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Articles

Dicesium *trans*-Tetraaquadichlorochromium(III) Chloride: Redetermination of the Crystal Structure and Infrared Study of the Water Spectrum

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Infrared spectral studies of the solid led us to believe that the published crystal structure of dicesium *trans*-tetraaquadichlorochromium(III) chloride, *trans*-$Cs_2[CrCl_2(H_2O)_4]Cl_3$ might be incorrect. Crystal data: $Cs_2CrCl_5{\cdot}4H_2O$, $a = 17.484(9)$ Å, $b = 6.099(3)$ Å, $c = 6.928(3)$ Å, $\beta = 106.06(5)°$, monoclinic, $C2/m$, $Z = 2$ molecules per cell. The redetermination has revealed disorder in the positions of the water molecules. Instead of *one* type of H_2O molecule being present as found in the original study, *two* sets of such molecules with four nonequivalent O···C*l* contacts were found. The presence, in the O−D stretching region of the spectra of samples with low deuterium content, of *three* bands with intensities close to 2:1:1 (rather than the expected four) is believed to be a consequence of different degrees of nonlinearity of the two hydrogen bonds formed by the water molecules of one of the two existing types.

Introduction

Data on the infrared spectra of the title compound (of both protiated and partially deuterated samples) have already been reported by us.[2] While it was found that our spectrum of the protiated *trans*-$Cs_2[CrCl_2(H_2O)_4]Cl_3$ agrees well with the spectra reported in 1983 by Michalska-Fong *et al.*,[3] the spectral picture in the O−D stretching region of the spectra of isotopically isolated HOD molecules was incompatible with the reported X-ray structure analysis of the crystal.[4] This analysis has Cr(III) hexacoordinated to four equivalent water molecules located in the equatorial plane and to two axial chlorine atoms. Thus only two ν(O−D) bands should be expected in the spectrum of the samples with low deuterium content. The number of observed bands led us to conclude that either a wrong space group had been assigned to the crystal or else the coordinated water molecules were disordered in some way not revealed by the crystal structure analysis. Our view that the published crystal structure might be wrong was strengthened by the fact that the residual R was somewhat high (at 0.083) but even more because the anisotropic temperature factors for the oxygen atoms were an order of magnitude greater than would be expected for an ordered structure. We report here a redetermination of the crystal structure showing that the coordinated water molecules are, in fact, disordered.

Experimental Section

Green crystals of the title compound were from the same sample as those used in the spectral analysis.[2] The crystal chosen for X-ray analysis was columnar, 0.08 × 0.1 × 0.4 mm, and preliminary X-ray photographs showed it to be of good quality.

Diffraction data were collected at 24 °C on an automated four-circle Picker diffractometer using Zr-filtered Mo Kα radiation ($\lambda = 0.7107$ Å) with pulse height analysis to a limiting 2θ of 50° covering the ranges $h = \pm18$, $k = 0-7$, and $l = 0-8$ (see Table 1 for details). Of 686 reflections measured, 660 were significant on the criterion $I_{net} > 2.5\sigma(I_{net})$. The systematic absences *hkl* for $h + k = 2n + 1$ were confirmed, thus allocating the space group to $C2$, Cm, or $C2/m$. McCarthy *et al.*[4] assumed $C2/m$, and we used this assignment also. Using NRCVAX computer software, after applying Gaussian absorption corrections to the intensity data[5] ($\mu = 67.4$ cm^{-1}; minimum and maximum transmission factors 0.18 and 0.36), we used the fractional atomic coordinates and anisotropic temperature factors listed by McCarthy *et al.*[4] to carry out refinement, varying only the scale factor and extinction coefficient. The resulting residual was somewhat better, at 0.070.[6]

A ΔF Fourier map showed immediately that, instead of four equatorial oxygen atoms associated with Cr, there were, in fact, eight partially occupied sites. The eight oxygen atoms had their occupancies set to 0.5. Full-matrix anisotropic least-squares refinement was uneventful, the final residual being 0.041. Attempts were made to refine the structure (with appropriately modified occupancies, etc.) in space groups $C2$ and Cm. In the former, the oxygen atoms could not be refined anisotropically, and the latter led to a false minimum showing high, but chemically unfeasible, disorder.

