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The Structures and Conformations of the Mixed Ethylenediamine 1,3-Propanediamine Complexes [Cr(en)$_2$(tn)]Br$_3$·H$_2$O and [Cr(en)(tn)$_2$]I$_3$·H$_2$O

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The crystal and molecular structures are reported for the two mixed diamine complexes [Cr(en)$_2$(tn)]Br$_3$·H$_2$O (**I**) *and [Cr(en)(tn)$_2$]I$_3$·H$_2$O* (**II**) *(en = ethylenediamine, tn = 1,3-propanediamine). Single crystal X-ray diffraction data were collected by automated counter techniques using θ–2θ scans. The intensity data were corrected for absorption and both structures refined by full-matrix least-squares methods. The number of independent reflection (and final weighted agreement factor) were 1847 (5.1%) and 2292 (5.05%) for* **I** *and* **II**, *respectively. Both salts crystallize in space group Pbca (D_{2h}^{15}) with similar structures. Unit cell constants are* a *= 11.571(3), 11.823(6);* b *= 13.152(3), 14.183(7); and* c *= 22.994(5), 24.023(9) Å for* **I** *and* **II**, *respectively. Both the cations of* **I** *and* **II** *have only C_1 point symmetry, although the coordination environment defines a pseudo-threefold axis. The [Cr(en)$_2$(tn)]$^{3+}$ cation in* **I** *exists in the Λδλa conformation (and its mirror image). In this conformation one of the five-membered Cr–en rings has its C–C bond parallel to the pseudo-threefold axis (δ) and the other ring is oblique to that axis (λ). The six-membered Cr–tn ring is in a chair conformation. The inner coordination geometry Cr–N bond lengths are equal within experimental error and average 2.073(4) Å. The Cr–en interior N–Cr–N bond angles average 82.9(2)° while the corresponding Cr–tn bond angle of 90.8(3)° is near that of an octahedron. The [Cr(en)(tn)$_2$]$^{3+}$ cation in* **II** *exists in the Λaaδ conformation (and its mirror image). In this conformation the five-membered Cr–en ring has its C–C bond parallel to the coordination pseudo-threefold axis (δ) and the six-membered Cr–tn rings are both in chair conformations. The inner coordination geometry has Cr–N bond lengths which are equal within experimental error and average 2.060(6) Å. The Cr–en interior N–Cr–N angle is 84.2(4)° while the corresponding Cr–tn angles average 88.6(9)°.*

Introduction

The effect of conformation on the optical activity of the d–d transitions of Co^{3+} and Cr^{3+} complexes has been the subject of active research dealing with structure-optical activity correlations. An interesting phenomenon in this area is the "ring size" effect. In the series [M(en)$_{3-n}$(tn)$_n$]$^{3+}$ (en = ethylenediamine, tn = 1,3-diaminopropane), the rotatory strength of the lowest energy d–d transition decreases with increasing n [1–4]. The same phenomenon is observed for [M(AA)$_2$(BB)]$^+$ where AA = en or chxn (chxn = *trans*-1,2-diaminocyclohexane) and BB = carbonate, oxalate and malonate [5]. These experimental investigations have correlated the decrease of the rotatory strength with the effective L–M–L angle expansion due to the increased ligand "bite" in the series. In addition, the tris chelates have provided a fertile testing ground for various models and computer programs for conformational energy calculations [6]. In order to determine the structures of the simplest of the mixed diamine chromium(III) complexes, we have prepared and structurally characterized the compounds [Cr(en)$_2$(tn)]Br$_3$·H$_2$O (Compound **I**) and [Cr(en)(tn)$_2$]I$_3$·H$_2$O (Compound **II**).

Experimental

[Cr(en)$_2$(tn)]Cl

Anhydrous [Cr(en)$_2$Cl$_2$]Cl was prepared by the thermal decomposition of [Cr(en)$_3$]Cl$_3$ under controlled conditions [7]. The product so obtained is generally a mixture of both the purple *cis* dichloro- and the green *trans* dichloro isomers which total to 90% yield (based on weight loss). The *cis* dichloro salt may be obtained by recrystallization of the mixture from cold, concentrated HCl; however, it was found that the subsequent reaction converted both isomers to the desired product.

The same procedure described in the synthesis of [Cr(tn)$_3$]Cl$_3$ [8] was used for [Cr(en)$_2$(tn)]Cl$_3$:

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9.7 g of dried [Cr(en)$_2$Cl$_2$] Cl (32 mmol) was placed in a 250 ml round bottom flask and covered with anhydrous ether. Five ml of dry tn (60 mmol) was diluted in 50 ml of anhydrous ether. The tn was previously distilled over sodium wire to eliminate water (a catalytic poison). The diluted amine was then added to the [Cr(en)$_2$Cl$_2$] Cl– ether slurry and the flask fitted with a water condenser. The temperature was adjusted so that the ether slowly distilled off, and after 12 hours the temperature was raised to boil off the remaining amine. The reaction was allowed to continue at the elevated temperature until signs of charring occurred. The crude reddish–yellow product was dissolved in 30 ml of 6*M* HCl at 40 °C and filtered through a sintered glass funnel. Upon cooling to 0 °C, the filtrate yielded a fine yellow powder corresponding to the luteo salt in 40% overall yield. A second fraction can be obtained by the addition of 50 ml of methanol to the filtrate, which gives a total yield of 50–60%. The product is extremely soluble in water and can be recrystallized from a methanol–water mixture (1:3) to give fine yellow needles with an average of 2.68 waters of hydration (determined by weight loss under vacuum). The extremely soluble chloride salts of these complexes do not form crystals of good diffraction quality. *Anal.* Calcd for $C_7H_{26}N_6Cl_3Cr$: C, 23.84%; H, 7.43%; N, 23.83%; Cl, 30.16%. Found: C, 23.52%; H, 7.59%; N, 23.61%; Cl, 30.00%.

