The Phenomenon of Conglomerate Crystallization. III [1]. Spontaneous Resolution in Coordination Compounds. III [1]. The Structures and Absolute Configuration of $\Lambda(\delta\lambda\delta)[(-)_{589}$-*cis*-$\alpha$-(triethylenetetraamine)$Co(NO_2)_2]Cl\cdot H_2O$ (I), $\Lambda(\delta\lambda\delta)[(-)_{589}$-*cis*-*bis*-ethylenediamine $Co(NO)_2)_2]Cl$ (II) and of $K[$*trans*-$Co(NH_3)_2(NO_2)_4]$ (III)— Stereoisomers Displaying *CLAVIC* Dissymmetry

IVAN BERNAL

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

Received April 9, 1984

Abstract

The crystal structures and absolute configurations of three *cis*-dinitro derivatives of Co(III) have been determined by single crystal X-ray diffraction data collected with a computer-controlled diffractometer. (I): $\Lambda(\delta\lambda\delta)[(-)_{589}$-*cis*-$\alpha$-(triethylenetetraamine)$Co(NO_2)_2]Cl\cdot H_2O$ crystallizes in the orthorhombic space group $P2_12_12_1$ with lattice constants: a = 8.070(1) Å, b = 12.506(3) and c = 13.741(1); V = 1386.67 Å^3. The calculated density (for z = 4 molecules/unit cell) is 1.679 g cm^{-3}. A total of 3467 data were collected of which 2082 were considered observed ($I > 3\sigma(I)$) and refinement converged to R = 0.0436 and R_w = 0.0456. Compound (II): $\Lambda(\delta\lambda)[(-)_{589}$ - *cis* - *bis* - ethylenediamine$Co(NO)_2]Cl$ crystallizes in the monoclinic system, space group $P2_1$. Cell constants are: a = 6.555(2) Å, b = 11.115(3), c = 8.254(2) and β = 106.59(2)°; volume = 576.34 Å^3 and density(calc) = 1.755 g cm^{-3}, for z = 2 molecules/unit cell. For compound (II), a total of 2866 data were collected of which 2423, having $I > 3\sigma(I)$, were considered observed. Using this set, the structure was refined to agreement indices of R = 0.0480 and R_w = 0.0466. Finally, (III): $K[$*trans*-$Co(NH_3)_2(NO_2)_4]$ crystallizes in the orthorhombic space group $P2_12_12_1$ with lattice constants of a = 11.275(3) Å, b = 12.806(5) and c = 6.696(3); cell volume = 316.118 Å^3 and the calculated density, for z = 4, is 2.170 g cm^{-3}. The data set collected for (III) consisted of 2749 measurements of which, by the same criterion as the other two, 2109 were found to be observed. Refinement of the atomic coordinates and thermal parameters converged, in this case, to R = 0.0367 and R_w = 0.0355. The absolute configurations of these substances, in the solid state, were established via the Bijvoet test and, for (I) and (II), correlations were made with other determinations.

All three substances are self-resolving stereoisomers forming crystalline conglomerates when crystallized from water at room temperature. Thus, each crystal consists of a single, pure, stereoisomer even if *other* crystals from the same batch contain the opposite enantiomer. While it is true that (I) and (II) are chiral due to the presence of non-planar five-membered ring ligands which lend chirality to those molecules by their very nature, this is not the case with (III). Instead, all three substances share an interesting source of asymmetry, not heretofore noticed, due to the arrangement of the pair of planar *cis*-dinitro ligands, which are held in position by hydrogen bonds with the adjacent $-NH_2$ or $-NH_3$ ligands present in all three compounds. Due to steric hindrance effects, these pairs of adjacent *cis*-dinitro ligands must, co-operatively, point in the same direction while each makes one short O···H and one long O···H bond, respectively, to a pair of hydrogens on the adjacent (*trans*) amino ligands. It is this co-operative steric and hydrogen bonded arrangement which gives rise to a form of atropisomerism which is referred to in the text as *CLAVIC* (from the Latin word for tillers or paddles) dissymetry.

Introduction

In their book 'Enantiomers, Racemates and Resolutions', Jacques, Collet and Wilen [2] define a *conglomerate* as a "mechanical mixture of crystals of pure enantiomers" and go on to say that "the separation of two enantiomers forming a conglomerate does not require any optically auxiliary agent since resolution occurred spontaneously during crystallization..." and that "taking advantage of this spontaneous resolution is actually the most economical route to the pure enantiomers when amounts ranging from a few grams to tons of material are needed." Therefore, it is desirable to reach a better understanding of the nature of the phenomenon of spontaneous resolution and of the factors leading to such resolutions. This paper is a contribution to such an understanding.

The project was initiated when the compound *cis*-α-(triethylenetetraamine)$Co(NO_2)_2]Cl\cdot H_2O$ was prepared to be used as a reagent for further synthetic

0020-1693/85/$3.30

work. Knowing from the work of Sargeson, Buckingham, Freeman, ... and their colleagues [3] and the review of Saito [4] that the structure of this substance was not known either as a racemate or as a pure enantiomer, work on it was begun. The structure and the absolute configuration were determined, at which point the question arose: what makes this substance undergo self-resolution? The question was made even more intriguing by the fact that the *cis*-dichloro derivative, from which the dinitro compound was made (see Experimental) crystallizes in two forms, both of whose structures have been determined [5], and both of which are racemic (space groups $P\bar{1}$ and $P2_1/n$). Furthermore, all derivatives of Co(III) and triethylenetetraamine whose structures have been published thus far [3, 4], are either racemic or, if not, were resolved *via* a chiral agent in the coordination sphere or outside. In other words, they appear not to form conglomerates.

Given the fact that a variety of other Co(III) derivatives of triethylenetetraamine are known in both the α and the β form [3–5] and that they do not to spontaneously resolve into antipodes or conglomerates, it is clear that the asymmetric backbone provided by neither the α-conformated nor the β-conformated Co(triethylenetetramine) moiety is sufficient to induce such self-resolution. The following questions are then pertinent: (a) is the presence of an additional pair of *cis* -NO_2 ligands necessary? (b) do they have to be associated with the Co(triethylenetetraamine) moiety, or is it possible to replace triethylenetetraamine and still obtain self-resolution? For example, is it possible to put two ethylenediamine ligands instead of one triethylenetetraamine? (c) is it possible to put other ligands, altogether different from *bi*- or poly-dentate ligands, plus a pair of *cis* -NO_2's and still obtain self-resolution? If so, which combination will suffice? And also, what is the connection between the successful sets of ligands?

Experimental

Synthesis and Crystal Growth for (I)

cis-α-[Co(trien)Cl_2]Cl was made by the procedure given by Basolo [6]. This substance was dissolved in a small volume of warm (*ca.* 60 °C) water and reacted with a small excess of $NaNO_2$ for about one hour. The solution was allowed to cool to room temperature and placed in a refrigerator. Crystals suitable for X-ray work were obtained in a day or so. One of these was selected for the structural determination.

Synthesis and Crystal Growth for (II)

Racemic *cis*-[Co(en)$_2$$Cl_2$]Cl was prepared by the method of Bailar [7]. 30 g of this substance were placed in a beaker with an excess of $NaNO_2$ over the (1:2) theoretical molar ratio and dissolved in the minimum amount of warm (60 °C) water. The solution was kept at *ca.* 60 °C for 1 hr and cooled in a refrigerator. The crystals of (I) were filtered, redissolved in distilled water and allowed to slowly crystallize at room temperature over a period of many days. Some of the larger ones were filtered, ground to spheres and used for X-ray data collection. Every one of these columnar crystals is chiral (see X-ray data collection and Bijvoet test) and some grow as large as 1.5 cm in length and girth of 0.70 × 0.50 cm. One weighed 0.637 g, which, given a density of *ca.* 1.755 g cm^{-3}, had a volume of 0.36 cc.

