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Redetermination of the double salt Λ-[tris(ethylenediamine)cobalt(III) trichloride]–sodium chloride–water (2/1/6)

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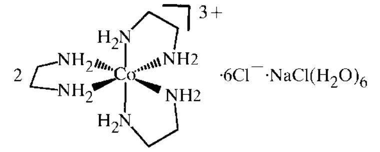
The structure of the title compound, $\{[Co(C_2H_8N_2)_3]Cl_3\}_2\cdot[Na(H_2O)_6]Cl$, has been redetermined to a higher degree of accuracy. The true space group is shown to be trigonal *P*3, but the structure is extremely close to hexagonal $P6_3$. Both of the independent Λ-$[Co(en)_3]Cl_3$ moieties (en is ethylenediamine) and the $[Na(H_2O)_6]Cl$ unit reside on sites of crystallographic threefold symmetry. The sodium and chloride ions share the same lattice positions and the whole $[Na(H_2O)_6]Cl$ unit is disordered over two positions in an approximate ratio of 0.73:0.27.

Comment

The complex cation $[Co(en)_3]^{3+}$ (en is ethylenediamine) has been of historic importance in the development of transition metal optical activity. The title complex, (I), was the first transition metal complex to have its absolute configuration determined by the anomalous scattering of X-rays (Saito *et al.*, 1954, 1955). The same compound was the first transition metal complex to have its electronic CD (circular dichroism) spectrum measured in both the solid state and in solution (Mathieu, 1953; McCaffery & Mason, 1963), and as such has been the complex of choice for testing the various theories of transition metal CD in the visible region (Mason & Seal, 1976; Ernst & Royer, 1993). The measurement of natural CD has recently been extended to the X-ray region (Alagna *et al.*, 1998) and the present redetermination was undertaken as a basis for *ab initio* and multiple scattering calculations of CD at the Co *K*-edge.

The crystal structure of (I) was first determined by Shiro and co-workers (Nakatsu *et al.*, 1957) from photographic data. On the basis of the observed 6/*m* Laue symmetry, the data were analysed in terms of a twinned structure in the hexagonal space group $P6_3$. However, these authors noted that the arrangement of the Na^+ and Cl^- ions, and the two independent water molecules was only consistent with the lower symmetry trigonal space group *P*3. Despite their clear statement in the summary that 'the space group is *P*3', the coordinates given in this paper and those deposited in the Cambridge Structural Database (refcode SAETCO; Allen & Kennard, 1993) refer to the hexagonal space group.



(I)

A distinction between the two space groups in terms of systematic absences can only be made from the intensities of the set of 00*l* reflections having *l* odd. These reflections are observed by us to be systematically weak, contributing *ca* 8.4% to the total 00*l* intensities, but are definitely present as Bragg reflections (see Table 2). The reflections $00\overline{3}$ and $00\overline{6}$ were monitored at several different azimuthal angles. They were found to have normal profiles and were not subject to the Renninger effect. Moreover, in concurrence with the earlier study (Nakatsu *et al.*, 1957), the $00\overline{3}$ reflection was found to be the strongest of these. The presence of these reflections in both the photographic (Nakatsu *et al.*, 1957) and diffractometric data precludes the possibility that they arise from scan overlap involving neighbouring strong reflections.

Although the Laue symmetry is very close to 6/*m* (R_{int} is 0.075 for 2473 observations of 629 independent data), the merging statistics are significantly better for the Laue symmetry $\overline{3}$ (R_{int} is 0.017 for 2218 observations of 915 independent data). Nevertheless, the overall crystal structure is very close to $P6_3$. The coordinates of the non-H atoms in cation 1 (x_1, y_1, z_1) are all nearly related to those in cation 2 (x_2, y_2, z_2) by the relationships $x_2 = \frac{1}{3} - x_1$, $y_2 = \frac{2}{3} - y_1$, $z_2 = \frac{1}{2} + z_1$, and all atoms are within 0.05 Å of the idealized $P6_3$ structure. The data may be satisfactorily refined in this space group (see supplementary material). Using the standard procedure of merging equivalent reflections (*SHELXL* instruction *MERG* 2), a final *R*(*F*) value of 0.0409 is obtained for 80 parameters and 719 independent data, suggesting this refinement is superior. However, the merging process forces the higher symmetry on the data and is slightly misleading. It is more illuminating to compare the refinements in both space