[Cr(en)$_2$(tn)]Br$_3$·H$_2$O

The less soluble bromide salt is readily obtained from a solution of the chloride by the addition of excess KBr to give well-formed yellow plates in quantitative yield. *Anal.* Calcd for $C_7H_{26}N_6Br_3Cr \cdot H_2O$: C, 16.68%; H, 5.60%; N, 16.67%. Found: C, 16.62%; H, 5.60%; N, 16.67%.

[Cr(en)(tn)$_2$] Cl

Anhydrous [Cr(tn)$_2$Cl$_2$] Cl was prepared by a modification of the reported synthesis of [Cr(en)$_2$Cl$_2$] Cl [7]. Thoroughly dried [Cr(tn)$_3$] Cl$_3$ was weighed and spread thinly onto an evaporating dish. The compound was heated in an oven at 175 °C. After two hours, the yellow luteo-salt lost one diamine and a mixture of the *cis*- and *trans*-dichloro isomers was obtained corresponding to 85% of the expected weight loss. If the *tris*-diamine chelate salt is first recrystallized from a 1% NH_4Cl aqueous solution, the thermal decomposition occurs at a temperature approximately 20 °C lower and the elimination of one ligand is much harder to control. The product was used directly after washing with ice-cold concentrated HCl and drying under vacuum. The yield of the purified product is 70%.

In a manner analogous to the preparation of [Cr(en)$_2$(tn)] Cl$_3$, the corresponding [Cr(en)(tn)$_2$] Cl$_3$ complex was obtained; the only difference is that a stoichiometric amount of dried ethylenediamine must be used, since the replacement of tn by en is much more facile than the reverse reaction. The product yield is 50–60%. If the reactants are not dry, the reaction takes place more slowly and results in much lower yields (30%). *Anal.* Calcd for $C_8H_{28}N_6Cl_3Cr$: C, 26.20%; H, 7.70%; N, 22.92%; Cl, 29.00%. Found: C, 25.90%; H, 8.00%; N, 22.90%; Cl, 29.10%.

[Cr(en)(tn)$_2$]I$_3$·H$_2$O

The less soluble iodide salt is obtained upon addition of excess KI and was found to be of better quality than the bromide. *Anal.* Calcd for $C_8H_{28}N_6I_3Cr \cdot H_2O$: C, 14.57%; H, 4.56%; N, 12.75%; I. 57.79%; Cr, 7.89%; H_2O, 2.72%. Found: C, 14.85%; H, 4.64%; N, 12.81%; I. 57.88%; Cr, 7.75%; H_2O, 3.0% (weight loss under vacuum).

X-Ray Diffraction Analyses

[Cr(en)$_2$(tn)] Br$_3$·H$_2$O Cell Data

The air- and water-stable crystals were mounted on glass fibers. Precession photographs (MoKα radiation, Zr filtered) showed mmm symmetry and the systematic absences: 0kl, k ≠ 2n; h0l, l ≠ 2n; and hk0, h ≠ 2n. These are consistent only with the space group Pbca (D_{2h}^{15}) [9]. The data crystal was highly regular; the bounding planes were easily identified as the (0 0 1), (1 1 2), ($\bar{1}$ $\bar{1}$ 2), ($\bar{1}$ 1 2) and the (1 $\bar{1}$ 2). An examination of the mosaicity along the crystallographic axes showed omega scan widths at half height of 0.04°, 0.04° and 0.06° for the (6 0 0), (0 6 0) and the (0 0 6) reflections, respectively. The unit cell parameters and crystal orientation were determined by a least squares fit to 18 carefully centered reflections whose Bragg 2θ angles were between 18 and 52°. The crystal data are summarized in Table I.

[Cr(en)(tn)$_2$] I$_3$·H$_2$O Cell Data

Precession photographs identified the space group as Pbca (D_{2h}^{15}) [9]. The mosaicities of 50 crystals were examined; the omega scan widths at half height ranged from 0.2° to 3° along *c* and from 0.1° to 2° for the other axes. The crystal chosen had mosaicities of 0.07°, 0.11° and 0.17° along the *a, b* and *c* directions, respectively. The crystals were thin diamond plates of irregular habit. The diffraction intensities observed diminished rapidly at high 2θ angles and so the fourteen reflections used to determine the cell constants and orientation matrix were limited to Bragg 2θ angles between 13.5 and 38°. The crystal data are summarized in Table I.

Data Collection

The data for both compounds were collected on an automatic Picker four-circle diffractometer using

TABLE I. Crystal and Experimental Data.

