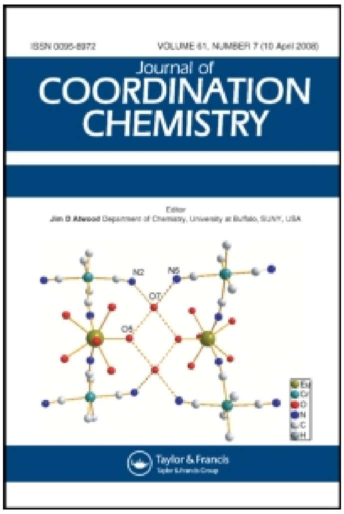

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THE CRYSTAL STRUCTURE OF TETRAMETHYLAMMONIUM *trans*-DIAQUOTETRACHLORO-RHODATE(III)

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The crystal structure of tetramethylammonium *trans*-diaquotetrachlororhodate(III) has been solved by X-ray diffraction using counter techniques. The compound crystallizes in the orthorhombic system with $a = 7.961\ (7)$ Å, $b = 8.439(7)$ Å, and $c = 9.222(9)$ Å. The space group is $D_{2h}{}^{13}$-$Pmmn$. The measured density of 1.82(3) g-cm^{-3} agrees with that of 1.90(1) g-cm^{-3} calculated for two formula units in the unit cell. A total of 353 independent reflections, up to $(\sin\theta)/\lambda$ of 0.50, and having $I \geqslant 3\sigma(I)$ was used in solving the structure which refined to a conventional R-factor of 0.051 and a weighted R-factor of 0.072. The $RhCl_4(H_2O)_2{}^-$ anion lies at a site of *mm* symmetry in the crystal as does the $(CH_3)_4N^+$ cation. There is slightly distorted, octahedral coordination about the rhodium ion with Rh-Cl distances of 2.300(7), 2.330(4) and 2.357(6) Å, and a Rh–O distance of 2.032(10) Å. There is apparently extensive hydrogen bonding between the chloroaquorhodate(III) anions in the crystal, with sheets of these anions being interleaved with sheets of cations parallel to the *ab* crystal plane.

INTRODUCTION

As part of a continuing interest in the structures and reactions of rhodium halocarbonyls,[1, 2] we wished to obtain the detailed molecular structure of the pentachlorocarbonylrhodate(III) complex, $RhCl_5CO^{2-}$. Dahm and Forster[3] have examined the crystal structure of the tetraethyl-ammonium salt of the iodo-analogue of this complex but found a disordered structure. Similarly, we found the easily isolatable cesium salt of the chlorocarbonyl rhodium complex also to be disordered[4] as is its ruthenium analogue.[5] In a further search for a suitable salt of this complex for crystal structure analysis, we then examined the tetramethylammonium one reported by Forster.[6] In attempting to grow a single crystal of this compound, we isolated instead a few crystals of the salt, tetramethylammonium *trans*-diaquotetrachlororhodate(III). Since this was not apparent until after we had computed a Patterson function, and since few structures,[7, 8] of *trans*-diaquo complexes appear in the literature, we completed the structural solution of $[(CH_3)_4N]\,[RhCl_4(H_2O)_2]$ and report it here.

EXPERIMENTAL

Preparation of the Crystals

Tetramethylammonium *trans*-diaquotetrachlororhodate(III) crystals were isolated accidentally from a recrystallization of the compound $[(CH_3)_4N]_2[RhCl_5CO]$ synthesized according to the method of Forster.[6] Hydrated rhodium trichloride, Matthey-Bishop Co., 40.0% Rh(361 mg; 1.40 mmol) was dissolved in 15 ml of methanol acidified with 2 ml of concentrated HCl, and CO bubbled through the solution at 60° until the solution was pale yellow, indicating the formation of the rhodium(I) dicarbonyl, $RhCl_2(CO)_2{}^-$. Tetramethylammonium chloride (310 mg; 2.84 mmol), dissolved in the minimum volume of methanol, was added, and Cl_2 bubbled through the solution for 15 minutes. During this time the solution turned orange and a green precipitate formed.[9] The solution was filtered and the orange filtrate evaporated in a stream of nitrogen. The resulting orange solid showed a single, sharp CO stretching frequency at 2095 cm^{-1} in the infrared (KBr pellet) in agreement with that previously reported[6] for the pentachlorocarbonylrhodate(III) compound. An amount of this compound was redissolved in 1 *M* HCl, filtered and set aside to evaporate. After several days the solution had almost evaporated to dryness and we were able to remove a few needle-shaped, orange crystals which we thought to be the monocarbonyl compound, but which we showed by X-ray later to be the diaquotetrachlororhodate(III) salt. There was also a quantity of red plates, presumably $[(CH_3)_4N]_2[RhCl_5(H_2O)]$ from their color. Since we isolated so few of the orange crystals, infrared or elemental analyses were not possible.

