Inorganica Chimica Acta, *121* (1986) 1–4

The Phenomenon of Conglomerate Crystallization.
VIII. Spontaneous Resolution in Coordination Compounds.
VI. The Chiral Behaviour of [*trans*-(*P*, or *M*)-$\mathrm{Co(NH_3)_2(NO_2)_4}]^-$ Anions, Dissymmetric by Virtue of their Propeller Conformation

IVAN BERNAL
Chemistry Department, University of Houston, Houston, Tex. 77004, U.S.A.

(Received March 4, 1986)

Abstract

Octahedral coordination compounds chiral by virtue of having fixed propeller conformations are, apparently, quite rare. Despite the fluxionality of the anion [*trans*-(*P*, or *M*)-$\mathrm{Co(NH_3)_2(NO_2)_4}]^-$, it is possible to establish its chiroptical properties in the solid. Our studies of its salts suggest that, conformationally, it is relatively impervious to the nature of the compensating cation and to variations in packing forces. Consequently, a useful method of determining the chiral symbol of this anion is proposed based on that of stereochemically rigid cations with which it forms diastereoisomeric salts.

In the case of solutions of the ions [*cis*-$\mathrm{Co(en)_2(NO_2)_2}]^+$ and [*trans*-$\mathrm{Co(NH_3)_2(NO_2)_4}]^-$, the crystals obtained from a conglomerate are expected to contain $\Lambda(\delta\lambda)$-$(-)_{589}$-[*cis*-$\mathrm{Co(en)_2(NO_2)_2}$][*trans*-(*P*)-$\mathrm{Co(NH_3)_2(NO_2)_4}$] and $\Lambda(\lambda\delta)$-$(+)_{589}$-[*cis*-$\mathrm{Co(en)_2(NO_2)_2}$][*trans*-(*M*)-$\mathrm{Co(NH_3)_2(NO_2)_4}$].

Introduction

In previous communications [1–3], the crystallization behaviour of the anion [*trans*-$\mathrm{Co(NH_3)_2(NO_2)_4}]^-$ was described for three salts:

	Space group
K[*trans*-$\mathrm{Co(NH_3)_2(NO_2)_4}$] (1) [1, 3]	$P2_12_12_1$
[*cis*-$\mathrm{Co(en)_2(NO_2)_2}$][*trans*-$\mathrm{Co(NH_3)_2(NO_2)_4}$] (**II**) [2]	$P2_1$
[*cis*-α-$\mathrm{Co(trien)(NO_2)_2}$][*trans*-$\mathrm{Co(NH_3)_2(NO_2)_4}$] (**III**) [1]	$P2_12_12_1$

Detailed structures of **I** and **II** have been described [1–3]. The space group of **III** was unambiguously determined [1]; unfortunately, given the number of atoms in the asymmetric unit, the available crystals were too small [1] to allow data collection for a meaningful, three-dimensional structural analysis. The structure of **I** was determined by both, X-ray [1], and neutron [3] diffraction methods in order to more precisely describe the orientation of the hydrogen atoms of the axial $-\mathrm{NH_3}$ ligands since they seem to play a vital role in the mechanism leading to the pronounced tendency for conglomerate resolution [1–3] exhibited by these species. After all, conglomerate crystallization is a phenomenon documented to be relatively rare in occurrence [4].

We knew that diastereoisomer formation was not the key to the high incidence of conglomerate crystallization since the cation of **I** (potassium) is achiral. The ammonium salt is isostructural with **I**. Therefore, hoping to find a link between properties of the anion and conglomerate crystallization, its geometrical characteristics in the above salts were compared and a remarkable consistency noted and commented on [1–3]; however, the potential this ion has for existence as a dissymmetric righthanded or lefthanded propeller was not discussed then.