Compound	$[Cr(en)_2(tn)Br_3 \cdot H_2O$	$[Cr(en)(tn)_2]I_3 \cdot H_2O$
Space group	Pbca	Pbca
Formula/unit cell	8	8
Density, observed	1.88	2.11 g cm^{-3}
Density, calculated	1.92	2.16 g cm^{-3}
Absorption coefficient (MoKα)	77.3	49.8 cm^{-1}
Cell parameters, λ = 0.70926 Å		
a	11.571(3)	11.823(6) Å
b	13.152(3)	14.183(7) Å
c	22.994(5)	24.023(9) Å
Maximum crystal dimensions		
along *a*	.21	.41 mm
b	.23	.16 mm
c	.10	.25 mm
Base width for scans	0.75	1.20 deg
Take-off angle	2.0	3.0 deg
Scan rate	1.0	2.0 deg min^{-1}
Background count	10.0	4.0 sec
Reflections collected (total)	7579	11350
Independent reflections with $F^2 > 3\sigma(F^2)$	1847	2292
Ignorance factor, p	0.04	0.06

graphite monochromatized MoKα radiation as described previously [10].

$[Cr(en)_2(tn)]Br_3 \cdot H_2O$

The crystal was mounted so that no symmetry axis was parallel to the spindle axis in order to minimize multiple diffraction effects [13]. The data were processed as previously reported [10, 11]. The crystal showed less than 0.1% decay in any of the monitored standards. An absorption correction was applied which corrected the intensities for a transmission factor range of 0.29 to 0.67 [12].

$[Cr(en)(tn)_2]I_3 \cdot H_2O$

The crystal showed less than 1% decay in any of the monitored standard reflections during data collection. An absorption correction was applied to the intensities, for a transmission factor range of 0.28 to 0.49 [12]. Since the crystal was irregularly shaped the bounding planes were difficult to identify, but after the absorption correction the symmetry equivalent reflections were averaged [13] to give a resultant R factor of 3.3% and an rms Δ/σ in equivalent reflections of 1.03. These parameters indicate that the model chosen adequately describes the crystal shape.

Solution and Refinement

$[Cr(en)_2(tn)]Br_3 \cdot H_2O$

Direct methods [14] were used to locate the heavy atoms. The remaining structure analysis employed standard Fourier and full-matrix least-squares refinement techniques. The atomic scattering factors for Cr, C, N and O were calculated from the values of Cromer and Mann [15]. Those of neutral hydrogen were of Stewart *et al.* [16]. Anomalous scattering factors for Cr and Br were also included [17]. The hydrogen atom positions for the chelate rings were calculated, assuming a tetrahedral disposition about the N and C with both N–H and C–H bond lengths equal to 1.0 Å. These were included before the final least squares refinements. The final least squares cycle allowed all the non-hydrogen atomic thermal parameters to vary anisotropically and used all 1847 independent reflections with $F^2 > 3\sigma(F^2)$. The final agreement factors are $R_1 = 5.90\%$, $R_2 = 4.82\%$ and the error in an observation of unit weight is 1.41 [18]. A final difference Fourier showed no peak greater than 25% of the height for a carbon atom in the structure. Final observed and calculated structure factor amplitudes may be obtained by applying to the Editor. The final values of the positional and thermal parameters are given in Table II [19].

$[Cr(en)(tn)_2]I_3 \cdot H_2O$

The structure was solved by standard heavy atom methods. The general structure is very similar to that of **I** and the fractional coordinates for all but the ring carbon and water oxygen atoms are near those found in **I**. The hydrogen atom positions for the chelate rings were calculated and included for the last least squares refinement where all non-hydrogen atomic

TABLE II. Positional and Thermal Parameters for $[Cr(en)_2(tn)]Br_3 \cdot H_2O$.[a]

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br_1	17373(8)	12562(7)	21453(4)	461(8)	325(6)	171(2)	−35(7)	36(4)	1(3)
Br_2	17798(11)	4094(8)	717(5)	1088(13)	586(8)	155(3)	61(9)	36(5)	122(4)
Br_3	37341(8)	31875(8)	32412(4)	530(8)	573(7)	125(2)	15(7)	14(4)	19(4)
Cr	47772(11)	32074(10)	14041(6)	300(11)	201(8)	65(3)	17(9)	3(5)	14(5)
N_1	3219(6)	3596(5)	1800(3)	46(6)	37(5)	9(2)	3(5)	−4(3)	−2(2)
N_2	4581(6)	1720(5)	1687(3)	38(6)	26(5)	14(2)	9(5)	−2(3)	1(2)
N_3	5722(5)	3519(5)	2153(3)	30(6)	30(5)	11(2)	2(4)	−2(3)	1(2)
N_4	3746(7)	3084(5)	675(3)	71(7)	43(5)	6(2)	4(5)	1(3)	1(2)
N_5	6252(6)	2819(5)	956(3)	54(7)	40(5)	10(2)	14(5)	5(3)	−4(2)
N_6	5088(6)	4733(5)	1231(3)	46(7)	22(5)	14(2)	7(5)	2(3)	5(2)
C_1	2283(7)	3713(7)	1352(4)	37(8)	45(6)	13(2)	10(7)	3(4)	5(3)
C_2	4882(9)	887(7)	1284(5)	65(11)	30(6)	22(3)	−1(7)	3(4)	−4(3)
C_3	5886(8)	4648(7)	2204(5)	44(9)	35(6)	19(3)	7(6)	−2(4)	−5(3)
C_4	2516(9)	2952(7)	863(4)	85(10)	49(8)	7(2)	−11(8)	−17(4)	7(3)
C_5	6365(8)	1792(8)	693(4)	68(9)	57(8)	15(3)	3(7)	5(4)	−6(4)
C_6	6048(8)	5090(7)	1614(5)	47(9)	25(6)	22(3)	−4(6)	7(4)	−2(3)
C_T	6096(9)	960(8)	1106(5)	62(10)	48(8)	23(3)	23(8)	2(5)	2(3)
H_2O	4219(9)	3388(8)	4690(4)	154(14)	248(13)	38(3)	−36(10)	−16(6)	45(5)