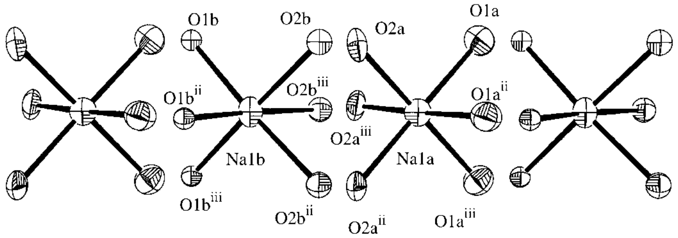


Figure 1
An *ORTEP*-3 (Farrugia, 1997) view of a section of the infinite chain comprising the $[Na(H_2O)_6]Cl$ unit (50% probability displacement ellipsoids). The Cl^- ions occupy the same lattice sites as the Na^+ ions, but only the Na^+ ions are labelled. [Symmetry codes: (ii) $-y, x - y, z$; (iii) $-x + y, -x, z$.]

groups without any data merging (*i.e.* treating all data as independent observations). The corresponding final $R(F)$ values are 0.0479 (space group $P3$, 130 parameters, 2484 data) and 0.0614 (space group $P6_3$, 80 parameters, 2478 data). This evidence, together with the $R_{\rm int}$ values, is strongly suggestive of the lower symmetry trigonal space group $P3$. Moreover, following the comment of Marsh (1995) that 'it is a solid tenet of crystallography that even a single violation of an extinction condition should be taken as proof that the symmetry is not present', we find that the strongest evidence in favour of space group $P3$ over $P6_3$ lies in the observed intensities of the $00l$ reflections for l odd (Table 2).

The asymmetric unit consists of two independent Λ-$[Co(en)_3]Cl_3$ moieties and an $[Na(H_2O)_6]Cl$ unit, all of which reside on sites of crystallographic threefold symmetry. As expected, the two independent $[Co(en)_3]^{3+}$ cations have very similar geometry (see Table 1). The Co—N distances within each molecule are significantly different from each other but are similar in the two independent molecules. In excess of 55 structural determinations on the $[Co(en)_3]^{3+}$ cation are found in the Cambridge Structural Database and the observed geometry in the title complex is unremarkable and merits no further comment. Each cation is associated with a Cl^- ion which shows no unusually short contacts to other atoms.

The $[Na(H_2O)_6]Cl$ unit effectively forms an infinite chain along the c axis (Fig. 1). A view of the unit cell contents is shown in Fig. 2. The problem of the unusual coordination geometry for the Na^+ and Cl^- ions which was discussed earlier (Nakatsu *et al.*, 1957) has been resolved with the observation of four partially occupied O-atom positions. The disordered O-atom positions are separated by *ca* 1 Å, allowing for anisotropic refinement of the more populated positions. The Na^+ and Cl^- ions occupy the same lattice positions in the structure and only the Na^+ ions are labelled in Fig. 1. Thus, the position indicated by Na1*A* is actually occupied by an Na^+ ion of occupancy 0.734 which is octahedrally coordinated by O atoms O1*A* and O2*A* at distances of 2.420 (12) and 2.488 (13) Å, respectively. This site is also occupied by a Cl^- ion (Cl3*B*) of occupancy 0.266, which is also coordinated octahedrally by the O1*B* and O2*B* atoms at distances of 3.19 (3) and 3.06 (3) Å, respectively. These latter Cl···O contact distances are suggestive of hydrogen bonding, but since the water H atoms could not be located directly, this conclusion is tentative. A similar situation pertains to the site labelled Na1*B*. In space group $P6_3$, there is only one independent Na/Cl lattice site and the Na^+ and Cl^- ions are thus required to be statistically (*i.e.* 50:50) disordered. This is the only significant difference arising between the two refinements.

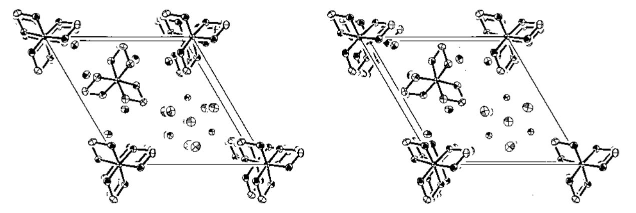


Figure 2
Unit-cell packing diagram of (I) viewed along the c axis (50% probability displacement ellipsoids).

