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# Revisiting the structure of (±)-$[Co(en)_3]I_3 \cdot H_2O$ – X-ray crystallographic and second-Harmonic results

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**Abstract:** As described in the Introduction, we became interested in the existing literature for the crystallization behavior of (±)-$[Co(en)_3]I_3 \cdot H_2O$ and the absolute configuration of its enantiomers because of our project on the historical sequence of chemical studies leading Werner to formulate his Theory of Coordination Chemistry. In so doing, we discovered a number of interesting facts, including the possibility that the published "*Pbca*" structure of the (±)-$[Co(en)_3]I_3 \cdot H_2O$ was incorrect, and that it really crystallizes as a kryptoracemate in space group $P2_12_12_1$. Other equally interesting facts concerning the crystallization behavior of $[Co(en)_3]I_3 \cdot H_2O$ are detailed below, together with an explanation why PLATON incorrectly selects, in this case, the space group *Pbca* instead of the correct choice, $P2_12_12_1$. As for the Flack parameter, (±)-$[Co(en)_3]I_3 \cdot H_2O$ provides an example long sought by Flack himself – a challenging case, differing from the norm. For that purpose, data sets (for the pure enantiomer and for the racemate) were collected at 100 K with *R*-factors of 4.24 and 2.82%, respectively, which are ideal for such a test. The fact that *Pbca* is unacceptable in this case is documented by the results of Second-Harmonic Generation experiments. CCDC nos: 1562401 for compound (I) and 1562403 for compound (II).

**Keywords:** cobalt complexes; enantiomers; Flack parameter; kryptoracemates; racemates; second-harmonic generation (SHG).

## 1 Introduction

We are currently preparing a series of historic/crystallographic studies of selected groups of Co(III) complexes which were the keys to Alfred Werner's discovery of Coordination Chemistry [1]. At the same time, Werner revolutionized stereochemistry by demonstrating that chirality was not the exclusive prerogative of tetrahedral atoms. Among our own studies, we examined the properties of $[Co(en)_3]I_3 \cdot H_2O$, which was the first complex Werner isolated in optically active form, and whose optical activity was a direct property, not of one or more chiral centers, but the result of the dissymmetry at the metal due to the helical arrangement of three bidentate ligands. Additionally, Werner realized that, in the case of non-planar ligands, such as ethylenediamine, the property of internal ligand dissymmetry contributes additional sources of chirality that play a role in the decision as to whether a pair of crystallographic entities are truly a racemic pair, or not. Prior to Werner's studies, optical activity was relegated to tetrahedral carbon atoms only; and later, and with considerable reluctance, it was attributed to other tetrahedral atoms of the first row, such as nitrogen. Thus, a consequence of Werner's study was that the octahedron was proven to be a viable entity for exhibiting chirality, even in the absence of any chiral centers, since it can be so even if the three ligands are planar, as is the case with three oxalates – a fact that added a new chapter to stereochemistry. Subsequently, Werner and one of his students, Victor L. King, demonstrated that solutions of the cations of the above-mentioned iodide rotated the plane of polarized light at room temperature. That result was instrumental in Werner receiving the Nobel Prize in 1913.

In the process of looking at these complexes, we repeated some of the work already in print, and found to

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our surprise that this simple looking molecule had a far richer crystalline behavior than one would normally expect. Details are expanded upon below. The history of the resolution of the $[Co(en)_3]^{3+}$ cation, using bromcamphorsulfonate anion as the resolving agent, has been described in detail by Kauffman [2] and, somewhat later, in a more abbreviated but more modern language, by Bernal and Kauffmann [3]. Briefly, racemic $[Co(en)_3]Cl_3{\cdot}H_2O$ was reacted with the silver salt of bromcamphorsulfonate in a 2:1 ratio, and the resulting solid contained the bromcamphorsulfonate salt of $(+)_{589}$-$[\Lambda\text{-}Co(en)_3]^{3+}$. The bromcamphorsulfonate anions, whose chirality would prejudice the optical-rotatory measurements, were removed by precipitation of the cations as the more insoluble iodide. Of major importance for this report is the fact that not all the enantiomer may have been extracted, given that no detection device was used to monitor the extent of separation of the enantiomers. Consequently, for a given experiment, either some $(+)_{589}$-[Λ] enantiomer was left in solution or some $(-)_{589}$-[Δ] was carried over into the “resolved” material. Subsequent precipitation of the leftover $(-)_{589}$-[Δ] would, perforce, be 100% pure if some of it went with the “resolved” $(+)_{589}$-[Λ], or it would be contaminated, if the former. Serendipitously, the latter occurred in our work, much to our great surprise and fortune, since it caused us to re-examine the structure of the (±)-$[Co(en)_3]I_3{\cdot}H_2O$ species, and the consequences of that are detailed below.

