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The incidence of kryptoracemic crystallization in $[Co^{III}(tren)XY]^+$ compounds: The case of *cis*-$[Co^{III}(tren)Cl_2]Cl \cdot H_2O$

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RESEARCH ARTICLE

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ABSTRACT

We are evaluating the proposition that compounds with pronounced tendencies to crystallize as kryptoracemates contain molecular fragments responsible for such a property. Why Sohncke space groups display such a tendency is not currently known, but one such fragment is the [*tris*(2-aminoethyl)amine-*N*,*N'*,*N''*,*N'''*] ligand when attached to cobalt(III). Therefore, proceeding to test the concept further, we examined the title compound and found a previously unknown kryptoracemic species, described in what follows. It seems then that the prescription has some merit and should be examined further inasmuch as guidelines for the occurrence of kryptoracemic crystallization are scant, if any exist. Crystal data for $C_6H_{20}Cl_3CoN_4O$: monoclinic, space group $P2_1$ (no. 4), $a = 7.6672(3)$ Å, $b = 15.7153(5)$ Å, $c = 10.7170(4)$ Å, $\beta = 92.964(2)°$, $V = 1289.59(8)$ Å^3, $Z = 4$, $T = 100(2)$ K, $\mu(CuK\alpha) = 16.026$ mm^{-1}, $Dcalc = 1.697$ g/cm^3, 13406 reflections measured ($8.26° \leq 2\Theta \leq 133.402°$), 3976 unique ($R_{int} = 0.0300$, $R_{sigma} = 0.0519$) which were used in all calculations. The final R_1 was 0.0220 ($I > 2\sigma(I)$) and wR_2 was 0.0459 (all data).

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1. Introduction

In 1995 [1], a new mode of crystallization was described, which was labeled “kryptoracemic crystallization”, alluding to the fact that a racemic pair was “hidden or buried” (in a krypt) in a Sohncke space group. In time, additional examples were added to the list of crystals in that class, as example IKERUL02 [2], and in the appearance of two reviews [3,4] recording examples of coordination compounds, organometallic, and organic species. Pertinent additional comments can be found in reference [5]. Interested readers are encouraged to peruse sources [1-5] to get an idea of the classes of compounds undergoing such crystallization modes, and of the variety of examples within those classes.

In the past, we have explored the concept that various recognizable factors may influence kryptoracemic and related modes of crystallization of chemical species, using a rather broad approach, and while concentrating on just species of composition $[CoN_4(XY)]$, where N_4 is any combination of amines occupying four sites of an octahedral Co(III) cation, we found many examples [3,5]. Here, we limit ourselves to $[Co^{III}(tren)(X)(Y)] \cdot$[counter-anions, if any] to produce kryptoracemates, given that X and Y are monodentate ligands and tren = *tris*-(2-aminoethyl)amine. From the vantage point of our previous experiences, we have begun to discern certain patterns which may be useful, as orderly guides, in predicting crystallization pathways - a very desirable goal, if for no other reason than there are few, if any, orderly guides available now. Some very useful, but somewhat dated references are, for example, the monographs by Bernstein [6] and by Jacques, Collet & Wilen [7], which we recommend for those beginning inquiries of their own. Some attempts, limited to predicting crystallization modes by analogy to cases where it does occur, have been made previously, with limited but encouraging results in NIXGIK [8] and FILGIQ [9].

2. Experimental

2.1. Materials

The chemicals used are all available from Sigma-Aldrich and were used without further purification.

2.2. Synthetic procedure and crystal growth

The synthesis of the title compound began with the preparation of the precursor $[Co^{III}(tren)(NO_2)_2]Cl$. This came

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Table 1. Crystal data and structure refinement for *cis*-[Co^{III}(tren)Cl$_2$]Cl·H$_2$O.