[a] Positional parameters, thermal parameters and deviations from Br and Cr are multiplied by 10^5, for other atoms by 10^4.

TABLE III. Positional and Thermal Parameters for $[Cr(en)(tn)_2]I_3 \cdot H_2O$.[a]

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
I_1	17420(7)	11139(6)	21768(4)	618(7)	446(5)	253(2)	7(5)	103(3)	−3(3)
I_2	20505(10)	6580(8)	1049(5)	1608(14)	749(7)	220(2)	59(8)	−47(4)	21(3)
I_3	38319(7)	30624(7)	32745(4)	462(6)	684(6)	189(2)	45(5)	3(3)	13(3)
Cr	47569(14)	29872(13)	13773(7)	326(12)	414(3)	114(3)	29(10)	−9(5)	−14(5)
N_1	3311(8)	3444(8)	1792(4)	52(7)	76(8)	14(2)	29(7)	2(3)	−2(3)
N_2	4602(8)	1657(6)	1723(4)	55(9)	35(5)	22(2)	−7(6)	−3(4)	−1(3)
N_3	5764(7)	3388(6)	2050(4)	45(7)	38(5)	15(2)	8(5)	−4(3)	−1(3)
N_4	3726(11)	2643(10)	718(5)	88(12)	96(11)	19(3)	−4(10)	−8(4)	4(4)
N_5	6188(8)	2535(7)	939(4)	71(9)	40(6)	18(2)	12(6)	14(4)	5(3)
N_6	5050(9)	4367(8)	1105(5)	44(8)	62(7)	46(4)	−7(7)	6(5)	20(5)
C_1	2351(11)	3754(11)	1464(6)	55(11)	76(11)	22(3)	29(9)	−17(5)	−11(5)
C_{14}	2087(18)	3234(17)	1001(9)	142(23)	122(18)	37(6)	−39(16)	4(9)	9(8)
C_4	2795(22)	3116(15)	607(11)	179(29)	95(14)	50(8)	13(17)	−43(12)	−8(9)
C_2	4822(15)	805(11)	1378(7)	122(16)	53(11)	29(4)	−33(10)	2(7)	7(5)
C_{25}	5972(19)	815(11)	1135(7)	204(27)	50(10)	29(5)	4(13)	18(9)	−7(5)
C_5	6264(14)	1557(11)	722(6)	140(18)	67(10)	25(3)	13(11)	29(6)	2(5)
C_3	5921(11)	4427(9)	2089(6)	71(11)	52(8)	21(3)	3(8)	−3(5)	−7(4)
C_6	6030(16)	4824(11)	1508(7)	152(20)	66(10)	36(4)	−5(12)	40(8)	1(5)
H_2O	4685(13)	2218(11)	4626(5)	200(18)	222(16)	28(3)	24(14)	5(6)	15(6)

[a] Positional parameters, thermal parameters and deviations are multiplied by 10^5 for I and Cr and by 10^4 for other atoms.

thermal parameters were allowed to refine anisotropically. The final agreement factors are R_1 = 5.05%, R_2 = 6.35% and the error in an observation of unit weight is 1.48 [18]. A final difference Fourier showed no peak larger than 25% of the height for a carbon atom in the structure. The final values of the positional and thermal parameters are given in Tables III and IV [19].

Description of the Structures

$[Cr(en)_2(tn)]Br_3 \cdot H_2O$

The strucure consists of discrete $[Cr(en)_2(tn)]^{3+}$ cations, bromide anions and water molecules. All atoms are in the general position 8(c) in Pbca. There is an extensive hydrogen bonding network involving the amine hydrogens and bromide anions (Table IV).

TABLE IV. Possible Hydrogen Bonds A—H···B with A—B Less than ~4 A.

