Alkylammonium Hexachlorometallates, IV[◇]

Synthesis and Crystal Structure of Bis(1,4-diammoniobutane) Diaquahydrogen Hexachlororhodate(III) Dichloride, $[H_3N-(CH_2)_4-NH_3]_2[H_5O_2][RhCl_6]Cl_2$

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Bis(1,4-diammoniobutane) diaquahydrogen hexachlororhodate(III) dichloride, $[H_3N-(CH_2)_4-NH_3]_2[H_5O_2][RhCl_6]Cl_2$ (**1**), was synthesized by the reaction of rhodium(III) chloride with 1,4-diaminobutane dihydrochloride in concentrated hydrochloric acid. The red compound slowly decomposes at room temperature, but is stable for months and up to 106 °C (DTA) under hydrogen chloride. Crystals of **1** were obtained by diffusion-controlled crystallization (space group $P\bar{1}$). The solid-state structure can be considered as a sequence of layers linked by hydrophobic interactions between the aliphatic chains of the 1,4-diammoniobutane ions. Within these layers the hydrophilic building blocks (hexachlororhodate and chloride anions, the diaquahydrogen cations and the ammonio groups of the diammoniobutane cations) are connected by a complex system of O–H···Cl and N–H···Cl hydrogen bonds. The $H_5O_2^+$ ion has a crystallographically imposed C_i symmetry and shows the typical 1:1 disorder of the central hydrogen atom for a symmetrically strong [O···O 2.406(10) Å] double-minimum potential O–H–O bond.

Only a few data concerning the physical and chemical properties, the conditions of crystallization, and the solid-state structures of alkylammonium, alkylenediammonium, and dialkylenetriammonium hexachlororhodates are known to date. This is surprising as the history of this class of compounds can be traced back to the first rhodium compound, isolated at the beginning of the 19th century. In 1804 by addition of ammonium chloride to aqua regia solutions, that he had obtained by dissolving residues of the platinum production process, Wollaston[2] precipitated tris(ammonium) hexachlororhodate(III) monohydrate $[NH_4]_3[RhCl_6]\cdot H_2O$ (**2**) and discovered the element rhodium. In 1854[3] Claus and in 1883[4] Wilm reported on alternative procedures for the synthesis and crystallization of this compound. A few years later Vincent[5] for the first time published a work on the synthesis and crystallization of rhodium salts by use of alkylamines. In 1914 v. Fraenkel[6] summarized his findings about the crystallization and composition of several alkylammonium hexachlororhodates and analogous hexachloroiridates. He was able to characterize all mono-, di-, tri-, and tetramethyl- as well as the corresponding ethylammonium hexachlororhodates. Gutbier[7] continued these investigations with different alkylamines and synthesized the first diammonioalkane hexachlororhodate, a compound with the formula $[H_3N-(CH_2)_2-NH_3]_2[RhCl_7]$ (**3**), which was discussed by Werner[8] with respect to its apparent heptacoordinated rhodium center, and which was also intensively dealt with by Meyer et al.[9] in the thirties of our century.

$[H_3N-(CH_2)_4-NH_3]_2[H_5O_2][RhCl_6]Cl_2$ **1**

$[NH_4]_3[RhCl_6]\cdot H_2O$ **2** $\quad$ $[H_3N-(CH_2)_2-NH_3]_2[RhCl_7]$ **3**

$[H_3N-CH(CH_3)-CH_2-NH_3]_2[RhCl_6]Cl$ **4**

$[H_3N-(CH_2)_2-NH_3]_2[RhCl_6]Cl\cdot H_2O$ **5** $\quad$ $[C(NH_2)_3][RhCl_6]\cdot H_2O$ **6**

$[H_3N-(CH_2)_2-NH_2-(CH_2)_2-NH_3][RhCl_6]$ **7**

To date the following ammonium salts with the hexachlororhodate anion were characterized by X-ray crystallography: The monohydrate **2** of the parent compound $[NH_4]_3[RhCl_6]$[10,11], the bis(diammonioalkane) hexachlororhodates **4**[12] and **5**[13], tris(guanidinium) hexachlororhodate monohydrate (**6**)[1], and diethylenetriammonium hexachlororhodate (**7**)[14]. In the course of the investigations of diammonioalkane hexachlororhodates exploring α,ω-diammonioalkane cations of different lengths as elements of crystal engineering, we succeeded in synthesizing and characterizing the structure of bis(1,4-diammoniobutane) diaquahydrogen hexachlororhodate(III) dichloride, $[H_3N-(CH_2)_4-NH_3]_2[H_5O_2][RhCl_6]Cl_2$ (**1**). In the literature only few ammonium oxonium double salts are described, either with tetraalkylammonium ions[15] or with

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species generated by protonation of complicated bicyclic nitrogen bases[16], both types being not capable of participating in extensive hydrogen bond formation.