The room temperature structures of the racemate (±)-$[Co(en)_3]I_3{\cdot}H_2O$ [4] and of the enantiomer $(+)_{589}$-$[\Lambda\text{-}Co(en)_3]I_3{\cdot}H_2O$ [5, 6] were determined previously. That of the latter was straightforward and was used to determine the absolute configuration of the cation; the former was stated to crystallize in space group *Pbca*, which was not surprising given the fact that (a) a racemate is usually expected to crystallize in a centrosymmetric or a polar space group; and (b) *Pbca* is one of the most common orthorhombic centrosymmetric space groups in recorded crystallography; see the Cambridge Crystallographic Structural Database (CSD) [7]. Due to the above observations, we decided to re-determine these structures, using redundant complete spheres of X-ray data over the temperature range 100–296 K. It is noteworthy to remind the readers that in the 1980s, data were collected over the asymmetric region only (if that much), which in this case, is 1/8 of the sphere of reflection since the crystal system is primitive orthorhombic. Moreover, the anomalous scattering, pertaining to whatever data were collected, were averaged out during the data processing by imposing the space group to be *Pbca*. The dataset herein reported is a redundant full sphere of 33,157 reflections (averaged to 5871 greater than $2\sigma$) and collected at 100 K. Additional data sets at room temperature were also collected and processed. At room temperature, we collected 34,419 reflections, which averaged to 6465 greater than $2\sigma$; the *R*-factor for this particular dataset was 3.22%. For details, see what follows.

# 2 Experimental section

## 2.1 Synthetic and crystal growth procedures

The racemate and both enantiomers were prepared according to the procedure of Girolami et al. [8]. Crystals were grown by saturating a water solution at 90 °C, filtering while hot, and allowing the solution to slowly cool to room temperature, filtering again, and placing the filtrate in a refrigerator (5 °C) overnight. The resulting crystals were filtered, washed with 50:50 ethanol:water and air-dried. Out of this mass of crystals, our X-ray diffraction samples were selected under the microscope. From the same batch, crystals were subsequently selected for the powder diffraction pattern, and for Differential Scanning Calorimetry (DSC) measurements reported herein.

## 2.2 Physical measurements

**2.2.1 Differential scanning calorimetry:** We studied the possibility of phase transitions above room temperature: a DSC trace was recorded on a 9.17 mg sample of (±)$[Co(en)_3]I_3{\cdot}H_2O$ (**II**) from 25 to 250 °C. There was only one exothermic transition which had an onset at 77.79 °C and which had a peak at 106.64 °C. This transition is ascribed to be the loss of the water of hydration since it did not reappear on the cooling curve. The enthalpy of this loss of water is $-32.80$ kJ $mol^{-1}$. DSC analyses were carried out using a TA Instruments Q20 series DSC equipped with a liquid nitrogen cooling system.

**2.2.2 Second-harmonic generation (SHG) experiments:** Well-formed, large-enough crystals of the racemate (±)-$[Co(en)_3]I_3{\cdot}H_2O$ (**II**), were used for the SHG measurements described below. Before the SHG measurements, the crystals were first tested by X-ray diffraction to make sure that they were the desired material. After the SHG measurements, the same exact crystals were again subjected to X-ray analysis to obtain the indices of the crystalline faces used in the SHG measurements and calculations.

**2.2.3 X-ray crystallography:** Using the crystalline mass described above, a 0.315 × 0.125 × 0.094 mm orange crystal of (**I**) was selected for X-ray examination for diffraction quality, oriented, and a sphere of data collected at 100 K. As expected, the crystal of $(-)_{589}$$[\Delta\text{-}Co(en)_3]I_3{\cdot}H_2O$ indexed in space group $P2_12_12_1$. The same crystal was allowed to warm to RT (296 K) and reoriented. The cell was the same, except for slight changes due to increased temperature; thus, there was no need to collect data since the 100 K data were of very good quality. During the selection of a crystal for the above experiments, we noted that there were a few beautiful crystals that seemed to be different in shape (orange plates as opposed to rods). A suitable one was selected and examined by X-ray diffraction. To our great surprise, it indexed with the same dimensions as the “known” racemic structure (±)-$[Co(en)_3]I_3{\cdot}H_2O$ [4], described as crystallizing in space group *Pbca*, whose crystals were described as grown from the (±) racemate (**II**). We collected a full dataset on ours at 100 K, and indeed, the space group seemed to be *Pbca* and the resulting structure was identical with that published by Whuler et al. [4], including the "disordered waters" with oxygens *ca.* 1.40 Å apart. The cell obtained with our crystal did not significantly change upon warming the crystal from 100 K to RT (296 K). We also prepared a sample of (±)-$[Co(en)_3]I_3 \cdot H_2O$ by mixing equivalent amounts of both enantiomers, (+)-$[\Lambda\text{-}Co(en)_3]I_3 \cdot H_2O$ and (−)-$[\Delta\text{-}Co(en)_3]I_3 \cdot H_2O$, in water, crystallizing this and collecting a dataset on one of those crystals, resulting in an identical structure to that described by Whuler et al. [4].

The diffraction data were collected on a Bruker Apex-II instrument using graphite-monochromated CuKα ($\lambda$ = 1.54178 Å) radiation. Inspection of many frames shows that the diffraction peaks are well-shaped and of good quality, with no streaking whatsoever; and the background is relatively uniform with no suggestion of fluorescence. Datasets were collected using ω and φ scans with the samples held in a cryoloop with Paratone oil and maintained at a constant temperature of 100 K using an Oxford cryostream. The data were reduced and processed using the Bruker Apex suite of programs [9]. Numerical absorption corrections were applied using Sadabs [10]. The diffraction data were solved using Shelxt and refined by full-matrix least-squares procedures using Shelxl-2016 [11, 12]. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were found in electron density difference maps and refined with a riding model, with isotropic displacement parameters equal to 1.2 times the isotropic equivalent of their carrier atoms (C or N). Specific refinement strategies are outlined in the crystallographic information files, CCDC 1562401 and 1562403. Structural and refinement parameters are presented in Table 1.