Collection of X-ray Data

Preliminary Weissenberg photographs of the zones $h0l$ and $h1l$ showed an orthorhombic lattice with extinction of the reflections $hk0$ for $h + k = 2n + 1$. The possible space groups are *Pmmn*, $P2_1mn$ or $Pm2_1n$. A negative pyroelectric test along with successful refinement of the structure in the centric choice indicates that the probable space group is $D_{2h}{}^{13}$–*Pmmn* (No. 59).[10]

Intensity data were collected on a Syntex four-circle, computer-controlled diffractometer. A needle-shaped crystal of approximate dimensions .1 × .3 × .1 mm along the *a*, *b*, and *c* crystal axes, respectively, was mounted with its *b* axis coincident with the ϕ axis of the goniostat. The unit cell dimensions, determined from a least-squares fit of the setting angles of nine reflections measured on the diffractometer, are $a = 7.961(7)$, $b = 8.439(7)$, and $c = 9.222(9)$ Å. The density, measured by flotation in a mixture of carbon tetrachloride and 1,2-dibromoethane, is 1.82 ± 0.03 g–cm^{-3}, compared with $1.90 \pm$ g-cm^{-3} calculated for two formula units in the unit cell. This requires that both the rhodium atom of the anion and the nitrogen atom of the cation be located at two-fold special positions in the unit cell.

The data were collected at $19 \pm 1°$ using Cu $K_{\bar{\alpha}}$ radiation (λ 1.5418 Å) filtered on the incident beam side through nickel foil. A 1 mm diameter collimator was used on the incident beam side of the crystal and a 2 mm diameter circular receiving aperture on the diffracted beam side. A take-off angle of 4°, which gave an approximately square focal spot, was used. The crystal-to-source and crystal-to-counter distances were both 13.5 cm. A θ–2θ scan mode was used with the scan ranging from -1.0 to $+1.0°$ from the calculated 2θ position. The scan rate was 1.0°/min and the background was counted for 15 seconds at each end of the scan range. Two check reflections were counted after every 24 reflections; their intensities remained constant to within $\pm 2\%$ throughout the data collection.

Of the 409 independent reflections collected within the sphere $2\theta \leqslant 100°$, 353 had $I \geqslant 3\sigma(I)$ and were used in the solution and refinement of the structure. The standard deviation of the intensity, $\sigma(I)$, was computed as $[S + (B_1 + B_2)\alpha^2 + (pS)^2]^{\frac{1}{2}, 11}$ where *S* is the scan count, B_1 and B_2 are the fixed time background counts, α is one-half the scan width divided by the scan rate, and *p* is a constant, here set equal to 0.02, which incorporates uncertainties in the measurements other than counting statistics. The linear absorption coefficient, μ, for this crystal is 191 cm^{-1}, and the calculated transmission factors range from .0442 to .1225; the data was therefore corrected for absorption.[12]