Preparation and Characterization

Mixing of hydrochloric acid solutions of 1,4-diaminobutane dihydrochloride and rhodium(III) chloride yields a microcrystalline carmine red precipitate of **1** within a few minutes, which is insufficiently soluble in the solvent up to the boiling point for recrystallization. Larger, dark red crystals of this compound could only be obtained by slow diffusion-controlled crystallization. The compound slowly decomposes in air at room temperature, but is stable under hydrogen chloride for a prolonged period. In a closed ampoule with a trace of mother liquor it is remarkably thermally stable. According to DTA measurements decomposition starts at 106°C under these conditions, yielding a mixture of amorphous black and red products.

For a long time we did not succeed in growing X-ray quality crystals of **1**. Therefore a closer inspection of the compound was first based mainly on elemental analysis and spectroscopic results. With respect to the percentage contents of C, H, N, and Cl and to the UV/Vis spectrum, that confirms the presence of $[RhCl_6]^{3-}$ in **1**, the components H_2O and H_3O^+ are both needed to obtain a satisfying formula for **1**.

The IR spectrum in the range between 4000 and 400 cm^{-1} shows the complete set of bands for the diammoniobutane cation known from its dichloride[17] with a maximum deviation of the band maxima of 5 cm^{-1}. Additional features in the spectrum of **1** in this region are (i) a very strong and broad band at 3350 cm^{-1}, (ii) a strong band at 1626 cm^{-1}, and (iii) a very broad band of medium intensity in the range between 800 and 350 cm^{-1} with the typical sharp bands of the diammoniobutane ion superimposed to it. The absorption band around 300 cm^{-1} is associated with the Rh–Cl asymmetric stretching mode $\nu_3(F_{1u})$. The triple of bands at 329, 303, and 275 cm^{-1} is related closely to the spectrum of $K_3RhCl_6 \cdot H_2O$ in this region [328, 305, and 277 cm^{-1}[18], 328, 306, 283 (276 sh) cm^{-1}[19]] suggesting similar low-site symmetry for $RhCl_6^{3-}$ in **1** and in this compound.

The presence of single water molecules and H_3O^+ ions not involved in further significant interactions can be ruled out by means of the IR data. Water of crystallization is typically indicated by two sharp bands ($[enH_2]_2[RhCl_6]Cl \cdot H_2O$: 3587, 3530 cm^{-1}[13]; $Na_2[Fe(CN)_5NO] \cdot 2\,H_2O$: 3616, 3545 cm^{-1}[20]). In the spectra of oxonium compounds usually four broad and intense bands are assignable to the fundamentals of the pyramidal H_3O^+ ion[21], a feature that was also found for $H_5O_2^+$ ions with a strong but asymmetrical central O–H···O bond[21]. In this context the present IR spectroscopic results may be interpreted satisfactorily, if not uniquely, according to centrosymmetric $H_5O_2^+$ ions. Further evidence is provided by a comparison with the IR spectra of $[H_5O_2][ClO_4]$[22] and $[H_5O_2]Cl$[23,24]. The spectrum of the first compound shows clearly distinguishable bands of the centrosymmetric $H_5O_2^+$ in the same three regions as **1**, whereas the spectrum of the second compound, that is known to contain an asymmetric O–H···O bond, is completely different[25].

The nature of **1** with its rather complicated looking formula can be described in several ways. First of all, it can be understood simply as a quasi-quaternary compound with the components 1,4-diammoniobutane, diaquahydrogen, hexachlororhodate, and chloride. Furthermore, it can be rationalized as a triple salt of the known compounds $[H_3N(CH_2)_4NH_3]Cl_2$[26] and $[H_5O_2]Cl$[23,24] and the unknown $[H_3N(CH_2)_4NH_3]_3[RhCl_6]_2$. As will be later shown in detail, a description of the solid-state structure as an addition compound of $[H_3N(CH_2)_4NH_3]_2[RhCl_6]_2Cl$, an example of the above-mentioned class of alkylammonium "heptachlorides"[7,8], with hydrogen chloride dihydrate might be more valid: $[H_3N(CH_2)_4NH_3]_2[RhCl_6]$-$Cl \cdot [H_5O_2]Cl$.