# 3 Results and discussion

## 3.1 The crystallographic results

We began our study with $(-)_{589}$-$[\Delta\text{-}Co(en)_3]I_3 \cdot H_2O$ (**I**) because the structure and absolute configuration of $(+)_{589}$-$[\Lambda\text{-}Co(en)_3]I_3 \cdot H_2O$ had already been determined [5, 6]. By doing so, we expected to verify that we had isolated the correct diastereoisomer, inasmuch as its helical chirality properties should be opposite of those described previously [5, 6]. The results are those expected, as shown in Figure 1.

In Figure 2, we describe the results of using space group *Pbca* for the racemate, (±)-$[Co(en)_3]I_3 \cdot H_2O$ **(II)**. N.B.: all structural solutions and refinements were carried out using the same data set, collected at 100 K, as described in Table 1, above.

Figure 3 describes the result of lowering the symmetry of the space group to the next proper subgroup, $Pca2_1$. It displays interesting results for the racemate (±)-$[Co(en)_3]I_3 \cdot H_2O$ (**II**), to wit: there two independent cations in the asymmetric unit, and associated with each is a well-defined water of crystallization.

**Table 1:** Crystallographic and refinement parameters for $(-)_{589}$-$[\Delta\text{-}Co(en)_3]I_3 \cdot H_2O$ (**I**) and (±)-$[Co(en)_3]I_3 \cdot H_2O$ (**II**).

| Identification code | $(-)_{589}$-$[\Delta\text{-}Co(en)_3]I_3 \cdot H_2O$ (**I**) | (±)-$[Co(en)_3]I_3 \cdot H_2O$ (**II**) |
|---|---|---|
| Empirical formula | $C_6H_{26}CoI_3N_6O$ | $C_6H_{26}CoI_3N_6O$ |
| Formula weight | 637.96 | 637.96 |
| Temperature/K | 100 | 100 |
| Crystal system | Orthorhombic | Orthorhombic |
| Space group | $P2_12_12_1$ | $P2_12_12_1$ |
| $a$/Å | 8.4012(1) | 11.4707(8) |
| $b$/Å | 11.2239(2) | 13.4157(9) |
| $c$/Å | 18.7210(3) | 23.1265(15) |
| $\alpha$/° | 90 | 90 |
| $\beta$/° | 90 | 90 |
| $\gamma$/° | 90 | 90 |
| Volume/Å$^3$ | 1765.28(5) | 3558.9(4) |
| $Z$ | 4 | 8 |
| $\rho_{calc}$/g cm$^{-3}$ | 2.400 | 2.381 |
| $\mu$/mm$^{-1}$ | 48.8 | 48.4 |
| $F$(000) | 1192 | 2384 |
| Crystal size/mm$^3$ | 0.315 × 0.125 × 0.094 | 0.500 × 0.304 × 0.119 |
| Radiation | CuKα | CuKα |
| $\theta$ range/° | 4.6 to 69.1 | 3.8 to 69.1 |
| Reflns collected | 16566 | 33157 |
| Independent reflns | 3151 [$R_{int}$ = 0.061, $R_\sigma$ = 0.031] | 6415 [$R_{int}$ = 0.058, $R_\sigma$ = 0.037] |
| Reflns observed [$I \geq 2\sigma(I)$] | 3074 | 5871 |
| Data/restraints/parameters | 3151/2/161 | 6415/151/308 |
| GOF on $F^2$ | 1.09 | 1.11 |
| Final $R$ indexes [$I \geq 2$ ($I$)] | $R_1$ = 0.0282,<br>w$R_2$ = 0.0689 | $R_1$ = 0.0422,<br>w$R_2$ = 0.1008 |
| Final $R$ indexes [all data] | $R_1$ = 0.0289,<br>w$R_2$ = 0.0694 | $R_1$ = 0.0468,<br>w$R_2$ = 0.1034 |
| Largest diff. Peak/hole/e Å$^{-3}$ | 1.21/−0.84 | 1.81/−0.91 |
| Flack parameter$^{13}$ | 0.012(14) | 0.48(3) |
| CCDC no. | 1562401 | 1562403 |

In Figure 5, we describe the stereochemical features that distinguish Co1 from Co2 when properly described in space group $P2_12_12_1$, specifically, by the use of a superposition diagram.

In Figure 6, we describe an interesting feature of the packing present in (±)-$[Co(en)_3]I_3 \cdot H_2O$ (**II**), which is of fundamental importance to the conclusions derived from this study, concerning space group assignments: namely, considerations of the distribution of species in the unit cell, as revealed by their Center of Mass (CM).

