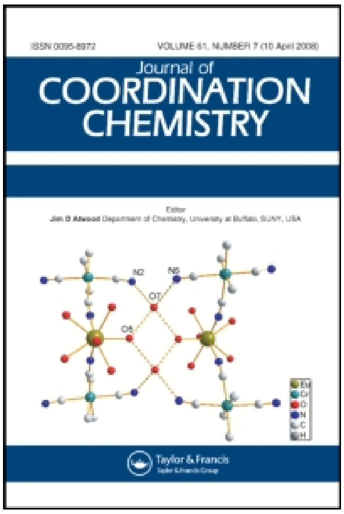

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THE CRYSTAL STRUCTURE OF CESIUM AQUOPENTACHLORORHODATE(III)

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The crystal structure of cesium aquopentachlororhodate(III) has been determined by X-ray diffraction using counter techniques. The complex crystallizes in the orthorhombic space group D_{2h}^{17}–*Amam* with $a = 8.023(3)$ Å, $b = 17.271(10)$ Å, and $c = 7.353(4)$ Å. The crystal sank in methylene iodide (density 3.32 g-cm^{-3}) in agreement with a density of 3.69 g-cm^{-3} calculated for four formula units in the unit cell. A total of 679 independent reflections was used in solving the structure, which was refined to a conventional R factor of 0.065 and a weighted R factor of 0.069. The complex is approximately octahedral, with Rh–Cl distances of 2.300 Å and 2.337 Å, and a Rh–O distance of 2.096 Å. The rhodium compound is isostructural with its ruthenium analogue.

INTRODUCTION

In a recent attempt to solve the structure of the salt tetramethylammonium pentachlorocarbonylrhodate(III), we mistakenly prepared and solved the crystal structure of the tetramethylammonium salt of the transdiaquotetrachlororhodate(III) complex, $[(CH_3)_4N][RhCl_4(H_2O)_2]$.[1] Since chloroaquocomplexes of rhodium(III) and ruthenium(III) show pronounced catalytic effects on certain hydration reactions of acetylene,[2,3] we thought it would be useful to complement our prior structural study by obtaining precise molecular dimensions of the pentachloroaquorhodate(III) complex, $[RhCl_5(H_2O)]^{2-}$. We report here the structure of the cesium salt of this latter complex, $Cs_2[RhCl_5(H_2O)]$.

EXPERIMENTAL

Preparation of the Crystals

Cesium aquopentachlororhodate(III) was prepared by dissolving a small amount of hydrated rhodium trichloride (Matthey-Bishop Co., 40.0% Rh) in a minimum amount of 3*M* HCl, adding the stoichiometric amount of cesium chloride, filtering and setting aside the solution to evaporate. After a few days red, needle-shaped crystals had formed and were collected. From X-ray examination and optical microscopy we ascertained that the crystals were bounded by the forms {120} parallel to the needle axis.

It should be stressed that when 3*M* HCl is used for the crystallization its volume should be kept to a minimum, since as evaporation takes place the effective concentration of HCl increases appreciably, which apparently favors formation of the hexachloro complex in solution. Indeed it has been observed[4] that under such conditions $Cs_3RhCl_6 \cdot H_2O$ crystallizes preferentially even though a stoichiometric ratio of Cs to Rh is present. Fortunately, though the two salts have very similar colors and morphologies, they are readily distinguishable from one another on the basis of their infrared[4,5] and visible-ultraviolet[6] spectra. *Anal.* Calc. for $Cs_2[RhCl_5(H_2O)]$: H, 0.35; Cl, 31.45. Found: H, 0.42; Cl, 31.50.

Collection of X-ray Data

Preliminary Weissenberg photographs of the zones *hk*0 and *hk*1, and precession photographs of the zones 0*kl*, 1*kl*, *h*0*l*, and *h*1*l*, showed an orthorhombic lattice. Observed extinction of reflections *hkl* for $k + l = 2n + 1$ and *h*0*l* for $h = 2n + 1$, is consistent with the possible space groups, for our choice of axes: (a) *Amam* (No. 63), (b) *Ama*2 (No. 40), or (c) *A*2$_1$*am* (No. 36).[7] A negative pyroelectric test and successful solution of the structure in the centric choice indicates that the most probable space group is *Amam* (D_{2h}^{17}—No. 63).

