps (Figs. 2 and 3) which display the hydrogens of the two –NH_3 ligands. The sections shown were defined by the planes containing the three hydrogens of the amino group in question. Note that (Fig. 2) H1, H2 and H3 appear as well-defined maxima and trigonally positioned about N1 whereas the other three hydrogens (Fig. 3) are not only much more diffuse but one can make a case for multiple maxima which, in the figure, are labelled as H4···H9. For obvious reasons, the X-ray study could not have revealed the details of the staggered arrangement of two possible potential minima for this –NH_3 ligand. However, something of the sort was suspected by the poor refinement of these hydrogens when compared with those of N1.

Discussion

Looking at Fig. 1, one is struck by the fact that the planes of –NO_2 groups defined by N5–O5–O6 and N6–O7–O8 are nearly orthogonal to the basal plane defined by N3···N6 whereas the other two –NO_2 ligands make an angle of *ca.* 45° to this plane. This latter arrangement is shown in Fig. 1 by N4–O3–O4 which is almost bisecting the angle defined

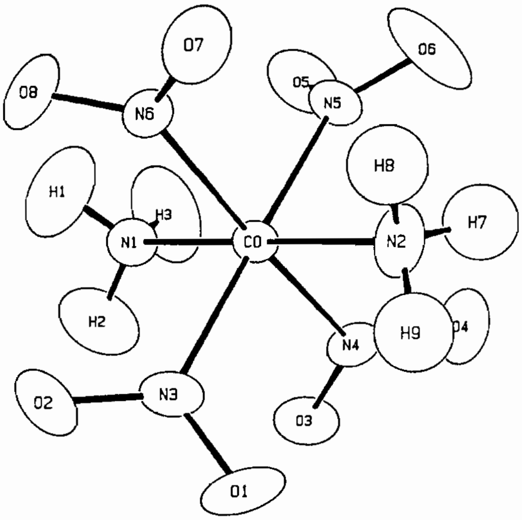

Fig. 1. A view of the molecule showing the numbering system employed in the X-ray and the neutron diffraction studies.

by N1–Co–N5. At the same time, H2 and H3 are so oriented as to approach O5 and O8, respectively, as closely as possible (the distances are 2.226 and 2.132 Å). The shortest hydrogen contact between H1 and an oxygen (O6 at $x, y, 1 + z$) is an intermolecular interaction (2.054 Å). Therefore, this amino group has three weak but well-defined hydrogen bonds, one for each of its hydrogens; two intramolecular and one intermolecular (strong NH•••O bonds are in the range of *ca.* 1.86 Å; see ref. 5). Given the trigonal symmetry of an $-NH_3$ ligand, it is impossible for two of its hydrogens to point to oxygens oriented as O5 and O8 are and avoid the fact that the third hydrogen has no chance for an intramolecular hydrogen bond to $-NO_2$ ligands in the square basal plane. After all, $-NO_2$ ligands bear a partial negative charge and their oxygens cannot bend in the direction of the third amino hydrogen without repelling each other. Thus, once one of the $-NH_3$ and two of the $-NO_2$ ligands are placed in the favorable positions occupied by N1–H1–H2–H3, N5–O5–O6 and N6–O7–O8, the other two $-NO_2$ ligands have to acquire a relatively fixed conformation. This conclusion is strengthened by the fact that in two salts with totally different charge compensating cations [1, 2] this anion has nearly identical conformations (maximum distance between any two atoms, as calculated by BMFIT (see ref. 2 for details) is 0.23 Å, and most are *ca.* 0.1 Å, or less).

