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Rare Earth Metal-Metal Halide Systems. XV. Crystal Structure of Gadolinium Sesquichloride. A Phase with Unique Metal Chains

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Received August 21, 1972

The crystal structure of gadolinium sesquichloride (a phase formerly identified as $GdCl_{1.58\pm0.06}$) was determined from Patterson, Fourier, and full-matrix least-squares techniques on three-dimensional X-ray data collected by an automated diffractometer. The compound crystallizes in the monoclinic space group *Cm* with $a = 15.237$ (4) Å, $b = 3.896$ (1) Å, $c = 10.179$ (3) Å, $\beta = 117.66$ (3)°, and $Z = 8$ for the composition $GdCl_{1.50}$ ($d_{calcd} = 5.23$ g cm^{-3}, $d_{obsd} = 5.14$ (30) g cm^{-3}). Final residuals were $R = 0.053$ and $R_w = 0.066$ using 1331 reflections with $F > 3\sigma_F$ and anisotropic and isotropic thermal parameters for gadolinium and chlorine, respectively. The striking feature of the structure is the occurrence of infinite chains of metal atoms which may be described as octahedra sharing opposite edges and elongated in the chain direction. The shortest metal–metal distance, the shared edge, is 3.349 (1) Å. An ionic formulation $[Gd_4^{6+}(Cl^-)_6]_n$ is suggested.

Introduction

Among the rare earth elements the formation of the dipositive cation is relatively common among the halides (except fluorides) existing either in a stoichiometric dihalide or as the (probable) reduced component in various phases with average oxidation states between 2 and 3.[2] The sole known exception to the formation of apparently simple M^{2+} ions occurs in the lower chloride of gadolinium for which a chloride to gadolinium ratio of 1.58 ± 0.06 has been deduced from analytical and powder pattern data on the purest samples obtainable.[3] Subsequent magnetic susceptibility studies have shown that the compound exhibits only the $4f^7$ core magnetism of gadolinium(III).[4] The present paper reports the results of a single crystal X-ray study which establishes that the compound has the simple stoichiometry Gd_2Cl_3 and contains a remarkable metal atom chain. A short communication has appeared previously.[5]

Experimental Section

Adequate single crystals could not be obtained from the reaction of the metal with liquid $GdCl_3$ in a temperature gradient as was employed in the original isolation.[3] Reaction of pieces of the metal with the trichloride *via* the vapor phase in a sealed tantalum tube at 610° for 9 days gave long chunks or bundles of the dark bronze to black product on the metal surface which exhibited exactly the same powder pattern as that obtained previously for "$GdCl_{1.6}$." Although these bundles were generally longer than optimal, efforts to cut them always led to fraying into "hairs." These were strong and flexible but attempts to cut them led only to still finer "hairs." Finally, several of the untrimmed chunks were mounted in 0.3-mm Lindemann glass capillaries in a drybox with the needle (*b*) axis parallel to the spindle axis. The single crystal finally selected from among these for data collection was prismatic with approximately pentagonal cross section and dimensions of 70 × 495 μ.

Other chunks from the same reaction were used for density measurements and for further work to ensure the absence of significant impurities. Emission spectroscopy measurements eliminated the presence of other heavy metals while an electron microprobe analysis eliminated extraneous elements heavier than chlorine at the level of a few hundred parts per million and also eliminated oxygen or nitrogen at a higher level.

The space group and approximate unit cell parameters were obtained from five levels (*hkl*, $k = 0$–4) of equiinclination Weissenberg photographs taken with Cu Kα radiation. The final unit cell parameters and their standard deviations were obtained by a least-squares fit to the 2θ angles of 12 independent reflections whose centers were determined at room temperature by left–right, top–bottom beam splitting on a Hilger-Watts four-circle diffractometer using Mo Kα radiation (λ 0.71069 Å). Values of each reflection were measured at $+2\theta$ and -2θ and averaged in order to eliminate any error in the instrumental zero. The final values, with estimated standard deviations, are $a = 15.237$ (4) Å, $b = 3.896$ (1) Å, $c = 10.179$ (3) Å, $\alpha = \gamma = 90.00°$, and $\beta = 117.66$ (3)°. The general extinctions for reflections with $h + k = 2n$ indicated the monoclinic space groups *C*2/*m*, *C*2, or *Cm*. Although a broad distribution of intensities suggested the centric group *C*2/*m*, the correct space group was subsequently shown to be *Cm* (No. 8). A density of 5.14 ± 0.3 g cm^{-3} was determined on 36 mg of the crystalline material by micropycnometric methods using chloroform. This value compared quite well with the calculated density of 5.23 g cm^{-3} for the composition $GdCl_{1.50}$ and $Z = 8$ that were subsequently established.

