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The Crystal and Molecular Structures of Diaquo-tetra-μ-(β-alaninatonium)-dirhodium(II) Tetraperchlorate Tetrahydrate

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The crystal structure of the binuclear carboxylato-bridged complex $[Rh_2(\beta\text{-}Ala)_4(H_2O)_2](ClO_4^-)_4\cdot 4H_2O$ *has been determined by X-ray crystallography. The compound crystallizes in the orthorhombic space group Pccn with four formula weights in a unit cell of dimensions* a = *14.435(7),* b = *19.177(5), and* c = *13.385(5)* Å. *The structure was solved by the Patterson method and refined to a final R value of 5.7%. The* $Rh_2(\beta\text{-}Ala)_4(H_2O)_2$ *tetravalent cation is located on a crystallographic inversion center, with a Rh–Rh distance of 2.386(3)* Å, *and the two water molecules are axially bound to Rh at a distance of 2.33* Å. *These values are the same as those found in* $Rh_2(OAc)_4(H_2O)_2$, *which indicates that these two carboxylate R groups have approximately equal inductive effects. The* trans *effect between the Rh–Rh and Rh–*OH_2 *bonds is noted, as is the unusually large carboxylate O–C–O angle of 127° – a value found only in the Rh series of tetracarboxylate complexes. There are three independent types of perchlorate anions in the lattice, two of which are disordered over two statistically equivalent positions. All hydrogens in the ammoniums and waters participate in hydrogen bonding. There are both intramolecular and intermolecular hydrogen bonds, involving all of the different molecular species in the cell.*

TABLE I. Summary of Data Collection and Processing Parameters.

Space Group	Pccn, orthorhombic
Cell Constants	a = 14.435(7) Å b = 19.177(5) c = 13.385(5) V = 3705 Å^3
Molecular Formula	$Rh_2Cl_4O_{30}N_4C_{12}H_{40}$
Formula Weight	1068.10
Formula Weights per Cell	4
Density	1.91 g cm^{-3}
Absorption Coefficient	11.6 cm^{-1}
Radiation (MoKα)	λ = 0.71073 Å
Collection Range	$4° \leqslant 2\theta \leqslant 45°$
Scan Width	$\Delta\theta = (1.10 + 0.35 \tan\theta)°$
Maximum Scan Time	300 s
Scan Speed Range	0.4 to 4.0° min^{-1}
Total Data Collected	2846
Independent Data with I > 3σ(I)	1063
Total Variables	165
R $\Sigma\lVert F_o\rvert - \lvert F_c\rVert/\Sigma\lvert F_o\rvert$	0.057
R $\lvert\Sigma_w(F_o\rvert - \lvert F_c\rvert)^2\Sigma_w\lvert Fo\rvert^2]^{1/2}$	0.049
Weights	$w = [\sigma(F)]^{-2}$

Introduction

We recently reported the synthesis and some of the preliminary structural details of the title compound $Rh_2(\beta\text{-}Ala)_4(H_2O)_2$, a binuclear carboxylato-bridged rhodium compound [1]. Many such complexes involving a variety of transition metals have lately been the subject of controversy regarding the nature of the metal–metal interaction – specifically in the case of rhodium(II), whether it should be considered a triple bond [2] or a very short single bond [3, 4]. The latter, more recent theory seems to be enjoying the most current favor, even though it has been pointed out that the shortness of the bond is not due to any strain on the part of the carboxylate bridge [5]. Another interesting facet of these complexes is the variable strength of the observed *trans* effect with regard to the axially bound ligands. A recent survey [5] shows that the M–M and M–L_{ax} bond lengths may or may not be altered by changing the nature of the carboxylate bridge ligand, and we wanted to investigate this further by using a zwitterionic amino acid bridge which is capable of multiple hydrogen bonding. The structure of the analogous acetate, $Rh_2(OAc)_4(H_2O)_2$, has already been reported [2] and can be compared with. Finally, we wish

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TABLE II. Atomic coordinates and Thermal Parameters (×1000, RH × 10000).

