

## Neutron Diffraction Structure of $\text{Cs}_3\text{CoCl}_5$ at 4.2 K

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### Abstract

The crystal structure of  $\text{Cs}_3\text{CoCl}_5$  [tetragonal,  $I4/mcm$ ,  $a = 9.063$  (5),  $c = 14.45$  (1) Å,  $U = 1186.9$  Å<sup>3</sup>,  $Z = 4$ ] has been determined at 4.2 K by single-crystal neutron diffraction methods. The Co–Cl bond length in the  $[\text{CoCl}_4]^{2-}$  ion is 2.263 (1) Å and the Cl–Co–Cl angles of the distorted tetrahedral Co environment are 107.22 (4) and 110.61 (4)°. The neutron scattering lengths of Cs and Co were found, by least-squares refinement, to be 0.538 (3) and 0.243 (5)  $\times 10^{-14}$  m respectively.

### Introduction

The compound  $\text{Cs}_3\text{CoCl}_5$  contains the  $[\text{CoCl}_4]^{2-}$  anion as a tetragonally distorted tetrahedron. The crystals are tetragonal, and this high symmetry, together with the simple chemical composition, has motivated a number of studies of the physical properties of the compound. The crystal structure has been determined at room temperature with increasing accuracy by X-ray diffraction (Powell & Wells, 1935; Figgis, Gerloch & Mason, 1964*a*; Figgis, Reynolds & White, 1979), the magnetic susceptibility has been measured over a large temperature range (van Stapele, Beljers, Bongers & Zijlstra, 1966; Mess, Lagendijk, Curtis & Huiskamp, 1967), the magnetic anisotropy has been measured to low temperature (Figgis, Gerloch & Mason, 1964*b*), the heat capacity has been measured at low temperatures (Wielinga, Blöte, Roest & Huiskamp, 1967), the electron spin resonance has been studied at very low temperatures (Beljers, Bongers, van Stapele & Zijlstra, 1964; van Stapele, Beljers, Bongers & Zijlstra, 1966) and the optical and Raman spectra have been taken to very low temperatures (Bird, Cooke, Day & Orchard, 1974). The electronic structure of the  $[\text{CoCl}_4]^{2-}$  ion has been treated in depth theoretically

(Bird, Cooke, Day & Orchard, 1974; Hillier, Kendrick, Mabbs & Garner, 1976). We have in hand a program of further study of this compound, including the analysis of the polarized neutron diffraction data in terms of the spin-density distribution (Figgis, Mason, Smith & Williams, 1979) and further theoretical work. To assist the polarized neutron data treatment in particular, and in the other areas as well, we have established the structure at 4.2 K by neutron diffraction.

### Experimental

Two crystals of  $\text{Cs}_3\text{CoCl}_5$  were studied; crystal (I) had dimensions 3.64  $\times$  2.76  $\times$  2.23 mm, and crystal (II) 3.16  $\times$  3.04  $\times$  1.67 mm. Neutron diffraction intensity data were obtained at 4.2 K ( $\lambda = 1.175$  Å) on the D15 normal-beam diffractometer with a motorized lifting counter at the Institut Laue–Langevin, Grenoble. Crystal (I) was mounted with the [111] direction as the rotation axis; 60 unique reflections, after averaging intensities of equivalent reflections, were obtained in the range  $0.128 < \sin \theta/\lambda < 0.356$  Å<sup>-1</sup>. However, it was apparent that the [111] mounting was not ideal for obtaining an extensive data set on the normal-beam diffractometer, and so crystal (II) was mounted with its rotation axis offset by about 5° from the crystallographic  $a$  axis in order to minimize multiple-diffraction effects, and 353 unique observations, after averaging intensities of equivalent reflections, were obtained in the range  $0.069 < \sin \theta/\lambda < 0.740$  Å<sup>-1</sup>.

The space group was verified to be  $I4/mcm$  by confirming the systematic absences  $hkl$  for  $h + k + l$  odd, and  $0kl$  for  $l$  odd, on the diffractometer. The absence of any significant intensity for the systematically absent reflections indicated that multiple-diffraction effects were not serious, as also did the observation that the intensities of symmetry-related reflections were in

excellent agreement in all cases. The unit-cell parameters were derived by a least-squares analysis of the setting angles determined for seven angularly well separated reflections; standard deviations were estimated from the agreement between several such determinations. Intensities were measured *via* an  $\omega$  scan, which was found to be more appropriate than an  $\omega$ - $n\theta$  scan indicating that the mosaic spread of the crystal was dominant over the wavelength spread of the neutron beam. No significant variation in the intensity of a standard reflection was observed throughout the data collections. Integrated intensities were obtained using a profile-analysis program, *COLL5* (Lehmann & Wilson, 1977), and geometrical corrections were applied. An absorption correction was not considered necessary [Cs<sub>3</sub>CoCl<sub>5</sub>,  $\mu = 0.060 \text{ mm}^{-1}$  at 4.2 K,  $\lambda = 1.175 \text{ \AA}$  (*International Tables for X-ray Crystallography*, 1968)].