Integrated intensities were measured for the same crystal at room temperature using Zr-filtered Mo radiation and the θ-2θ scan technique on the automated diffractometer cited earlier. Data were collected for each reflection with thirty 0.4-sec counts separated by 0.01° in θ, with one additional counting added for each degree in θ to allow for the increase in peak width with θ. Periodic counts were made on three standard peaks to check for instrument and crystal stability. Data were collected for the asymmetric unit HKL + $\bar{H}KL$ over the range $0 < \theta < 35°$. The crystal was a good diffractor and 1331 of the possible 1378 reflections were observed to be greater than $3\sigma_F$. The standard deviations were computed as previously described.[6] The data were corrected for background and then for Lorentz-polarization and for absorption ($\mu = 266.7$ cm^{-1}) using a general polyhedral crystal description. Transmission factors varied from 0.146 to 0.243.

Structure Determination and Refinement

A three-dimensional Patterson function generated from the intensity data contained peaks only in the sections $v = 0$ and 0.5, thus indicating a layering in the structure normal to the short *b* axis. A structural solution was first sought in the centric space group *C*2/*m*. However, the unit cell could not accommodate all apparent gadolinium atoms with unit occupancy of the indicated fourfold general positions, and the chloride atoms could not be located by Fourier synthesis. On the other hand a solution was found readily in the acentric space group *Cm* (the alternate *C*2 is the same as *C*2/*m* with the indicated layering). Diagnosis of gadolinium positions from the Patterson function followed by successive Fourier syntheses yielded four gadolinium and six chlorine atoms, all in twofold general positions. Three cycles of full-matrix least-squares refinement using isotropic thermal parameters gave a conventional reliability index of 0.090 for $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. The difference Fourier computed at this point was quite flat indicating that the correct stoichiometry was indeed $GdCl_{1.5}$. Further least-squares refinements were carried out using absorption correc-

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Table I. Final Positional and Thermal Parameters for Gd_2Cl_3[a]

	x/a	y/b	z/c	B, Å^2	B_{11}[b]	B_{22}	B_{33}	B_{13}
Gd(1)[c]	0.0	0.0	0.0		45 (8)	31 (8)	112 (9)	17 (7)
Gd(2)	0.2731 (2)	0.0	0.7572 (3)		42 (8)	52 (8)	104 (9)	21 (6)
Gd(3)	0.5456 (2)	0.0	0.3422 (3)		50 (8)	70 (9)	58 (8)	6 (6)
Gd(4)	0.8208 (1)	0.0	0.1029 (2)		45 (8)	95 (9)	59 (8)	9 (6)
Cl(5)	0.1787 (13)	0.0	0.9356 (18)	1.23 (21)				
Cl(6)	0.0704 (9)	0.0	0.5625 (14)	0.83 (17)				
Cl(7)	0.4594 (9)	0.0	0.7794 (13)	0.79 (16)				
Cl(8)	0.3599 (10)	0.0	0.3156 (15)	1.05 (19)				
Cl(9)	0.7524 (11)	0.0	0.5375 (16)	1.26 (21)				
Cl(10)	0.6404 (10)	0.0	0.1697 (15)	0.71 (16)				

[a] Standard deviations of least significant figures are given in parentheses. Symmetry-related atoms occur at $x/a + {}^1/_2, {}^1/_2, z/c$. [b] The form of the thermal ellipsoid is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{13}hla^*c^*)]$. The values of B_{ij} have been multiplied by 10^2. $B_{12} = B_{23} = 0$. [c] Coordinates of Gd(1) fixed to define origin.

tions appropriate to the correct stoichiometry and with unit weights since most reflections were strong and counting statistics did not make significant contributions. The values of R and R_w $\{[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}\}$ obtained with isotropic thermal parameters were 0.073 and 0.083, respectively. Further refinement with anisotropic thermal parameters for the metal atoms and isotropic parameters for chlorine gave respective R values of 0.053 and 0.066, and with all atoms anisotropic the values became 0.052 and 0.065. Only five of the 24 B_{ij} parameters obtained in the last step for chlorine were greater than $3\sigma_B$ and the 0.001 reduction in R thereby was judged not to be significant. All features in the final difference map were less than 1.5 e Å^{-3}.