Synthesis and Crystal Growth for (III)

The compound was synthesized according to the procedure given by Schlessinger [8]. Crystals were grown over a period of over one year by the slow evaporation of 300 cc of a saturated aqueous solution set aside in an enclosed shelf and at a temperature *ca.* 21–22 °C. Crystals were prismatic for the first few months and some were very large, before they began to develop side growths, and easily reached 1 cm along the longest dimension. Spheres were ground from large crystals using an ENRAF-NONIUS spherizer and one, *ca.* 0.4 mm in diameter, was used for data collection.

X-Ray Data Collection and Processing

Data were collected by identical procedures using a computer-controlled ENRAF-NONIUS CAD-4 diffractometer. The details of data collection and processing are summarized in Tables I, II and III. When refinement was finished, a set of F_c tables was calculated for the (+++) coordinates and for the inverted (− − −) coordinates. A suitable set of reflections was selected and the Bijvoet test [9] performed. The coordinates of (I) were, accidentally, the correct ones for the enantiomer present in the crystal chosen. Those of (II) and (III) needed to be inverted, which was done and the structures refined enough more cycles of full-matrix least-squares that the refinements converged. The final coordinates for (I), (II) and (III) in their correct absolute configurations are given in Tables IV, V and VI. Tables of bond lengths and angles (VII, VIII and IX) are provided.

All crystallographic calculations were carried out with SHELX-76 [10], all the molecular plots were generated with Johnson's ORTEP [11] and the molecular overlap stereo plots with BMFIT [12].

The crystal structure and absolute configuration of $(-)_{589}$-*cis*-α-dinitro-(L-*3,8*-dimethyltriethylenetetraamine)Co(III) perchlorate (IV) were determined by Saito *et al.* [13] and we determined the structure and absolute configuration of $(-)_{589}$-*cis*-α-dinitro-(L-*2,7*-dimethyltriethylenetetraamine)Co(III) perchlorate [14]. In both cases, the absolute configuration of the $(-)_{589}$ rotating stereoisomer was established to be

TABLE I. Summary of Data Collection and Processing Parameters for (I)

Space group	$P2_12_12_1$
Cell constants	$a = 8.070(1)$ Å $b = 12.506(3)$ $c = 13.741(1)$
Cell volume	$V = 1386.67$ Å^3
Crystal aligned approximately along	[0,1,0] direction
Molecular formula	$[C_6H_{18}N_6O_4ClCo]\cdot H_2O$
Molecular weight	350.6497 g mol^{-1}
Density (calc.; $z = 4$)	1.679 g cm^{-3}
Radiation	MoKα ($\lambda = 0.71073$ Å)
Absorption coefficient	15.49 cm^{-1}
Data collection range	$4.0° \leqslant 2\theta \leqslant 70.0°$
Scan width	$\Delta\theta = (0.95 + 0.35 \tan\theta)$
Maximum scan time	120 sec
Scan speed range	0.72 to 6.70 deg min^{-1}
Total data collected	3467
Data with $I > 3\sigma(I)$	2082*
Total variables	173
$R = \Sigma\lvert F_o - F_c\rvert/\Sigma F_o$	0.0436
$R_w = [w^2(F_o - F_c)^2/\Sigma w^2F_o{}^2]^{1/2}$	0.0456
Weights	$w = [0.3823/(\sigma(F_o))^2 + 0.000345F_o{}^2)]^{-2}$
Goodness of fit	0.980

*The difference between this figure and that above is due to the removal of the standard reflections, some redundant data and those which do not meet the 3σ criterion.

TABLE II. Summary of Data Collection and Processing Parameters for (II).

Space group	$P2_1$
Cell constants	$a = 6.555(2)$ Å $b = 11.115(3)$ $c = 8.254(2)$ $\beta = 106.59(2)°$
Crystal aligned near	$[0,\bar{1},1]$
Cell volume	$V = 576.34$ Å^3
Molecular formula	$C_4H_{14}N_6O_4ClCo$
Molecular weight	304.580 g mol^{-1}
Density (calc.; $z = 2$)	1.755 g cm^{-3}
Radiation	MoKα ($\lambda = 0.71069$ Å)
Absorption coefficient	16.09 cm^{-1}
Data collection range	$4.0° \leqslant 2\theta \leqslant 60.0°$
Scan width	$\Delta\theta = (1.0 + 0.35 \tan\theta)$
Maximum scan time	240 sec
Scan speed range	0.39 to 5.03 deg min^{-1}
Total data collected	2866
Data with $I > 3\sigma(I)$	2423*
Total variables	120
$R = \Sigma\lvert F_o - F_c\rvert/\Sigma F_o$	0.0480
$R_w = [w^2(F_o - F_c)^2/\Sigma w^2F_o{}^2]^{1/2}$	0.0466
Weights	$w = [\sigma(F_o)]^{-2}$
Goodness of fit	3.63

*This is the total left after removing standard reflections which are included in the total (2866) quoted above.

TABLE III. Summary of Data Collection and Processing Parameters for (III).

Space group	$P2_12_12_1$
Cell constants	$a = 11.275(3)$ Å $b = 12.806(5)$ $c = 6.696(3)$
Cell volume	$V = 966.762$ Å^3
Molecular formula	$K[Co(NH_3)_2(NO_2)_4]$
Molecular weight	316.118 g mol^{-1}
Density (calc.; $z = 4$)	2.170 g cm^{-3}
Absorption coefficient	33.37 cm^{-1}
Data collection range (2θ)	4° to 70°
Scan width	$\Delta\theta = (1.0 + 0.35 \tan\theta)$
Maximum scan time	180 sec
Scan speed range	0.57 to 6.70 deg min^{-1}
Total data collected	2749 data points*
Data with $I > 3\sigma(I)$	2109
Total variables	146†
$R = \Sigma\lvert F_o - F_c\rvert/\Sigma F_o$	0.0367
$R_w = [\sigma w^2(F_o - F_c)^2/\Sigma w^2F_o{}^2]^{1/2}$	0.0355
Weights	$w = [\sigma(F_o)]^{-2}$

*A total of 2749 data points were collected of which 190 were standards, 350 were unobserved on the criterion that their I was less than 3 standard deviations. Standard deviations were estimated on the basis of Poisson statistics.

†The 16 heavy atoms were refined anisotropically; the positions of the 6 hydrogens recalculated after each cycle of L.S. and a single, isotropic, thermal parameter was refined for the set of 6 independent hydrogen atoms of the two amine ligands.

$\Lambda(\delta\lambda\delta)$. Since the particular crystal of (I) chosen for X-ray data collection was found to be $\Lambda(\delta\lambda\delta)$ configurated, the $(-)_{589}$ symbol used in the title was assigned to it. The same was done with compound (II) since it is expected that the cation present in solutions of (II) will be configurated $\Lambda(\delta\delta)$ (*i.e.*, the most energetically preferred [15] conformation of the *en* rings for the Λ configuration). Saito [16] has already discussed the absolute configuration for such a cation in a salt bearing a different anion (*i.e.*, the resolving agent $(-)_{589}$-*cis*-dinitrooxalatodiaminecobaltate(III)). Also, we note that $(+)_{589}$-*cis*-dinitrobis-[$(-)_{589}$-1,2-propylenediamine] cobalt(III) chloride has the inverse $[\Delta(\lambda\lambda)]$ absolute configuration for the cobalt cation [17]. Consequently, compound (II) was assigned the label $(-)_{589}$.

Finally, we come to compound (III): this substance is optically active in the solid state but the onset of free rotation for the $-NO_2$ and $-NH_3$ is immediate upon dissolving the substance. Consequently, the anion of (III) is achiral in water and its CD spectrum cannot be checked. It is hoped this situation can be remedied in the future when CD spectra of orthorhombic crystals are measured.

TABLE IV. Atomic Coordinates and Thermal Parameters (×1000; Co & Cl × 10 000).

