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Cs_3CoCl_5 at 10 K

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The crystal structure of tricaesium cobalt pentachloride has been determined by X-ray diffraction at 10 K. The Co atom is at a site with $\overline{4}2m$ symmetry, one Cs atom is at a site with 42 symmetry, the other has mm site symmetry, one Cl ligand has $4/m$ symmetry and the other has m symmetry. The accurate and extensive data set collected should be suitable for charge–density analysis studies. In the $CoCl_4^{2-}$ ion, as the temperature is lowered, the Co—Cl bond length increases a little and the small distortion of the tetrahedron (site symmetry $\overline{4}2m$) is slightly reduced.

Comment

Cs_3CoCl_5 is of interest in inorganic chemistry as it provides a well defined example of a high-spin Co^{II} complex with four monatomic ligands and only slightly distorted tetrahedral stereochemistry. We have determined the crystal structure of Cs_3CoCl_5 by X-ray diffraction at 10 (2) K. It is made up of Cs^+ cations, and $[CoCl_4]^{2-}$ and Cl^- anions, and the unit-cell contents are illustrated in Fig. 1. The structural features, including the coordination polyhedra, have been described before for higher temperature studies both by X-ray (Reynolds *et al.*, 1981; Figgis *et al.*, 1989*a*) and neutron diffraction (Williams *et al.*, 1980), and also at 4.2 K by neutron diffraction (Figgis, Mason *et al.*, 1980); our new results present no unusual features. The relationship between the charge density at 115 K (Figgis *et al.*, 1989*a*) and the spin density obtained from polarized neutron diffraction (Figgis, Reynolds & Williams, 1980; Figgis, Reynolds, Williams *et al.*, 1980) and theoretical calculations has been discussed (Chandler *et al.*, 1982; Figgis *et al.*, 1989*b*; Li *et al.*, 2001). The bond lengths and angles for the $[CoCl_4]^{2-}$ ion at various temperatures by the two methods are given in Table 1.

The $[CoCl_4]^{2-}$ ion consists of a regular tetrahedron distorted along one of its ($\overline{4}$) axes so as to reduce the Cl2—Co—Cl2^i angle by 2.3° at 10 K. As determined by X-rays, the Co—Cl2 bond length increases very slightly (0.008 Å) as the temperature falls from ambient to 115 K, but then is unchanged to very low temperatures. The Cl_2—Co—Cl_2^i angle rises slightly (0.2°) from ambient to 115 K, but then remains constant to 4 K. Over the same temperature ranges, the Cl_2—Co—Cl_2^v angle falls by 0.15° and similarly remains constant (see Table 1 for symmetry codes).

The unbonded Cl^- ion has approximate octahedral coordination by Cs^+ ions, two Cs^+ at ~3.6 Å and four Cs^{2+} at ~3.4 Å, but the Cs^+ environments are not simple – roughly, that of Cs1$^+$ is a bicapped square antiprism and that of Cs2$^+$ a bicapped trigonal prism.

The atomic displacement parameters (ADP) decrease with temperature largely as expected. At higher temperatures, they are approximately proportional to temperature; the average value of $U_{\rm eq}^{115}/U_{\rm eq}^{295}$ is 0.45, but this becomes 0.31 if Cs1, which hardly changes, is excluded. For reference, the temperature ratio, 115/295, is 0.39. This proportionality is not seen at lower temperatures because of zero-point motion. The average value of $U_{\rm eq}^{10}/\ U_{\rm eq}^{115}$ is 0.40, whereas the temperature ratio is 0.09. The $U_{\rm eq}$ value for Cs1 falls rapidly in this range, so that at 10 K it is not markedly different from the other atoms, as it was at 115 K. Complexities of the thermal motion of Cs1 which restricted the reliability of the charge–density analysis at 115 K should be much reduced in the present 10 K data.

The agreement between the ADP at 10 K with those found for the compound by neutron diffraction at 4.2 K is not good. The average value for $U_{\rm eq}$ reported here is some 30% larger than for the 4.2 K neutron study. Good agreement is expected for non-H atoms at these very low temperatures, as has been shown for $(ND_4)_2Cu(SO_4)_2\cdot 6D_2O$ at 15 K (Iversen *et al.*, 1994), $Ni(ND_3)_4(NO_2)_2$ at 13 K (Iversen *et al.*, 1996) and $(ND_4)_2Fe(SO_4)_2\cdot 6D_2O$ at 12 K (Figgis *et al.*, 1998). For the latter, two cases of neutron diffraction structures at 4.2 K (Figgis *et al.*, 1981; Figgis, *et al.*, 1989) were also available and showed disagreement with the latter neutron studies at 13 and 12 K, and of a similar magnitude to the present instance. The