$[Cr(en)_2(tn)]Br_3\cdot H_2O$				$[Cr(en)(tn)_2]I_3\cdot H_2O$			
A	B	Length (A)	Symmetry Operation Applied to B[a]	A	B	Length (A)	Symmetry Operation Applied to B[a]
N_1	Br_1	3.614(11)	1	N_1	I_1	3.887(12)	1
	Br_1	3.590(11)	2*		I_1	3.912(12)	4
	Br_3	3.421(9)	1		I_3	3.653(10)	1
N_2	Br_1	3.495(9)	1	N_2	I_1	3.629(10)	1
	Br_1	3.717(10)	4*		I_1	3.753(10)	3*
N_3	Br_1	3.596(8)	4*	N_3	I_1	3.894(9)	3*
	Br_3	3.420(9)	1		I_3	3.737(9)	3*
	Br_3	3.641(9)	4*		I_3	3.755(10)	1
N_4	Br_2	3.440(11)	2*	N_4	I_2	3.731(12)	1
	H_2O	3.043(16)	6		H_2O	2.877(18)	8
N_5	Br_3	3.383(10)	5	N_5	I_2	3.736(10)	7
	Br_3	3.435(10)	4*		I_3	3.731(11)	3
	H_2O	3.815(18)	4				
				N_6	I_2	3.747(11)	7
N_6	Br_1	3.576(10)	2*		I_2	3.900(11)	4
	Br_2	3.598(10)	5				
	Br_2	3.555(9)	5*				
H_2O	Br_2	3.353(18)	3*				
	Br_3	3.387(18)	1				

[a] Numbers denote the followihg symmetry operations:

1. x, y, z	5. 1/2 + x, 1/2 − y, −1 − z
2. 1/2 + x, 1/2 − y, z	6. x, 1/2 − y, −1/2 + z
3. $\bar{x}$, 1/2 + y, 1/2 − z	7. 1/2 − x, −1 − y, 1/2 + z
4. 1/2 x, y, 1/2 + z	8. 1/2 + x, −1/2 − y, $\bar{z}$

*Indicates inversion on the fractional coordinates, x, y and z of symmetry operation n [*e.g.* (1/2 + x)* = (1/2 − x)].

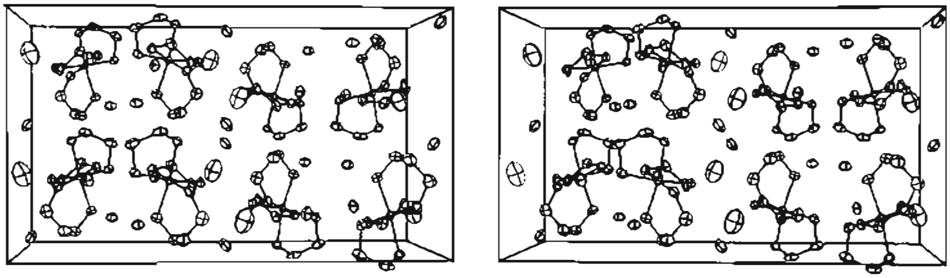

Figure 1. A stereo packing diagram of one unit cell of $[Cr(en)_2(tn)]Br_3\cdot H_2O$. The horizontal axis is *c*, and the vertical axis is *b*.

The cation complex, $[Cr(en)_2(tn)]^{3+}$, is in the enantiomorphic Λδλa and Δλδa conformations (Figure 1) [20]. It sits in an environment of seven bromide anions and one water molecule. The configuration of these eight atoms about the chromium is that of a trigonally bicapped octahedron with a mean distance from the chromium of 4.7 Å. Other anions and water molecules are more than 1.1 Å further removed. The water molecule makes a close approach to the N_4 amine protons. This apparently stabilizes the λλ ring in this structure. The stabilization of energetically unfavored conformes by hydrogen bonding in crystals has been observed before and a model for the mechanism of this stabilization has been proposed [10, 21].

The six-membered tn ring is in a chair conformation (Figures 2 and 3). The observed bond lengths in this chelate ring are about three standard deviations from the normal C–C and C–N bond lengths (Table V). Similar deviations have been noticed in the crystal structure determinations of $(+)[Co(en)_2(tn)]Br_3$ [22] and (±) $[Cr(tn)_3][Ni(CN)_5]\cdot 2H_2O$ [23].

TABLE V. $[Cr(en)_2(tn)]Br_3 \cdot H_2O$ Bond Lengths and Angles.

Bond	Length (Å)	Group	Angle (°)
$Cr–N_1$	2.083(7)	$N_1–Cr–N_2$	90.0(3)
$Cr–N_2$	2.074(7)	$N_1–Cr–N_3$	92.5(3)
$Cr–N_2$	2.081(7)	$N_2–Cr–N_4$[a]	82.8(3)
$Cr–N_4$	2.065(7)	$N_1–Cr–N_5$	175.8(3)
$Cr–N_5$	2.058(7)	$N_1–Cr–N_6$	89.9(3)
$Cr–N_6$	2.077(6)	$N_2–Cr–N_3$	89.0(3)
$N_1–C_1$	1.503(10)	$N_2–Cr–N_4$	96.8(3)
$C_1–C_4$	1.529(12)	$N_2–Cr–N_5$[b]	90.8(3)
$C_4–N_4$	1.498(11)	$N_2–Cr–N_6$	172.0(3)
$N_2–C_2$	1.477(11)	$N_3–Cr–N_4$	172.5(3)
$C_2–C_T$	1.467(13)	$N_3–Cr–N_5$	91.6(3)
$C_T–C_5$	1.481(13)	$N_3–Cr–N_6$[a]	83.0(3)
$C_5–N_5$	1.485(11)	$N_4–Cr–N_5$	93.0(3)
$N_3–C_3$	1.501(10)	$N_4–Cr–N_6$	91.1(3)
$C_3–N_6$	1.488(13)	$N_5–Cr–N_6$	90.0(3)
$C_6–N_6$	1.494(11)	$Cr–N_1–C_1$	110.4(5)
		$N_1–C_1–C_4$	108.1(7)
		$C_1–C_4–N_4$	107.7(7)
		$C_4–N_4–Cr$	108.9(5)
		$Cr–N_2–C_2$	118.5(6)
		$N_2–C_2–C_T$	110.7(8)
		$C_2–C_T–C_5$	115.4(8)
		$C_T–C_5–N_5$	113.1(8)
		$C_5–N_5–Cr$	120.2(6)
		$Cr–N_3–C_3$	109.0(5)
		$N_3–C_3–C_6$	109.4(8)
		$C_3–C_6–N_6$	108.8(7)
		$C_6–N_6–Cr$	108.6(5)