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*11	*U*22	*U*33	*U*12	*U*13	*U*23
Co	0.24075(6)	0.75185(6)	0.21012(4)	229(2)	234(2)	198(2)	11(3)	-15(2)	31(3)
Cl	0.1988(3)	0.5734(1)	0.6002(1)	838(13)	487(9)	570(10)	58(9)	45(10)	51(8)
O1	0.0291(7)	0.6750(4)	0.0703(4)	73(3)	62(3)	70(3)	0(3)	-42(3)	-16(3)
O2	-0.0585(5)	0.8183(4)	0.1335(3)	33(2)	86(4)	52(3)	16(2)	-8(2)	10(3)
O3	0.2936(7)	0.9138(3)	0.0785(3)	98(4)	47(3)	46(2)	12(3)	24(3)	23(2)
O4	0.2910(6)	0.9687(3)	0.2251(3)	59(3)	29(2)	58(3)	-7(2)	-4(2)	0(2)
OW	0.1918(7)	0.0907(3)	0.9654(3)	82(3)	43(2)	46(2)	4(3)	13(2)	12(2)
N1	0.1041(6)	0.8049(3)	0.3170(3)	34(2)	28(2)	28(2)	4(2)	4(2)	2(2)
N2	0.1963(5)	0.6098(3)	0.2649(3)	28(2)	23(2)	26(2)	-3(2)	1(2)	0(2)
N3	0.4459(4)	0.7530(4)	0.2871(3)	26(1)	27(2)	29(2)	4(2)	-6(1)	1(2)
N4	0.3786(6)	0.6938(4)	0.1046(3)	38(2)	36(2)	22(2)	2(2)	2(2)	-2(2)
N5	0.0463(5)	0.7469(5)	0.1289(3)	35(2)	46(2)	29(2)	1(3)	-7(2)	8(3)
N6	0.2812(5)	0.8947(3)	0.1664(3)	27(2)	33(2)	38(2)	7(2)	3(2)	10(2)
C1	0.0369(7)	0.7182(5)	0.3782(4)	42(3)	38(3)	33(3)	3(2)	12(2)	9(2)
C2	0.0361(7)	0.6158(5)	0.3195(4)	36(3)	38(3)	40(3)	-5(3)	8(2)	9(3)
C3	0.3395(7)	0.5741(4)	0.3266(4)	34(3)	26(2)	37(3)	4(2)	1(2)	7(2)
C4	0.4330(7)	0.6700(5)	0.3651(4)	41(3)	38(3)	32(3)	5(2)	-15(2)	1(2)
C5	0.5898(6)	0.7400(6)	0.2197(4)	30(2)	53(4)	47(3)	-3(3)	1(2)	6(4)
C6	0.5463(8)	0.6704(6)	0.1365(5)	51(4)	53(4)	48(3)	14(3)	11(3)	-1(3)
H1	0.0095(6)	0.8465(3)	0.2891(3)	54(4)					
H2	0.1732(6)	0.8529(3)	0.3587(3)	54(4)					
H3	0.1080(7)	0.7090(5)	0.4372(4)	54(4)					
H4	-0.0787(7)	0.7362(5)	0.3986(4)	54(4)					
H5	-0.0589(7)	0.6163(5)	0.2728(4)	54(4)					
H6	0.0257(7)	0.5529(5)	0.3640(4)	54(4)					
H7	0.1348(5)	0.5546(3)	0.2127(3)	54(4)					
H8	0.2968(7)	0.5310(4)	0.3825(4)	54(4)					
H9	0.4159(7)	0.5292(4)	0.2865(4)	54(4)					
H10	0.5467(7)	0.6475(5)	0.3855(4)	54(4)					
H11	0.3727(7)	0.7004(5)	0.4223(4)	54(4)					
H12	0.4639(4)	0.8225(4)	0.3215(3)	54(4)					
H13	0.6843(6)	0.7073(6)	0.2562(4)	54(4)					
H14	0.6234(6)	0.8118(6)	0.1946(4)	54(4)					
H15	0.5536(8)	0.5938(6)	0.1570(5)	54(4)					
H16	0.6253(8)	0.6837(6)	0.0817(5)	54(4)					
H17	0.3835(6)	0.7474(4)	0.0506(3)	54(4)					
H18	0.3266(6)	0.6263(4)	0.0801(3)	54(4)					

TABLE V. Atomic Coordinates and Thermal Parameters (×1000, Co × 10 000).

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*11	*U*22	*U*33	*U*12	*U*13	*U*23
Co	-0.31047(7)	-0.32831(0)	-0.30694(6)	129(2)	156(2)	191(2)	-4(2)	35(1)	-37(3)
Cl	0.0282(3)	-0.1873(2)	-0.6976(2)	86(1)	47(1)	54(1)	-11(1)	20(1)	1(1)
O1	-0.6835(5)	-0.3184(7)	-0.2208(4)	26(1)	67(3)	59(2)	-8(2)	22(1)	-12(3)
O2	-0.4693(7)	-0.1824(4)	-0.0998(6)	49(2)	59(3)	85(3)	-2(2)	33(2)	-42(3)
O3	-0.4087(7)	-0.1163(3)	-0.4898(6)	45(2)	23(2)	70(3)	5(2)	-5(2)	9(2)
O4	-0.1082(8)	-0.1102(4)	-0.3080(6)	59(3)	46(2)	54(3)	-33(2)	-11(2)	10(2)
N5	-0.5121(6)	-0.2677(4)	-0.1974(5)	20(2)	33(2)	31(2)	5(1)	9(1)	-5(2)
N6	-0.2718(6)	-0.1663(3)	-0.3752(5)	26(2)	19(2)	33(2)	-1(1)	7(1)	-3(1)
N1	-0.0758(5)	-0.3068(3)	-0.0996(4)	26(1)					
H1	-0.1177(5)	-0.2458(3)	-0.0259(4)	34(14)					
H2	0.0532(5)	-0.2780(3)	-0.1298(4)	33(14)					
N2	-0.3403(5)	-0.4891(3)	-0.2189(4)	22(1)					
H7	-0.2719(5)	-0.5501(3)	-0.2757(4)	16(11)					
H8	-0.4945(5)	-0.5090(3)	-0.2403(4)	36(15)					

(continued on facing page)

TABLE V *(continued)*

Atom	*x/a*	*y/b*	*z/c*	*U*11	*U*22	*U*33	*U*12	*U*13	*U*23
N3	−0.1169(6)	−0.3863(3)	−0.4348(4)	22(1)					
H9	−0.0153(6)	−0.4463(3)	−0.3652(4)	56(18)					
H10	−0.0354(6)	−0.3168(3)	−0.4620(4)	20(10)					
N4	−0.5388(5)	−0.3549(3)	−0.5163(4)	20(1)					
H15	−0.6352(5)	−0.2833(3)	−0.5395(4)	41(16)					
H16	−0.6219(5)	−0.4280(3)	−0.5034(4)	35(14)					
C1	−0.0266(8)	−0.4224(5)	−0.0070(6)	30(1)					
H3	0.0736(8)	−0.4707(5)	−0.0523(6)	12(10)					
H4	0.0396(8)	−0.4069(5)	0.1162(6)	44(16)					
C2	−0.2327(7)	−0.4891(4)	−0.0329(6)	29(1)					
H5	−0.3240(7)	−0.4476(4)	0.0284(6)	27(13)					
H6	−0.2045(7)	−0.5735(4)	0.0095(6)	104(31)					
C3	−0.2433(7)	−0.4438(4)	−0.5938(5)	26(1)					
H11	−0.1615(7)	−0.4424(4)	−0.6792(5)	19(12)					
H12	−0.2765(7)	−0.5289(4)	−0.5714(5)	27(13)					
C4	−0.4479(7)	−0.3729(4)	−0.6589(6)	28(1)					
H13	−0.5504(7)	−0.4186(4)	−0.7513(6)	65(20)					
H14	−0.4172(7)	−0.2932(4)	−0.7031(6)	42(17)					

TABLE VI. Atomic Coordinates and Thermal Parameters (×1000, K & Co × 10 000).

