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The Crystal and Molecular Structure of Triamminetriaquocobalt(III) Perchlorate, $[Co(NH_3)_3(H_2O)_3](ClO_4)_3$. A Highly Disordered Structure

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The structure of triamminetriaquocobalt(III) perchlorate has been determined by the Patterson method. It crystallizes in the cubic space group Pm3 with a unit cell dimension of a = *11.213(2)Å. The structure was refined to final weighted and unweighted R factors of 0.062 and 0.082, respectively. The two independent cobalt centers were found to exhibit different degrees of ligand disorder. One center appears to have a meridional distribution of ligands while it is not possible to determine whether the distribution about the second cobalt center is meridional or facial. The three independent perchlorate groups are also disordered.*

Introduction

Recently, Davies and his coworkers [1] investigated the product distribution resulting from the reaction of ammonium salts with carbonatocobaltate(III) species in alkaline bicarbonate solution. Acidification of the product mixture followed by gradient elution from a cation exchange column with perchloric acid gives strongly acidic perchlorate solutions from which pure, crystalline ammineaquocobalt(III) perchlorates can be isolated by slow evaporation [1]. One such product is a carmine-red crystalline solid with the empirical formula $Co(NH_3)_3(H_2O)_3(ClO_4)_3$, which, from consideration of the likely mechanism of its formation and comparison with earlier spectral data for triamminecobalt(III) products obtained by a different route [2], was tentatively concluded to be the complex salt *fac*-$[Co(NH_3)_3(H_2O)_3](ClO_4)_3$ [1].

Structural data, which would be a valuable aid in understanding the interesting reactivity variations [1, 3] in the ammineaquocobalt(III) series $Co(NH_3)_n(H_2O)_{6-n}^{3+}$ is scarce. To date, the only triammineaquocobalt(III) complex which has been structurally characterized [4] is the species $[(NH_3)_3Co(OH,OH,OH)Co(NH_3)_3]^{3+}$, which was obtained from alkaline solution; available evidence indicates that a trihydroxobridged dimer, which necessarily has a *facial* arrangement of ammine ligands, is also present in solution under the isolation conditions [4].

In this study we have investigated the crystal and molecular structure of $[Co(NH_3)_3(H_2O)_3](ClO_4)_3$ in an attempt to establish the ligand distribution about the cobalt(III) center.

Experimental

Single crystals used in this determination were prepared as described by Bodek, Davies and Ferguson [1]. The crystals of triamminetriaquocobalt(III) perchlorate are carmine red and have a stoichiometric ammonia:cobalt(III) ratio of 3.03 ± 0.04 (ten determinations) and contained 9.02 ± 0.03% nitrogen (two determinations). Calculated nitrogen for $Co(NH_3)_3(H_2O)_3(ClO_4)_3$ is 9.07%. They belong to the cubic system with unit cell dimensions: a = 11.213(2) Å. The measured density of 2.16 g/cm^3 agrees well with the calculated density of 2.18 g/cm^3 for Z = 4 formula weights per unit cell. The lack of any systematic absences and indication of a centrosymmetric distribution of normalized structure factor amplitudes ($|E_{hkl}|$) are consistent with the space group Pm3.

Three dimensional intensity data were collected on a Syntex P2$_1$ automated diffractometer using monochromatized molybdenum ($K\bar{\alpha}$) radiation (λ = 0.71069 Å) up to a 2θ limit of 55°. The θ–2θ scan technique was used to measure 293 unique reflections of which 265 were considered observed ($I \geq 1.25\ \sigma$

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(I)). Lorentz and polarization corrections were applied to the data. Corrections for absorption were not made ($\mu[\lambda(\text{Mo}K\bar{\alpha})] = 19.2\ \text{cm}^{-1}$).

Solution and Refinement of the Structure

Interpretation of the three-dimensional Patterson function suggested that two independent cobalt atoms were located in special positions at the origin (0, 0, 0) and on the cube faces (0, 1/2, 1/2) and three independent chlorine atoms in special positions on the cube edges (0, 0, 1/2), on the body diagonal (x, x, x) and at the center of the unit cell (1/2, 1/2, 1/2). Positions of the ammine and aquo ligands around the cobalt atom were revealed in subsequent Fourier synthesis maps. The oxygen atoms of all three independent perchlorate ions showed a considerable degree of disorder but all oxygens were accounted for with partial site occupancies given to each one. Refinement of the structure using individual isotropic temperature factors resulted in an R-value of 0.19.