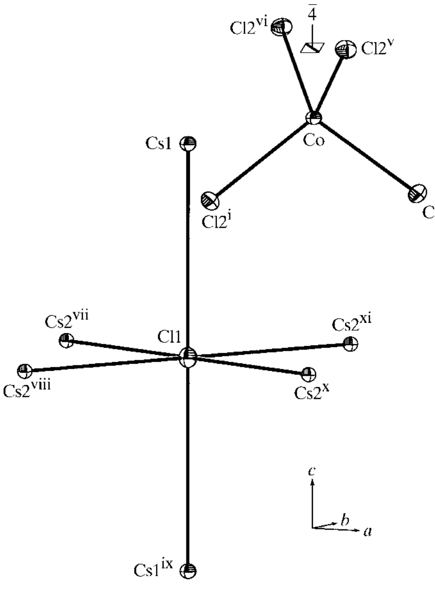

Figure 1
The $CoCl_4^{2-}$ distorted tetrahedron and the $ClCs_6^{5+}$ distorted octahedron coordination polyhedra in Cs_3CoCl_5 at 10 K. Displacement ellipsoids are shown at the 75% probability level. [Symmetry codes: (i) $-x, -y+1, z$; (v) $y-\frac{1}{2}, -x+\frac{1}{2}, -z+\frac{1}{2}$; (vi) $-y+\frac{1}{2}, x+\frac{1}{2}, -z+\frac{1}{2}$; (vii) $x-1, y-1, z$; (viii) $-y+1, x-1, z$; (ix) $-x, -y, -z$; (x) $-x+1, -y+1, -z$; (xi) $y-1, -x+1, -z$.]

disagreement in positional parameters was less marked. It seems likely that data collected on the D15 diffractometer at the Institute Laue–Langevin on this substance, and also on $Ni(ND_3)_4(NO_2)_2$ and on $(ND_4)_2Fe(SO_4)_2{\cdot}6D_2O_2O$, contained some systematic error. The error does not seem to be associated with the normal beam Weissenberg diffraction geometry of D15, as the good agreement for $(ND_4)_2Cu(SO_4)_2{\cdot}6D_2O$ was obtained with a diffractometer employing that configuration.

Experimental

Cs_3CoCl_5 was prepared by evaporation of an aqueous solution of $CoCl_2$ containing an excess of CsCl.

Crystal data

Cs_3CoCl_5
$M_r = 634.91$
Tetragonal, *I*4/*mcm*
$a = 9.0793$ (3) Å
$c = 14.4862$ (8) Å
$V = 1194.15$ (9) Å^3
$Z = 4$
$D_x = 3.532$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 32 reflections
$\theta = 29.67–35.25°$
$\mu = 11.503$ mm^{-1}
$T = 10$ (2) K
Prism, dark blue
0.32 × 0.28 × 0.28 mm

Data collection

Huber 512 goniometer diffractometer
ω–2θ scans
Absorption correction: Gaussian (*Xtal*3.7; Hall *et al.*, 2000)
$T_{\min} = 0.120$, $T_{\max} = 0.141$
23863 measured reflections
1708 independent reflections

$R_{\rm int} = 0.026$
$\theta_{\max} = 50.13°$
$h = -19 \rightarrow 19$
$k = -19 \rightarrow 19$
$l = -31 \rightarrow 31$
3 standard reflections every 100 reflections intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.021$
$wR(F^2) = 0.045$
$S = 1.442$
1708 reflections
18 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0092P)^2 + 6.8514P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 3.41$ e Å^{-3} (0.468 Å from Cs1)
$\Delta\rho_{\min} = -1.52$ e Å^{-3} (1.872 Å from Cl1)
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0118 (2)

The very low temperature data set was collected on a locally assembled Huber 512 goniometer equipped with a Displex 202D cryogenic refrigerator (Henriksen *et al.*, 1986; Larsen, 1995). A full sphere of data was collected. Lists of calculated and observed structure factors are given in the supplementary material. The correction for absorption by the beryllium thermal shields was performed using the *PROFIT* (Streltsov & Zavodnik, 1989) program.

Data collection and cell refinement: local diffractometer control software; data reduction: *PROFIT* (Streltsov & Zavodnik, 1989); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

Table 1
Bond lengths (Å) and angles (°) in the $CoCl_4^{2-}$ anion and Cs—Cl distances (Å) at various temperatures by X-ray (X) and neutron (N) diffraction.

M is multiplicity.

Parameter	*M*	295 K (X)	295 K (N)	115 K (X)	10 K (X)	4.2 K (N)
Co—Cl2	4	2.260 (1)	2.2653 (3)	2.2677 (6)	2.2679 (4)	2.2625 (6)
Cl1—Cs1	2	3.6384 (6)	3.6384 (6)	3.625 (1)	3.6215 (2)	3.6125 (3)
Cl1—Cs2$^{\rm i}$	8	3.815 (1)	3.8148 (5)	3.765 (1)	3.7460 (3)	3.739 (2)
Cs2—Cl1$^{\rm ii}$	2	3.4442 (7)	3.4446 (7)	3.414 (1)	3.4023 (1)	3.396 (2)
Cs2—Cl2$^{\rm iii}$	2	3.428 (1)	3.4235 (5)	3.3975 (9)	3.3896 (4)	3.3826 (9)
Cs2—Cl2$^{\rm iv}$	4	3.639 (1)	3.6383 (6)	3.601 (1)	3.5844 (4)	3.577 (1)
Cl2—Co—Cl2$^{\rm i}$	2	106.98 (4)	106.97 (1)	107.22 (3)	107.20 (2)	107.22 (1)
Cl2—Co—Cl2$^{\rm v}$	4	110.75 (3)	110.74 (1)	110.60 (3)	110.62 (1)	110.61 (1)

Symmetry codes: (i) $-x, -y+1, z$; (ii) $x+1, y+1, z$; (iii) $-x+1, -y+2, z$; (iv) $y, -x+1, -z$; (v) $y-\frac{1}{2}, -x+\frac{1}{2}, -z+\frac{1}{2}$.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1294). Services for accessing these data are described at the back of the journal.

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