ATOM	X/A	Y/B	Z/C	U11	U22	U33	U12	U13	U23
RH	.5499(1)	-.0388(1)	.9558(1)	378(9)	318(7)	268(6)	97(10)	-25(12)	-65(12)
O4	.596(1)	.045(1)	.879(1)	76(13)	56(10)	28(8)	-12(10)	6(7)	7(9)
O5	.503(1)	.118(1)	.956(1)	16(8)	57(9)	41(8)	3(7)	-1(9)	-29(9)
O6	.445(1)	-.057(1)	.856(1)	40(0)	60(10)	24(7)	22(9)	1(0)	-14(7)
O7	.352(1)	.018(1)	.941(1)	31(9)	56(10)	33(8)	11(7)	6(8)	-9(8)
O8	.649(1)	-.115(1)	.872(1)	64(13)	45(10)	46(10)	23(8)	-9(8)	-5(8)
C1	.561(2)	.106(1)	.899(2)	75(23)	26(12)	49(15)	20(15)	-17(15)	-18(12)
C2	.612(2)	.162(1)	.842(2)	60(19)	10(11)	68(16)	-8(11)	24(13)	11(11)
C3	.589(2)	.235(1)	.870(2)	49(20)	103(0)	157(30)	-6(19)	23(22)	56(23)
N4	.494(1)	.251(1)	.877(2)	111(23)	96(16)	109(0)	-21(18)	43(18)	28(17)
C5	.369(2)	-.024(1)	.871(1)	58(18)	34(15)	42(14)	-6(12)	-5(13)	2(11)
C6	.288(1)	-.045(1)	.802(1)	44(16)	43(14)	44(13)	15(12)	-13(12)	15(13)
C7	.199(2)	-.011(1)	.834(1)	46(18)	88(20)	30(14)	10(15)	-20(13)	-7(13)
N8	.190(1)	.064(1)	.832(1)	101(20)	98(19)	52(14)	42(14)	-50(13)	-8(12)
O9	-.003(1)	.100(1)	.841(1)	53(11)	46(9)	59(10)	-12(8)	4(8)	-11(8)
O10	.028(2)	.227(1)	.648(1)	148(9)					
CL1	.086(1)	.410(1)	.606(1)	64(2)					
O1A	.001(1)	.376(1)	.581(1)	128(6)					
O1B	.083(1)	.481(1)	.575(1)	128(6)					
O1C	.100(1)	.406(1)	.711(1)	128(6)					
O1D	.160(1)	.375(1)	.556(1)	128(6)					
CL1'	.087(1)	.399(1)	.611(1)	64(2)					
O1E	.062(1)	.342(1)	.550(1)	128(6)					
O1F	.010(1)	.444(1)	.622(1)	128(6)					
O1G	.162(1)	.436(1)	.567(1)	128(6)					
O1H	.115(1)	.375(1)	.707(1)	128(6)					
CL2	.250(0)	.250(0)	.884(1)	73(3)					
O2A	.190(1)	.213(1)	.818(1)	118(5)					
O2B	.198(1)	.297(1)	.943(1)	118(5)					
CL3	.750(0)	.250(0)	.101(1)	82(3)					
O3A	.748(1)	.306(1)	.033(1)	134(8)					
O3B	.660(1)	.220(1)	.110(1)	134(8)					
O3C	.813(1)	.198(1)	.066(1)	134(8)					
O3D	.780(1)	.273(1)	.197(1)	134(8)					
H2A	.685(0)	.156(0)	.853(0)	60(0)					
H2B	.596(0)	.156(0)	.764(0)	60(0)					
H3A	.622(0)	.248(0)	.940(0)	60(0)					
H3B	.617(0)	.271(0)	.813(0)	60(0)					
H4A	.468(0)	.220(0)	.931(0)	60(0)					
H4B	.486(0)	.300(0)	.898(0)	60(0)					
H4C	.464(0)	.242(0)	.813(0)	60(0)					
H6A	.303(0)	-.029(0)	.726(0)	60(0)					
H6B	.278(0)	-.101(0)	.805(0)	60(0)					
H7A	.144(0)	-.030(0)	.786(0)	60(0)					
H7B	.185(0)	-.026(0)	.910(0)	60(0)					
H8A	.201(0)	.082(0)	.764(0)	60(0)					
H8B	.126(0)	.078(0)	.855(0)	60(0)					
H8C	.236(0)	.085(0)	.880(0)	60(0)					