### Refinement

The data sets of 60 (crystal I) and 353 (crystal II) unique observations were treated separately, using the least-squares program *CRYLSQ* (Stewart, 1976) to refine the atomic coordinates, temperature factors, isotropic extinction coefficient and Cs and Co scattering lengths in the case of the larger data set. The starting parameters were obtained from the room-temperature structure of Cs<sub>3</sub>CoCl<sub>5</sub>. In the case of the larger data set, refinement, using unit weights and minimizing the function  $\sum w(\Delta F)^2$ , where  $w$  is the weight assigned to the  $|F_o|$  values and  $\Delta F = |F_o| - |F_c|$ , converged with  $R = \sum |\Delta F| / \sum |F_o| = 0.036$  (19

variables including scale, three positional and 13 anisotropic thermal parameters, and Co and Cs scattering lengths). A small secondary-extinction effect was evident from an examination of observed and calculated structure factors, and inclusion of an isotropic extinction coefficient in the refinement resulted in  $R = 0.024$ . The low-intensity reflections systematically appeared to have  $|F_o| > |F_c|$ , so a weighting scheme of the type  $w = (0.06 - 0.0184|F_o| + 0.0015|F_o|^2)^{-1}$  was employed to downweight them and also the very high-intensity reflections. This weighting scheme gave  $\sum w(\Delta F)^2/N_i \approx 1.0$  for the various ranges of the data containing  $N_i$  observations within particular  $|F_o|$  limits. Refinement (20 variables) then converged with  $R = 0.024$  and  $R_w = [\sum w(\Delta F)^2 / \sum w|F_o|^2]^{1/2} = 0.020$ . The maximum parameter shift-to-error ratio at convergence was 0.007:1, and a final difference synthesis was featureless. The extinction coefficient was refined to  $3.3(1) \times 10^2$  assuming an average transmission path length,  $t$ , of 3 mm. The neutron scattering lengths of Cs and Co were refined to  $0.538(3)$  and  $0.243(5) \times 10^{-14} \text{ m}$  respectively, with the scattering length of Cl fixed at  $0.958 \times 10^{-14} \text{ m}$  (*International Tables for X-ray Crystallography*, 1974).

In the case of the smaller data set (60 observations), refinement using isotropic temperature factors and the weighting scheme described above converged with  $R = 0.039$  and  $R_w = 0.033$  (10 variables including scale, isotropic extinction coefficient, three positional and five isotropic thermal parameters). The maximum parameter shift-to-error ratio at convergence was 0.04:1. The extinction coefficient was refined to  $3.5(4) \times 10^2$  assuming  $t = 3 \text{ mm}$ . The neutron scattering lengths

Table 1. Final atomic positional coordinates and thermal parameters for Cs<sub>3</sub>CoCl<sub>5</sub>

The first and second sets of values for each atom are from the refinements of crystal (I) and crystal (II) neutron data, respectively, at 4.2 K. The third set of values is from the 295 K X-ray refinement (Figgis, Reynolds & White, 1979).  $U$  tensors in  $\text{\AA}^2$ . Anisotropic and isotropic thermal parameters are defined by  $T = \exp[-2\pi^2(h^2 a^{*2} U_{11} + k^2 b^{*2} U_{22} + l^2 c^{*2} U_{33} + 2hka^* b^* U_{12} + 2hla^* c^* U_{13} + 2klb^* c^* U_{23})]$  and  $T = \exp[-8\pi^2 U_{11}(\sin^2 \theta)/\lambda^2]$ , respectively.