The site symmetry of the cobalt atom at the origin (m3) dictates that its six ligands are equivalent. As a result, its lone unique ligand, designated as X(1), is an aquo group half of the time and an ammine group the other half of the time. This means that the triammine triaquocobalt(III) ion at this position is completely disordered and that it is not possible to determine whether it is a *fac* or a *mer* isomer. The ligand atom X(1) was refined as a hybrid oxygen–nitrogen atom. The cobalt atoms on the faces have mmm site symmetry requiring that ligands *trans* to each other be equivalent. On the basis of the three different cobalt–ligand distances, the three independent ligand atoms around this cobalt atom were assigned as an ammine group (N(2)), an aquo group (O(2)) and a disordered ammine–aquo hybrid (X(2)). There is a paucity of data for cobalt ammine–aquo complexes. A survey of the literature [4, 5] indicates that it is difficult to distinguish between Co–N and Co–O bonds but that the Co–N distance generally is the shorter. The ligand atom involved in the shortest bond distance with Co(2) was assigned as an ammine nitrogen (N(2)), that involved in the intermediate distance as an aquo oxygen (O(2)) and that involved in the longest distance as an oxygen-nitrogen hydrid (X(2)). This latter assignment of X(2) was made on the basis of the similarity in the Co(1)–X(1) and Co(2)–X(2) bond distances as well as the similarity of the anisotropic temperature factors of X(1) and X(2). Both X(1) and X(2) have a flattened ellipsoidal shape. The arrangement of disordered ligands about Co(2) is consistent only with the all *trans(mer)* isomer, precluding the presence of the *fac* isomer.

TABLE I. Positional and Thermal Parameters of Nonhydrogen Atoms.

Atom	x	y	z	U11[a]	U22	U33	U12	U13	U23	Occupancy
Co(1)	0.0000	0.0000	0.0000	2.2(2)[b]	0.0	0.0	0.0	0.0	0.0	1.0
Co(2)	0.5000	0.0000	0.5000	7.7(4)	1.9(2)	3.6(3)	0.0	0.0	0.0	1.0
Cl(1)	0.5000	0.0000	0.0000	3.3(4)	8.3(6)	1.3(4)	0.0	0.0	0.0	1.0
Cl(2)	0.7492(4)	0.7492(4)	0.7492(4)	6.0(1)	6.0(1)	6.0(1)	0.4(2)	0.4(2)	0.4(2)	1.0
Cl(3)	0.5000	0.5000	0.5000	3.3(3)	3.3(3)	3.3(3)	0.0	0.0	0.0	1.0
X(1)	0.1737(8)	0.0000	0.0000	0.6(5)	5.5(8)	6.8(11)	0.0	0.0	0.0	1.0
X(2)	0.5000	0.0000	0.3249(11)	10.4(14)	7.7(14)	2.2(7)	0.0	0.0	0.0	1.0
O(2)	0.5000	0.1715(15)	0.5000	9.0(15)	8.2(12)	6.8(11)	0.0	0.0	0.0	1.0
N(2)	0.3323(15)	0.0000	0.5000	6.4(12)	2.7(7)	4.8(12)	0.0	0.0	0.0	1.0
O(11)	0.4213(9)	0.0785(11)	0.0681(8)	4.8(5)	10.0(9)	3.8(6)	3.2(10)	−1.4(7)	−1.8(7)	0.5
O(21)	0.2560(22)	0.3817(16)	0.2493(16)	14.7(25)	10.8(16)	9.5(13)	8.6(18)	8.0(16)	6.0(14)	0.42
O(22)	0.1793(15)	0.1793(15)	−.1793(15)	5.5(7)	5.5(7)	5.5(7)	1.1(11)	−1.1(11)	−1.1(11)	0.40
O(23)	0.1740(17)	0.3085(24)	0.3283(25)	7.8(14)	8.1(12)	10.4(17)	1.2(17)	5.7(14)	−1.4(17)	0.39
O(24)	0.1073(17)	0.2321(20)	0.2331(25)	9.5(7)[c]	–	–	–	–	–	0.39
O(31)	0.4316(10)	0.4316(10)	0.4316(10)	9.5(9)	9.5(9)	9.5(9)	−3.1(10)	−3.1(10)	−3.1(10)	0.50

[a] The anisotropic temperature factors are multiplied by 100 and are of the form $T = \exp[-2\pi^2 * U11(ha^*)^2 + \ldots]$. [b] Estimated standard deviations are given in parentheses and refer to the least significant digits. [c] Atom O(24) would not refine anisotropically and was therefore refined isotropically.

TABLE II. Calculated Hydrogen Atom Positional Parameters.[a]

Atom	x	y	z	Occupancy
H(1)	0.2026	0.0596	0.0596	2.5/12
H(2)	0.2034	–.0811	0.0218	2.5/12
H(3)	0.2034	0.0218	–.0811	2.5/12
H(4)	0.4404	0.1992	0.4404	2/12
H(5)	0.4782	0.2000	0.5811	2/12
H(6)	0.5811	0.2000	0.4782	2/12
H(7)	0.3017	0.0596	0.4404	3/12
H(8)	0.3008	–.0811	0.4782	3/12
H(9)	0.3008	0.0208	0.5811	3/12
H(10)	0.4404	0.0596	0.2946	2.5/12
H(11)	0.5811	0.0218	0.2937	2.5/12
H(12)	0.4782	–.0811	0.2937	2.5/12

[a] The hydrogen atom thermal parameters were not refined but were given a fixed isotropic value of B = 4.0.