Crystal Structure

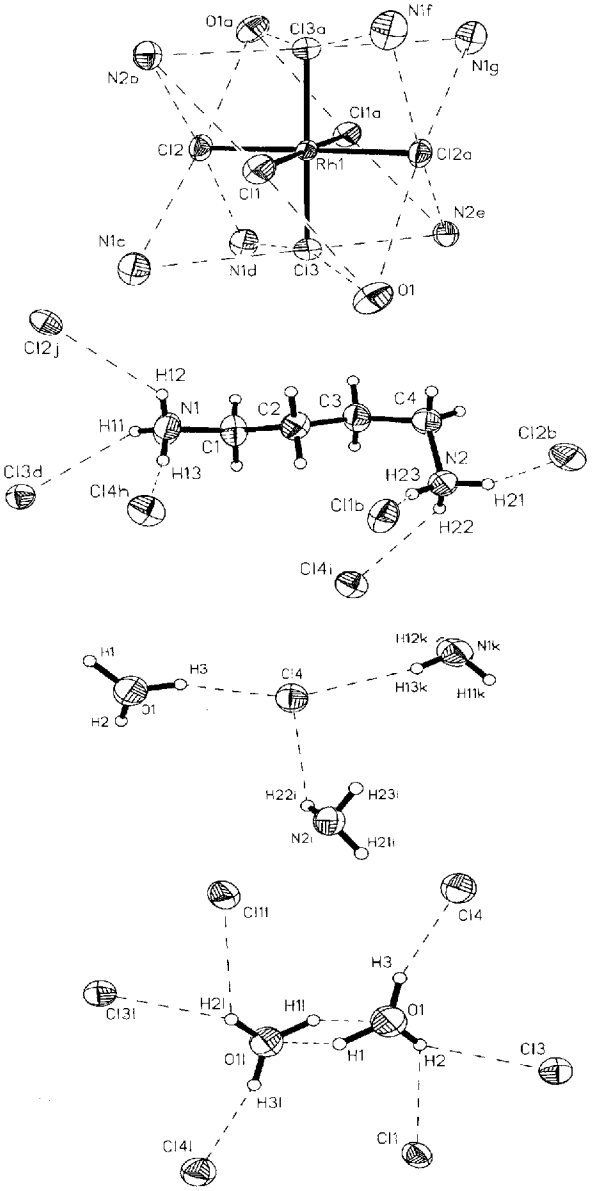
Compound **1** crystallizes in the triclinic space group $P\bar{1}$. The structure determination shows $[RhCl_6]^{3-}$, $[H_3N-(CH_2)_4-NH_3]^{2+}$, Cl^-, and $[H_5O_2]^+$ ions to be present in the crystal in a 1:2:2:1 ratio and thus confirms the ideas of the nature of the compound developed before. The rhodate and the hydronium ions have a crystallographically imposed C_i symmetry, the diammoniobutane and the chloride ions are in general positions. Bond lengths and angles in all the complex units are as expected, taking into account their solid-state interactions. Figure 1 shows all the building blocks of the structure of **1** together with their direct environments.

The $[RhCl_6]^{3-}$ ion is surrounded by six NH_3 groups of six diammoniobutane cations and two H_2O groups of two diaquahydrogen cations, the central N and O atoms of these groups forming a rather regular cube. The Cl ligands of the rhodate ion are in good approximation arranged in the middle of the faces of the cube. All the hydrogen bonds between the $[RhCl_6]^{3-}$ ion and the neighboring groups are weak.

The 1,4-diammoniobutane ion has six near chlorine neighbors lying approximately in the direction of the six N–H bonds. The interactions must be considered weak according to the N···Cl and O···Cl (3.17–3.56 Å) and H···Cl (2.43–2.69 Å) distances. In its given conformation the dication reminds of a walking stick (please note the torsion angles given in the caption to Figure 1). From N1 to C4 the aliphatic chain has an *all-trans* (zig-zag chain-like) arrangement, and N2 is about 65° bent out of the plane defined by these atoms.