Recently, we realized the conglomerate crystallization of this anion provides an opportunity to document another apparently rare [5] phenomenon; namely, the isolation, in optically active form, of an octahedral coordination species with a 'fixed propeller conformation'. As Utsuno [5], pointed out in 1982, there is a dearth of information about the properties of species chiral by virtue of having such a conformational property, partly because they are stereochemically non-rigid. In fact, he was able to find only two examples [6–8] recorded prior to his resolution and isolation of [$(+)_{589}$-[*trans*-dichlorotetrapyridineCo(III)]][(*R*, *R*)-dibenzoyltartrateH], a species containing a fluxional [5] cation like ours.

In what follows, we summarize our results and suggest a method of characterizing the absolute configuration of stereochemically non-rigid, fixed propeller ions such as Utsuno's [5] and ours.

Discussion

The X-ray studies of crystals of **II** [2] produced a geometric description of the anion which was nearly identical with that found in the potassium salt **I**

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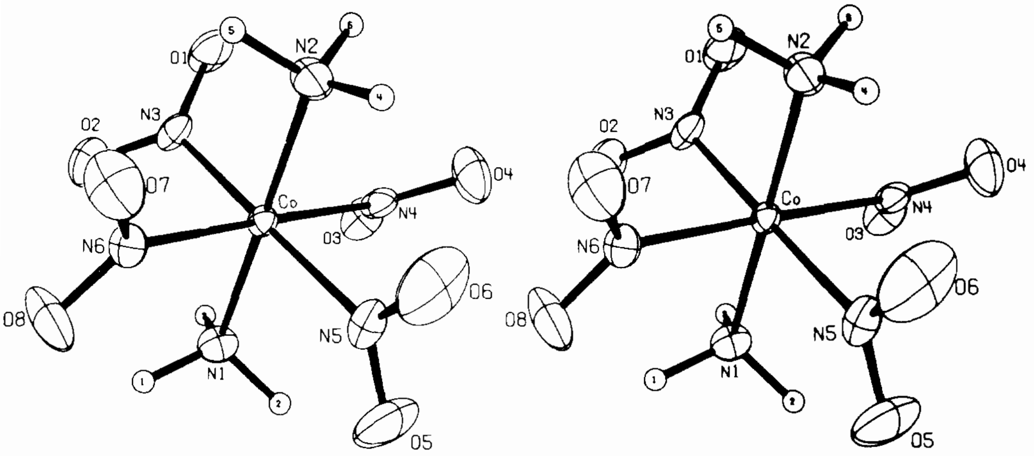

Fig. 1. A stereoview of the anion $[trans\text{-}Co(NH_3)_2(NO_2)_4]^-$ showing the atomic labelling system used in Table I.

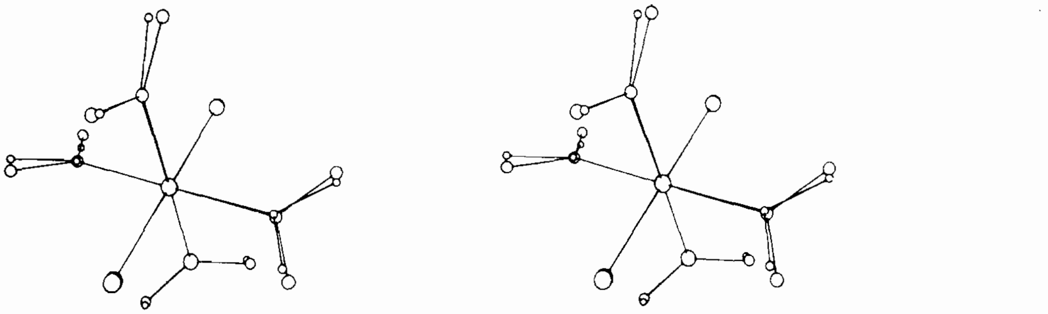

Fig. 2. BMFIT [9] comparison of the anion of **I** with that of **II**. Note how remarkably close the 'flexible, singly bonded' $-NO_2$ ligands match stereochemically. The largest deviation between oxygens in these two anions is *ca.* 0.25 Å. The larger circles belong to the anion as described by the structural study of **I**. The orientation of the axes is identical with that in Fig. 1; hydrogens of $-NH_3$ omitted. For details see refs. 1–3.