Empirical formula	$C_6H_{18}Cl_2CoN_4$, Cl, H_2O
Formula weight	329.54
Temperature (K)	100(2)
Crystal system	Monoclinic
Space group	$P2_1$
a (Å)	7.6672(3)
b (Å)	15.7153(5)
c (Å)	10.7170(4)
β (°)	92.964(2)
Volume (Å^3)	1289.59(8)
Z	4
ρ_{calc} (g/cm^3)	1.697
μ (mm^{-1})	16.026
F(000)	680.0
Crystal size (mm^3)	0.279 × 0.254 × 0.232
Radiation	CuKα (λ = 1.54178 Å)
2Θ range for data collection (°)	8.26 to 133.402
Index ranges	$-8 \le h \le 9$, $-18 \le k \le 18$, $-12 \le l \le 12$
Reflections collected	13406
Independent reflections	3976 [R_{int} = 0.0300, R_{sigma} = 0.0519]
Data/restraints/parameters	3976/1/320
Goodness-of-fit on F^2	0.888
Absorption correction	Numerical
T_{min}, T_{max}	0.054, 0.243
Final R indexes [I≥2σ (I)]	R_1 = 0.0220, wR_2 = 0.0455
Final R indexes [all data]	R_1 = 0.0235, wR_2 = 0.0459
(sin θ/λ)$_{max}$ (Å^{-1})	0.596
Largest diff. peak/hole (e Å^{-3})	0.37/-0.24
Flack parameter	-0.004(3)
H-atom treatment	Treated by a mixture of independent and constrained refinement
Computer programs	SAINT [11], APEX2 [12], SADABS [13], SHELXL [14], DIAMOND [15]
CCDC number	1978094

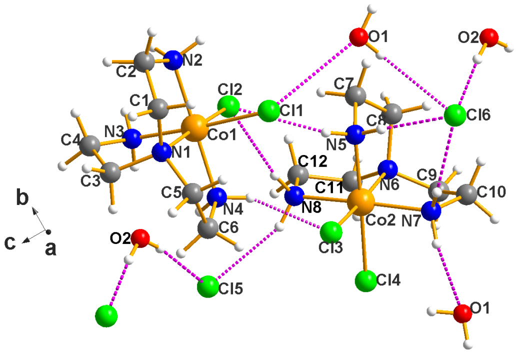

Figure 1. The two cations, chloride anions, and waters of crystallization as observed in *cis*-[Co^{III}(tren)Cl$_2$]Cl·H$_2$O.

from the process of Uprety *et al.,* 2018 [10]. 7.267 g of NaNO$_2$ was added to a solution of 11.992 g of CoCl$_2$·6H$_2$O in 10 mL deionized water in a 100 mL side-arm flask. To this solution, 4.4 mL of 32% HCl and 7.5 mL *tris*-(2-aminoethyl)amine (tren) in 10 mL deionized water were added and placed in an ice bath until the solution was ice-cold. Then air was pulled through the solution for 2 hours to oxidize the cobalt(II) to cobalt(III). A yellow-brown product was observed. The product was collected by suction filtration and recrystallized from a minimum amount of warm water (enough to dissolve the crystallized product); the crystals were then collected by suction filtration and dried. This product was then used to synthesize, *cis*-[Co^{III}(tren)Cl$_2$]Cl·H$_2$O, again following Uprety *et al.*'s process, 2018 [10]. 7.056 g of the above precursor were dissolved in the minimum amount of deionized H$_2$O in a 100 mL beaker and 50 mL of 30% HCl were added to it. The solution was heated on a hot water bath all the way to dryness. The precipitate was dissolved in a minimum amount of warm deionized water. After leaving this solution to crystallize, it was isolated by vacuum filtration and washed with cold deionized water. Crystals appeared to be purple in color. Note that our product molecular formula is different from that described in Uprety's paper [10]; our complex has H$_2$O of crystallization instead of hydroxonium chloride, H$_7$O$_3$$^+Cl^-$.

2.3. X-ray diffraction study, solution and refinement of the data

A crystal of compound *cis*-[Co^{III}(tren)Cl$_2$]Cl·H$_2$O was mounted on a Bruker APEXII X-ray diffractometer using graphite-monochromated CuKα (λ = 1.54178 Å) radiation, oriented, and data were collected using ω and φ scans. After data collection at 100 K using an Oxford Cryostream, the crystal was brought to 296 K and reoriented. The cell was essentially the same, except for slight changes due to increased temperature. Data processing, Lorentz-polarization, and face-indexed numerical absorption corrections were performed using SAINT, APEX, and SADABS computer programs [11-13]. The structure was solved by direct methods and refined by full-matrix least-squares methods on *F*^{2}, using the SHELXTL V6.14 program package (Figure 1) [14]. All non-hydrogen atoms were refined with anisotropic displacement parameters; the H atoms of the nitrogen atoms and the oxygen atoms were refined positionally. For *cis*-[Co^{III}(tren)Cl$_2$]Cl·H$_2$O, the structural and refinement parameters and the CCDC deposition number can be found in Table 1.