to clarify the nature of the hydrogen bonding in the unit cell and the amount of water of crystallization present, both of which were given erroneously in our preliminary report [1]. The disorder of the perchlorates also turns out to be not quite so complicated as we originally thought, albeit somewhat more perplexing.

Experimental

All details of the synthesis have been reported previously [1]. The crystal used for all X-ray measurements was a dark green plate of approximate dimensions ½ X ½ X ¼ mm. An Enraf-Nonius CAD-4 automatic diffractometer was used, with MoKα radiation monochromatized by a dense graphite crystal assumed for all purposes to be ideally imperfect. The unit cell constants used in data collection were obtained from a least squares fit of 25 centered reflections, and these values are listed in Table I, along with other pertinent crystal data. The Laue symmetry was found to be mmm, and from the systematic absences noted, the space group was determined to be Pccn. Intensity data were measured using

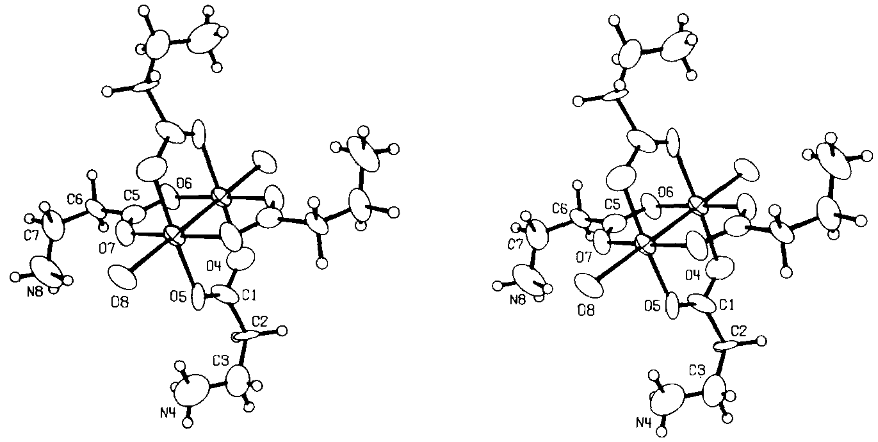

Fig. 1. Stereoscopic view of the $Rh_2(\beta\text{-}Ala)_4(H_2O)_2$ tetravalent cation showing the atom labelling scheme. The atoms are shown as 50% equiprobability ellipsoids, with hydrogens as spheres of arbitrary diameter. There are probable intramolecular hydrogen bonds between each β-alanine zwitterion.

the $\theta-2\theta$ scan technique in bisecting position. The crystal had to be coated with acrylic polymer (Krylon®) to prevent decomposition by loss of water, and this tended to raise the backgrounds somewhat. Two standard reflections were monitored after every two hours of exposure time to check crystal stability, and a third was recentered periodically to test for any crystal shifting. No abnormalities were noted in any of the three sets of reflections at the conclusion of data collection.