[1, 3], showing that its gross stereochemistry is largely independent of the choice of compensating cation and of the nature of the crystal lattice forces. This last fact is emphasized by the observation that **I** [1] and **II** [2] crystallize in different space groups and, as expected, the nearest neighbors of the anion differ. Thus, the packing forces must differ in magnitude and in the direction they act upon the 'flexible, singly bonded' $-NH_3$ and $-NO_2$ ligands. Nonetheless, we found that in both salts $Co(NO_2)$ fragments are fixed in approximately constant, dissymmetric arrangements by anchoring the *clavic* [1–3] $-NO_2$ ligands to the adjacent $-NH_3$ ligands through hydrogen bonds. The reader is referred to the original papers [1–3] for details of the structural analyses; for convenience of discussion, the relevant results can be summarized as follows:

(a) If one uses the bond lengths and angles measured for this anion [1], and assumes the four $-NO_2$ ligands could lie flat in the equatorial plane of $[trans\text{-}Co(NH_3)_2(NO_2)_4]^-$ the interligand O....O distances would be approximately 2.1 Å*, which is about 1 Å less than known values of van der Waals' contacts between oxygens of polyoxo anions (*ca.* 3.2 Å) [9]. Consequently, this anion belongs in the category of the sterically hindered, 'fixed propeller' systems described by Utsuno [5].

(b) The stereochemistry of the $[trans\text{-}Co(NH_3)_2(NO_2)_4]^-$ anions can be summarized by Figs. 1 and 2 and Table I. Figure 1 shows the overall geometry of the anion as found in **I** [1]. Figure 2 shows a BMFIT [9]** stereoplot of the superposition of the anion, as found in **I** and in **II**. The table gives the torsional angles measured by $N2-Co-N_x-O_y$.

(c) Since salts **I** → **III** crystallize as conglomerates, anions with a geometry enantiomorphic to that

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*Estimated using Co–N = 1.95 Å, N–O = 1.23 Å and <O–N–O = 119.3°. Reference 10 gives the van der Waals distance of the CO_3^- anion, in calcite, as 3.17 Å.

**This program does a least-squares fit of the two molecular fragments such that the distances between pre-specified groups of atoms are minimized.

TABLE I. Torsional angles (°)[a]

	I	II
N2–Co–N3–O1	43.28	46.13
N2–Co–N4–O4	40.66	29.36
N2–Co–N5–O6	5.39	−0.76
N2–Co–N6–O7	12.53	0.13

[a] Note these torsional angles indicate the planes of two $-NO_2$ ligands lie close to the equatorial plane (average deviation for the planes of N5 and N6 of **I** and **II** is 4.3°) while the planes of two of them (N3 and N4) lie, on the average (for **I** and **II**), 40° above a base defined by N3, N4, N5 and N6. Two are canted such that one of their oxygens forms as strong an intramolecular hydrogen bond as possible [1–3] with the hydrogens of the $-NH_3$ ligands.

described for a given sample are found in crystals antipodal to those accidentally selected for crystallographic studies. However, for a given set of crystallization conditions, once an enantiomorph of a rigid, chiral cation is selected, the absolute geometry of the anion is fixed.

Chirality Assignment for the [trans-Co(NH$_3$)$_2$(NO$_2$)$_4$]$^-$ Anion

The absolute stereochemistry of salts **I** → **III** can be determined [1–3] either by the Bijvoet test or least-squares refinement. Either test can fix the absolute configuration of a chiral species present in the crystal selected; however, no chiroptical symbol was assigned to this anion [1–3] since it has been traditional to view it, and other non-rigid species like it, from a solution standpoint; *i.e.*, 'the substance is achiral on the average'.