Dihedral Angles for Chelate Rings

1. Crossing Angle of C–C Bond with N–N Axis (en ring)

Planes	Angle (°)
$C_1–Cr–C_4$	–26.8(3)
$N_1–Cr–N_4$	
$C_2–Cr–C_6$	27.1(3)
$N_3–Cr–N_6$	

2. Dihedral Angles for 6-membered Rings

Planes	Angle (°)
$C_2–C_T–C_5$	33.0(3)
$N_5–Cr–N_2$	
$Cr–N_2–C_2$	–14.6(3)
$C_T–C_5–N_5$	

Average Bond Lengths[c]

Cr–N	2.073(4) Å
C–N	1.493(4) Å

[a] Interior angle for Cren ring. [b] Interior angle for Crtn ring. [c] Mean values and standard deviations of the mean are computed by the formulas $\bar{x} = 1/n \sum_{i=1}^{n} x_i$ and $\sigma(\bar{x}) = \sqrt{\frac{\Sigma(x_i - \bar{x})^2}{n(n-1)}}$

TABLE VI. $[Cr(en)(tn)_2]I_3 \cdot H_2O$ Bond Lengths and Angles.

Bond	Length (Å)	Group	Angle (°)
$Cr–N_1$	2.080(9)	$N_1–Cr–N_2$	91.2(4)
$Cr–N_2$	2.064(9)	$N_1–Cr–N_3$	90.4(4)
$Cr–N_3$	2.085(9)	$N_1–Cr–N_4$[b]	87.7(5)
$Cr–N_4$	2.063(12)	$N_1–Cr–N_5$	178.6(4)
$Cr–N_5$	2.095(10)	$N_1–Cr–N_6$	89.3(5)
$Cr–N_6$	2.094(11)	$N_2–Cr–N_3$	89.4(4)
$N_1–C_1$	1.447(14)	$N_2–Cr–N_4$	91.6(5)
$C_1–C_{14}$	1.357(23)	$N_2–Cr–N_5$[b]	89.5(4)
$C_{14}–C_4$	1.276(26)	$N_2–Cr–N_6$	173.6(4)
$C_4–N_4$	1.304(23)	$N_3–Cr–N_4$	178.0(5)
$N_2–C_2$	1.471(17)	$N_3–Cr–N_5$	90.1(4)

(continued on facing page)

TABLE VI. *(continued)*

Bond	Length (A)	Group	Angle (°)
C_2–C_{25}	1.490(19)	N_3–Cr–N_6[a]	84.2(4)
C_{25}–C_5	1.490(23)	N_4–Cr–N_5	91.2(5)
C_5–N_5	1.458(16)	N_4–Cr–N_6	94.8(5)
N_3–C_3	1.486(16)	N_5–Cr–N_6	90.1(4)
C_3–C_6	1.514(20)	Cr–N_1–C_1	118.7(8)
C_6–N_6	1.652(20)	N_1–C_1–C_{14}	118.2(15)
		C_1–C_{14}–C_4	122.0(22)
		C_{14}–C_4–N_4	119.6(25)
		C_4–N_4–Cr	121.3(14)
		Cr–N_2–C_2	120.3(9)
		N_2–C_2–C_{25}	112.3(12)
		C_2–C_{25}–C_5	117.9(16)
		C_{25}–C_5–N_5	115.1(12)
		C_5–N_5–Cr	120.8(9)
		Cr–N_3–C_3	112.9(8)
		N_3–C_3–C_6	109.1(11)
		C_3–C_6–N_6	109.7(12)
		C_6N_6–Cr	107.2(8)

Dihedral Angles for Chelate Rings

1. Crossing Angle of C–C Bond with N–N Axis (en ring)

Plane	Angle (°)
C_3–Cr–C_6 N_3–Cr–N_6	24.0

2. Crossing Angle of C–C–C Plane with N–N Axis (tn ring)

Plane	Angle (°)
C_1–C_{14}–C_4 N_1–Cr–N_4	25.7
C_2–C_{25}–C_5 N_2–Cr–N_5	23.2

Average Bond Lengths

Cr–N	2.080(6) A
C–N	1.47(5) A

[a] Interior angle for Cren ring. [b] Interior angle for Crtn ring.