The Cl^- ion (C14) in the structure is enclosed by one $H_5O_2^+$ ion and two NH_3 groups of different dications. The arrangement of C14, O1, N1k, and N1i is nearly planar. Considering the shorter H3···C14 distance of 2.12(4) Å compared to the two longer distances H13k···C14 [2.43(5) Å] and H22i···C14 [2.54(5) Å], it can be stated that Cl^- is primarily fixed at $H_5O_2^+$. The $H_5O_2^+$ ion lies on a crystallographic inversion center, and the central H1 atom shows [torsion angle H2–O1···O11-H31 79(5)°] the typical dy-

Figure 1. Diagram of the ions of **1** with their environments (displacement ellipsoids at the 50% probability level)[a]



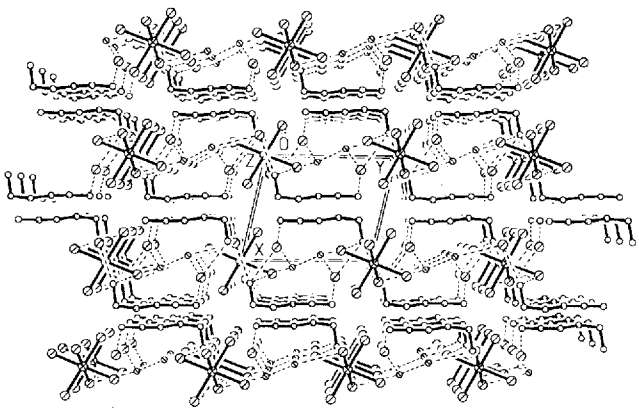
[a] Selected bond lengths [Å], angles [°], and torsion angles [°]: Rh1–Cl1 2.3546(6), Rh1–Cl2 2.3473(7), Rh1–Cl3 2.3551(7), N1–C1 1.480(3), N2–C4 1.487(3), C1–C2 1.505(3), C2–C3 1.527(4), C3–C4 1.507(3), O1–H1 1.06(8), O1–H2 0.98(4), O1–H3 0.87(4), all N–H 0.89 and all C–H 0.97; Cl1–Rh1–Cl2 90.58(2), Cl1–Rh1–Cl3 88.88(2), Cl2–Rh1–Cl3 91.41(2), N1–C1–C2 113.7(2), C1–C2–C3 109.2(2), C2–C3–C4 115.9(2), N2–C4–C3 112.2(2), H2–O1–H3 96(3), N1–C1–C2–C3 −170.7(2), C1–C2–C3–C4 −172.0(2), C2–C3–C4–N2 64.1(3); selected data concerning hydrogen-bonding geometry [Å]: Cl1···O1 3.399(4), Cl1···N2b 3.259(3), Cl2···N2b 3.345(4), Cl2···N1c 3.354(4), Cl2···N1d 3.578(4), Cl3···O1 3.163(4), Cl3···N1c 3.525(4), Cl3···N1d 3.291(4), Cl3···N2c 3.227(4), Cl4···O1 3.015(4); symmetry codes: a: $-x, -y, -z$; b: $1-x, -y, 1-z$; c: $x, 1+y, z$; d: $1-x, -1-y, -z$; e: $-1+x, y, -1+z$; f: $-1+x, 1+y, z$; g: $-x, -1-y, -z$; h: $1+x, -1+y, 1+z$; i: $1-x, -y, -z$; j: $x, -1+y, z$; k: $-1+x, 1+y, -1+z$; l: $-x, 1-y, -z$.

namic 1:1 disorder for a symmetrical double-potential well hydrogen bond[27]. The O···O bond length, the O–$H_{term.}$ bond lengths, the H_{term}–O–$H_{term.}$ angles, and the geometric parameters concerning the disordered H atom site are very similar to the corresponding parameters found by X-ray diffraction studies of good quality[28].

One of the two crystallographically independent terminal H atoms (H2) is engaged in a weak bifurcated hydrogen bond to two Cl atoms of one hexachlororhodate anion, the second (H3) participates in the much stronger C14···H3–O1 bond mentioned above in context with the Cl^- ion.