Atom	*x/a*	*y/b*	*z/c*	*U*11	*U*22	*U*33	*U*12	*U*13	*U*23
K	−0.3645(1)	0.0235(1)	−0.1866(2)	469(6)	339(5)	407(6)	19(5)	21(5)	−26(5)
Co	−0.0835(0)	−0.3102(0)	−0.2572(1)	193(2)	145(2)	196(2)	6(2)	8(3)	−12(3)
N1	0.0306(3)	−0.2464(3)	−0.0762(5)	33(2)	29(2)	25(2)	−4(2)	−1(2)	−6(2)
N2	−0.1982(3)	−0.3744(3)	−0.4334(6)	32(2)	25(2)	41(2)	4(2)	−10(2)	−9(2)
N3	−0.1497(4)	−0.3899(3)	−0.0371(6)	36(2)	14(2)	36(2)	0(2)	8(2)	0(2)
N4	−0.1923(3)	−0.1966(2)	−0.2062(5)	25(2)	15(1)	45(2)	−3(1)	4(2)	−2(2)
N5	−0.0191(4)	−0.2277(3)	−0.4774(6)	41(2)	26(2)	29(2)	3(2)	5(2)	7(2)
N6	0.0289(3)	−0.4220(3)	−0.3205(5)	29(2)	23(2)	23(2)	4(1)	2(2)	−1(1)
O1	−0.2577(3)	−0.3971(3)	−0.0217(6)	37(2)	36(2)	71(3)	−5(2)	20(2)	14(2)
O2	−0.0838(3)	−0.4300(2)	0.0881(5)	61(2)	38(2)	34(2)	0(2)	−1(2)	14(2)
O3	−0.2045(3)	−0.1590(2)	−0.0361(5)	51(2)	29(2)	39(2)	2(2)	17(2)	−6(2)
O4	−0.2514(3)	−0.1601(3)	−0.3469(6)	56(2)	36(2)	57(2)	21(2)	−20(2)	−8(2)
O5	0.0473(3)	−0.1560(3)	−0.4461(6)	73(3)	61(2)	53(3)	−33(2)	10(2)	17(2)
O6	−0.0547(4)	−0.2415(3)	−0.6465(5)	130(4)	72(3)	20(2)	−30(3)	−3(2)	7(2)
O7	0.0100(3)	−0.4814(3)	−0.4605(5)	55(2)	50(2)	46(2)	16(2)	−7(2)	−23(2)
O8	0.1204(3)	−0.4327(3)	−0.2254(6)	38(2)	55(2)	67(3)	25(2)	−21(2)	−22(2)
H1	0.1014(3)	−0.2893(3)	−0.0698(5)	127(12)					
H2	−0.0041(3)	−0.2408(3)	0.0560(5)	127(12)					
H3	0.0511(3)	−0.1774(3)	−0.1246(5)	127(12)					
H4	−0.1872(3)	−0.3483(3)	−0.5682(6)	127(12)					
H5	−0.2776(3)	−0.3575(3)	−0.3879(6)	127(12)					
H6	−0.1876(3)	−0.4496(3)	−0.4323(6)	127(12)					

Discussion

Description of the Molecules

Molecule (**I**) has the *cis*-α-conformation and absolute configuration Λ(δλδ), as shown in Fig. 1. The geometrical characteristics of the Co(trien) moiety are similar to those obtained by Dwyer and Maxwell [3f] for the racemic *cis*-α-aminechlorotriethylenetetraamine)Co(III) nitrate, by Bernal [5] for racemic [*cis*-α-dichlorotriethylenetetraamine chloride]·nH$_2$O ($n = 2$ and 3) and also with the results obtained by Saito *et al.* [13] for the resolved compound (**IV**). Exactly how well (**I**) and (**IV**) agree in their geometrical characteristics is shown in Fig. 4, which depicts, in stereo, attempts to overlap those molecules using program BMFIT [12]. It is clear that the agreement is remarkable since the largest deviation for the non-hydrogen atoms is either 0.395 or

TABLE VII. Distances (Å) and Angles (°) and Estimated Standard Deviations for Compound (I).

A. *Distances*			
Co–N6	1.914(4)	N1–C1	1.476(7)
Co–N5	1.926(4)	C1–C2	1.513(8)
Co–N1	1.953(4)	C2–N2	1.497(7)
Co–N2	1.963(4)	N2–C3	1.501(7)
Co–N3	1.965(3)	C3–C4	1.513(8)
Co–N4	1.967(4)	C4–N3	1.496(7)
		N3–C5	1.494(6)
N5–O1	1.216(8)	C5–C6	1.479(9)
N5–O2	1.231(7)	C6–N4	1.453(8)
N6–O3	1.235(6)		
N6–O4	1.230(6)		
B. *Intramolecular Hydrogen Bonds*			
O1–H18	2.480(7)	O2–H1	2.113(7)
O1–H17	3.012(7)	O3–H17	2.237(7)
C. *Intermolecular Hydrogen Bonds*			
Cl–H18	2.522(5)	O2–H17	2.701(6)
Cl–H1	3.099(5)	O4–H1	2.876(6)
O1–H17	2.255(7)	OW–H2	1.958(6)
D. *Water–Oxygen Contacts*			
OW–O3	2.825(6)		
OW–N1	2.929(6)		
E. *Angles*			
N1–Co–N2	85.2(2)	N1–C1–C2	108.6(4)
N1–Co–N3	93.9(2)	Cl–C2–N2	107.8(5)
N1–Co–N4	178.1(2)	C2–N2–C3	113.3(4)
N1–Co–N5	89.2(2)	N2–C3–C4	110.3(4)
N1–Co–N6	90.9(2)	C3–C4–N3	109.5(4)
N2–Co–N3	87.4(2)	C4–N3–C5	115.0(4)
N2–Co–N4	93.0(2)	N3–C5–C6	111.0(5)
N2–Co–N5	92.5(2)	C5–C6–N4	109.6(5)
N2–Co–N6	175.7(2)	C6–N4–Co	112.2(4)
N3–Co–N4	85.6(2)	Co–N5–O1	120.1(4)
N3–Co–N5	176.8(2)	Co–N5–O2	120.4(4)
N3–Co–N6	91.1(2)	Co–N6–O3	120.1(4)
N4–Co–N5	91.2(2)	Co–N6–O4	120.4(3)
N4–Co–N6	91.0(2)	Co–N2–C2	107.7(3)
N5–Co–N6	89.2(2)	Co–N2–C3	110.2(3)
O1–N5–O2	119.5(5)	Co–N3–C4	108.8(3)
O3–N6–O4	119.4(5)	Co–N3–C5	108.7(3)
Co–N1–C1	112.7(3)		

TABLE VIII. Bond Lengths (Å) and Angles (°) for (II) with Estimated Standard Deviations Given in Parentheses.