While true that many of these substances are stereochemically non-rigid in fluid media, it is expected that brief though their lifetimes may be for specific, dissymmetric, conformations not all of them are beyond current fast spectroscopic methods. Thus, looking forward to such future measurements, it is worth examining potential candidates for such studies, determining their absolute stereochemistry in solids and assigning chiroptical symbols to them even if, momentarily, these are only valid in rigid media. With that approach in mind, we note that:

(1) When the cation used is $\Lambda(\delta\lambda)$-$(-)_{589}$-[*cis*-(Co(en)$_2$(NO$_2$)$_2$]$^+$, the absolute configuration of the [*trans*-Co(NH$_3$)$_2$(NO$_2$)$_4$]$^-$ compensating anion is that described by the torsional angles in Table I. For a given set of crystallization conditions, this cation–anion pair is expected to always form this, preferred, diastereoisomeric salt; its mirror image will be found in antipodal crystals always present in a conglomerate mixture.

(2) It is irrelevant which $-NH_3$ group is used as a reference axial ligand since, if (as above) the torsional angle N2–Co–N$_x$–O$_y$ is clockwise with value $+\theta°$, that for N1–Co–N$_x$–O$_y$ will also be clockwise with value $+(180 - \theta)°$. Thus, the propeller conformation of the anion would have *P* chirality. Therefore, in our sample crystal of **II** the full chiral symbol for the molecule is $\Lambda(\delta\lambda)$-$(-)_{589}$-[*cis*-Co(en)$_2$(NO$_2$)$_2$][*trans*-(*P*)-Co(NH$_3$)$_2$(NO$_2$)$_4$].

(3) If physical measurements on a crystal for which the chirality of the anion is known are desirable, one needs only dissolve a portion of a large crystal (ref. 2 describes the growth of crystals as large as 1 cm in length and 0.4 cm in diameter) and measure the CD spectrum of the rigid cation. This fixes the chiroptical properties of the anion present in that crystal. The remaining portion of the crystal can then be used for the other measurements. Alternatively, the CD spectrum can be checked at the end of the physical measurements by dissolving the entire crystal specimen.

Conclusions

(a) We have demonstrated that the [*trans*-Co(NH$_3$)$_2$(NO$_2$)$_4$]$^-$ anion is a genuine example of the apparently rare [5] class of dissymmetric, octahedral coordination compounds in which the source of dissymmetry is due, exclusively, to having a propeller conformation. This is the octahedral coordination compound's analogue of classical axial dissymmetry present in substances such as hindered biphenyls.

(b) The conformation of the [*trans*-Co(NH$_3$)$_2$(NO$_2$)$_4$]$^-$ anion is relatively constant for salts we studied before [1–3] even though the compensating cations are quite different and the space groups they crystallize in belong to different crystal systems.

(c) Despite the problem of fluxionality in solution, it is possible to establish the absolute conformation and configuration of cations and anions, such as [*trans*-(*P*)-Co(NH$_3$)$_2$(NO$_2$)$_4$]$^-$. When they are crystallized in diastereoisomeric salts containing a rigid counterion whose absolute configuration is known, a solution CD suffices to establish the absolute stereochemistry of both ions present in that crystal. For the particular case of conglomerates crystals of **II**, $\Lambda(\delta\lambda)$-$(-)_{589}$-[*cis*-Co(en)$_2$(NO$_2$)$_2$][*trans*-(*P*)-Co(NH$_3$)$_2$(NO$_2$)$_4$] and $\Lambda(\lambda\delta)$-$(+)_{589}$-[*cis*-Co(en)$_2$(NO$_2$)$_2$][*trans*-(*M*)-Co(NH$_3$)$_2$(NO$_2$)$_4$] will be the two diastereoisomeric pairs expected.

Acknowledgements

We thank the Robert A. Welch Foundation for support of this study through Grant E-594. The National Science Foundation generously provided funds for the X-ray diffraction facilities used.

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