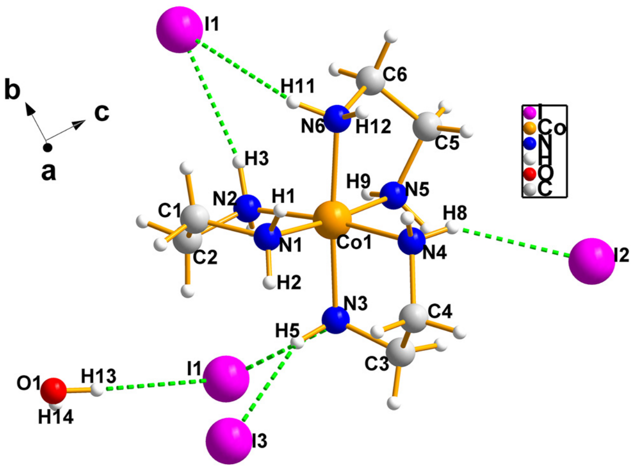


**Figure 1:** The $(-)_{589}$-[Δ-$Co(en)_3]I_3{\cdot}H_2O$ (**I**) diastereoisomer obtained from our X-ray study, showing the water of crystallization hydrogen-bonded to iodide I1.

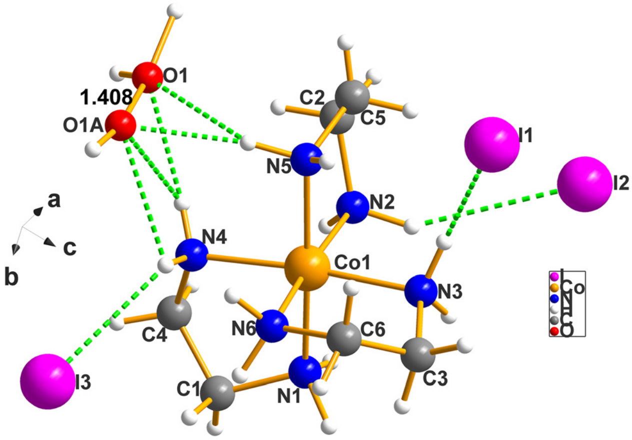


**Figure 2:** This figure represents the structure drawn either from the original coordinates, or from ours, in space group *Pbca*.

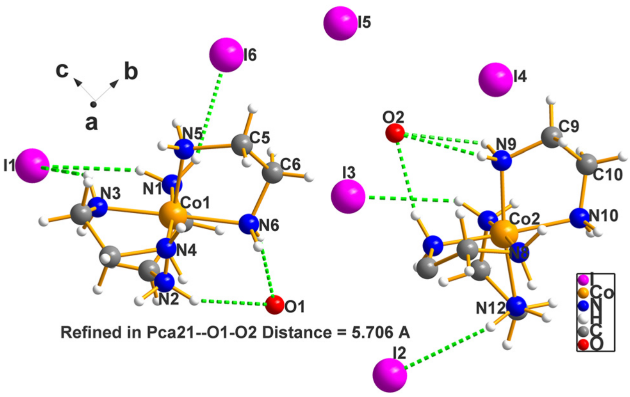


**Figure 3:** In space group $Pca2_1$, two water molecules, separated by a distance of 5.71 Å, now emerge. However, the hydrogen atoms of those waters cannot be found at acceptable positions. Platon [13] suggests that the correct space group is *Pbca*; hence, if Platon is to be trusted, $Pca2_1$ is incorrect, and safely ignored. When the space group is further lowered to the next proper subgroup $P2_12_12_1$, then the missing hydrogen atoms appear, as shown in Figure 4. Note that, once again, Platon suggests that the correct space group is *Pbca*.

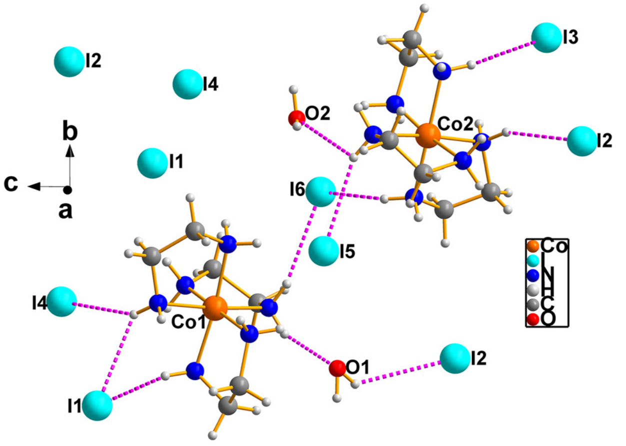


**Figure 4:** Structure of the kryptoracemic crystals of the racemate (±)-$[Co(en)_3]I_3{\cdot}H_2O$ (**II**). Each Co (1 or 2) has a separate hydrogen-bonded water, the distance between them being 7.54 Å. One iodide (I6) helps link the cobalt cations by hydrogen bonds by their $-NH_2$ fragments. Torsional angle differences in the *en* ligands of the two independent Co cations keep them from achieving full enantiomeric symmetry – see below for more details on torsional angles, and consequences thereof.

Given the above, we finished the solution and refinement of our dataset in the subgroup $P2_12_12_1$ with $Z = 8$ and $Z' = 2$. The results are as follows: (a) there are two independent $[Co(en)_3]I_3{\cdot}H_2O$ units in the asymmetric unit; (b) the cobalt cations are a racemic pair insofar as the helical chirality around the cobalt; (c) each cation has a hydrogen-bonded water, and these are 7.54 Å apart; (d) the average value of the torsional angles of the two $[Co(en)_3]^{3+}$ cations match exactly the value of the *en* torsional angles obtained in the "*Pbca*" structure, despite the independent refinement of the data in $P2_12_12_1$, implying a totally artificial assignment of the space group as the centrosymmetric *Pbca*; (e) nonetheless, the fact is that (1) the usual tests by Platon [13] unequivocally suggests the space group is *Pbca*; and (2) the statistics of the data say that the data are centrosymmetric, but we prefer the Sohncke choice for reasons detailed below. This is clearly a case of a kryptoracemic crystallization, and the results we obtained with our "odd crystal", those reported previously [4], and those we obtained with our sample of (±)-$[Co(en)_3]I_3{\cdot}H_2O$, prepared from its chiral components, are all identical. Finally, and unequivocally, the Second Harmonic Generation results below demonstrate the correctness of our space group assignment.