A. *Bond Lengths*			
Co–N1	1.962(3)	C2–N2	1.495(3)
Co–N2	1.960(3)	N3–C3	1.482(5)
Co–N3	1.976(4)	C3–C4	1.515(6)
Co–N4	1.959(3)	C4–N4	1.477(6)
Co–N5	1.924(4)	N5–O1	1.222(6)
Co–N6	1.925(4)	N5–O2	1.224(5)
N1–C1	1.483(6)	N6–O3	1.235(5)
C1–C2	1.501(7)	N6–O4	1.227(5)
B. *Intramolecular Bonds*			
O1–H8	2.483(8)	O3–H15	2.340(5)
O1–H16	2.761(6)	O4–H2	2.424(5)
O1–H15	2.766(5)	O4–H1	2.789(6)
O2–H1	2.319(6)		
C. *Intermolecular Bonds*			
Bond	Length	Symmetry Operation*	
Cl–H15	2.463(4)	65501	
Cl–H1	2.684(4)	55401	
O1–H2	2.112(6)	45501	
O3–H16	2.105(5)	45402	
O4–H16	2.843(5)	45402	
D. *Angles*			
N1–Co–N2	85.6(1)	N5–Co–N6	88.6(2)
N1–Co–N3	92.4(1)	Co–N1–C1	110.2(3)
N1–Co–N4	177.8(2)	N1–C1–C2	107.4(4)
N1–Co–N5	91.1(2)	C1–C2–N2	106.7(4)
N1–Co–N6	90.3(2)	C2–N2–Co	108.2(3)
N2–Co–N3	92.8(1)	Co–N3–C3	109.4(3)
N2–Co–N4	93.3(1)	N3–C3–C4	107.7(4)
N2–Co–N5	89.4(2)	C3–C4–N4	107.8(3)
N2–Co–N6	175.5(2)	C4–N4–Co	110.0(3)
N3–Co–N4	85.7(1)	O1–N5–O2	119.3(4)
N3–Co–N5	175.9(2)	O3–N6–O4	117.9(4)
N3–Co–N6	89.4(2)	Co–N5–O1	119.2(4)
N4–Co–N5	90.7(1)	Co–N5–O2	121.4(3)
N4–Co–N6	90.8(1)	Co–N6–O3	121.2(3)
		Co–N6–O4	120.9(3)

*In ORFFE FORMAT (Operations: xyz; $\bar{x}$, $1/2 + y$, $\bar{z}$).

TABLE IX. Distances (Å) and Angles (°) for (III) with Estimated Standard Deviations in Parentheses.

A. *Distances*			
Co–N1	1.947(3)	K–O7	2.807(4)
Co–N2	1.934(4)	K–O2	2.825(4)
Co–N3	1.942(4)	K–O8	2.870(3)
Co–N4	1.933(3)	K–O4	2.881(4)
Co–N5	1.954(4)	K–O6	2.949(4)
Co–N6	1.959(3)	K–O8	2.998(4)
N3–O1	1.225(5)	K–O3	3.016(4)
N3–O2	1.232(4)	K–O5	3.118(4)
N4–O3	1.244(4)	K–O3	3.119(4)
N4–O4	1.246(5)	K–O4	3.153(4)
N5–O5	1.203(5)		
N5–O6	1.214(5)		
N6–O7	1.226(4)		
N6–O8	1.220(4)		
B. *Intramolecular Hydrogen Bonds*			
O1–H6	2.497(5)	O4–H4	2.944(7)
O1–H2	2.508(7)	O5–H2	2.125(5)
O2–H3	2.581(8)	O5–H1	3.162(6)
O2–H1	2.978(7)	O6–H4	2.032(8)

(continued on facing page)

TABLE IX *(continued)*

O3–H3	2.549(7)	O7–H5	2.238(7)
O3–H2	2.981(7)	O7–H4	2.932(7)
O4–H6	2.551(8)	O8–H1	2.063(7)
C. *Intermolecular Hydrogen Bonds*			
O1–H5	2.049(7)	O3–H1	2.293(7)
O1–H4	3.117(5)	O5–H6	2.199(7)
O2–H4	2.711(6)	O5–H4	3.015(7)
O2–H5	2.969(7)	O6–H3	1.964(5)
O2–H6	3.113(8)	O7–H2	2.587(8)
D. *Angles*			
N1–Co–N2	179.1(2)	N3–Co–N5	178.9(2)
N1–Co–N3	90.1(2)	N3–Co–N6	91.6(2)
N1–Co–N4	89.6(2)	N4–Co–N5	87.8(1)
N1–Co–N5	89.9(2)	N4–Co–N6	177.3(1)
N1–Co–N6	90.8(2)	N5–Co–N6	89.5(1)
N2–Co–N3	89.0(2)	O1–N3–O2	120.7(4)
N2–Co–N4	90.2(1)	O3–N4–O4	119.2(3)
N2–Co–N5	91.0(2)	O5–N5–O6	118.6(4)
N2–Co–N6	89.4(1)	O7–N6–O8	118.5(4)

0.449 Å. Since these molecules have an almost exact 2-fold axis of symmetry, they can be fitted in two ways. Table XII gives the details of two such fits between (I) and (IV). Similar comments can be made about (II) and (III) when compared with (I) or related molecules (see Table XII).

The stereochemical information presented in Tables XII and XIII suggest that:

(a) a pair of NH_2 (or NH_3) ligands above and below the plane defined by Co and the two NO_2 nitrogens orients, through hydrogen bonding, the plane of the NO_2 ligands so as to maximize the strength of the O•••H interactions.

In solution, the strength of these hydrogen bonds (certainly 1–2 Kcal/mol, at most) is not enough to prevent free rotation of the -NO_2 ligand plane about the Co–N bond. However, in the solid, they are frozen at the conformations in question.

(b) packing forces have, at best, a secondary role in dictating conformation of the NO_2 ligands. This is strongly implied by the numerical results on Table XII and by the BMFIT drawings such as that in Fig. 4.

(c) the presence of NO_2 ligands has little effect on the $Co(en)_2$ or Co(trien) fragments as shown by the fact that $[cis\text{-}\alpha\text{-}Co(trien)(NO_2)_2]^+$ fragment matches equally well Saito's (IV) cation as well as the cations of two crystalline forms of $[cis\text{-}\alpha\text{-}Co(trien)Cl_2[Cl\cdot nH_2O$ ($n = 2$, monoclinic $P2_1/n$; and $n = 3$, triclinic, P1). The stereochemistry of the two *cis*-dichloro compounds match almost exactly Dwyer and Maxwell's [*cis*-α-aminochloroCo(trien)]Cl, *etc.* These observations can be extended to other related systems using the comparisons afforded by BMFIT. Table XII provides some relevant numbers; others will appear in papers dealing with related molecules [5, 14].

(d) Note in Figs. 1–3 that the plane of the NO_2 ligand is rotated so as to follow the hydrogens on the NH_2 or NH_3 ligands. For example, let us examine the values of the hydrogen bonds on (II): Table VIII (B) shows that O2 and H1 form a short bond (2.32 Å) while O1 and H15 and H16 form nearly equally long (and weaker) bonds of *ca.* 2.76–2.77 Å. Meantime, O3 interacts with H15 (2.34 Å) and O4 interacts with H2 (2.42 Å). That is, as the conformation of the amine ligands of the Co moiety changes with respect to the plane defined by Co, N5 and N6, the oxygens of NO_2 follow the amine hydrogens (whose conformation is fixed by the stereochemistry of the more rigid trien or en ligands) so as to maximize hydrogen bond interactions.

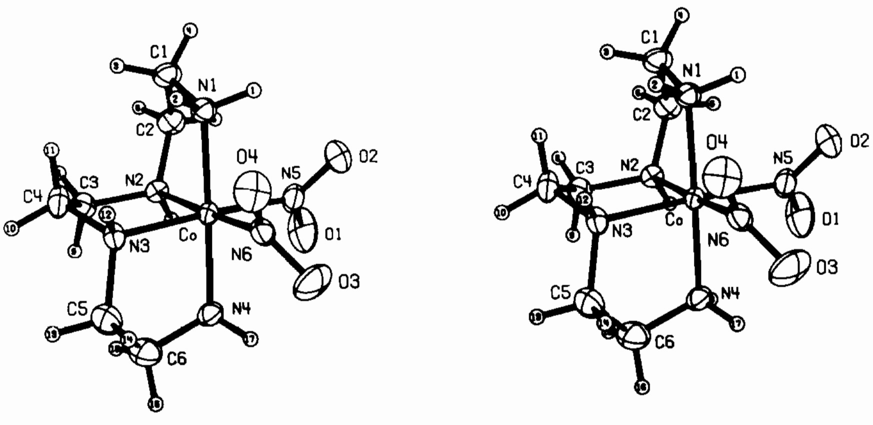


Fig. 1. Stereo view of molecule (I) showing the numbering system used in the crystallographic study. The ellipsoids of thermal motion for the non-hydrogen atoms are 50% probability envelopes. Hydrogen atoms were drawn as spheres of size to be convenient for representational purposes and to avoid unnecessary cluttering of the drawing. These statements are equally true for Figs. 2 and 3.