Intensity data were collected on a Syntex computer-controlled, four-circle diffractometer. A needle-shaped crystal of dimensions .04 × .04 × .28 mm along the *a*, *b* and *c* crystal axes, respectively, was mounted with its *c* axis coincident with the ϕ axis of the goniostat. The unit cell dimensions determined from a least squares fit of the 2θ's of eighteen reflections are $a = 8.023(3)$ Å, $b = 17.271(10)$ Å, and $c = 7.353(4)$ Å. The crystal sank in methylene iodide (density 3.32 g–cm^{-3}) in agreement with a density of 3.69 g–cm^{-3} calculated for four formula units in the unit cell.

The intensity data were collected at 22.5 ± 1° using zirconium filtered Mo $K_{\bar{\alpha}}$ radiation (λ 0.71069 Å). Details of data collection and the counter system are identical to those described in ref. 1. Of the 872 independent reflections collected within one octant of the sphere defined by $0° \leqslant 2\theta \leqslant 60°$, 679 had $I \geqslant 3\sigma(I)$ and were used in the solution and refinement of the structure. The linear absorption coefficient, μ, for this crystal is 100 cm^{-1}; and the transmission factors range from .5275 to .6636; therefore the data were corrected for absorption.[8]

Solution and Refinement of the Structure

Since it was noticed that the space group of $Cs_2[RhCl_5(H_2O)]$ was identical with that of the ruthenium(III) analogue, $Cs_2[RuCl_5(H_2O)]$,[9] and that the unit cell dimensions were quite similar, we thought it likely that the compounds were isostructural. Therefore, we first attempted refining an overall scale factor, the final atomic coordinates found by Hopkins and coworkers for $Cs_2[RuCl_5(H_2O)]$, and isotropic temperature factors for all atoms. This refinement converged to $R_1 = .126$ and $R_2 = .180$, where R_1, R_2, and the weighting scheme are as previously defined.[1] Further refinement, with all atoms allowed to vibrate anisotropically, converged to $R_1 = 0.059$ and $R_2 = .063$, but β_{22} for the water oxygen atom refined to a physically unreal, slightly negative number. Removal of some low-angle reflections which it appeared might have been suffering from extinction had no effect on this temperature factor. Refinement of data sets taken on two other crystals also showed this anomaly. We then thought that this behavior of the oxygen atom might be indicative of some amount of disorder of the water ligand with the chloride ligand *trans* to it. However a difference Fourier map computed at this stage showed no residual peaks in the neighborhood of the water oxygen nor its trans chloride which would lend support for the introduction of a disordered model. Two other observations that may be related to the observation of the anisotropic temperature factor anomaly with the oxygen atom are 1) the β_{22} parameter of each of the other atoms in the structure is small relative to those for the other axes, and 2) careful examination of the F_o, F_c list show a fair number of high angle reflections associated with the *b* axis to have significantly higher values of F_o than of F_c. These characteristics appear to be associated with refinement of the data sets from two other crystals also. Though we have no convincing explanation for these observations, we feel their occurrence may be related to some significant degree of anisotropic mosaic character of the crystals, particularly relative to the *b* crystal axis.

In a final set of least squares calculations the

TABLE 1

Coordinates[a] and anisotropic thermal parameters[b] for $Cs_2[RhCl_5(H_2O)]$

Atom	*X*	*Y*	*Z*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rh	.2500[c]	.1142(1)	.0000	445(21)	103(5)	475(26)	0	0	0
Cs(1)	.2500	.4699(1)	.0000	579(21)	213(5)	1178(32)	0	0	0
Cs(2)	.2500	.7540(1)	.0000	1284(29)	145(5)	900(31)	0	0	0
Cl(1)	.2500	.2472(3)	.0000	1144(100)	90(16)	748(106)	0	0	0
Cl(2)	.4582(3)	.1119(2)	.2225(4)	703(37)	205(9)	791(47)	−47(16)	−425(36)	76(19)
O	.2500	.9922(10)	.0000	1.91(30)[d]					

[a] Coordinates in fractions of unit cell edge. Estimated standard deviations in parentheses.

[b] βs and standard deviations (in parentheses) $\times 10^5$. The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl = 2\beta_{23}kl)]$.

[c] Parameters without standard deviations were constrained by symmetry and were not refined.

[d] Isotropic thermal parameter B.

oxygen atom thermal parameter was reset to an isotropic value. After two cycles the refinement converged to $R_1 = .065$ and $R_2 = .069$; no parameter change in the final cycle was greater than 1/6 of its standard deviation. The observed and calculated structure factor amplitudes are available as detailed in ref. 10, final positional and thermal parameters in Table I, and selected interatomic distances and angles in Table II. Figure 1 is an illustration of the crystal structure viewed down the *a* axis; only two formula units are shown for clarity.