Atomic scattering factors for the foregoing refinement were taken from Hanson, *et al.*[7] Correction for the real and imaginary parts of anomalous dispersion were applied to the gadolinium atoms.[8] All calculations were carried out on the IBM 360/65 computer at the Iowa State University Computer Center with the following programs: ABCOR[9] for absorption correction, LCR[10] for lattice constant least-squares refinement, ALF[11] for Fourier summation, ORFLS[12] for least-squares parameter refinement, ORFFE[13] for structure parameters and estimations of errors, and ORTEP[14] for figure illustrations.

Structure Description

The final positional and thermal parameters (gadolinium anisotropic, chlorine isotropic) are given in Table I.[15] Important interatomic distances and angles calculated therefrom are listed in Table II. Figure 1 gives a projection of the structure down the 3.90-Å b axis and defines the atomic notation. A stereoscopic view of the structure is shown in Figure 2.

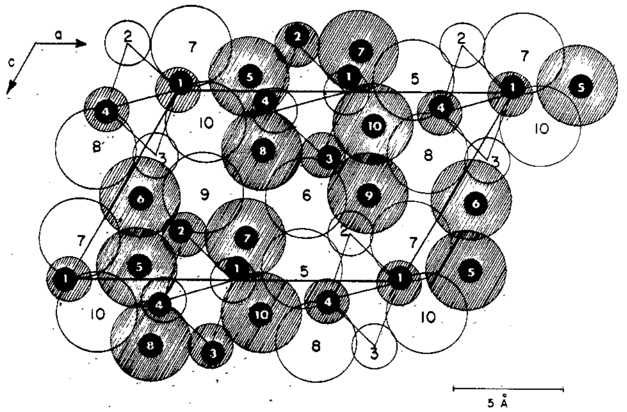

Figure 1. Projection of the structure of Gd_8Cl_{12} onto the (010) plane, with metal chains outlined. Atoms at $y/b = 0.5$ are represented by open circles while those at $y/b = 0$ are shaded. The numbers on the atoms correspond to those used in Tables I and II. Atomic boundaries are drawn with ionic radii, $Cl^- = 1.81$ Å, $Gd^{3+} = 1.02$ Å.

The most remarkable feature of the structure is the occurrence of all the gadolinium atoms in infinite chains oriented parallel to the b axis. A section of one of these chains with the pertinent distances and angles is shown in Figure 3. The elements of the chain can be described as octahedra sharing opposite edges, though the variation in edge lengths from 3.35 (shared edge) to 3.90 Å (repeat distance) suggests an alternate description in terms of a string of parallel Gd(1)-Gd(4) dimers separated by the b dimension and capped by more distant Gd(2) and Gd(3) atoms in a plane also parallel to b and at 88.7° to the plane of the dimers.

The chlorine atoms are all located over triangles formed by three gadolinium atoms (Figures 1 and 2). Thus four chlorines are located over the metal triangles 1-1′-3, 4-4′-3, 1-1′-2, and 4-4′-2, the side faces of the "octahedra." The other two chlorines, Cl(6) and Cl(9), bind (or separate) two adjacent metal chains. Identical metal chains occur above and below the apices of each chain but displaced by $b/2$, and the remaining two chlorine atoms alternate in front of and behind the triangles of metal atoms formed by the apex gadolinium atoms in adjacent chains, that is, 3-3′-2″ and 2-2′-3″. This last construction generates sheets of bridged chains which lie in the $20\bar{1}$ planes of the structure (Figure 1). These sheets in turn pack loosely and, again, with relative displacements of $b/2$. This last process gives Gd(4) a fifth more distant chlorine neighbor formally from another sheet (Cl(10)), and Gd(1), likewise, another neighbor (Cl(5)). Such chlorine atoms are shown dashed in Figure 2. The fraying characteristics of the crystals seem explicit in the structure.