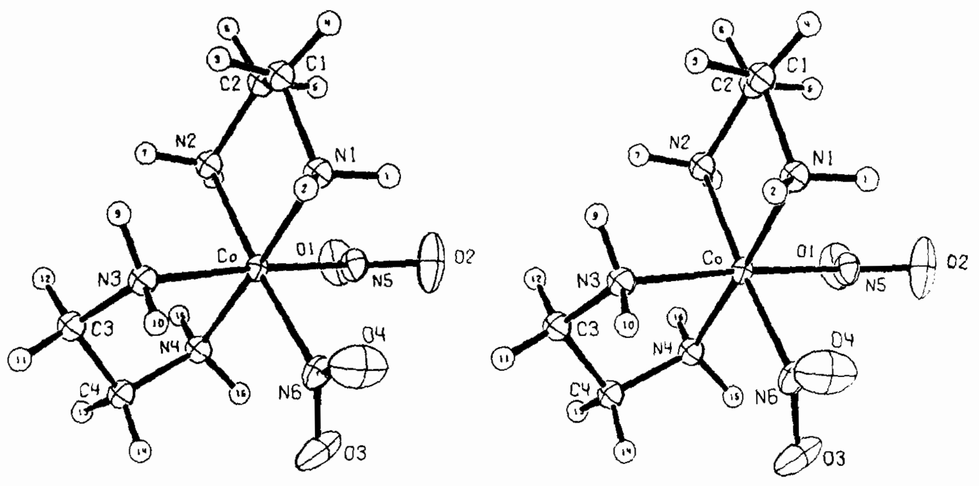


Fig. 2. Stereo view of compound (II).

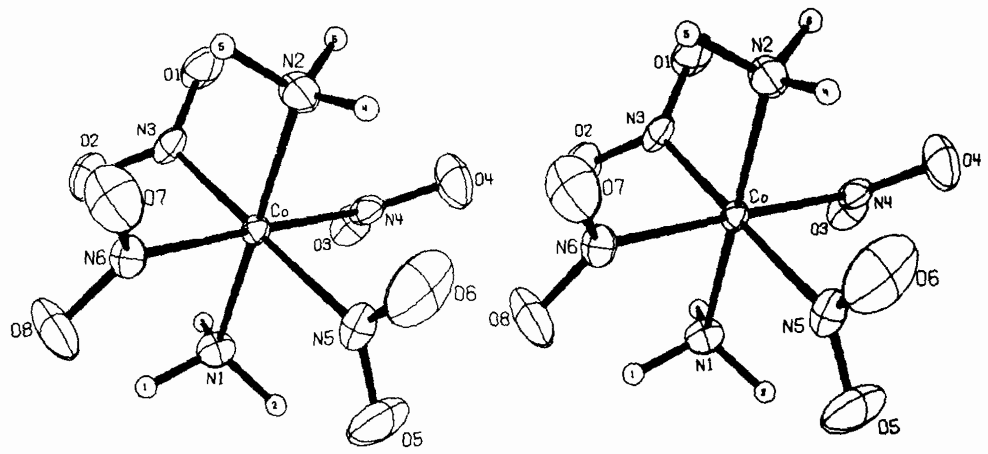


Fig. 3. Stereo view of compound (III).

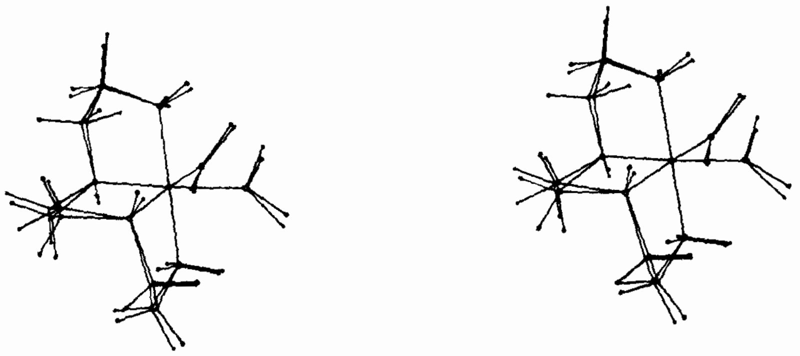


Fig. 4. BMFIT stereo pair comparing the geometrical properties of compound (I) with Saito's [13] *cis*-α-Co(3,8-dimethyltriethylenetetraamine)$(NO_2)_2^+$ (see Discussion).

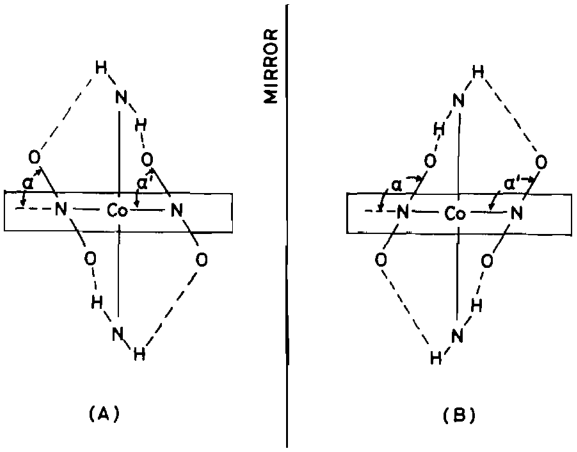
Implications of the Above Results and CLAVIC Dissymetry

Referring to the sketches (A) and (B) in Scheme 1 one notes that the pattern of hydrogen bonds between the *cis*-dinitro oxygens and the hydrogens on either $-NH_2$ or $-NH_3$ ligands can be defined by two angles α and α', which may or may not be the same (in (I) they are 54.92° and 58.31°) but which are either smaller or larger than 90°.

TABLE X. Selected Torsional Angles (°) for (I) and (II).

	(I)	(II)
N1–Co–N5–O1	–143.10	–137.29
N1–Co–N5–O2	39.42	39.93
N4–Co–N5–O1	35.08	41.63
N4–Co–N5–O2	–142.41	–141.15
N1–Co–N6–O3	–144.91	–165.45
N1–Co–N6–O4	33.30	15.86
N4–Co–N6–O3	35.53	16.41
N4–Co–N6–O4	–146.26	–162.28
N1–C1–C2–N2	42.59	50.21
N2–C3–C4–N3	–40.39	–
N3–C5(3)–C6(4)–N4^a	39.31	–48.09
N5–Co–N1–H1	–29.70	–22.05
N5–Co–N1–H2	–148.73	–141.83
N6–Co–N1–H1	59.53	66.56
N6–Co–N1–H2	–59.51	–53.22
N5–Co–N4–H17(15)^a	66.19	44.44
N5–Co–N4–H18(16)^a	–52.97	–75.39
N6–Co–N4–H17(15)^a	–23.07	–44.18
N6–Co–N4–H18(16)^a	–142.23	–164.01
Co–N1–C1–C2	–22.16	–34.57
Co–N4–C6(4)–C5(3)^a	–26.43	36.95
Co–N3–C5(3)–C6(4)	–33.67	36.85
Co–N2–C3–C4	25.54	–
Co–N3–C4–C3	35.94	–

[a] The first number applies to compound (I); the one in parentheses applies to (II). See Figs. 1 and 2 for numbering.



Scheme 1.

TABLE XI. Torsional Angles (°) for (III).

