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The Phenomenon of Conglomerate Crystallization. XIII. Spontaneous Resolution in Coordination Compounds.
X. The Effect of Intramolecular Hydrogen Bonding on Ring Conformations of Polyamine Ligands

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Sometime ago, we reported [1] that [*cis*-Co(en)$_2$(NO$_2$)$_2$]Cl (hereafter, **I**) crystallizes as a conglomerate and attributed the phenomenon to the formation of relatively strong hydrogen bonds between the $-NO_2$ oxygens and the hydrogens of the $-NH_2$ of the ethylenediamine rings. We have since noted that, as a result of such hydrogen bonding, the en rings about the Co ion of **I** and related species do not have the lowest energy conformation. In Table I, we summarize the structural data available for [*cis*-Co(en)$_2$(NO$_2$)$_2$]$^+$ cations as well as cases of [*cis*-Co(en)$_2$(NO$_2$)$_{2-x}$(SO$_3$)$_x$] and related species which display the structural feature mentioned above.

Note that in every case the torsional angle(s) of the one or more (*i.e.* **IV**) ethylenediamines has the wrong (higher energy) conformation, given the configuration about the metal ion. This is probably due to the possibility of enhancing the O...H–N interactions upon inversion of the en ring torsional angle(s). Interestingly, such a change in ring conformation has never been observed in the [*cis*-α-Co(trien)(NO$_2$)] or [*cis*-β-Co(trien)(NO$_2$)] series of compounds, probably as a result of the increased barrier to inverting a terminal ring in the trien compounds. This observation places a definite bracket to the magnitude of the strength of the ON–O...H–N hydrogen bonds in the species under discussion.

We also note that the entire [*cis*-Co(en)(SO$_3$)] portion of **VI** and **VIII** are identical, as shown in Figs. 1 and 2. The major difference between the two compounds is that in **VIII** the $-N_3$ cannot form hydrogen bonds with the $-NH_2$ hydrogens, whereas the oxygens of the $-NO_2$ in **VI** do so [1].

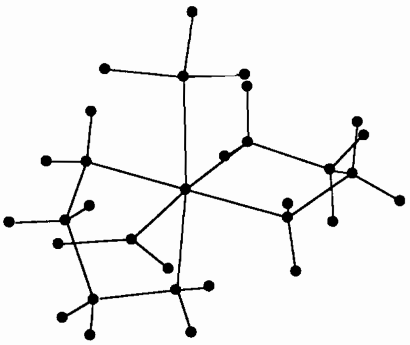

Fig. 1. A view of the [*cis*-Co(en)$_2$(SO$_3$)(NO$_2$)] molecule showing the Δ configuration of the two en rings about the Co ion, the λ conformation on the lower lefthand side of the figure and the δ conformation on the right.

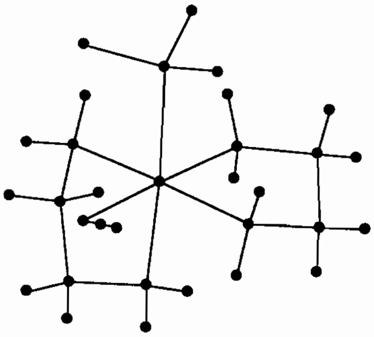

Fig. 2. A view of the [*cis*-Co(en)$_2$(SO$_3$)(N$_3$)] molecule showing the Δ configuration of the two en rings about the Co ion and the λ conformation of the two N–C–C–N fragments.

A few comments are in order:

(1) The phenomenon is independent of space group inasmuch as the cation [*cis*-Co(en)$_2$(NO$_2$)$_2$]$^+$

TABLE I. Structural Data

Compounds	Symbol	Space group	Reference
[*cis*-Co(en)$_2$(NO$_2$)$_2$]Cl (I)	Λ(δλ)	$P2_1$	1
[*cis*-Co(en)$_2$(NO$_2$)$_2$](NO$_3$) (II)	Λ(δλ)	$P2_1/n$	2
[*cis*-Co(en)$_2$(NO$_2$)$_2$][Co(NH$_3$)$_2$(NO$_2$)$_4$] (III)	Λ(δλ)	$P2_12_12_1$	3
[*cis*-Co(en)$_2$(NO$_2$)$_2$][*cis*-Co(mal)$_2$(en)] (IV)	Δ(δδ)	$P2_1$	4
[*cis*-Co(en)$_2$(NO$_2$)$_2$][Co(NH$_3$)$_2$(NO$_2$)$_2$ox] (V)	Δ(λδ)	$P2_12_12_1$	5
[*cis*-Co(en)$_2$(NO$_2$)(SO$_3$)] (VI)	Λ(δλ)	$P2_1/c$	6
[*cis*-Co(en)$_2$(NO$_2$)(S-SO$_3$)] (VII)	Λ(δλ)	$P2_1$	7
[*cis*-Co(en)$_2$(N$_3$)(SO$_3$)] (VIII)	Λ(δδ)	$P2_1/n$	6

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is present in a variety of salts (see above) which crystallize in different space groups. Therefore, since the charge compensating anion and the packing forces are different, it seems reasonable to assign an intramolecular origin to the phenomenon.

(2) The torsional phenomenon described has nothing to do with chirality and/or with conglomerate crystallization since **I** crystallizes as a conglomerate and **II** as a racemate – yet, both display oppositely conformated en rings. The only common feature they share is the composition of the cation.

(3) Comparison of the behaviour of the en rings in **VI** is very instructive (see Figs. 1 and 2). The ring forming a hydrogen bond with the $-NO_2$ ligand is normal, as is always the case with one of the en rings of the above compounds. Those bearing either a second $-NO_2$, and $-SO_3$ or an $-SSO_3$ have an abnormally conformated ring. We believe this comes about because, once the $-NO_2$ ligand finds the best torsional angle to maximize hydrogen bonding, the geometry of the second group ($-NO_2$, and $-SO_3$ or an $-SSO_3$) is fixed by the need to preserve sensible intramolecular O...O contacts, which must be [8] about 3.2 Å. The second ligand ($-NO_2$, and $-SO_3$ or an $-SSO_3$) cannot form equally meaningful hydrogen bonds with the $-NH_2$ hydrogens of the second en ligand unless the latter is twisted into the conformation opposite the lowest energy one. For instance in Fig. 1, the normal en ring is that bonded to the $-NO_2$ oxygen (O...H = 2.20 Å), the abnormal one is that bonded to the $-SO_3$ (O...H = 2.17 Å). Thus, it appears that in competition for the amino hydrogens, $-NO_2$ has precedence over $-SO_3$ in selecting a hydrogen bonding partner.

(4) Comparison of **VI** with **VIII** is also instructive (see Figs. 1 and 2). In the latter species, both rings are normal, which means that there is no need to twist the ring forming a hydrogen bond with the $-SO_3$. The azide anion does not form hydrogen bonds with the en rings and, thus, the $-SO_3$ oxygens have their choice of en partner, without increasing the energy of the molecule by unnecessarily inverting the torsional angle of the N–C–C–N fragment.

(5) The behaviour of **VII** is also of interest. The molecule is $\Lambda(\delta\lambda)$ and the ring with the incorrect conformation is that forming a hydrogen bond with an oxygen of the $-SSO_3$ ligand (*i.e.* the $-NO_2$ has first choice as in **VI**). The observations made in (3) to (5) suggest that, in competition with other oxo ligands capable of forming hydrogen bonds with terminal $-NH_2$ hydrogens, the $-NO_2$ ligand always has first choice.

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