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(15) A table of the observed and calculated structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-556.

Table II. Interatomic Distances and Selected Angles in Gd_2Cl_3[a]

Distances, Å					
Gd(1)-Gd(2)	3.725 (3)	Gd(2)-Cl(5)	2.78 (2)	Cl(5)-Cl(6)	3.22 (2)
Gd(1)-Gd(2)[b]	5.741 (6)	Gd(2)-Cl(6)	2.77 (1)	Cl(5)-Cl(7)	3.53 (2)
Gd(1)-Gd(3)	3.764 (3)	Gd(2)-Cl(7)	2.74 (1)	Cl(5)-Cl(8)	3.60 (2)
Gd(1)-Gd(4)	3.349 (1)	Gd(2)-Cl(9)	2.85 (1)	Cl(5)-Cl(10)	3.34 (1)
Gd(1)-Gd(4)[b]	4.902 (5)	Gd(3)-Cl(6)	2.88 (1)	Cl(6)-Cl(7)	3.87 (2)
Gd(2)-Gd(3)	5.453 (3)	Gd(3)-Cl(8)	2.72 (2)	Cl(6)-Cl(8)	3.60 (2)
Gd(2)-Gd(3)[b]	4.479 (5)	Gd(3)-Cl(9)	2.86 (1)	Cl(6)-Cl(9)	3.50 (1)
Gd(2)-Gd(4)	3.785 (3)	Gd(3)-Cl(10)	2.75 (1)	Cl(7)-Cl(8)	4.24 (3)
Gd(3)-Gd(4)	3.711 (3)	Gd(4)-Cl(5)	2.83 (1)	Cl(7)-Cl(9)	3.54 (2)
Gd(3)-Gd(4)[b]	5.744 (6)	Gd(4)-Cl(8)	2.78 (1)	Cl(7)-Cl(10)	3.62 (2)
Gd(1)-Cl(5)	3.09 (2)	Gd(4)-Cl(10)	3.12 (1)	Cl(8)-Cl(9)	3.87 (2)
Gd(1)-Cl(7)	2.79 (1)			Cl(8)-Cl(10)	3.56 (2)
Gd(1)-Cl(10)	2.81 (1)			Cl(9)-Cl(10)	3.36 (2)

Angles, Deg			
Gd(1)-Gd(2)-Gd(4)	52.96 (4)	Cl(7)-Gd(1)-Cl(7)	88.4 (3)
Gd(1)-Gd(3)-Gd(4)	53.22 (4)	Cl(10)-Gd(1)-Cl(10)	87.7 (4)
Gd(1)-Gd(3)-Gd(4′)	93.17 (6)	Cl(9)-Gd(2)-Cl(9)	86.1 (4)
Gd(2)-Gd(4)-Gd(3)	93.35 (6)	Cl(6)-Gd(3)-Cl(6)	85.1 (3)
Gd(2)-Gd(1)-Gd(3)	93.49 (6)	Cl(5)-Gd(4)-Cl(5)	87.1 (4)
Gd(1)-Gd(2)-Gd(1)	63.07 (6)	Cl(8)-Gd(4)-Cl(8)	89.0 (3)
Gd(1)-Gd(3)-Gd(1)	62.34 (6)	Cl(5)-Gd(1)-Cl(10)	68.7 (3)
Gd(4)-Gd(2)-Gd(4)	61.95 (5)	Cl(7)-Gd(1)-Cl(10)	79.8 (3)
Gd(4)-Gd(3)-Gd(4)	63.32 (7)	Cl(6)-Gd(2)-Cl(9)	76.9 (3)
Gd(3)-Gd(1)-Gd(4)	62.56 (5)	Cl(7)-Gd(2)-Cl(9)	78.6 (3)
Gd(3)-Gd(4)-Gd(1)	64.18 (5)	Cl(6)-Gd(2)-Cl(5)	73.4 (4)
Gd(2)-Gd(4)-Gd(1)	62.60 (6)	Cl(9)-Cl(10)-Cl(7)	164.9 (5)
Gd(2)-Gd(1)-Gd(4)	64.44 (5)	Cl(6)-Cl(5)-Cl(8)	162.4 (6)
Gd(1)-Gd(4)-Cl(10)	174.8 (2)		
Gd(4)-Gd(1)-Cl(5)	175.1 (3)		

[a] Estimated standard deviations are in parentheses. [b] Distance to gadolinium atom in another chain.