N1–Co–N3–O1	–136.54	N2–Co–N3–O1	43.28
N1–Co–N3–O2	41.37	N2–Co–N3–O2	–138.81
N1–Co–N4–O3	39.71	N2–Co–N4–O3	–139.39
N1–Co–N4–O4	–140.23	N2–Co–N4–O4	40.66
N1–Co–N5–O5	12.50	N2–Co–N5–O5	–167.30
N1–Co–N5–O6	–174.80	N2–Co–N5–O6	5.39
N1–Co–N6–O7	168.35	N2–Co–N6–O7	–12.53
N1–Co–N6–O8	–9.91	N2–Co–N6–O8	169.20

TABLE XII. Distances (Å) between Chemically Related Atoms when Their Molecules are Superimposed by BMFIT [11] Pair Being Compared.

Atom	(I)–(IV)^a	(I)–(IV)	(I)–(V)^a	(I)–(V)	(I)–(II)	(I)–(III)
Co	0.004^b	0.035^b	0.044^b	0.018^b	0.013^b	0.027^b
N5	0.055^b	0.022^b	0.032^b	0.014^b	0.070^b	0.065(N3)^b
N6	0.041^b	0.039^b	0.031^b	0.013^b	0.066^b	0.070(N4)^b
N1	0.067^b	0.044	0.112	0.043	0.041^b	0.015(N2)
N2	0.060^b	0.102	0.215	0.207	0.158^b	0.174(N6)
N3	0.019^b	0.083	0.104	0.063	0.073^b	0.122(N5)
N4	0.031^b	0.104	0.066	0.133	0.053^b	0.038(N1)
O1	0.304	0.146	0.535	0.947	0.128	0.186(O2)
O2	0.449	0.048	0.619	0.806	0.125	0.040(O1)
O3	0.127	0.395	0.792	0.603	0.376	0.150(O3)
O4	0.154	0.261	0.920	0.500	0.357	0.177(O4)
C1	0.159	0.054	0.465	0.346	0.155^b	–
C2	0.101	0.079	0.188	0.164	0.055^b	–
C3	0.234	0.215	–	–	–	–
C4	0.258	0.234	–	–	–	–
C5(3)^c	0.211	0.113	0.068	0.043	0.644	–
C6(4)^c	0.129	0.089	0.257	0.367	0.479	–

[a] There are two ways of matching a pair of these molecules. This and the next column give the two possible matches. [b] Atoms used in the least-squares fitting routine of BMFIT [11]. [c] The number in parenthesis belongs to compound (II) or (III); see Discussion.

In order to define a symbol which conveys the chirality inherent to the Co(NO_2)$_2$ moiety, as oriented by hydrogen bonds, one can take the upper NH_2 (or NH_3) ligand and move from the nitrogen (N1 on Figs. 1–2) to the *short* hydrogen-bonded oxygen (O2 on Figs. 1–2) and onto the next NH_2

(or NH_3) nitrogens. This defines the sense [(+) = (*R*); (−) = (*S*)] as shown on drawings (A) and (B). Since NO_2 ligands look like broad-bladed paddles or twin tillers, this source of dissymmetry has been named *CLAVIC* (from the Latin for tiller). It is interesting to observe that all three compounds (**I**) → (**III**) having this source of dissymmetry, which can be anchored by hydrogen bonds, self-resolve into crystalline conglomerates.

One may at this point inquire whether this phenomenon of self-resolution is more general: the answer is *YES*. Table XIII was prepared to illustrate the point. This table lists the structures of all of the relevant substances available in the literature up to August of 1982. Together with the three examples discussed here, seven other known cases of spontaneous resolutions of Co(III) compounds bearing -NO_2 (nitro) ligands were found. Except for two cases of -ONO (nitrito)-bearing compounds which also spontaneously resolve [21], there are no other cases of spontaneous resolutions reported, thus far, for *any* other compound of Co bearing one or more monodentate ligands. Note that -ONO is also *clavic*.

Further Observations

(1) Recently, equimolar solutions of (**I**) and (**III**) and of (**II**) and (**III**) were mixed with the hope of obtaining crystals suitable for X-ray work of [*cis*-α-Co(trien)$(NO_2)_2$][*trans*-$Co(NH_3)_2(NO_2)_4$] and of [*cis*-$Co(en)_2(NO_2)_2$][*trans*-$Co(NH_3)_2(NO_2)_4$]. In both cases conglomerate formation occurs and both substances crystallize in the chiral, orthorhombic space group $P2_12_12_1$. Their structures are currently being examined [5].

(2) It should be clear, however, that the energies involved in these spontaneous resolutions of *clavic* dissymmetric compounds are very small (one needs only *ca.* 3 kcal/mol for 100% discrimination) and, thus, the balance may be altered readily by other factors. For instance, Bortin [22] reported that [*cis*-$Co(en)_2(NO_2)_2$](NO_3) crystallizes as a racemate (space group $P2_1/n$) while the *trans*- derivative crystallizes in $P2_1/a$. Interestingly, he states [22] that the cations are strongly hydrogen bonded to the nitrate anions and that the shortest hydrogen bonds are: *cis*-case, 2.08 Å; *trans*-case, 2.24 Å. These numbers are interesting when viewed against the background of our *intra-molecular* hydrogen bonds: 2.11 to 2.48 Å for (**I**), 2.32 to 2.48 Å for (**II**) and 2.03 and 2.06 to *ca.* 2.50 Å for (**III**), which means that the presence of NO_3^- as compensating anions can disturb the fine balance of *intramolecular* hydrogen bonds in dinitro species and prevent cations such as [*cis*-$Co(en)_2(NO_2)_2$]$^+$ from spontaneously resolving into conglomerates.

(3) While it seems NO_3^- can disrupt the possibility of conglomerate formation in species such as the cations of (**I**) and of (**II**) by disturbing the intramolecular hydrogen bond framework, it can constructively act as a source of stereochemical stability in other cases: we reported already [1] that the nitrate salts of the cations $M(en)_3^{2+}$ (M = Mn, Ni, Co, Cu and Zn) undergo spontaneous resolution into conglomerates. In these cases the labile and stereochemically nonrigid cations seem to be stabilized (at least at the time of crystal formation) by an elaborate network of hydrogen bonds linking terminal -NH_2 hydrogens to the oxygens of the anions. The reader is referred to those papers [1] for details. It is also interesting to note that other salts of these trisethylenediamine cations do not appear to undergo spontaneous resolution.

(4) Conglomerate formation seems to be a common phenomenon in Werner complexes both of the robust (*i.e.*, Co(III) complexes) as well as in labile ones (Ni(II), Co(II), Mn(II) derivatives of en, for example [1]). The common factor which seems to aid such substances to spontaneously resolve is the possibility of specific conformational stabilization *via* such phenomena as hydrogen bond formation (inter or intra) or steric hindrance, or both (see below, conclusion (6)).

(5) A type of chemical species which seems prone to providing the means of enhancing the chances of such occurrence are broad, planar ligands such as -NO_2 (or -O–NO) particularly when anchored into specific, dissymmetric arrangements brought about by the agency of hydrogen bonds or steric hindrance.

TABLE XIII. Other Examples of Self-Resolution Available in the Literature.

Formula	Characteristics	Space group	Ref.
$Co(NH_3)_3(NO_2)_3$	*mer*-NH_3	$P2_12_12_1$	18
$[Co(NH_3)_4(NO_2)_2]NO_3$	*cis*-dinitro	$P2_12_12_1$	19
$[Co(NH_3)_4(NO_2)_2]NO_3$	*trans*-dinitro	$P2_12_12_1$	20
$[Co(en)_2XY]Z$	two *trans* derivatives with X = NCS, Y = NO_2 and Z = I^- or ClO_4^-	Both $P2_1$	21
[Co(tetraazacyclododecane$(NO_2)_2$]Cl	*cis*-dinitro	$P2_1$	22
$Co(DMG)_2(NO_2)P\phi_3)$[a]	*trans*-NO_2)$(P\phi_3)$	$P2_12_12_1$	23

[a] DMG = dimethylglyoxime.