Figure 2 shows a packing diagram of **1** viewed along [0 0 −1]. The structure can be considered as a sequence of layers parallel to the *b*, *c* plane of the unit cell linked by hydrophobic interactions between the aliphatic chains of the 1,4-diammoniobutane ions. Whithin these layers the hydrophilic building blocks (hexachlororhodate and chloride anions, the diaquahydrogen cations and the ammonio groups of the diammoniobutane cations) are connected by a complex system of O–H···Cl and N–H···Cl hydrogen bonds in particular described above. Figure 3 shows the structure along [−1 0 0], i.e. viewed in the direction perpendicular to the layers. A system of approximately brick-shaped cavities with their longer edges oriented parallel to [0 2 1] can easily be recognized. Every second of the cavities is filled with $H_5O_2^+$ ions. In view of crystal engineering, the α,ω-diammonioalkane cations act as intelligent building blocks, because their conformational flexibility enables them to act as cavity building elements with exactly the right lengths for the inclusion of the given guest ions. In this context attempts seem to be fruitful to synthesize compounds with enlarged cavities by use of longer-chain diamines with the aim to enclose larger $H(H_2O)_n^+$ ions or other species.

Figure 2. Packing diagram of **1** along [0 0 −1]; hydrogen atoms are omitted for clarity; O–H···Cl and N–H···Cl hydrogen bonds are represented by dashed lines between N and O atoms, respectively, and Cl atoms



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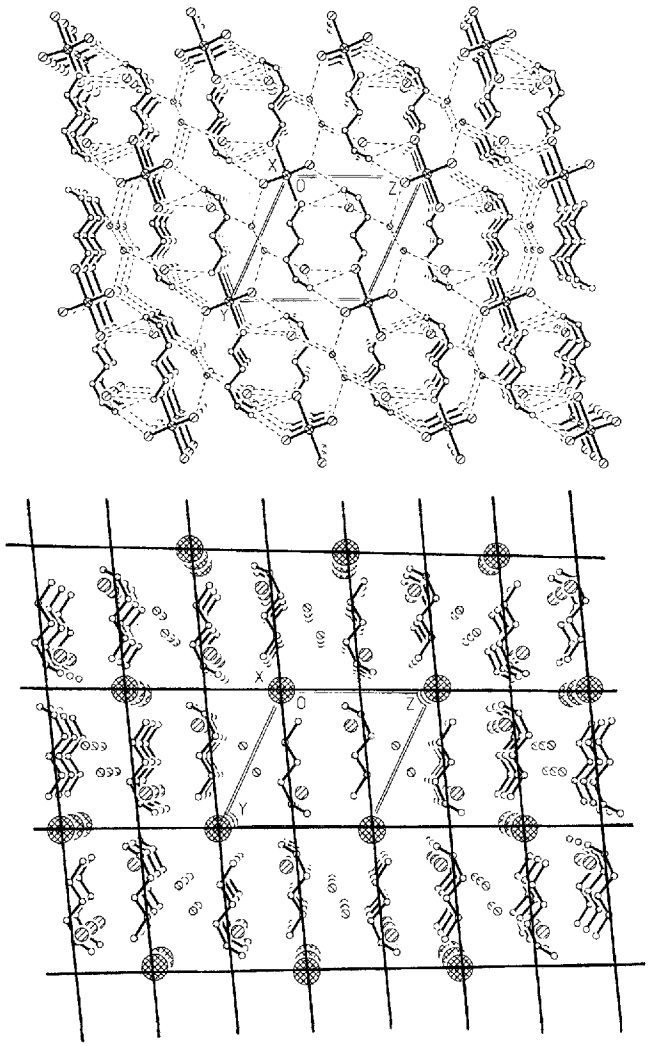
Experimental

Rhodium trichloride was used as a 6 M hydrochloric acid solution of $RhCl_3 \cdot n\ H_2O$ containing 20% of $RhCl_3$ (Degussa AG). 12 M Hydrochloric acid (99.9%, Riedel-de Haen) was used as received.

Figure 3. Packing diagram of **1** along [−1 0 0] as described for Figure 2 (top) and with cross-hatched circles for hexachlororhodate ions and grid lines demonstrating a system of nearly brick-shaped cavities, every second filled with $H_5O_2^+$ ions (bottom)



– Elemental analysis: Perkin Elmer Microanalyzer 240 – IR: nujol mull and KBr disk spectra, Perkin Elmer IR 883. – UV/Vis: Carl Zeiss, Spectralphotometer, Modell DMR 10.