Table 2. Bond lengths for *cis*-[Co^{III}(tren)Cl_2]Cl·H_2O.

Atom	Atom	Length (Å)	Atom	Atom	Length (Å)	Atom	Atom	Length (Å)
Co1	N4	1.939(3)	Co2	Cl3	2.2459(10)	N5	C9	1.499(5)
Co1	N3	1.940(3)	Co2	Cl4	2.2833(11)	N5	C8	1.512(5)
Co1	N1	1.944(3)	N4	C6	1.499(5)	C2	N2	1.495(5)
Co1	N2	1.973(3)	N3	C4	1.482(5)	C2	C1	1.513(5)
Co1	Cl2	2.2771(11)	N8	C12	1.499(5)	N7	C10	1.501(5)
Co1	Cl1	2.2783(11)	N1	C5	1.489(5)	C4	C3	1.516(5)
Co2	N5	1.946(3)	N1	C1	1.494(5)	C10	C9	1.530(5)
Co2	N8	1.948(3)	N1	C3	1.514(4)	C6	C5	1.525(5)
Co2	N7	1.951(4)	N6	C7	1.477(5)	C12	C11	1.521(5)
Co2	N6	1.956(3)	N5	C11	1.496(5)	C8	C7	1.503(6)

Table 3. Bond angles for *cis*-[Co^{III}(tren)Cl_2]Cl·H_2O.

Atom	Atom	Atom	Angle (°)	Atom	Atom	Atom	Angle (°)	Atom	Atom	Atom	Angle (°)
N4	Co1	N3	93.80(15)	N7	Co2	N6	94.42(15)	C11	N5	C9	111.9(3)
N4	Co1	N1	84.71(14)	N5	Co2	Cl3	174.06(11)	C11	N5	C8	111.9(3)
N3	Co1	N1	87.92(14)	N8	Co2	Cl3	93.83(10)	C9	N5	C8	109.6(3)
N4	Co1	N2	170.59(15)	N7	Co2	Cl3	92.50(11)	C11	N5	Co2	106.4(2)
N3	Co1	N2	90.27(15)	N6	Co2	Cl3	87.81(10)	C9	N5	Co2	107.0(2)
N1	Co1	N2	86.97(14)	N5	Co2	Cl4	93.73(10)	C8	N5	Co2	109.8(2)
N4	Co1	Cl2	92.01(10)	N8	Co2	Cl4	88.09(11)	N2	C2	C1	109.6(3)
N3	Co1	Cl2	86.84(10)	N7	Co2	Cl4	87.16(11)	C2	N2	Co1	110.4(2)
N1	Co1	Cl2	173.62(10)	N6	Co2	Cl4	178.42(11)	C10	N7	Co2	111.4(3)
N2	Co1	Cl2	96.68(11)	Cl3	Co2	Cl4	92.12(4)	N3	C4	C3	107.7(3)
N4	Co1	Cl1	89.10(11)	C6	N4	Co1	112.9(2)	N7	C10	C9	109.1(3)
N3	Co1	Cl1	176.57(11)	C4	N3	Co1	110.9(3)	N4	C6	C5	109.5(3)
N1	Co1	Cl1	94.17(10)	C12	N8	Co2	110.9(2)	N8	C12	C11	109.2(3)
N2	Co1	Cl1	87.13(11)	C5	N1	C1	110.7(3)	N1	C1	C2	109.2(3)
Cl2	Co1	Cl1	91.24(4)	C5	N1	C3	108.6(3)	N5	C11	C12	109.3(3)
N5	Co2	N8	87.42(13)	C1	N1	C3	112.8(3)	C7	C8	N5	110.9(3)
N5	Co2	N7	86.75(14)	C5	N1	Co1	108.1(2)	N5	C9	C10	108.5(3)
N8	Co2	N7	172.22(15)	C1	N1	Co1	108.0(2)	N1	C5	C6	108.1(3)
N5	Co2	N6	86.37(14)	C3	N1	Co1	108.5(2)	N6	C7	C8	107.1(3)
N8	Co2	N6	90.34(15)	C7	N6	Co2	110.8(3)	N1	C3	C4	110.8(3)