Solution and Refinement of the Structure

The structure was solved using conventional heavy-atom methods. A Patterson function showed the intermolecular Rh–Rh vector, and a square of four chloride ligands about the rhodium was indicated from the distribution of the intramolecular Rh–Cl vectors. A Fourier synthesis phased on the Rh and three independent chlorine atoms revealed all the other atoms except hydrogens and indicated that the compound was indeed $[(CH_3)_4N][RhCl_4(H_2O)_2]$, and not the desired pentachlorocarbonyl compound. Full-matrix least squares refinement of an overall scale factor, twelve coordinates, and twenty-eight anisotropic thermal parameters for the eight atoms of the asymmetric unit excluding hydrogens, converged to $R_1 = 0.051$ and $R_2 = 0.072$. R_1 and R_2 are the weighted and unweighted *R* factors, defined respectively as $R_1 = \Sigma\,||F_o| - |F_c||/\Sigma\,|F_o|$ and $R_2 = [\Sigma w(|F_o| - F_c|)^2/\Sigma w(F_o{}^2)]^{1/2}$ where F_0 and F_c are the observed and calculated structure factors and *w* is the weight. The weight *w* was defined as $1/\sigma^2(F_0)$, where $\sigma(F_0)$ is the standard deviation of the structure factor and is related to the standard deviation of the measured intensity, $\sigma(I)$, through the formula $\sigma(F_0) = .5\sigma(I)[LpTI]^{-\frac{1}{2}}$, *Lp* being the Lorentz-polarization factor, and *T* the transmission factor.[13] Atomic scattering factors were taken from the following compilations: Rh^{3+}, from Cromer and Waber,[14] and Cl^-, C°, N°, O°, and H° from Ibers.[15]

A difference Fourier synthesis computed at this

TABLE I

Coordinates[a] and anisotropic thermal parameters[b] for $[(CH_3)_4N][RhCl_4(H_2O)_2)$[c]

Atom	*X*	*Y*	*Z*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rh	.2500	.2500	.0781(2)	58(4)	27(3)	47(3)	0	0	0
Cl(1)	.2500	.2500	.3337(7)	82(12)	108(11)	49(8)	0	0	0
Cl(2)	.2500	.2500	−.1713(7)	127(14)	182(14)	39(8)	0	0	0
Cl(3)	.2500	.5261(5)	.0817(5)	91(9)	33(7)	127(7)	0	0	6(6)
O	.5052(13)	.2500	.0812(11)	57(21)	87(17)	66(14)	0	−19(14)	0
N	.2500	.7500	.5009(25)	170(51)	161(46)	66(28)	0	0	0
C(1)	.2500	.5963(24)	.6040(25)	255(56)	105(39)	164(38)	0	0	−12(31)
C(2)	.0936(30)	.7500	.4099(22)	153(44)	364(65)	95(29)	0	−41(33)	0

[a] Coordinates in fractions of unit cell edge. Estimated standard deviations ($\times 10^4$) in parentheses.

[b] βs and standard deviations (in parentheses) $\times 10^4$. 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 not refined.

stage showed residual electron density near the carbon atoms of the cation, but attempts to refine hydrogen atom coordinates were unsuccessful. An application of Hamilton's test[16] after inclusion of the methyl hydrogens at calculated positions showed the reduction in the *R*-factor to be insignificant. The hydrogens of the water ligands could not be located.

The observed and calculated structure factor amplitudes are available as detailed in Ref. 17, and the final positional and anisotropic thermal parameters for each atom of the asymmetric unit are listed in Table I. Figure 1 is an ORTEP drawing of the unit cell, viewed down the *a* axis of the crystal. Selected interatomic bond distances and angles are given in Table II.

RESULTS AND DISCUSSION

The $[RhCl_4(H_2O)_2]^-$ anion has been prepared previously by aquation of $[RhCl_5(H_2O)]^{2-}$,[18] and