The structure was solved by interpretation of the Patterson map, which yielded the location of the rhodium atom. The remaining non-hydrogen atoms were all located in subsequent difference Fourier syntheses, including the partially disordered perchlorate oxygens. These latter atoms refined quite poorly due to the obvious high positional correlations, however, and finally each of the perchlorate groups had to be treated as a rigid body. The parameters used to define the rigid groups were taken from a recent crystal structure which we were working on [6]. When the temperature factors of the disordered groups were fixed at equal values, the population parameters all refined to between 49 and 51% occupancy, and so in the final cycles the populations of the two orientations in each of the two disordered perchlorate groups were fixed at 50%. The ordered perchlorate chlorine (Cl2) and one of the disordered ones (Cl3) lie on two-fold crystallographic axes. The other disordered group was found to have two slightly different chlorine coordinates (Cl1 and Cl1′) in general positions. There are thus four ordered perchlorates and twelve disordered perchlorates in the unit cell. Sixteen water molecules (O9 and O10) were also found in the cell (four per Rh_2 dimer), although their hydrogens could not be located. The hydrogens on the β-alaninatonium ions were entered ideally and held fixed, those on $-NH_3^+$ being staggered with respect to the adjacent ones on methylenes. In the final cycle of refinement, a few of the anisotropic thermal parameters had to be held constant to prevent the tensors from going non-positive definite, and these are indicated in the final list of positional and thermal parameters (Table II) by e.s.d.s of zero. The idealized hydrogens also have zero e.s.d.s.

TABLE III. Intramolecular Bond Distances (Å)*.

Rh–Rh′	2.386(3)	C1–C2	1.51(3)
Rh–O4	2.03(1)	C2–C3	1.48(3)
Rh′–O5	2.06(1)	C3–N4	1.40(3)
Rh–O6	2.05(1)	C5–O6	1.27(3)
Rh′–O7	2.02(1)	C5–O7	1.27(2)
Rh–O8	2.33(1)	C5–C6	1.55(3)
C1–O4	1.30(2)	C6–C7	1.50(3)
C1–O5	1.16(3)	C7–N8	1.44(3)

*All Cl–O distances were held fixed at 1.42 Å, all C–H distances at 1.08 Å and all N–H distances at 1.00 Å.

In the final cycle of full-matrix least squares, 165 variables were refined, including an overall scale factor. The final agreement factors are $R = 0.057$ and $R_w = 0.049$, and the goodness-of-fit is 1.63. Final shifts in all parameters were less than one-half of their standard deviations. The atomic scattering factors for the non-hydrogen atoms were computed from numerical Hartree–Fock wave functions [7]; for hydrogen those of Stewart, Davidson, and Simpson [8] were used. The anomalous dispersion coefficients of Cromer and Liberman [9] were assumed for rhodium and chlorine. All calculations were made with the SHELX-76 series of programs [10]. The atom labelling scheme for the Rh_2 dimer is shown in Fig. 1, which shows the inversion center between the

TABLE IV. Intramolecular Bond Angles (°).*

O4–Rh–O6	92.6(5)	O4–C1–C2	111(2)
O4–Rh–O8	92.9(5)	O5–C1–C2	123(2)
O6–Rh–O8	91.9(5)	C1–C2–C3	116(2)
O4–Rh–O5	174.5(5)	C2–C3–N4	116(2)
O6–Rh–O7′	176.8(5)	Rh–O6–C5	117(1)
O8–Rh–Rh′	179.0(3)	Rh′–O7–C5	120(1)
O4–Rh–Rh′	87.5(4)	O6–C5–O7	127(2)
O6–Rh–Rh′	89.0(4)	O6–C5–C6	116(2)
Rh–O4–C1	119(1)	O7–C5–C6	117(2)
Rh′–O5–C1	120(1)	C5–C6–C7	112(2)
O4–C1–O5	127(2)	C6–C7–N8	121(2)

*All O–Cl–O angles were held fixed at 110°. All hydrogens were held at essentially tetrahedral sites, with ammonium hydrogens staggered with respect to adjacent ethylene hydrogens.

TABLE V. Selected Torsion Angles (°).

O4–Rh–Rh′–O7	92.3
O5–Rh′–Rh–O6	−91.1
O4–Rh–Rh′–O5	1.6
O6–Rh–Rh′–O7	−0.4
Rh–O4–C1–O5	−1.7
Rh–O4–C1–C2	173.8
O4–C1–C2–C3	−170.1
C1–C2–C3–N4	−47.8
Rh–O6–C5–O7	−0.0
Rh–O6–C5–C6	−173.0
O6–C5–C6–C7	173.0
C5–C6–C7–N8	62.3

TABLE VI. Possible Hydrogen Bonds (Å).