	$x$	$y$	$z$	$10^3 U_{11}$	$10^3 U_{22}$	$10^3 U_{33}$	$10^3 U_{12}$	$10^3 U_{13}$	$10^3 U_{23}$
Co	0	0.5	0.25	1.2 (58)					
	0	0.5	0.25	3.2 (9)	3.2 (9)	1.7 (10)	0	0	0
	0	0.5	0.25	29.9 (4)	29.9 (4)	24.5 (7)	0	0	0
Cs(1)	0	0	0.25	0.7 (33)					
	0	0	0.25	3.8 (4)	3.8 (4)	2.7 (4)	0	0	0
	0	0	0.25	45.0 (3)	45.0 (3)	41.1 (5)	0	0	0
Cs(2)	0.6623 (5)	1.1623 (5)	0	-0.3 (35)					
	0.66225 (7)	1.16225 (7)	0	2.5 (3)	2.5 (3)	2.2 (3)	0.5 (3)	0	0
	0.66574 (3)	1.16574 (3)	0	29.4 (2)	29.4 (2)	39.1 (3)	-1.4 (2)	0	0
Cl(1)	0	0	0	6.4 (24)					
	0	0	0	4.3 (2)	4.3 (2)	6.5 (2)	0	0	0
	0	0	0	32.0 (7)	32.0 (7)	52.1 (14)	0	0	0
Cl(2)	0.1421 (2)	0.6421 (2)	0.1570 (2)	2.8 (28)					
	0.14210 (3)	0.64210 (3)	0.15711 (2)	5.4 (1)	5.4 (1)	4.7 (1)	-1.1 (1)	0.8 (1)	0.8 (1)
	0.13963 (9)	0.63963 (9)	0.15753 (8)	46.1 (4)	46.1 (4)	42.0 (8)	-12.0 (5)	7.3 (4)	7.3 (4)
	0.14030 (9)†	0.64030 (9)†	0.15703 (8)†						

† 295 K atomic positional coordinates corrected for rigid-body libration effects by the TLS method of Schomaker & Trueblood (1968).

used for Co and Cl were the tabulated values (*International Tables for X-ray Crystallography*, 1974) while for Cs the value  $0.538 \times 10^{-14}$  m, found in the refinement described above, was used.

Final atomic positional coordinates and thermal parameters are listed in Table 1 for both refinements, together with the room-temperature values from X-ray studies (Figgis, Reynolds & White, 1979).\*

### Results and discussion

The unit-cell dimensions of  $\text{Cs}_3\text{CoCl}_5$  at 4.2 K, together with the bond lengths and angles in the  $[\text{CoCl}_4]^{2-}$  ion are presented in Table 2, along with the room-temperature X-ray values for comparison.

The crystal structure of  $\text{Cs}_3\text{CoCl}_5$  is shown in Fig. 1, and interatomic distances at 4.2 K less than 4 Å are given in Table 3. The main feature of the low-temperature structure compared to that at room

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34813 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Unit cell, bond lengths and angles in  $\text{Cs}_3\text{CoCl}_5$

	4.2 K		295 K	
	Crystal (I)	Crystal (II)	A	B
$a$ (Å)	—	9.063 (5)	9.2315 (15)	—
$c$ (Å)	—	14.45 (1)	14.5535 (24)	—
$U$ (Å <sup>3</sup> )	—	1186.9	1240.26	—
Co—Cl (Å)	2.264 (2)	2.263 (1)	2.266 (1)	2.277 (1)
Cl—Co—Cl (°)	107.13 (8)	107.22 (4)	107.13 (4)	107.09 (4)
	110.66 (6)	110.61 (4)	110.66 (3)	110.67 (3)

(A) Values taken from the X-ray study of Figgis, Reynolds & White (1979).  
(B) Bond length and angles of (A) corrected for rigid-body libration effects by the TLS method of Schomaker & Trueblood (1968).

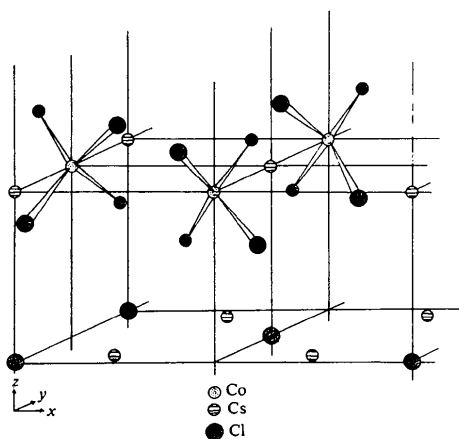


Fig. 1. The crystal structure of  $\text{Cs}_3\text{CoCl}_5$ .