$[H_3N-(CH_2)_4-NH_3]_2[H_5O_2][RhCl_6]Cl_2$ (**1**): 4 ml of 12 M hydrochloric acid containing 0.15 g (0.72 mmol) of $RhCl_3$ was carefully added to a solution of 0.10 g (1.13 mmol) of 1,4-diaminobutane (putrescine) in 4 ml of the same 12 M acid to form a lower layer. After about one week, 0.23 g (52%) dark red prismatic crystals with medium diameters between 0.05 and 0.3 mm were isolated from the lower region of the still colorless top layer. – $C_8H_{33}Cl_8N_4O_2Rh$ (603.9): calcd. C 15.91, H 5.51, Cl 46.96, N 9.28; found C 15.6, H 5.4, Cl 46.6, N 9.1. – IR: $\tilde{\nu}$ = 3394 (s), 3099 (s), 2550 (w), 2010 (w), 1626 (m), 1605 (sh), 1580 (sh), 1464 (m), 1444 (m), 1401 (w), 1330 (w), 1279 (m), 1109 (m), 1024 (w), 915 (w), 870 (w), 760 (w), 580 (w, vb), 493 (w), 434 (w), 329 (w), 303 (w), 275 (w). – UV/Vis (12 M hydrochloric acid): λ_{max} (lg ε) = 250 nm (4.506), 413 (1.912), 518 (2.000)[29].

Differential Thermal Analysis: For investigation with an instrument Linseis L62 DTA, 20 mg of the dark red crystals of **1**, grown as described above, were taken from the crystallization medium and sealed in a glass ampoule without drying. For calibration of the apparatus the melting points of potassium (63.3 °C) and indium (156.6 °C) were used, while the heating rate was 2 °C/min in all cases. Only one exothermic effect owing to the decomposition of **1** could be detected (room temp. to 200 °C; T_{onset}: 106.5 °C; $T_{react.}$: 111.5 °C; T_{max}: 116.0 °C; T_{offset}: 120.8 °C). With dry material continuous decomposition occurred already at room temp., and DTA curves strongly depend on the heating rate and on the history of the material.

Crystal Structure Analysis: Crystal sealed in thin-walled glass capillary; Siemens P4 diffractometer controlled by the XSCANS 2.10b[30] program, graphite monochromator, Mo-K_α radiation (λ = 0.71073), SHELXS-86[31] and SHELXL-93 programs[32] for structure solution by Patterson method and refinement by full-matrix least-squares. Semiempirical absorption corrections were applied to the intensity data by use of Ψ scans, max./min. transmission: 0.373/0.248. Hydrogen atoms at the carbon atoms of the diammoniobutane ion were included by using a riding model and one common U_{iso} value for each group. Hydrogen atoms of the ammonio groups were allowed to rotate around the C–N bond direction by starting from positions taken from the difference Fourier map; common U_{iso} value for each group. Hydrogen atom positions at the diaquahydrogen cation were obtained from a difference Fourier map and included in the refinement with individual isotropic displacement parameters; the site occupation factor of the disordered H1 atom was set to 0.5 and not refined. Anisotropic displacement parameters for all nonhydrogen atoms were used. $C_8H_{33}Cl_8N_4O_2Rh$, M = 603.93, triclinic, space group $P\bar{1}$, a = 7.4781(8), b = 9.2363(6), c = 9.8471(8) Å, α = 111.637(6), β = 109.585(7), γ = 94.177(8)°, V = 580.46(9) Å^3 (38 centered reflections between 12.53 < 2Θ < 30.02°), Z = 1, D_{calc} = 1.728 g·cm^{-3}, T = 293 K. Crystal size 0.1 × 0.2 × 0.4 mm; ω scan with variable scan speed: 4–25°/min; scan range: 4.8 ≤ 2Θ ≤ 52.5° (−1 ≤ h ≤ 9, −10 ≤ k ≤ 10, −12 ≤ l ≤ 11), 2386 reflections collected, 2191 symmetry-independent reflections (R_{int} = 0.0264), 2191 reflections used for refinement and 1752 reflections with $F^2 > 2.0\sigma(F^2)$; 145 parameters refined; $w^{-1} = 1/\sigma^2(F^2)$, refined extinction coefficient χ = 0.0008(3) ($F_c^* = kF_c[1 + 0.001\ \chi F_c^2\lambda^3/\sin(2\Theta)]^{-1/4}$), $R^1[F^2 > 2.0\ \sigma(F^2)]$ = 0.0379, wR^2 [all data] = 0.0657, $\Delta_{max}/\Delta_{min}$ = 0.53/−0.46 eÅ^{-3}[33].

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