Intramolecular			
N4···O5	2.76(3)	N8···O7	2.90(2)
Intermolecular			
N4···O9	2.91(3)	N8···O8	2.96(2)
N4···O10	3.12(3)	N8···O9	2.86(2)
N4···O1E	3.01(3)	N8···O2A	2.86(3)
N4···O2A	2.86(3)		
N4···O2B	3.05(2)		
O1B···O9	2.80(2)	O3B···O10	2.77(3)
O1D···O8	2.92(2)	O8···O10	2.78(2)
O1E···O10	2.60(2)	O6···O9	2.86(2)

two rhodium atoms. The perchlorate oxygens are labelled with the same numbers as the chlorines to which they are bonded (O1A–D on Cl1, O1E–H on Cl1′). Intramolecular bond lengths and angles are given in Tables III and IV based on the positions in Table II. Table V lists selected torsion angles and Table VI shows the close contacts which are most likely to be hydrogen bonds, both intra- and intermolecular.

Results and Discussion

$Rh_2(\beta\text{-}Ala)_4(H_2O)_2$ Dimer

The tetravalent cation consists of a pair of Rh(II) atoms axially bound by two waters and bridged by four β-alanine zwitterions. There is a crystallographic inversion center between the rhodiums, and the carboxylate bridges are in nearly a D_{4h} arrangement about them (Fig. 1). The disposition of bonded atoms about each rhodium is essentially octahedral (see Table IV). The bond distances and angles between the rhodiums and the surrounding oxygens are identical, within experimental error, to the values reported for the analogous molecules $Rh_2(CO_3)_4(H_2O)_2$ [11], and $Rh_2(OAc)_4(H_2O)_2$ [2], and only marginally different from those of $Rh_2(piv)_4(H_2O)_2$ [12].

The Rh–Rh distance of 2.386 Å is one of the shortest known in these complexes, equal to that observed in $Rh_2(OAc)_2(H_2O)_2$ [2], while the Rh–OH_2 bond length of 2.33 Å is quite long and indicative of a very weak coordination. These observations are quite in keeping with qualitative *trans*-influence theory, which predicts stronger M–M bonding as the strength of the M–L_{ax} σ bond decreases. As [13] point out, the sensitivity of the M–M bond to this effect should be inversely proportional to the strength of the M–M bond, the stronger bonds exhibiting the least perturbation. And it has been shown that the Mo–Mo quadruple bond is a limiting case, in which the extremely strong M–M bond actually *precludes* axial ligation [14]. Although it was originally hoped that the determination of the degree of the *trans* effect in Rh_2 dimers might reveal the true formal bond order of the Rh–Rh bond, the Rh_2 case has actually been found to be anomalous [5] with respect to the other metals studied (Mo, Cr, Cu), the only conclusion being that "...the Rh–Rh bond is intermediate in strength between that of the Mo–Mo and Cr–Cr bonds, irrespective of its bond order" [13]. Since our Rh–Rh and Rh–OH_2 distances are indistinguishable from those already known [2], we are unable to shed any new light on this particular point.

One area in which we do contribute new and potentially valuable information is in regard to the question of whether the Rh–Rh distance depends on the inductive effect of the R group of the carboxylate bridge (RCO_2^-). In the case of the very strong Mo_2 dimers, the nature of the R group has no effect on the Mo–Mo bond [14]. However, both the Cr_2 [15] and Rh_2 dimers [11, 12] exhibit such an effect, with the most sensitive measure apparently being the O–C–O angle [5]. Our angles average 127° (Table IV), which for an M–M separation of 2.386 Å falls within the cluster of Rh_2 data in Fig. 7 of Koh and Christoph. As they explain, these angles are exceptionally large in the Rh_2 complexes, with the speculation that "...the carboxylate bridges, perhaps through the π system, facilitate bonding interactions between the metal centers that would not occur in the absence of the bridges". Oddly enough, they do not pursue the idea to what we feel is the logical conclusion – that the Rh–Rh bond is indeed a formal single bond which has been abnormally shortened through just such a synergistic interaction as they propose. They do point out that their idea is in accord with the very strong mixing of metal and ligand atomic orbitals noted by Norman and Kolari [3], but in a separate paper they conclude that such extensive mixing makes formal bond order not a useful measure of Rh–Rh interactions [16]. In a series of unrelated compounds of the type $M_2Br_2(E_2L_{2n})$ which we have been working on for several years [17–20], we have been led to the conclusion of the existence of extraordinarily short single bonds instead of formal multiple bonds, and these results will be forthcoming shortly [21].