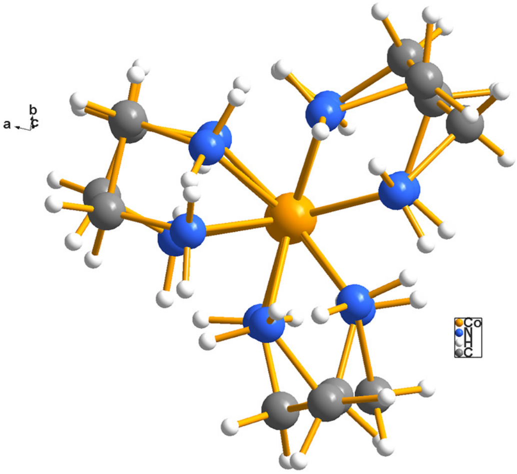


**Figure 5:** This is a superposition diagram of Co1 and Co2 from our structural refinement in $P2_12_12_1$. The ring of the *en* ligand at left matches reasonably well, but the two at right are very far off, as expected from the torsional angle values of Co1 = −41(2), −40(2), +50(2)°; and, for Co2 = +56.1(18), −45(2), +55.1(19)°. These values are far from those expected for a racemic pair, especially since the signs for the second and third "pairs" are the same, whereas they must be *opposite* for all three coordinates in a true racemate. Thus, this test reinforces the idea that the space group cannot be the centrosymmetric one, *Pbca*. Also note that when the rings of Co1 and Co2, refined in $P2_12_12_1$, are averaged, the resulting values match, nearly perfectly, those obtained by solving and refining the structure in space group *Pbca*. The overlay diagram was generated by Mercury [14] and then used in the program Diamond [15].

## 3.2 Second-harmonic generation (SHG) studies

Allowing for the fact that there is still room for insisting that the correct space group is *Pbca*, we decided to definitely pin down the centricity or the non-centricity of the complex (±)-$[Co(en)_3]I_3·H_2O$ (**II**) by resorting to Second-Harmonic Generation (SHG) measurements, described next.

### 3.2.1 Second-harmonic generation (SHG) measurements

We carried out SHG measurements at room temperature (290 K), 200, and 100 K, respectively. The pulsed laser used in our SHG measurements is of 50 fs pulse duration and 200 kHz repetition rate, and the laser beam is focused down to a 20 µm diameter spot on the samples at a power of 0.88 mW, corresponding to a fluence of 1.4 $mJ/cm^2$. The 800 nm incident laser light is directed normal to the sample surface, which is identified to be close to the (0 0 1) crystal facet via X-ray diffraction measurements, and the reflected 400 nm SHG signal is collected by a photomultiplier-tube (PMT) whose signal is demodulated through a lock-in amplifier. The incident and the reflected light polarizations can be selected to be either parallel or crossed to each other via a half-wave plate and an analyzer, respectively. The laser beam can further be scanned across the sample surface from point to point with a constant fluence and be used to construct high resolution SHG scanning images at selected polarization geometries. Figure 7(a)–(b) shows the SHG scanning images of the (±)-$[Co(en)_3]I_3·H_2O$ crystal at 290, 200, and 100 K, respectively. One can observe that the overall SHG signal strength shows minor variations across the sample and maintains the same order of magnitude at various temperatures. The effective susceptibility strengths are calculated to be around 0.01 pm/V, which is about two orders of magnitude larger than those of electric quadrupole SHG from centrosymmetric crystals [16]. The strong

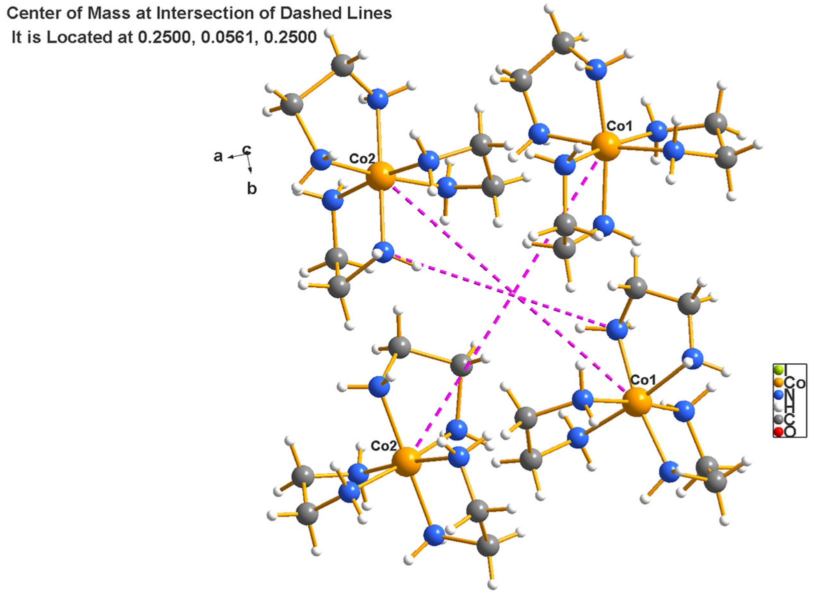


**Figure 6:** For the racemate (±)-$[Co(en)_3]I_3·H_2O$ (**II**), the dotted lines drawn from Co1 to Co2 cations (which necessarily have to be enantiomeric in space group *Pbca*), intersect at a common point (their center of mass) located at 0.2500, 0.0561, 0.2500, which is a nearly perfect inversion center, despite the fact the structure was refined in $P2_12_12_1$.