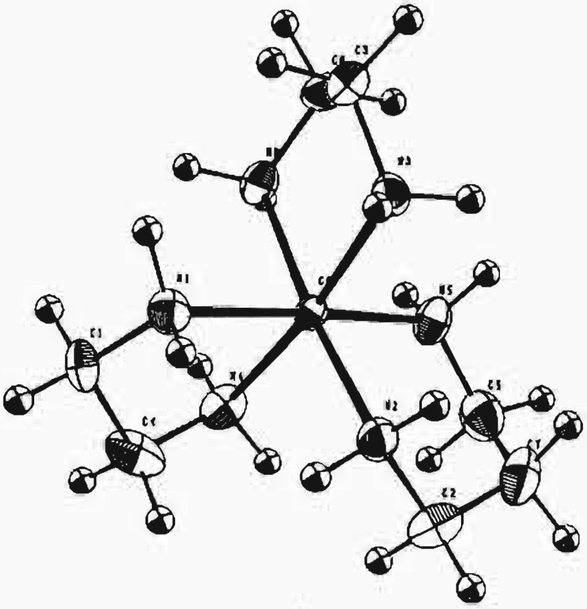

Figure 2. The $[Cr(en)_2(tn)]^{3+}$ ion (Λδλa conformation) viewed down the coordination pseudo threefold axis. The inversion operation produces the enantiomeric Δλδa conformer.

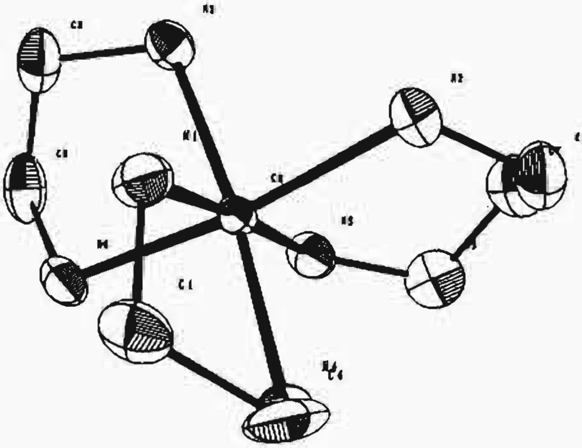

Figure 3. A side view of the $[Cr(en)_2(tn)]^{3+}$ complex which shows the relative orientations of the chelate rings.

These deviations may be artifacts of the thermal motion. The Cr–N bond lengths are all equal within experimental error and average 2.073(4) Å. The Cr–en interior N–Cr–N bond angles are compressed from octahedral geometry and average 82.9(2)° while the corresponding Cr–tn bond angle is 90.8(3)°.

The Λλ ring and the water molecule to which it hydrogen bonds have large rms amplitudes of displacement – the water molecule is not rigidly held in place. It is positioned such that it can hydrogen bond with both the amine protons of N_4 (Table IV). Since it cannot form simultaneous hydrogen bonds to both protons, it is disordered

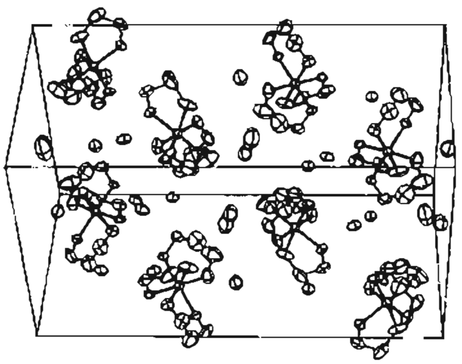

Figure 4. A stereo packing diagram of one unit cell of $[Cr(en)(tn)_2]I_3 \cdot H_2O$. The horizontal axis is c. The cell is rotated counterclockwise about the c axis such that the b axis is pointing out of the plane and the a axis points below the plane of projection.

between the two N_4 amine protons in the structure. This results in a dispersion of the water molecule electron density over an average displacement of 0.36 Å directed mostly along the principal axis of N_4.

$[Cr(en)(tn)_2]I_3 \cdot H_2O$

The structure consists of discrete $[Cr(en)(tn)_2]^{3+}$ cations, iodide anions and water molecules. All atoms occupy the general position 8(c) in Pbca. The packing is a complex network of hydrogen bonds which link the cations, water molecules and iodide anions (Table IV and Figure 4) and is approximately the same as that in $[Cr(en)_2(tn)]Br_3 \cdot H_2O$, although the details of hydrogen bonding and ring structures are very different. The cation is surrounded by a second coordination sphere of eight iodide anions and one water molecule in a low symmetry arrangement within an average Cr–X distance of 4.7 Å. The next possible coordination occurs at distances greater than 6.4 Å. The water molecule makes a very close approach (2.8 Å) to one of the tn amine nitrogens, N_4. The observed conformation in this structure is Λδaa and its enantiomorph Δλaa (Figures 5 and 6) [20]. Selected bond lengths and angles are in Table VI [24]. The crystal quality of II is low, as measured by the large ω scan widths. The high thermal motion of the central atoms of the chelate rings may be due to some partial, unresolved disorder in this structure, which could also explain the high mosaicity of the crystal. Because of this, the geometric parameters of the central atoms of the chelate rings are of lower precision than those of I. The inner coordination sphere shows all Cr–N bond lengths are equal within experimental error and average 2.080(6) Å. The Cr–en interior N–Cr–N angle is 84.2(4)° while the corresponding Cr–tn angles average 88.6(9)°.