Since our Rh–Rh separation is the same as in the tetra-acetate analog [2], the obvious conclusion is that the relative inductive effects of the two R groups, CH_3 and $CH_2CH_2NH_3^+$, are approximately equal. This is not very surprising, although there may be some perturbation caused by the considerable hydrogen bonding which the NH_3^+ group undergoes (*vide infra*). The bond lengths and angles in the β-alaninatoniums are not unusual, but the standard deviations are a bit too high to allow any meaningful comparisons with literature values. A very similar complex involving Mo and glycine has been reported [22] with the most noticeable difference being the telltale O–C–O angle.

Additional Cell Contents and Hydrogen Bonding

Along with the four dimeric cations in the unit cell there are sixteen perchlorates and sixteen waters of crystallization. Figure 2 shows the particular cation centered about ½, ½, ½ and all of the smaller moieties in the cell. The four ordered perchlorates (type 2) and four of the disordered ones (types 3) are on two-fold crystallographic axes parallel to *c*, while the remaining eight (type 1) are generally distributed along with the water molecules. In order to make sense out of the molecular packing, and hopefully to explain why some perchlorates are ordered while others adopt two equally stable orientations, we calculated all of the close intermolecular contacts involving O and N out to 3.5 Å to check for possible hydrogen bonding. Those likely candidates are listed in Table VI. Unfortunately, since the water hydrogens could not be located and since the ammonium hydrogens were ideally fixed, the usual parameters involving the protons were either unobtainable or open to skepticism, so we have omitted them from the table. As can be seen there are intramolecular hydrogen bonds from the ammonium nitrogens to carboxylate oxygens within each of the β-alaninatoniums. In fact, Fig. 1 shows that the idealized hydrogen positions (calculated so as to be staggered with respect to the methylene hydrogens) are quite nicely directed towards the oxygens. The O•••N separations show both to be stronger than the average hydrogen bond of this type as found by Whuler *et al.* [23], with a length of 3.05 Å. The pseudo-six-membered ring thus formed would be expected to be quite stable, as has been noted previously [24].

There are several types of intermolecular hydrogen bonds, of varying strengths, shown in the lower part of Table VI. The N•••O type involve perchlorate oxygens and waters of crystallization, and there is even one which bridges two dimers (N8•••O8). Most of these appear stronger than the normal NH•••O bond, probably due to the formal charge on the ammonium nitrogen. Wallwork [25] concluded that NH_n^+ donor groups should be about 0.14 Å closer than NH_n donors, on the average, because of the excess charge density, and this is in the neighborhood of what we see. The large range of values (2.86 to 3.12 Å) is not unusual, and is in good agreement with the 2.82 to 3.09 Å range found in hydroxylammonium perchlorate [26]. Unfortunately the authors of the Mo-glycine paper [22] chose to completely ignore the possible hydrogen bonding in their zwitterionic complex, and so we do not have these values to compare with. The O•••O hydrogen bonds shown in Table VI involve the water, carboxylate, and perchlorate oxygens. Most would be considered to be strong attractions when compared to the average value of 2.90 Å in the literature [23]. The overall hydrogen bonding is as follows: one terminal nitrogen (N4) bonds to six oxygens– one carboxyl, two water, and three from perchlorates. This can only be accomplished if each hydrogen is shared, which is a fairly common occurrence in, for example, trisethylenediamine complexes [27, 28]. The shared pairs appear to be H4A (O5 and O2B), H4B (O9 and O1E), and H4C (O10 and O2A). N8, on the other hand, is not nearly so intricately engaged, with close contacts to one carboxylate, one perchlorate, and two water oxygens. The sole shared hydrogen goes to O8 and O2A. It is interesting to note that the cation hydrogen bonds to all the other species except perchlorate type 3, although type 3 bonds to O10 which then bonds to N4, thus providing a weak link perhaps. The remaining O•••O contacts are between