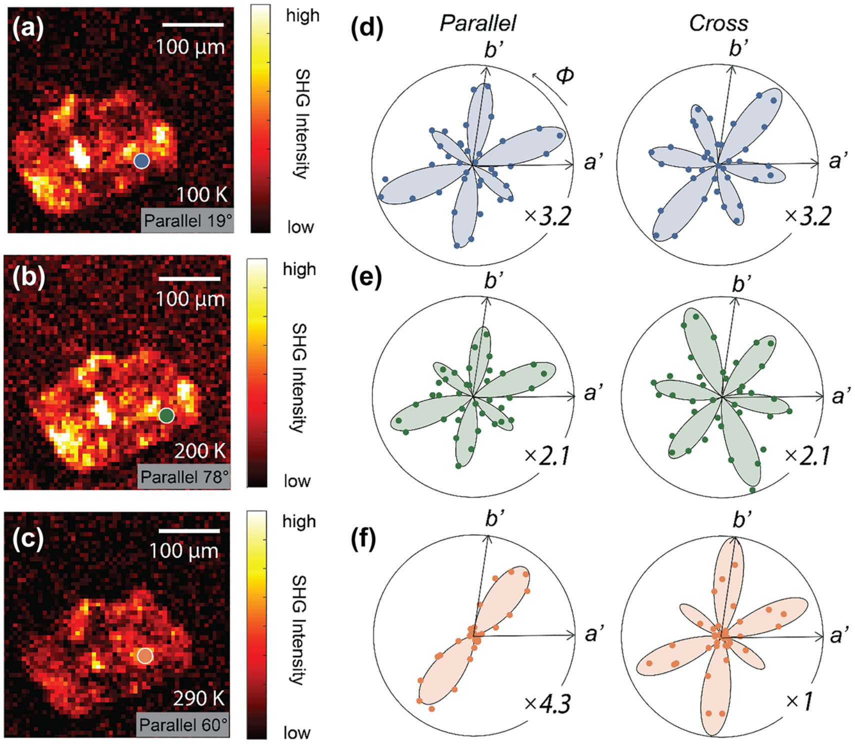


**Figure 7:** SHG scanning images of the (±)-[Co(en)$_3$]I$_3$·H$_2$O crystal at (a) 100 K (b) 200 K and (c) 290 K. Color scales of all three images are set to be identical. (d–f) RA SHG measurements taken at various locations at 100, 200, and 290 K, respectively. Colors correspond to the sites shown in (a), (b) and (c). Data (markers) are fitted to point group $D_2$ simulations (solid lines). *a'* and *b'* correspond to the crystal *a*- and *b*-axes projected onto the crystal surface. Matlab and Adobe illustrator generated these figures.

SHG signal level indicates that the crystal breaks inversion symmetry and possesses a non-centrosymmetric crystal structure, activating the leading order electric dipole SHG. We then performed rotational anisotropy (RA) SHG measurements, which is the angular dependence of SHG, in both parallel and crossed polarization channels at various sample locations at 290, 200, and 100 K. As is shown in Figure 7(d)–(f), the data are well fitted by the simulated functional form of RA SHG under the $D_2$ point group [17], further confirming the proposed **polar** crystal structure. We finally note that the RA SHG patterns at 100 and 200 K are qualitatively similar, but are dramatically different from those at 290 K, indicating a possible structural phase transition between 200 and 290 K, which is however beyond the scope of the current study.

## 4 Conclusions

So, what is the origin of our “odd crystal” obtained from a crystalline mass that was supposed to be a pure enantiomer? As mentioned above, it is impossible to stop a tiny fraction of the (+)-enantiomer to crystallize together with the main portion of the desired (−) product, and vice-versa, because such crystallizations are never monitored with a device so precise that it tells you when to stop recovering the (+) or (−) material. Thus, it is not unreasonable that a tiny fraction of the (+)-enantiomer appears in the yield of the (−) one, or vice-versa. We, accidentally, found an attractive crystal with a slightly different external color and shape from that of the optically-active material, and decided to examine it. To our great surprise it turned out to be identical with a genuine sample of (±)-[Co(en)$_3$]I$_3$·H$_2$O as reported by Whuler et al. [4] and later verified by us by purposely synthesizing the racemate directly and by crystallizing a (50:50) mixture of the pre-resolved diastereoisomers.

Perusal of the literature leads to some interesting observations which help strengthen our arguments since they are (a) independent of our study by virtue of the fact that they were carried out elsewhere, using totally different techniques; (b) the nature of the compounds studied elsewhere differ from ours; nonetheless, the authors reached precisely the same conclusions we did, to wit: the centrosymmetric space group choice was incorrect. The heavy atoms in their structures dominate the scattering of their “centrosymmetric” space groups, which “swamp out” the contributions from the dissymmetric arrays of light atoms responsible for the break in the symmetry expected from a true racemate.