The positions for hydrogen atoms could not be determined with any certainty, but the most likely positions for them appear to be those which allow both O1 and O2 to be hydrogen bonded to C*l*1 and C*l*3. (Because the oxygen atoms are disordered, they cannot be simultaneously bonded this way in any one Cr coordination polyhedron). The geometries then are as follows: O1−C*l*1, 3.009 Å; O1−C*l*3, 3.045 Å; C*l*1···O1···C*l*3 angle, 88.7°; O2−C*l*1, 3.086 Å; O2−C*l*3, 3.178 Å; C*l*1···O2···C*l*3 angle, 85.0°.

Final fractional atomic coordinates are given in Table 2. Figure 1 shows an ORTEP diagram[7] of the coordination sphere, and Figure 2 shows a packing diagram with putative hydrogen bonds marked in.

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(1) (a) King's College, London. (b) Institut za hemija, Skopje.
(2) Šoptrajanov, B.; Stefov, V.; Petruševski, V. M. *Spectrosc. Lett.* **1993**, *26*, 1839.
(3) Michalska-Fong, D.; McCarthy, P. J.; Nakamoto, K. *Spectrochim. Acta* **1983**, *39A*, 835.
(4) McCarthy, P. J.; Lauffenburger, J. C.; Skonezny, P. M.; Rohrer, D. C. *Inorg. Chem.* **1981**, *20,* 1566.
(5) Gabe, E. J.; Le Page, Y.; Charland, J.-P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22,* 384.
(6) In order to obtain the correct U_{ij} factors from the β_{ij} values as published, those with $i \neq j$ had to be divided by two.
(7) Johnson, C. K. *ORTEP*; Report ORNL-3794, Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

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Table 1. Crystal Data

empirical formula $Cs_2CrCl_5{\cdot}4H_2O$	fw 567.13
$a = 17.484(9)$ Å $(17.604(1))$†	space group *C2/m* No. 12
$b = 6.099(3)$ $(6.140(1))^a$	$T = 24$ °C
$c = 6.928(3)$ $(6.979(1))$	$\lambda = 0.7107$ Å
$\beta = 106.06(5)°$ $(106.040(7))$	$\rho_{calcd} = 2.653$ g cm^{-3}
$V = 709.9(6)$ Å^3	$\mu = 67.4$ cm^{-1}
$Z = 2$	$R(F_o) = 0.0403^b$
	$R_w(F_o)$ 0.0530^b

[a] Parameters in parentheses are from McCarthy *et al.*[4] Differences of the order 0.7% could be due to a higher ambient temperature. [b] $R(F_o) = \sum(F_o - |F_c|)/\sum F_o$; $R_w(F_o) = (\sum(w(F_o - |F_c|)^2)/\sum(wF_o^2))^{1/2}$ with w based on counting statistics.

Table 2. Atomic Parameters and B_{iso} Values, Where Esd's Refer to the Last Digit(s) Printed

	x	y	z	$B_{iso}{}^a$ (Å^2)
Cs	0.29779(5)	0	0.25146(12)	2.84(6)
Cr	0	0	0	1.72(11)
C*l*1	0.19339(19)	$^1/_2$	0.2433(5)	2.71(14)
C*l*2	−0.10693(19)	0	0.1296(5)	2.55(14)
C*l*3	0	$^1/_2$	$^1/_2$	2.72(20)
O1	0.0329(8)	0.2810(24)	0.1362(21)	2.5(6)
O2	0.0647(7)	0.153(3)	0.2410(19)	2.5(6)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