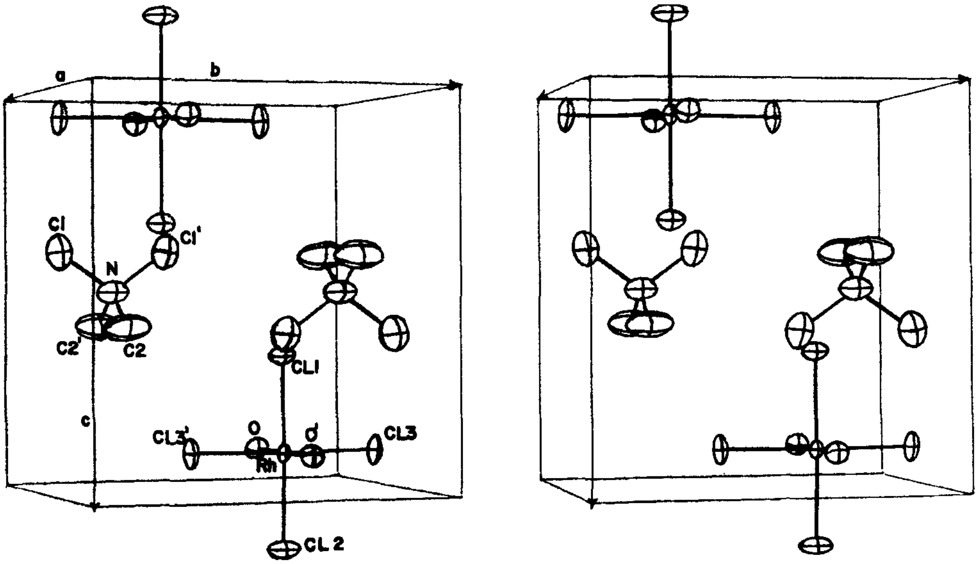

FIGURE 1 Stereo view of the crystal structure of tetramethylammonium *trans*-diaquotetrachlororhodate (III), down the *a* crystal axis. The *b* axis runs horizontally and the *c* axis vertically. 50 % probability thermal ellopsoids are plotted.

TABLE II

Selected intramolecular bond distances and bond angles[a]

Bond	*Bond length* (Å)	*Bond*	*Bond angle(deg.)*
Rh—Cl(1)	2.357(6)	Cl(1)—Rh—Cl(2)	180.0[b]
Rh—Cl(2)	2.300(7)	Cl(1)—Rh—Cl(3)	89.2(1)
Rh—Cl(3)	2.330(4)	Cl(1)—Rh—O	89.2(3)
Rh—O	2.032(10)	Cl(2)—Rh—Cl(3)	90.8(1)
Cl(1)—Cl(3)	3.290(6)	Cl(2)—Rh—O	90.8(3)
Cl(1)—O	3.090(11)	Cl(3)—Rh—Cl(3′)	178.3(3)
Cl(2)—Cl(3)	3.298(6)	Cl(3)—Rh—O	90.0(0)
Cl(2)—O	3.091(11)	O—Rh—O′	178.4(6)
N—C(1)	1.608(25)	C(1)—N—C(2)	109.3(6)
N—C(2)	1.501(26)	C(1)—N—C(1′)	107.5(2.1)
Cl(3)—O	3.091(8)	C(2)—N—C(2′)	112.0(2.2)

[a] Standard deviations in the least significant digits in parentheses.

[b] Bond angles constrained by symmetry and not refined.

the *cis* and *trans* isomers separated by column chromatography.[19] The present work, however, to our knowledge, is the first report of the isolation of a solid compound of this anion.

The $[RhCl_4(H_2O)_2]^-$ anion has *mm* site symmetry in the crystal with Rh, Cl(1) and Cl(2) required to lie at the intersection of the two mirror planes. The other two chlorides, Cl(3) and Cl(3′) and the water oxygens, O and O′, lie on, and are related by, the mirror planes. The Rh atom is slightly displaced (0.032 Å) from the plane defined by Cl(3), Cl(3′), O, and O′.

There are very few Rh(III)-Cl distances reported in the literature, but those we find for $[RhCl_4(H_2O)_2]^-$ (2.300(7), 2.330(4) and 2.357(6) Å) are similar to those found in trichloro-bis-(*o*-methoxyphenyldimethylarsine)-rhodium(III) (2.33(1), 2.35(1) and 2.39(2) Å)[20] and trichloro-bis-(*o*-phenylenedimethylaminedimethylarsine)rhodium(III)