## 5 Additional information from the literature

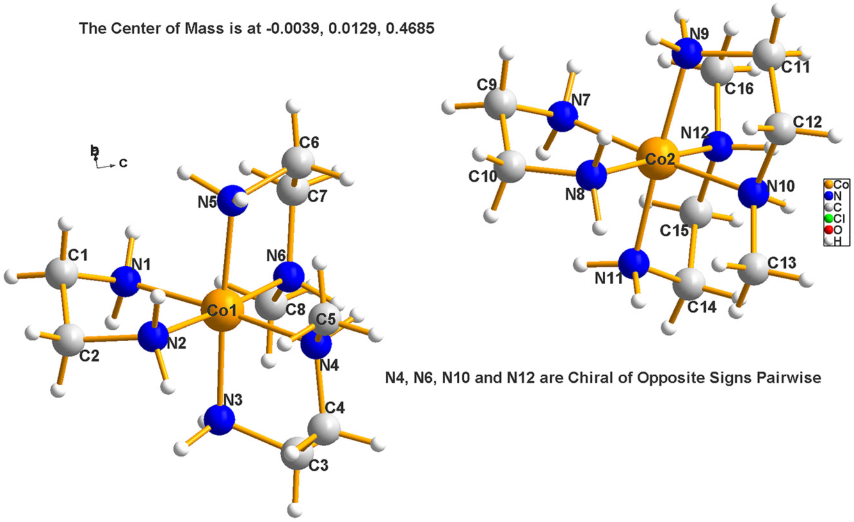
*Caveat:* Note that the so-called “*Pbca*” crystal of (±)-[Co(en)$_3$]I$_3$·H$_2$O (**II**) turned out to be a very interesting case of kryptoracemic crystallization – an unknown phenomenon at the time of the original publication by Whuler et al. [4], given that it was first clearly recognized in 1995 [18–21].

(1) In 1988, Fuertes et al. [22] discovered a case closely related to ours, namely the structure of $[(\pm)Co(en)_3](C_2O_4)I \cdot 1.5H_2O$ (REFCODE = **GAPHUA**). Despite the fact that this substance was synthesized as a racemate, they determined that the correct space group for their crystals is $P2_12_12_1$ and not *Pbca*. What they discovered is closely related to our results. Therefore, we think it is informative to quote them directly since what they observed was exactly what we did, but with a somewhat different substance. Namely, "two 'nearly enantiomeric' crystallographically independent octahedral $[Co(en)_3]^{3+}$ are distinctively different. The configurations are Λδδδ and Δλλλ." Moreover, when discussing the solution and refinement of their structure, they said: "From a chemical standpoint of view, and taking into account the synthesis procedure, the yield of this 'active racemic' compound is unique, considering the reported structures of $[M(en)_3]L_m \cdot xH_2O$ complexes." Indeed, their structure was one of the rare species discovered up to that time which behaved that way. Still, they recognized the phenomenon and correctly identified the real space group to be $P2_12_12_1$ and not *Pbca*. Unfortunately, they did not follow-up this interesting lead. Some years later, this mode of crystallization was recognized to be relatively poorly documented for coordination compounds [23] and much more extensively available for organic ones [24], likely due to the fact that there are orders of magnitude more organic species in the crystallographic literature [7].

(2) Another example of the same dilemma occurred in the case of **KARFAK** [25], which is ethane-1,2-diamine-*N*,*N'*)-bis(*N*-methylethane-1,2-diamine-*N*,*N'*)-cobalt(III) dichloride perchlorate mono-hydrate, and whose structure they were also forced to assign to space group $P2_12_12_1$ and which bears a remarkable similarity to ours. Compare Figures 4 and 6 (above) and Figure 8 (below).

As shown above, the Center of Mass of those species is located very close to the special position 0, 0, 1/2. That is, there is a pseudo-inversion center in that lattice which is imperfect in view of the torsional angle values listed above. Moreover, another important fact that must be emphasized, is that the cobalt and the three chlorides in the asymmetric unit constitute 30.7% of the scattering power of this compound, and that it is only the small failure in the torsional angles of the *en* ligands that destroy an otherwise perfect inversion center.

(3) Finally, there is an even more interesting article by Sunatsuki et al. [26] which directly takes us to the heart of the matter, and that is, the case of ROPRUL, a chiral complex of $[Fe(HL)_2](PF_6)_2$, where HL denotes 2-pyridylmethylidenehydrazono-4-(2-methylimidazolyl)methane sesquihydrate. The difficulty with the correct interpretation of the space group in our case, as well as in the case of the problem forcefully described by the above authors, is namely: the heavy atoms of the molecule are located very close to a "near-perfect" inversion center; therefore, the diffraction pattern is skewed such that it very closely appears to be centrosymmetric, as in our case, because their heaviest atoms, Fe and $PF_6^-$, (as is the case of the Co ion and the three iodide anions in our structure)