We come now to the disorder of N2–H4–H5–H6: the strongest intermolecular hydrogen contact for this ligand is between H5 and O1 (2.167 Å); however, H4 and O5 form a nearly equally strong bond (2.245 Å). Finally H5 is close to O7 (2.41 Å). If we allow an anticlockwise rotation of the amino ligand (see Fig. 1) then H6 can form a stronger bond with O1, H5 with O7 and H4 with O4. This is the

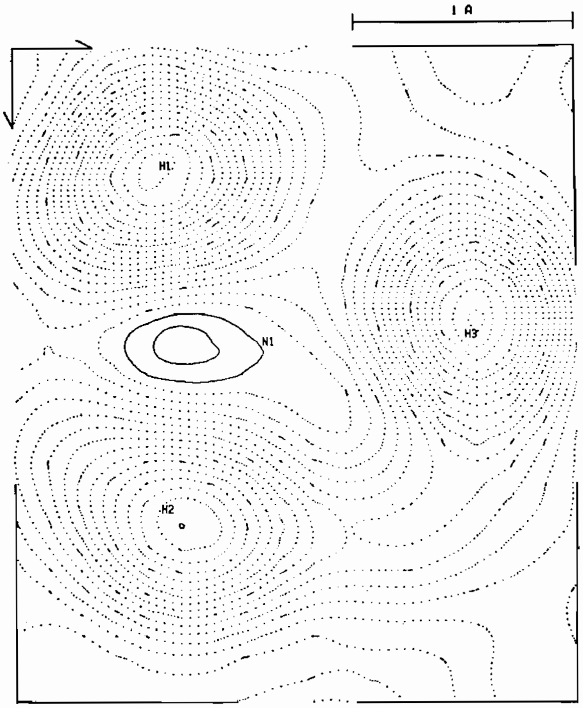

Fig. 2. Contour of neutron diffraction amplitudes in the region of N1H1H2H3 ligand. Note the clearly defined maxima for the three hydrogens indicative of relatively small amplitudes of librational motion about the Co–N1 axis.

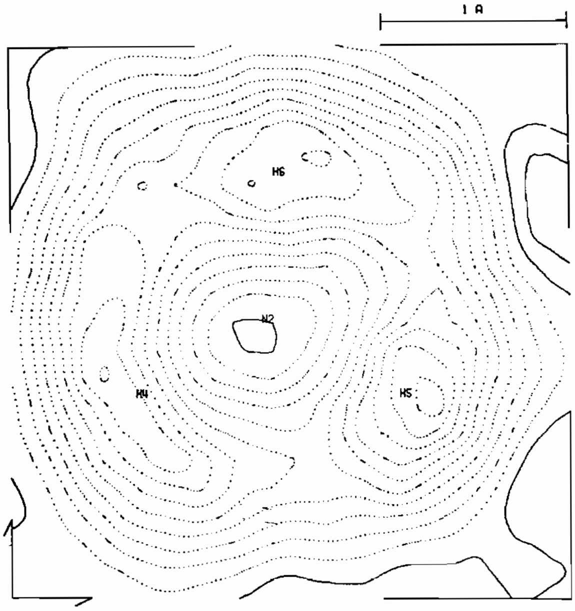

Fig. 3. Contour of neutron diffraction amplitudes in the region of N2H4H5H6. Note the large amplitude of librational motion about the Co–N2 axis and the fact that there are more than three maxima in the region of the hydrogen atoms. For details, see 'Discussion'. H7, H8 and H9 are located between H4, H5 and H6, respectively.

origin of the second potential well for this amino ligand, shown in Fig. 3 as H7, H8 and H9. Again, a similar stereochemical configuration was found for the anion ligands of [*cis*-Co(en)$_2$(NO$_2$)$_2$][*trans*-Co(NH$_3$)$_2$(NO$_2$)$_4$] (ref. 2) a salt which provides a totally different kind of crystal packing environment and symmetry of intermolecular hydrogen-bonded contacts, thereby eliminating packing forces as the dominant source of conformation for the [*trans*-Co(NH$_3$)$_2$(NO$_2$)$_4$] anion.

Conclusions

We have provided a rationale for the conformational behavior of the –NH$_3$ ligands of the [*trans*-Co(NH$_3$)$_2$(NO$_2$)$_4$] anion by revealing their behavior through neutron diffraction and by comparison with its behavior in another, very different, salt. In both, the anion exists in a common conformation despite environmental changes introduced by the nature of the two charge compensating cations used; thus, intramolecular hydrogen bonds render the species chiral in the solid state by fixing the *clavic*–NO$_2$ ligands in a dyssymmetric arrangement.

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