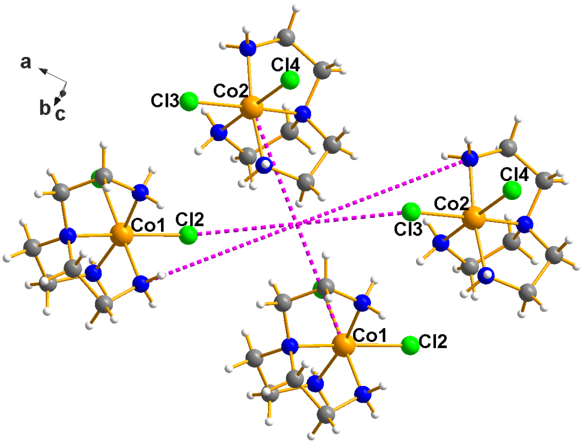

Figure 2. Center of mass is at the intersection of the dotted lines. The center of mass is located at 0.2453, 0.2416, 0.2333.

The bond lengths, bond angles, and hydrogen bonding values are summarized in Tables 2-4. Figures were drawn using the graphics program DIAMOND [15]. In this article, six-letter acronyms used by CSD [16], such as IKERUL, are provided for the convenience of the interested reader who wishes to further examine the data provided here. Thus, access to the CSD entry will be automatic.

3. Results and discussion

A view of the contents of the asymmetric unit in *cis*-[Co^{III}(tren)Cl_2]Cl·H_2O is given in Figure 1. Figure 2 depicts the packing of two pairs of the cations alone. Their center of mass is located at 0.2453, 0.2416, 0.2233 (see further, Figure 3). Note that in the polar space group, $P2_1$, the *y*-coordinate of the origin is arbitrary, and must be fixed.

The fact that there is a *pseudo-inversion center* relating the cations does not limit that relationship to them alone. The entire unit cell, depicted in Figure 3, also demonstrates that such a relationship exists for the overall contents of the lattice. In fact, the lattice, as a whole, is closer to a true inversion center of a higher symmetry supergroup. Note in that regard that the Flack parameter (Table 1) assures that the space group belongs in the Sohncke class.

Using an overlay technique, Figure 4 illustrates the stereochemical difference(s) between the cations present in an overlay of the cations in *cis*-[Co^{III}(tren)Cl_2]Cl·H_2O. For comparison, Figure 5 depicts a comparable overlay for the cations in IKERUL02, which was one of the earliest kryptoracemates described [1,2].

Inasmuch as it is difficult to observe differences in superimposed 3D objects when depicted in 2D, we illustrate their difference by the torsional angles of their respective Tren ligands in Table 5.

While there is a very close racemic relationship between the first two sets, the last pair is very far from that, given that there is no inversion of sign. Thus, effectively, they differ from being a racemic pair by 77.86°.

Table 4. H-bonding interactions in *cis*-[Co^{III}(tren)Cl$_2$]Cl·H$_2$O.

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	∠ D-H···A (°)
N4-H6···O2^{i}	0.83(4)	2.17(5)	2.977(5)	163(4)
N4-H5···Cl3	0.92(5)	2.42(4)	3.263(3)	152(4)
N3-H4···Cl6^{ii}	1.00(4)	2.40(4)	3.307(3)	150(3)
N3-H3···O2^{i}	0.83(4)	2.12(5)	2.901(5)	156(4)
N8-H12···Cl6^{iii}	0.92(4)	2.54(4)	3.380(3)	154(3)
N8-H11···Cl2	0.88(4)	2.56(4)	3.413(3)	165(4)
N6-H8···Cl2	0.87(4)	2.70(4)	3.426(4)	143(4)
N6-H7···Cl5^{ii}	1.00(4)	2.24(4)	3.231(4)	169(3)
N2-H2···Cl1	0.83(4)	2.54(4)	2.938(4)	110(3)
N2-H1···Cl6^{ii}	0.86(4)	2.40(4)	3.244(4)	170(4)
N7-H10···Cl5^{ii}	0.76(4)	2.61(5)	3.302(4)	153(4)
N7-H9···O1^{ii}	0.96(4)	2.38(4)	3.223(6)	146(3)
O1-H13···Cl1	0.93(7)	2.24(7)	3.164(3)	175(6)
O1-H14···Cl5^{ii}	1.01(6)	2.42(7)	3.401(4)	164(5)
O2-H15···Cl5^{ii}	0.77(5)	2.40(5)	3.160(3)	167(5)
O2-H16···Cl6^{iv}	0.77(5)	2.33(5)	3.088(3)	172(5)

Symmetry codes: *i* = *x*, *y*, *z*+1; *ii* = -*x*+1, *y*-1/2, -*z*+1; *iii* = *x*-1, *y*, *z*+1; *iv* = *x*-1, *y*, *z*.