Refinement of the structure by the full matrix least-squares technique with anisotropic temperature factors for individual atoms resulted in an R-factor of 0.088. Calculated hydrogen atom positions consistent with hydrogen bonding between the ammine and aquo donor ligands and the perchlorate oxygen acceptor atoms of Cl(2) were included with isotropic temperature factors though not refined. As a result of the space group symmetry the three independent hydrogen atom positions for each ligand are disordered over a total of twelve sites. Depending on the nature of the ligand, the appropriate occupancy was used (see Table II). The observed intensity data were corrected for the anomalous dispersion of molybdenum radiation by the cobalt and chlorine ions and an isotropic extinction correction was applied to the strong reflections. The final weighted and unweighted R values are 0.062 and 0.082, respectively. The final positional and thermal parameters for the nonhydrogen atoms are given in Table I and the calculated hydrogen atom positions in Table II. The function minimized was $\Sigma w(|F_o|-|F_c|)^2/\Sigma|Fo|^2$ where $w = 2.0/\sigma^2$ (I).

The atomic scattering factors for cobalt, chlorine, oxygen and nitrogen were taken from Cromer and Mann [7] and those for hydrogen from Stewart *et al.* [8]. For the hybrid oxygen-nitrogen atoms X(1) and X(2) the scattering factors for oxygen and nitrogen were interpolated and averaged. The XRAY76 [9] computer program system was used throughout for data processing, structure determination and least-squares refinement.

Description of Structure and Discussion

Figure 1 shows a labelled drawing of the structure of the two independent cobalt octahedra and the three independent perchlorate moieties [10]. The corresponding interatomic bond distances and their estimated standard deviations are listed in Table III. As indicated above, the cobalt 1 center at the origin contains six equivalent hybrid ammine–aquo disordered groups. It is not possible to determine whether the disordered triamminetriaquocobalt(III) groups are *fac* or *mer* at this position. On the other hand, the cobalt 2 center at the face shows three distinct cobalt–ligand distances (see Table III) and requires amine–aquo disorder along only one axis. This can be accommodated only by the presence of the *mer* triamminetriaquocobalt(III) isomer at these face centers. Thus there are two possibilities for this crystal structure: (1) the presence of the *mer* isomer completely disordered about Co(1) at the origin and the *mer* isomer disordered along only one axis about

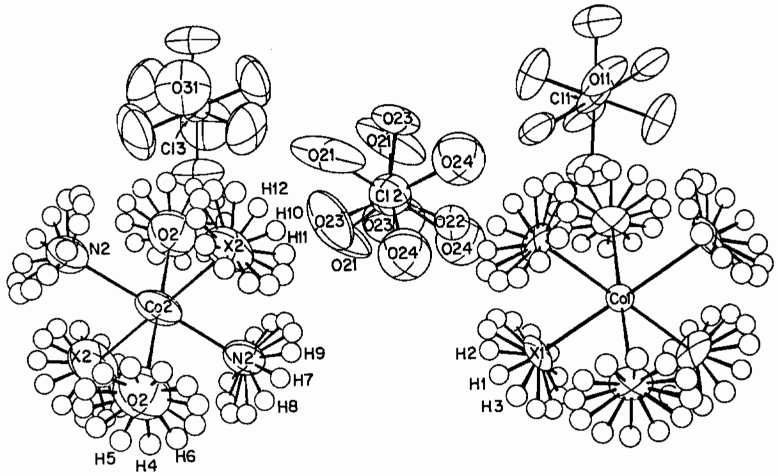

Figure 1. A view of the two cobalt centers and three perchlorate groups showing 50% probability ellipsoids for the nonhydrogen atoms.

TABLE III Interatomic Distances

Atoms	Bond Length[a] (Å)	Atoms	Bond Length (Å)
Co(1)–X(1)	1 948(9)	Cl(1)–O(11)	1 462(11)
Co(2)–X(2)	1 964(13)	Cl(2)–O(21)	1 468(18)
Co(2)–O(2)	1 923(17)	Cl(2)–O(22)	1 389(10)
Co(2)–N(2)	1 880(17)	Cl(2)–O(23)	1 384(24)
		Cl(2)–O(24)	1 635(20)
		Cl(3)–O(31)	1 329(7)

Atoms	Nonbonded Contact Distance (Å)	Positions of Second Atom
O(11)····O(21)	2 882	y, z, x
O(11)····O(24)	2 774	y, z, x
O(11)····O(24)	2 819	z, x, y
O(31)····O(21)	2 892	x, y, z, z, x, y, y, z, x