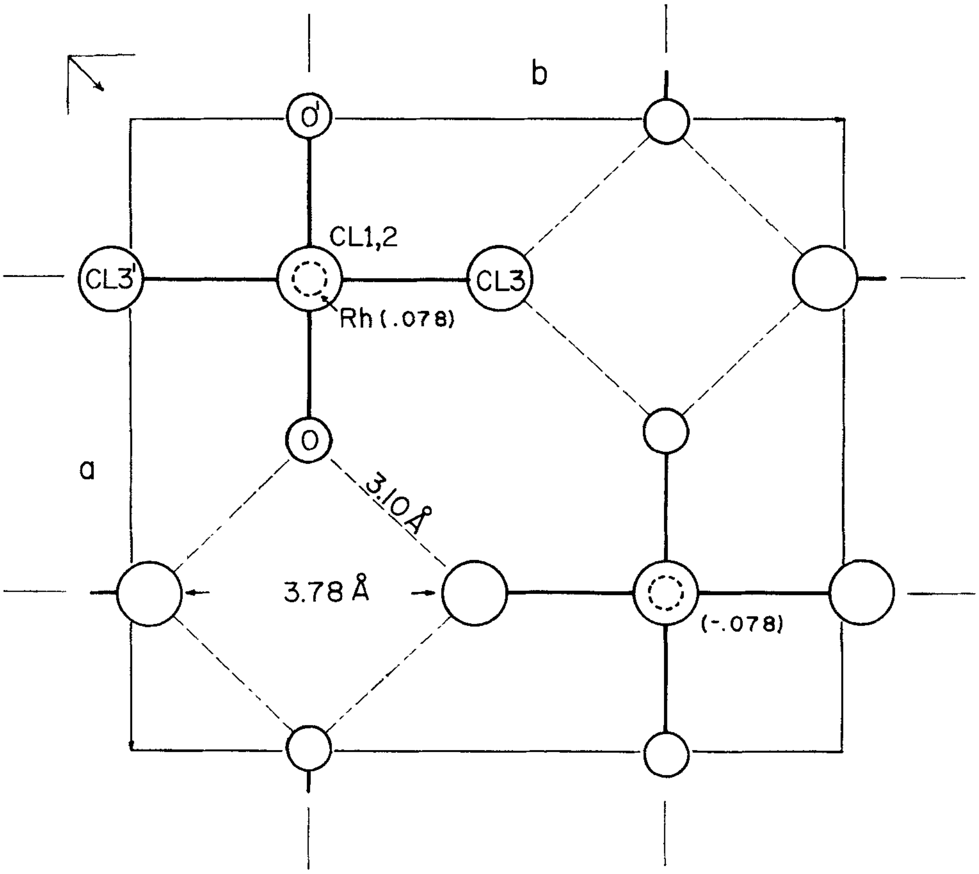

FIGURE 2 View of the proposed hydrogen bonding scheme between diaquotetrachlororhodate(III) anions in the crystal. The *z* coordinates of the n-glide-related rhodium atoms are given on the figure, as well as the intermolecular Cl–O and Cl–Cl distances. For other bond distances and angles consult Table II and the text.

(2.33, 2.35 and 2.39 Å),[21] although slightly less than the distance of 2.41 Å found in $[Rh(NH_3)_5Cl]Cl_2$.[22] They are also in the range of reported Rh(I)–Cl distances, some of which are reviewed in Ref. 2.

The Rh(III)–O distance to the coordinated water molecule of 2.032(10) Å is not unusual. The average of six Rh(III)–O distances in $K_3[Rh(C_2O_4)_3]\cdot 4.5H_2O$ is 2.016 Å,[23] and the Rh(III)–O distance in the salt $Cs_2[RhCl_5(H_2O)]$ is 2.096(13) Å.[24]

As can be seen from Figure 1, the crystal is built up of oppositely charged layers perpendicular to the *c* axis. Sheets of anions (Rh coordinates $\frac{1}{4}$, $\frac{1}{4}$, .0781; $\frac{3}{4}$, $\frac{3}{4}$, −.0781) parallel to the *ab* plane are interleaved with sheets of cations (N coordinates $\frac{1}{4}$, $\frac{3}{4}$, .5009; $\frac{3}{4}$, $\frac{1}{4}$, .4991). There appears to be extensive hydrogen bonding between the diaquotetrachlororhodate(III) complexes within the anion layer judging from the fact that the *intermolecular* Cl(3)–O distance is only 3.103(9) Å, effectively the same as the *intramolecular* Cl(3)–O distance of 3.091(8) Å, although the Cl(3)–O–Cl(3′) *intramolecular* hydrogen bonding angle is rather narrow at 78°. Figure 2 illustrates this anion–anion interaction.

The tetramethylammonium cations are found to be tetrahedra with slightly inequivalent N–C bond lengths of 1.50(3) and 1.61(3) Å. There are no carbon–chlorine contacts between cations and anions less than 3.5 Å in the structure.

ACKNOWLEDGMENT

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