Experimental

The Λ-enantiomer of the title complex was synthesized according to the method of Broomhead *et al.* (1960) and crystallized by evaporation from an aqueous solution.

Crystal data

$[Co(C_2H_8N_2)_3]_2Cl_6\cdot NaCl\cdot 6H_2O$
$M_r = 857.72$
Trigonal, $P3$
$a = 11.415\ (4)$ Å
$c = 8.0552\ (8)$ Å
$V = 909.0\ (5)$ Å^3
$Z = 1$
$D_x = 1.567$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 11.6$–$22.5°$
$\mu = 1.484$ mm^{-1}
$T = 293\ (2)$ K
Approximate trapezoid cleaved from larger crystal, orange–brown
0.7 × 0.6 × 0.4 mm

Data collection

Enraf–Nonius Turbo CAD-4 diffractometer
Non-profiled $\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\rm min} = 0.419$, $T_{\rm max} = 0.552$
2484 measured reflections
1180 independent reflections (plus 260 Friedel-related reflections)
1429 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.017$
$\theta_{\rm max} = 25.86°$
$h = -14 \rightarrow 12$
$k = -1 \rightarrow 14$
$l = -9 \rightarrow 1$
6 standard reflections every 118 reflections frequency: 120 min intensity decay: 26%

Refinement

Refinement on F^2
$R(F) = 0.047$
$wR(F^2) = 0.144$
$S = 1.198$
1440 reflections
130 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0620P)^2 + 3.2274P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.002$
$\Delta\rho_{\rm max} = 0.64$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.61$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.040 (5)
Absolute structure: Flack (1983)
Flack parameter = 0.07 (5)

A linear correction for crystal decomposition was applied. H atoms were placed in calculated positions (C—H = 0.96 Å) and refined with a riding model. The H atoms of the disordered water molecules could

Table 1
Selected geometric parameters (Å, °).

Co1—N12	1.938 (7)	C22—N22	1.498 (13)
Co1—N11	1.983 (7)	Na1*A*—O2*A*	2.420 (12)
C11—N11	1.487 (12)	Na1*A*—O1*A*	2.488 (13)
C11—C12	1.499 (14)	Na1*A*—Na1*B*	4.023 (10)
C12—N12	1.494 (12)	Na1*B*—O1*B*	2.41 (2)
Co2—N22	1.942 (8)	Na1*B*—O2*B*$^{\rm i}$	2.55 (3)
Co2—N21	1.965 (8)	O1*A*—O1*B*	1.03 (3)
C21—N21	1.454 (12)	O2*A*—O2*B*	0.90 (3)
C21—C22	1.538 (14)		
N12$^{\rm ii}$—Co1—N12	91.5 (3)	N22$^{\rm iv}$—Co2—N22	91.7 (3)
N12$^{\rm ii}$—Co1—N11	92.9 (3)	N22$^{\rm iv}$—Co2—N21	92.5 (3)
N12—Co1—N11	85.3 (3)	N22—Co2—N21	85.1 (3)
N12—Co1—N11$^{\rm iii}$	92.9 (3)	N21$^{\rm iv}$—Co2—N21	91.0 (3)

Symmetry codes: (i) $x, y, 1+z$; (ii) $-y, x-y, z$; (iii) $-x+y, -x, z$; (iv) $1-y, 1+x-y, z$.

Table 2
Observed and calculated intensities for the 00*l* reflections.

l	F^2(calc)	F^2(obs)	σ
−9	72.76	177.30	3.57
−8	2097.26	2106.88	14.15
−7	32.59	21.10	1.42
−6	1078.48	1091.35	8.24
−5	58.99	111.37	1.73
−4	1847.87	1652.23	7.03
−3	370.18	1176.73	4.99
−2	18204.96	19443.56	74.78
−1	18.84	44.08	0.56
1	18.78	50.40	0.59

not be observed and were omitted from the model. Calulations were carried out using the *WinGX* package (Farrugia, 1999).

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1992); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1996); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1333). Services for accessing these data are described at the back of the journal.

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