[a] The site symmetries of Co(1) and Co(2) atoms require that all bond angles involving the ligands about these atoms are equal to 90° or 180°

TABLE IV Hydrogen Bonds

D–H···A	D····A Distance (Å)	D–H···A Angle (°)	H···A Distance (Å)
X(1)–H(1)···O(22)	2 84	153	1 92
X(1)–H(2)···O(22)	2 84	130	2 10
X(1)–H(3)···O(22)	2 84	130	2 10
X(1)–H(1)···O(24)	2 94	150	2 04
X(1)–H(2)···O(24)	2 95	163	1 98
X(1)–H(3)···O(24)	2 94	163	1 98
X(2)–H(10)···O(23)	2 74	155	1 80
X(2)–H(11)···O(23)	2 74	130	1 99
X(2)–H(12)···O(23)	2 74	131	1 98
O(2)–H(4)···O(23)	2 88	153	1 96
O(2)–H(5)···O(23)	2 88	136	2 11
O(2)–H(6)···O(23)	2 88	127	2 18
N(2)–H(7)···O(23)	2 90	151	1 98
N(2)–H(8)···O(23)	2 90	126	2 19
N(2)–H(9)···O(23)	2 90	132	2 13

Co(2) on the face, (2) the presence of the *fac* isomer completely disordered about Co(I) at the origin and the *mer* isomer disordered along only one axis about Co(2) on the face For possibility (1) the cobalt complexes are all in the *meridional* configuration whereas possibility (2) requires 3/4 of the cobalt complexes to be *meridional* and 1/4 to be *facial* since there are three times as many face centers as origin centers per unit cell

A structure containing hexaammine cobalt(III) at the origin and *trans*-diamminetetraaquocobalt(III) on the faces was also considered since it obeys the measured stoichiometry and also fits the space group The structure was rejected for the following reasons 1) Hexaamminecobalt(III) salts are not very soluble in aqueous solution while the crystals under consideration are very soluble in concentrated aqueous perchloric acid 2) Dissolution of the crystals in water gave the same spectrum as that obtained from the original fraction from cation exchange chromatography If disproportionation had occurred in the solid state, the spectrum would very likely be different [1] 3) If the facial cobalt atom had four waters and two ammines as ligands, only two distinct bond lengths would be expected (symmetry demands *trans* ammines) Alternatively, random distribution of indistinguishable ammines and waters would show only one bond length, presumably equal to that for Co–X1

The oxygen atoms of all three independent perchlorate groups in this structure are disordered Perchlorate groups appear to have a propensity for disorder [11, 12] The oxygen atoms about Cl(1) and Cl(3) exhibit similar behavior in that each perchlorate group has one independent oxygen atom, O(11) and O(31) respectively, occupying eight equivalent positions about the chlorine atom at 50% occupancy. There is still greater disorder of oxygen atoms about Cl(2). There are four independent oxygen atoms which partially occupy ten positions around Cl(2) with occupancies ranging from 39 to 42%. One of the latter oxygen atoms, O(24), could not be refined anisotropically and exhibited a rather long bond distance to Cl(2) (see Table III). The remaining Cl–O bond lengths for all three perchlorate groups fall within the range of values reported by others [12].

The crystal structure is stabilized by an extensive scheme of hydrogen bonding which involves the ammine and aquo ligands of both cobalt centers as donor atoms and the disordered oxygen atoms of the number 2 perchlorate group as acceptor atoms (see Table IV). It appears that the maximization of these hydrogen bond interactions is the driving force behind the disordering of the ammine and aquo groups and their respective hydrogen atoms as well as the oxygen atoms of perchlorate group 2. The disorder exhibited by the remaining perchlorate groups, 1 and 3, seems to be correlated with the disorder of group 2 as indicated by the non-bonded contact distances of the disordered oxygen atoms of groups 1 and 3 with those of group 2 (see Table III). These contact distances would be prohibitive if the oxygen atom locations were fully occupied.

Conclusion

Despite the extensive disorder exhibited by this structure we are able to conclude that the ligand distribution about the cobalt is *meridional* at least for 75% of the triamminetriaquocobaltate(III) ions. It is not known whether the remaining 25% are the *mer* or *fac* isomer. These results are for crystals grown in concentrated perchloric acid. Under basic conditions a bridged *fac* dimer structure crystallizes. It was primarily on the basis of this latter structure that the solution species was tentatively assigned as the *fac* isomer. The present results leave that assignment in doubt. In the hopes of further clarifying the problem we plan to grow crystals of the nitrate salt, $Co(NH_3)_3(H_2O)_3(NO_3)_3$, which hopefully will not have the disorder found in the present perchlorate salt.

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