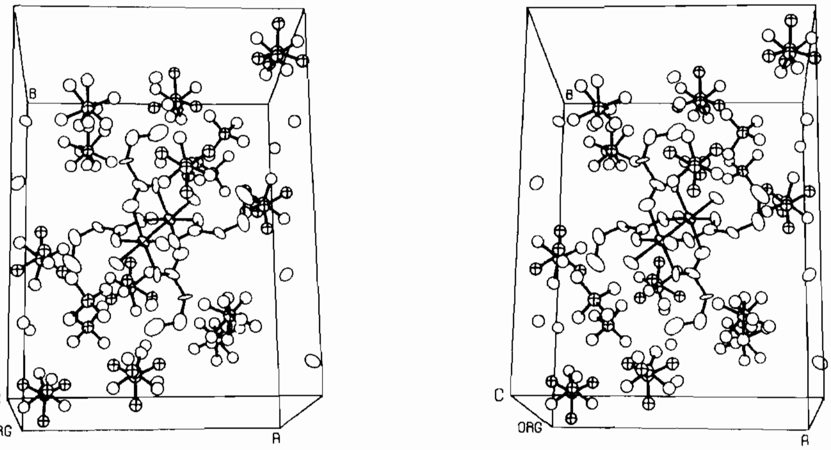

Fig. 2. Stereoscopic packing diagram showing the contents of the unit cell minus partial cation fragments. Type 1 perchlorates have 'crossed' oxygens for one orientation and clear for the other. Type 2 is ordered and shows four clear oxygens. Type 3 shows eight clear oxygens which upon careful inspection can be seen to comprise two ideal tetrahedra about chlorine. The eight O9 waters appear as ellipsoids, while the eight O10 waters show as spheres. Note how sets of two 'arms' of the cation lock the ordered perchlorates into position.

waters and perchlorates, except for the O6···O9 water–carboxylate bond which occupies the carboxylate oxygen not tied up by the ammonium nitrogen. It seems odd that O4 is not similarly engaged since there is a large void around it, and perhaps a hexahydrate version of this complex exists in which the additional waters fill this role. As is, every single hydrogen on the ammoniums and waters seems to be involved in hydrogen bonding: O8 donates to O1D and O10, O9 to O1B and O6, and O10 to O1E and O3B; the others were discussed above. Both of the free waters have two hydrogen bonds directed at them, presumably through the lone electron pairs, thus completely filling their coordinations. This, combined with the multiple bifurcation of the ammonium hydrogens, makes it hard to imagine a more totally involved complex.

Lastly there remains the question of the perchlorates. It is fairly easy to see why type 3 is disordered – it bonds to practically nothing else in the cell, and merely occupies space and balances charge in the lattice. Similarly, the ordered arrangement of type 2 is sensible when Fig. 2 is viewed, and it is seen that two of the 'arms' of the cation grasp it from opposite sides so strongly that there exists a classic transmission of symmetry whereby one of the three-fold axes of the perchlorate is forced into parallel with the Rh–Rh axis. The disorder of the type 1 perchlorates, however, is a bit more unusual. As can be seen in Fig. 2, two of the type 1 Cl–O vectors are nearly co-linear (Cl1–O1C, Cl1′–O1H), while the remaining ones are neatly staggered. In both positions the perchlorate has two reasonably strong hydrogen bonds available – one from a free water molecule and one from the cationic unit. Apparently, since the population parameters refined to about 50%, each of these environments is equally attractive. Such statistical disorder of the oxygens caused by alternative hydrogen bonding possibilities has been encountered before, in the case of sulfate ions [29], but in our case some slight additional difficulty must arise when the choice is being made during crystallization since the chlorines refine to different locations.

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