The Center of Mass is at -0.0039, 0.0129, 0.4685

N4, N6, N10 and N12 are Chiral of Opposite Signs Pairwise

**Figure 8:** Structure of ethane-1,2-diamine-*N*,*N'*)-bis(*N*-methylethane-1,2-diamine-*N*,*N'*)-cobalt(III) dichloride perchlorate mono-hydrate, (REFCODE = **KARFAK**) [25]. There are two cobalt cations in the asymmetric unit. Each has two *en* and one N-methylene disymmetric ligands, in which Co1, with torsional chirality of the ethylenediamine rings of −53.2(8), −52.5(8) and +51.9(8)°, and Co2 = with torsional chirality of +53.5(8), +52.5(8), +45.9(8)°. There cannot be a true inversion center connecting them because the signs of the torsional angles cannot be inverted, inasmuch as Co1 = (−, −, +) and Co2 = (+, +, +). For additional details of this interesting substance, the readers are referred to the lengthy, original report [25].

account for over 40.7% of the scattering power of the lattice; therefore, a statistical analysis, such as the Flack parameter test [27] is bound to incorrectly identify these crystals as being centrosymmetric. And that is exactly what Sunatsuki et al. [26] proved by showing that (a) the refinement was much better in $P2_12_12_1$; and (b) that a single crystal of that iron compound rotated the plane of polarized light. There is no way to challenge the choice of space group after that last experiment.

## 6 Closings comments

Kryptoracemic crystals [18–21] contain one or more pairs of molecules (or ions) that, in solution, would be perfect racemic pairs. In the solid, however, they are not "exact racemic pairs" due to the fact that they contain diastereoisomeric components that do not obey operations of the second kind (e.g., inversion centers, mirror planes, etc.). Therefore, they differ, for example, in the angles of dissymmetric elements such as in those of the ethylenediamine ligands. Thus, as long as they are trapped in crystalline lattices, the contents of the asymmetric unit will always be *pseudo-racemic pairs* whose scattering pattern will always be "almost, but not exactly, centrosymmetric". That property therefore prejudices the recognition of the Sohncke nature of the correct space group. Note that, if dissolved, such crystals will produce an exact racemic solution; therefore, that solution will not rotate the plane of polarized light even though individual crystals will, as forcefully shown by Sunatsuki et al. [26].

The structure reported by Whuler et al. [4] was an early but unrecognized example of kryptoracemic crystallization. That it was not recognized as such is not surprising since the phenomenon was not identified, described, and named until 15 years [18] after the publication of their paper [18–21].

Platon [13] and the Flack parameter test [27] are very reliable for those cases in which the distribution of intensities reflect the scattering of an array of atoms with *more or less equal* scattering powers; but when there is a large discrepancy in the diffracting power between the "heavy atoms" and the "light ones" in the structure, the latter being those breaking the center of symmetry, then the calculations break down and predict a centrosymmetric space group. In so far as the Flack parameter is concerned, recall that light atoms, with atomic number less than sulfur, contribute practically nothing to the anomalous portion of the scattering power of a crystalline lattice.

When the composition of the asymmetric unit is such that a large fraction is made up of elements of the 3d-series, or above, and the space group assignment is controversially between a centrosymmetric choice and one of its proper subgroups, and, if in the lowest subgroup, $Z' > 1$, we suggest the following procedure to avoid the trap of a case of kryptoracemic crystallization:

(1) Solve the structure in the lowest symmetry space group selection and refine it to convergence.
(2) Find the center of mass (CM) of the entire unit cell, and if it is near a "special position" such as above, then
(3) Submit the results of refining in the lowest space group to Platon [15] for an evaluation of the space group assignment and for a value of the Flack parameter [27].
(4) If the issue is not clearly resolved, then compare the structural results obtained for all of the space group choices and see which one is most chemically satisfying, because if chemical results are unacceptable in a given space group, that assignment should be viewed, at least, *cum grano salis*, as above.
(5) As a last resort, the substance should be examined by an independent method, such as described above for the Fe compound [*i.e.*, measure the circular dichroism (CD), as in [26], or SHG, or piezoelectricity test, etc.]. One of those should be useful in making a satisfying conclusion. As a last piece of evidence that we have the correct material, i.e., (±)-$[Co(en)_3]I_3{\cdot}H_2O$, we supply the actual powder diffraction experiment and compare it to the simulated powder pattern from the single crystal work. These are in the Supporting Information.

## 7 Supporting Information

The original structures of all species herein described were deposited and their information is available through the CCDC. The codes are 1562401 and 1562403

CCDC- See above. The Cambridge Structural Database, C. R. Groom, I. J. Bruno, M. P. Lightfoot and S. C. Ward, Acta Cryst. (2016). B72, 171-179.

Figure S1: ORTEP Diagram for $(-)_{589}$-$[\Delta\text{-}Co(en)_3]I_3{\cdot}H_2O$ (I) structure: anisotropic atoms are at the 30% probability level.

Figure S2: ORTEP Diagram for (±)-$[Co(en)_3]I_3{\cdot}H_2O$ (II) structure: anisotropic atoms are at the 30% probability level.

Figure S3: Actual Powder Pattern for the (±)-$[Co(en)_3]I_3{\cdot}H_2O$ (II) structure.

Figure S4: Simulated Powder Pattern for the (±)-$[Co(en)_3]I_3 \cdot H_2O$ (II) structure generated from the single crystal data.

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NOTE: The six letter acronyms, such as JOKKAV, are used by the Cambridge File [7] to identify the crystals within that database.

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