TABLE XIV

Compound	Space Group	Ref.
(a) 3-methyl-4-nitropyridine oxide	$P2_12_12_1$	23
(b) 3,5-dimethyl-4-nitropyridine oxide	$P4_12_12$ (or $P4_32_12$)*	23
(c) 4-aminopyridine	$P2_12_12_1$	24
(d) phenol	$P222_1$	25
(e) 2,4-dinitrophenol	$P2_12_12_1$	26
(f) *o*-cresol(2-methylphenol)	$P3_1$ (or $P3_2$)*	27
(g) 3-methyl-4-isopropylphenol	$P4_1$ (or $P4_3$)*	28
(h) pentachloronitrobenzene	$R3$	29
(i) 2,3-dichlorophenol	$P3_1$ (or $P3_2$)*	30
(j) 1,8-dihydroxyanthraquinone	$P4_1$ (or $P4_3$)*	3q
(k) picryl iodide	$P4_12_12$ (or $P4_32_12$)*	32
(l) 2,5-dimethylphenol	$P2_1$	33

*Depending on the crystal accidentally picked from the crystalline (conglomerate) mass.

(6) In order to test the generality of this suggestion in systems other than Werner complexes, a search was instituted in the area of substituted planar aromatics, substances normally not associated with dissymmetry (see Table XIV).
This list is by no means exhaustive, and no substantial effort was made to make it complete. It is, however, an impressive list in that every one of those substances accidentally self-resolved into antipodes whose sole source of asymmetry (or dissymmetry) is the orientation of a paddle-like substituent (-NO_2, NH_2, OH, *etc.*) into a fixed position which destroys the symmetry of such molecules when the angle between the aromatic ring and the paddle is not 0 or 90°. Thus, these are also examples of *CLAVIC* dissymmetry and the phenomenon is perfectly general and free of special features associated with octahedral Werner complexes such as **(I)**, **(II)** or **(III)**.

By now it should be clear why urea and thiourea derivatives frequently crystallize in optically active space groups—the amide linkage has the paddle or tiller shape needed for *CLAVIC* dissymmetry. It has, thus, not escaped us that this type of dissymmetry bears on the question of spontaneous resolution in the early stages of life on Earth, particularly for such substances as amino acids and peptides since they, too, share the property of clavic dissymmetry.

Acknowledgements

Thanks are due to the Robert A. Welch Foundation for support of this study and the USA National Science Foundation for the equipment with which these structures were determined. Finally, I thank the Alexander von Humboldt Foundation for a US Senior Scientist Award which allowed me to work at the laboratory of Professor Henri Bunner, whom I also thank for his hospitality. It was this award which provided me with the opportunity to think about this problem both in the framework of coordination chemistry and, later, about its general implications for stereochemistry.

References

1 For the two previous papers on spontaneous resolutions of coordination compounds, see (a) J. D. Korp, I. Bernal, R. A. Palmer and J. C. Robinson, *Acta Cryst., B36*, 680 (1980) and (b) I. Bernal and R. A. Palmer, *Inorg. Chem., 20*, 295 (1981).

2 J. Jacques, A. Collet and S. H. Wilen, 'Enantiomers, Racemates and Resolutions', New York, Wiley–Interscience, 1981.

3 See for example: (a) G. H. Searle and A. M. Sargeson, *Inorg. Chem., 12*, 1014 (1973); (b) A. M. Sargeson and G. H. Searle, *Inorg. Chem., 4*, 45 (1965); (c) D. A. Buckingham, I. E. Maxwell, A. M. Sargeson and H. C. Freeman, *Inorg. Chem., 9*, 1921 (1970); (d) H. C. Freeman, L. G. Marzilli and I. E. Maxwell, *Inorg. Chem., 9*, 2408 (1970); (e) H. C. Freeman and I. E. Maxwell, *Inorg. Chem., 6*, 1293 (1969); (f) M. Dwyer and I. Maxwell, *Inorg. Chem., 9*, 1459 (1970).

4 Y. Saito, 'Absolute Stereochemistry of Chelate Complexes', appearing in *Topics in Stereochemistry*, E. L. Eliel and N. L. Allinger, Eds.; New York, Wiley, 1978. Also, references therein.

5 Ivan Bernal, to be published. Presented at the Tulsa, Oklahoma, *39th Southwest Regional ACS Meeting*, December 7–9, 1983. See Abstract No. 121.

6 F. Basolo, *J. Am. Chem. Soc., 70*, 2634 (1948).

7 J. C. Vailar, Jr., 'Inorganic Syntheses Vol. 2', New York, McGraw–Hill, 1946, p. 223.

8 C. G. Schlessinger, 'Inorganic Syntheses Vol. 9', New York, McGraw–Hill, 1967, p. 170.

9 J. M. Bijvoet, A. F. Peerdeman and A. J. van Bommel, *Nature, 168*, 271 (1951).

10 G. Scheldrick, 'SHELX-76, A System of Computing Programs', Cambridge University, Cambridge, England, 1976.

11 C. K. Johnson, ORTEP-2. 'A Fortran-Ellipsoid Plot Program for Crystal Structure Illustration', Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, Tenn., 1968.

12 L.-K. Liu, Program BMFIT for Molecular Comparisons, University of Texas, Austin, 1967. Modified by S. F. Watkins, J. D. Korp and M. W. Creswick, University of Houston, 1978–1980.

13 M. Ito, F. Marumo and Y. Saito, *Acta Cryst., Sect. B:, 28*, 457 (1972).

14 I. Bernal and R. Job, to be published.

15 See Y. Saito's article 'Absolute Configuration of Transition Metal Complexes' in *Stereochemisty of Optically Active Transition Metal Complexes*, B. E. Douglas and Y. Saito, Eds., ACS Symposium Series, Volume 119, pp. 13–42; but particularly pp. 14–16.

16 H. Shintani, S. Sato and Y. Saito, *Acta Cryst., Sect. B:, 32,* 1184 (1976).

17 G. A. Barclay, E. Goldschmied and N. C. Stephenson, *Acta Cryst., Sect. B:, 26,* 1559 (1970).

18 (a) Y. Tanito, Y. Saito and H. Kuroya, *Bull. Chem. Soc. Japan, 25,* 188 (1952); (b) Structure redone by M. Laing, S. Baines and P. Sommerville, *Inorg. Chem., 10,* 1057 (1971).

19 I. Oonishi, H. Fujimaki, F. Muto and Y. Komiyama, *Bull. Chem. Soc. Japan, 43,* 733 (1970).

20 I. Oonishi, F. Muto and Y. Komiyama, *Bull. Chem. Soc. Japan, 42,* 2791 (1969).

21 I. Grenthe and E. Nordin, *Inorg. Chem., 18,* 1109 (1979).

22 O. Bortin, *Acta Chem. Scand., A30,* 657 (1976).

23 M. Shiro, M. Yamakawa and T. Kubota, *Acta Cryst., Sect. B:, 33,* 1549 (1977).

24 M. Chao and E. Schempp, *Acta Cryst., Sect. B:, 33,* 1557 (1977).

25 H. Gillier-Pandraud, *Bull. Soc. Chim. France,* 1988 (1967).

26 H. Gillier-Pandraud, *Bull. Soc. Chim. France,* 1933 (1967).

27 C. Bois, *Acta Cryst., B28,* 25 (1972).

28 M. Perrin, C. Bavoux and A. Thozet, *Acta Cryst., Sect. B:, 33,* 3516 (1977).

29 I. Tanaka, F. Iwazaki and A. Aihara, *Acta Cryst., Sect. B:, 30,* 1546 (1974).

30 A. Bavoux and A. Thozet, *Crystal Struct. Commun., 5,* 259 (1976).

31 A. Prakash, *Z. Kristall., 122,* 272 (1965).

32 G. Huse and H. M. Powell, *J. Chem. Soc. (London),* 1398 (1940).

33 H. Gillier-Pandraud, *Bull. Soc. Chim. France,* 3267 (1965).