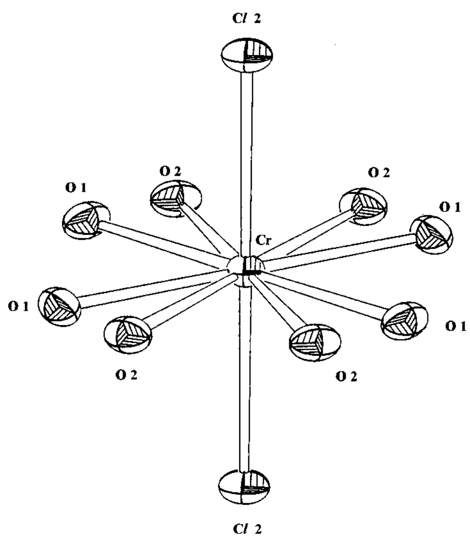

Figure 1. ORTEP plot[7] of the coordination sphere showing 50% probability ellipsoids.

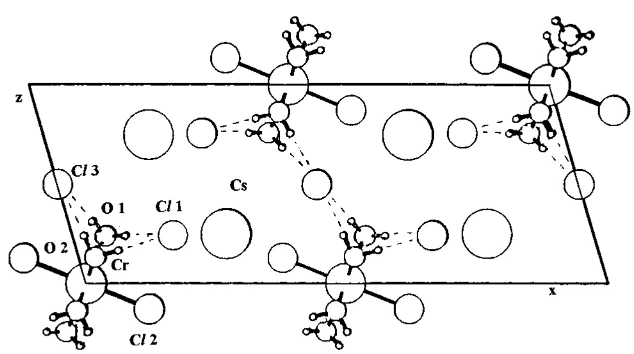

Figure 2. Packing diagram showing putative hydrogen bonds. (Only two of the four shown can be present together.)

The Fourier-transform infrared (FTIR) spectra were recorded on a Perkin-Elmer System 2000 FT-IR (resolution 2 cm^{-1}, OPD rate 0.2 cm/s, 32 background and 64 sample scans) from pellets in CsCl. Mulls in Nujol between CsBr plates were also used. The spectra were identical, thus guaranteeing that no reactions occurred during pellet preparation. For low-temperature work, a P/N 21525 low-temperature cell (Graseby Specac) with a temperature controller was used. Liquid

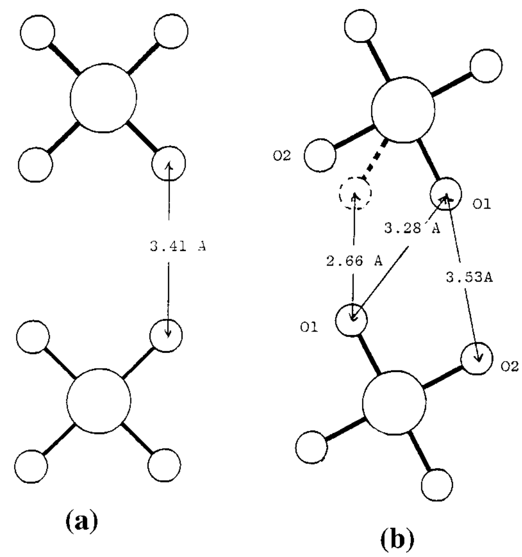

Figure 3. Left: (a) View normal to plane containing oxygen atoms (as reported by McCarthy, *et al.*[4]). (b) Right: Disordered, structure, showing that the rotational sense of disordering must be preserved in any one column.

Table 3. Selected Interatomic Distances (Å) and Bond Angles (deg)[a]

Cs−C*l*1	3.546(2)	Cs−C*l*3	3.478(2)
Cs−C*l*1a	3.461(4)	Cr−C*l*2	2.287(3)
Cs−C*l*2c	3.683(2)	Cr−O1	1.964(13)
Cs−C*l*2b	3.637(4)	Cr−O2	1.972(13)
O1−C*l*1	3.005(13)	O2−C*l*1	3.086(13)
O1−C*l*3	3.045(13)	O2−C*l*3	3.178(13)
O1−Cr−O2d	91.0(7)	O2−Cr−C*l*2	90.4(3)
O1−Cr−C*l*2	88.5(3)		
C*l*1−O1−C*l*3	88.7(10)	C*l*1−O2−C*l*3	85.0(9)

[a] Symmetry operations: (a) $^1/_2 - x$, $^1/_2 - y$, $1 - z$; (b) $-x, -y, -z$; (c) $^1/_2 + x$, $-^1/_2 + y$, z; (d) $-x, y, -z$.

nitrogen was employed as a cooling agent. The temperature was maintained at 100 K, which is close to the lowest temperature attainable with this system.