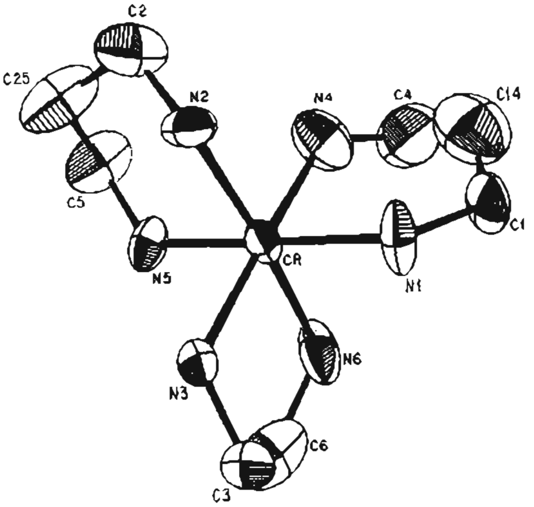

Figure 5. The $[Cr(en)(tn)_2]^{3+}$ ion (λaaδ conformation) viewed down the coordination pseudo three-fold axis. The inversion operation produces the enantiomeric Δaaλ conformer.

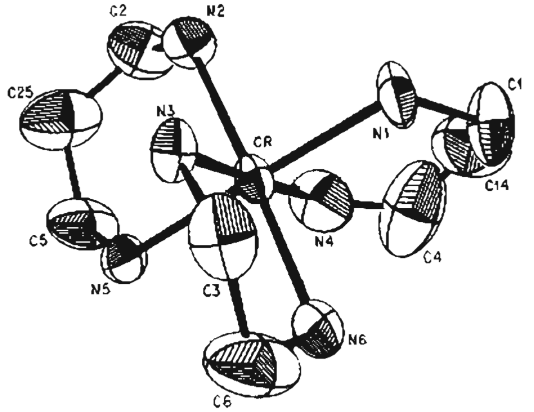

Figure 6. A side view of the $[Cr(en)(tn)_2]^{3+}$ cation complex.

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11 In addition to local programs for the CDC 6400 and 7600 computers, modifications of the following programs were employed: Ibers' NUCLS, a group least squares version of the Busing–Levy ORFLS program; Zalkin's FORDAP Fourier program; ORFFE, a function and error program by Busing, Martin and Levy; Johnson's ORTEP thermal ellipsoid plot program. Programs for the PDP8/I computer used in the automated diffractometer are those of Busing and Levy as modified by Picker Corp.

12 AGNOST, an absorption correction program by Coppens, Leiserowitz and Rabinovich as modified by Hamilton, Edmonds, Cahen and Ibers. The absorption correction was calculated by a Gaussian numerical integration with the crystal divided into grids.

13 EQUIV, a local modification of a program to average equivalent reflections originally written by Doedens and Ibers. The R factor for averaging is defined as

$$R_{av} = 100\frac{\sum_{i=1}^{Y}\sum_{j=1}^{Z}\langle F_i^2\rangle - F_{ij}^2}{\sum_{i=1}^{Y} Z\langle F_i^2\rangle}$$

where Y is the number of unique reflections observed more than once, Z is the number of times a unique reflection can be observed, taking into account its equivalent forms, and $\langle F_i^2\rangle$ is the average value of the intensity for a unique reflection i. The rms Δ/σ is the average value of the intensity for a unique reflection i. Ideally, this parameter is 1.

14 LSAM, a program package written by Main, Woolfson and Germain to phase centrosymmetric crystal structures. The solutions are based on the probability of assigning phases to the triple-product sign relationships [D. Sayre, *Acta Cryst.*, *5*, 60 (1952) and Woolfson, "Direct Methods in Crystallography", Oxford, 1961].

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18 $R_1 = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$, $R_2 = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, and the final error in an observation of unit weight is defined as $[\Sigma w(|F_o|-|F_c|)^2/N_o - N_v]^{1/2}$ where F_o and F_c are the observed and calculated structure factors and N_o and N_v are the number of observations and number of variables used in the least squares refinements.

19 Supplementary tabulated material is available in: E. N. Duesler, *Ph.D. Thesis*, University of California, Berkeley (1973).

20 The nomenclatrue used here is the IUPAC convention, *Inorg. Chem.*, *9*, 1 (1970). (a) The conformations Λδδδ and Δλλλ are enantiomorphous and so identical in energy. A Λ configuration about the metal ion is assumed when not specified. (b) To specifiy the optical isomer, the notation (+) and (−) are used, which signify the sign of the specific rotation, $[\alpha]_D$, at the sodium doublet, 589 nm. If the rotation was measured at a different energy, the wavelength (nm) is indicated in the subscript, *e.g.* $(+)_{745}$ $[M(en)_3]^{3+}$. Where necessary, racemic mixtures are denoted as (±), *e.g.* $(\pm)[M(\text{-pn})_3]^{3+}$; this specifies the unresolved complex mixture $(+)[M(\text{-pn})_3]^{3+}$ and $(-)[M(\text{-pn})_3]^{3+}$, where the ligand is optically active and rotates the plane of polarization negatively at the sodium doublet. For the notation used in describing the parallel (p) and antiparallel (a) chair conformation of the six-membered chelate rings see F. A. Jurnak and K. N. Raymond, *Inorg. Chem.*, *11*, 3149 (1972).

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24 For a more detailed discussion of the conformations of these compounds and speculations regarding their comparisons with related complexes see Ref. 19.