Table 5. Torsional angles of tren observed for cations 1 and 2.

Atoms	Angle (°)	Atoms	Angle (°)
N1-C1-C2-N2	-41.28	N5-C8-C7-N6	41.28
N1-C3-C4-N3	41.43	N5-C11-C12-N8	-40.10
N1-C5-C6-N4	38.30	N5-C9-C10-N7	39.56

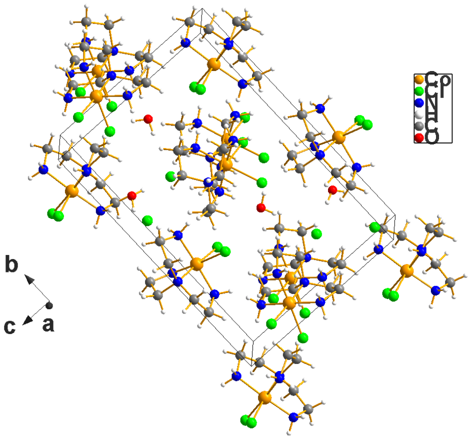

Figure 3. Packing diagram of the unit cell for *cis*-[Co^{III}(tren)Cl$_2$]Cl·H$_2$O. The center of mass located at 0.5028, 0.4915, 0.5072 is a *pseudo-inversion* center which is remarkably close to ½, ½, ½. Dotted lines have been omitted to avoid cluttering. This diagram displays the characteristic kryptoracemic packing described previously [1-5]; *e.g.*, the center of mass is expected to be near a special position of a centrosymmetric supergroup.

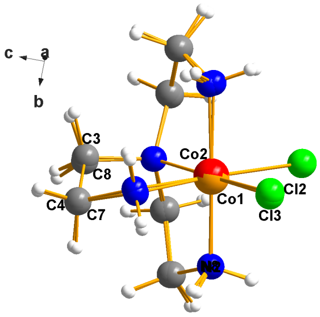

Figure 4. Overlay of cation 2 onto cation 1. The differences appear tiny and it is difficult to separate the images of chemically related atoms, except for some of the hydrogen atoms.

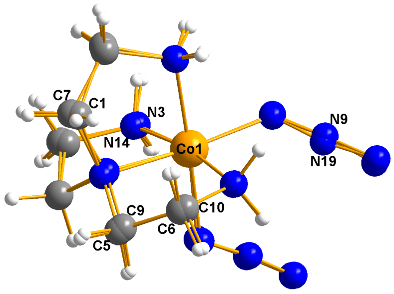

Figure 5. The stereochemical differences between the cations present in IKERUL02, which was one of the earliest kryptoracemates described [2].

4. Conclusions

We began with the premise that experimentally observed examples of interesting modes of crystallization of a given substance may be used as clues for which other related species may crystallize likewise [8]; and having the example of IKERUL02 [2] as a guide, we tested that premise with *cis*-[Co^{III}(tren)Cl$_2$]Cl·H$_2$O. It is encouraging that both are krypto-racemates, as attested by the Flack parameter test, see Table 1. How far this concept may be extended can only be ascertained by experiments, which we are currently examining with the tren derivatives of 3d metals, using variations of the mono-dentate ligands at the fifth and sixth positions, as well as variations of the charge-compensating anions.

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Supporting information

CCDC-1978094 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

Disclosure statement

Conflict of interest: The authors have declared that no competing interests exist.
Author contributions: Mina Mikhael, Mary Hanna, and Evana Halaka are undergraduate students who prepared the complexes under the direct supervision of Roger Lalancette. Ivan Bernal and Roger Lalancette wrote the manuscript.
Ethical approval: All ethical guidelines have been adhered.
Sample availability: Samples of the compounds are available from the author.

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