The software package GRAMS 2000[8] was used in the spectra acquisition, and GRAMS/386[9] was used to analyze the spectra.

Discussion

The Cr atoms lie along 0, y, 0 and $^1/_2$, y, 0 equally spaced at one cell dimension (i.e. b) apart with their C*l*2−Cr−C*l*2 polar axes all parallel in the xz-plane (see Figures 2 and 3). The O atoms lie in planes containing the Cr atoms and normal to the polar axes. Had the oxygen atoms been ordered (as in the published structure[4]), they would be disposed as in Figure 3a. The disordered structure presents the O atoms with two choices, either a clockwise or a counterclockwise rotation (of 28.2°) about the polar axes through Cr (Figure 3b). Whichever sense of rotation is adopted for a particular row along y, it must be the same throughout the entire row. This is because any change in the sense of rotation at a point along the row would result in an unacceptably short O···O distance. Figure 3 provides the geometric details, and Table 3 gives selected interatomic distances and angles.

The existence of two crystallographically different types of water molecule is consistent with the appearance (both at room and at liquid-nitrogen temperature) of two bands due to

(8) GRAMS ANALYST for PE 2000 FT-IR, Version 3.01B, Galactic Industries Corp., 1991−1994.
(9) GRAMS/386 for Microsoft Windows, Version 2.02, Galactic Industries Corp., 1991−1993.

Figure 4. HOH bending region in the spectrum of isotopically isolated H_2O molecules in practically perdeuterated $Cs_2[CrCl_2(H_2O)_4]Cl_3$: (Top) room temperature; (bottom) liquid-nitrogen temperature.

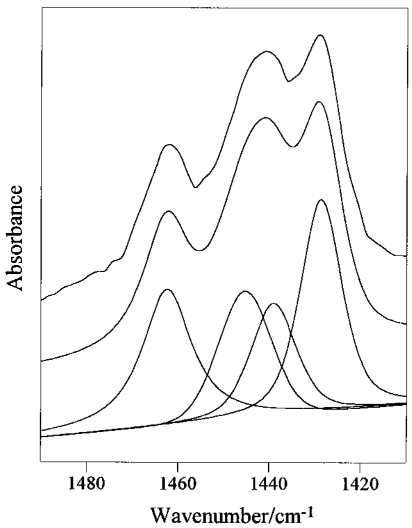

Figure 5. FT-IR liquid-nitrogen temperature difference spectrum of slightly deuterated (≈2% D) and protiated $Cs_2[CrCl_2(H_2O)_4]Cl_3$ in the region of the HOD bendings: (Top) actual difference spectrum; (middle) spectrum obtained by curve-fitting; (bottom) component profiles of the fitted spectrum.

H−O−H bending (Figure 4) in the spectra of samples with a high deuterium content. As has been pointed out,[2] under such circumstances the H_2O molecules are isotopically isolated by HOD and D_2O molecules and all interactions between identical oscillators (correlation-field effects) are excluded. The two bands then must originate from vibrations of two distinct types of water molecule. This is confirmed by the analysis of the HOD bending region. For two types of water molecule, four types of half-deuterated molecules should be present (with each of the protons being alternatively substituted by deuterons). In the difference spectrum[10] of the slightly deuterated sample, a complex feature with three maxima is observed (Figure 5), but the envelope could be better reproduced by assuming that it consists of four components (Table 4).

As seen from Figures 4 and 5, as well as from Table 4, the intensities of the individual components of the HOH/HOD bending modes vary considerably. This is, however (perhaps contrary to the intuitive expectations), a common behavior of

(10) The spectrum of the protiated compound, appropriately scaled, was subtracted from the spectrum of the deuterate. The same procedure was performed in the region of the OD stretching bands.