Table 3. Interatomic contacts (Å) less than 4 Å in  $\text{Cs}_3\text{CoCl}_5$  at 4.2 K

Cs(1)···Cl(1) × 2	3.613 (3)	Cl(2)···Co	2.263 (1)
···Cl(2) × 8	3.739 (2)	···Cs(1) × 2	3.739 (2)
Cs(2)···Cl(1) × 2	3.396 (2)	···Cs(2)	3.383 (1)
···Cl(2) × 2	3.383 (1)	···Cs(2) × 2	3.577 (2)
···Cl(2) × 4	3.577 (2)	···Cl(2)	3.643 (1)
Cl(1)···Cs(1) × 2	3.613 (3)	···Cl(2) × 2	3.720 (2)
···Cs(2) × 4	3.396 (2)	···Cl(2)	3.855 (2)

temperature is the relatively small contraction of the unit cell, and the corresponding reductions of the non-bonded interatomic contact distances. In particular, the tetragonal distortion of the  $[\text{CoCl}_4]^{2-}$  ion, as defined by the non-equivalence of the two Cl—Co—Cl angles, is independent of temperature. This is despite the fact that the shortest Cl···Cl contact between  $[\text{CoCl}_4]^{2-}$  ions undergoes the largest reduction of all non-bonded contact distances on changing from 295 to 4.2 K [3.943 (2) Å at 295 K; 3.941 (2) Å at 295 K using Cl coordinates corrected for rigid-body libration effects; 3.855 (2) Å at 4.2 K]. This Cl···Cl contact has been suggested as a pathway for the antiferromagnetic interaction between the Co atoms (Figgis, Gerloch & Mason, 1964b), and as a possible origin of the distortion of the  $[\text{CoCl}_4]^{2-}$  tetrahedron (Figgis, Gerloch & Mason, 1964a). A detailed 'molecular-mechanics' calculation of the anionic distortions in relation to the intermolecular environment of the ion at different temperatures will be undertaken.

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## Bonding in [S<sub>2</sub>O<sub>6</sub>]<sup>2-</sup>: Refinement and Pictorial Representation from an X-ray Diffraction Study of Na<sub>2</sub>S<sub>2</sub>O<sub>6</sub>·2H<sub>2</sub>O and Na<sub>2</sub>S<sub>2</sub>O<sub>6</sub>·2D<sub>2</sub>O

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### Abstract

Conventional refinements of room-temperature data sets for Na<sub>2</sub>S<sub>2</sub>O<sub>6</sub>·2H<sub>2</sub>O and Na<sub>2</sub>S<sub>2</sub>O<sub>6</sub>·2D<sub>2</sub>O led to  $R = 0.0198$  and  $R = 0.0229$  respectively. Ensuing difference density syntheses showed significant charge accumulations in the S–S and S–O bonds. Further studies of the electron distribution in the [S<sub>2</sub>O<sub>6</sub>]<sup>2-</sup> anion were based on four models, which resulted in significantly improved  $R$  values. In the first three models, applicable to conventional least-squares programs, no external constraint was imposed on the anion charge, which was proved to be doubly negative within the limits of tolerance. (a) Ionic model: variation of the S and O occupancies ( $R = 0.0192/0.0224$ ). The anion charge was shown to be uniformly distributed on the O atoms, while the S atoms remained unaffected. (b) Bond model: conventional refinement plus free point charges initially placed between each pair of bonded atoms ( $R = 0.0162/0.0210$ ). The anion charge was found to be distributed on the seven bonds. (c) Core model: as (b) but representation of S and O by Ne and He cores respectively. Initially additional free point charges were placed on the atomic positions ( $R = 0.0139/0.0191$ ). The final atomic parameters were used for ( $X$ – $X$ ) syntheses yielding improved dynamic deformation densities. (d) Multipole model: refinement with neutral S and O atoms plus atomic deformation functions ( $R = 0.0129/0.0172$ ). Refined multipole coefficients were used to calculate static deformation densities and their e.s.d.'s. The features of the static

deformation densities of both compounds are in good qualitative agreement. Examples of three-dimensional pictorial representations of individual atomic deformation density and total static density distributions are given. All refinement results show [S<sub>2</sub>O<sub>6</sub>]<sup>2-</sup> to behave like a charged molecular fragment held together by strong covalent bonds.

### Introduction

In a previous paper (Kirfel, Will & Weiss, 1980; hereafter called part I) the crystal structures of Na<sub>2</sub>S<sub>2</sub>O<sub>6</sub>·2H<sub>2</sub>O and its deuterated homologue have been reinvestigated and refined by conventional least-squares methods from X-ray diffraction data. As in part I, the compounds are referred to as NAH and NAD respectively. A study of the electron density distribution in the unit cell beyond the configurational analysis of the structure, *i.e.* the study of bond densities, imposes requirements on the data, which are matched only partially in the present work, since both data sets suffer from a limited scattering angle,  $2\theta_{\max} = 60^\circ$ , corresponding to a cut-off at  $s = 0.70 \text{ \AA}^{-1}$ . This prevents high-order refinements and also excludes some experimental information from the bonding contributions of the core electrons and of charge concentrations in the vicinity of the nuclei-like lone-pair electrons. In spite of these shortcomings, we decided to look more closely at the electron distribution, since the data sets are of good quality and we were interested in testing various refine-