TABLE II

Selected interatomic distances and bond angles in $Cs_2[RhCl_5(H_2O)]$

	Intramolecular Distances		
Rh-Cl(1)	2.300(5)	Cl(1)-4Cl(2)	3.305(5)
Rh-4Cl(2)	2.337(3)	O-Cl(2)	3.115(9)
Rh-O	2.096(13)	Cl(2)-Cl(2)	3.268(5)
		Cl(2)-Cl(2)	3.342(5)
	Interionic distances		
Cs(1)-4Cl(2)	3.413(3)	Cl(1)-4Cl(2)	3.943(4)
Cs(1)-4Cl(2)	3.604(3)		
Cs(1)-2O	3.698(3)	Cl(2)-O	3.380(7)
Cs(1)-Cl(1)	3.844(6)	Cl(2)-Cl(2)	3.927(6)
		Cl(2)-Cl(1)	3.943(4)
Cs(2)-4Cl(2)	3.602(3)		
Cs(2)-4Cl(2)	3.675(3)		
Cs(2)-2Cl(1)	3.678(2)		
	Angles		
Cl(1)-Rh-Cl(2)	90.91(8)		
Cl(1)-Rh-O	180.00		
O-Rh-Cl(2)	89.09(8)		
Cl(2)-Rh-Cl(2)	91.25(13)		
Cl(2)-Rh-Cl(2)	88.72(13)		
Cl(2)-Rh-Cl(2)	178.19(15)		

[a] Standard deviations in the least significant digits in parentheses. Angle with no standard deviation is constrained by symmetry.

DESCRIPTION OF THE STRUCTURE

The $RhCl_5H_2O^{2-}$ anion has *mm* site symmetry in the crystal with Rh, Cl(1) and O required to be located at the intersection of the two mirror planes. These mirror planes also bisect the Cl(2)-Rh-Cl(2′) bond angles between the equatorial chloride ligands. The Rh(III)-Cl distances of 2.300(5) Å and 2.337(3) Å to the *trans* and equatorial chlorides are comparable to those of 2.357(6) Å, 2.300(7) Å, and 2.330(4) Å found in the tetrachlorodiaquorhodate (III) complex.[1] However it should be noted that the bond between rhodium and the chloride *trans* to the water in the pentachloroaquocomplex is shortened by 0.04 Å, a result also observed in the analogous ruthenium complex, $[RuCl_5(H_2O)]^{2-}$ by Hopkins and coworkers.[9] The Rh(III)—O bond length of 2.096(13) Å is significantly longer than the distance of 2.034(10) Å in the *trans*-diaquo complex,[1] but is comparable to that of 2.104(28) Å found in the ruthenium analogue.[9]

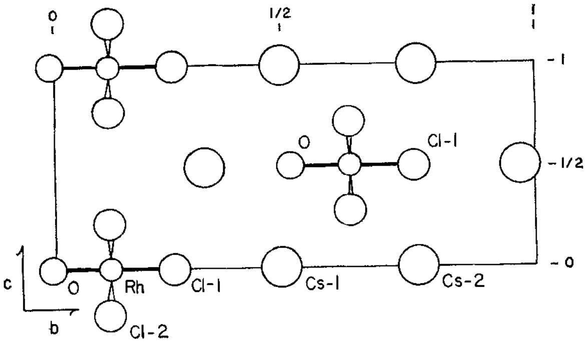

FIGURE 1 Crystal structure of $Cs_2[RhCl_5(H_2O)]$ viewed down the **a** crystal axis. All atoms in the figure have an **x** coordinate of 0.2500, with the exception of the equatorial chlorines (shown super-imposed) which have **x** coordinates of 0.0418 and .4582. For clarity, only two of the four formula units in the cell are shown. The omitted two may be derived through the operation of the **a** glide plane of the space group (*Amam*) at y = 0 and 1/2.

The four equatorial Cl(2) ligands lie at the corners of a rectangle, rather than a square, the Cl(2)-Rh-Cl(2′) bond angles being 88.7(1)° and 91.3(1)°. Stanko and Chaipayungpundhu[11] observe a similar distortion in the structure of $Cs_2[RuCl_4(CO)(H_2O)]$, as do Hopkins *et. al.*[9] in $Cs_2[RuCl_5\text{–}(H_2O)]$. Both attribute it to hydrogen bonding between water and chloride ligands of adjacent anions. Although we could not locate the water hydrogen atoms on final difference Fourier maps, we feel that this is also the probable explanation for the distortion in the present structure since the Cl(2)-O hydrogen bond distance of 3.380(7) Å is close to that observed in the ruthenium salts.

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