Table 4. Spectral Parameters (Obtained by Curve-Fitting) for the OD Stretching and HOD Bending Bands of Isolated HDO Molecules in the Difference Liquid-Nitrogen-Temperature IR Spectra of *trans*-$Cs_2[CrCl_2(H_2O)_4]Cl_3$

ν/cm^{-1}	height/arbitrary units	width/cm^{-1}	area/arbitrary units
2427.6	0.1838	16.7	4.0751
2322.1	0.1428	13.2	2.8232
2300.6	0.1228	14.1	2.3532
1462.4	0.0204	13.0	0.3758
1445.3	0.0191	13.7	0.2924
1439.1	0.0169	11.9	0.2495
1428.6	0.0316	10.9	0.4340

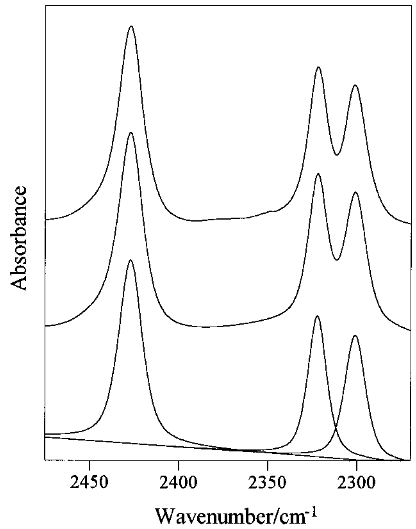

Figure 6. Difference spectrum of slightly deuterated (≈2% D) and protiated $Cs_2[CrCl_2(H_2O)_4]Cl_3$ in the O−D stretching region: (top) actual difference spectrum; (middle) spectrum obtained by curve-fitting; (bottom) component profiles of the fitted spectrum.

the *bending* vibrations of water isotopomers in crystalline hydrates.[11] The reasons for such behavior remain unclear.

Since the true positions of the hydrogen atoms are unknown, the geometry and the details for the bonding of the water molecules could not be determined with any degree of confidence by crystallographic means. It is here that the infrared spectra, particularly those of samples containing isotopically isolated HOD molecules, may shed some light.

The appearance (Figure 6) of *three* distinct bands in the O−D stretching region (the one at highest frequency being more intense) suggests that the four crystallographically distinct hydrogen bonds are grouped in pairs—two of them must be stronger than the remaining ones. That this is indeed so is shown by the ratio of the measured intensities of these three bands (1.73:1.20:1) which is close to the ideal 2:1:1 ratio expected for a quartet with two overlapping bands. The half-width of the 2427.6 cm^{-1} band is larger (at approximately 17 cm^{-1}) than that of the two bands at lower frequencies (at 13 and 14 cm^{-1}, respectively). Qualitatively, this is consistent with the hydrogen-bonding scheme outlined above since the O1−C*l* distances were found to be shorter than the O2−C*l* ones and, furthermore, the two O1−C*l* contacts differ slightly from each other. It is then safe to conclude that the bands at 2322 and 2301 cm^{-1} originate from O−D stretching modes of isotopically isolated H−O1−D molecules. What remains unclear is why there is only a *single* (albeit stronger and broader) band at 2427.6 cm^{-1}, contrary to the fact that the difference between the two O2−C*l* distances (≈0.09 Å) is much larger

(11) Cvetković, J.; Petruševski, V. M.; Šoprajanov, B. *J. Mol. Struct.*, in press.

than the difference between the two O1−C*l* distances. Our attempts to resolve (either experimentally or by curve-fitting procedures) this band into two components were unsuccessful so that the frequency difference between the components must be less than some 7 cm^{-1}. One of the possible explanations for the discrepancy between our expectations and the experimental results is the conjecture that the two O2···C*l*2 hydrogen bonds deviate to a different degree from linearity and that thus they are, accidentally, almost identical in strength.

Full crystal data and anisotropic temperature factors are provided as Supporting Information.

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Supporting Information Available: Tables of crystal data and anisotropic temperature factors (2 pages). Ordering information is given on any current masthead page.

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