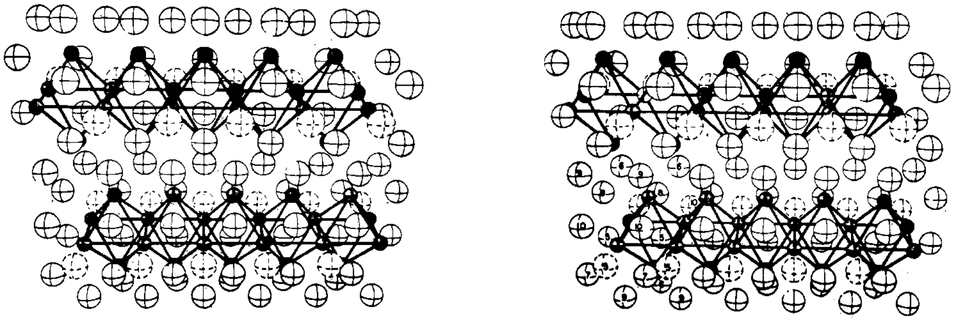

Figure 2. Stereoscopic view of the structure of Gd_2Cl_3 with gadolinium atoms represented by small shaded circles and chlorine atoms by larger open circles. The *b* axis is horizontal in the plane of the paper to the right while *a* is approximately toward the viewer. "Bridging" atoms Cl(5) and Cl(10) from a neighboring sheet are shown dashed.

Discussion

Consideration of the structure in terms of the chain polymer with a charge distribution approximating $[Gd_4^{6+}(Cl^-)_6]_n$ appears to be both useful and reasonable. Indeed, the structure found is difficult to understand if the metal chain is not considered to be the principal structure-determining feature. The chloride ion arrangement is entirely plausible and a likely way in which to maximize coulombic interactions between gadolinium and chlorine (or any other type of interaction which likewise depends on the number of Cl-Gd contacts). If the localized "metal-metal bonding" is presumed to be effectively concentrated "within" the chain, it is natural that the effective distances outward toward chlorine closely approximate those of the Gd^{3+} metal cores. Close comparisons for the latter distances are made somewhat uncertain by the unusual coordination spheres found (both in kind and in number). But in general the observed Gd-Cl distances are quite similar to the sum of "ionic radii"[16] and to those found in $GdCl_3$[17] where ionic interactions appear to be predominant and covalency is supposedly "small but not quite negligible".[18] The Gd-Cl distances in the sesquichloride range from 2.72 to 2.88 Å (2.81 Å average) with the longer associated with the Cl(6) and Cl(9) atoms which are involved in interchain bridging (2.85 Å average). These distances are closely comparable to Gd-Cl distances in the trichloride, six at 2.82 Å and three at 2.92 Å. The metal in the present structure is nine- or

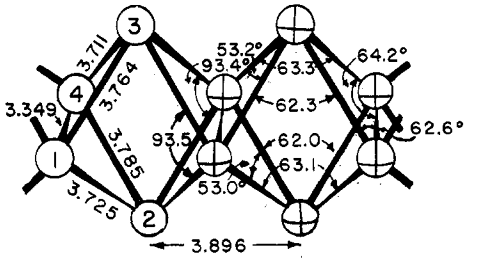

Figure 3. Portion of the metal chain with distances (Å) and angles (degrees). The pairs of gadolinium atoms 1–4 and 2–3 lie on mirror planes perpendicular to the chain.

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ten-coordinate but only five of these neighbors are chlorine. Lacking a clear notion of how to handle the effect of this coordination on radius, we simply note that the sum of radii for chloride and six- or eight-coordinate Gd^{3+} is 2.75 or 2.87 Å.[16] The comparison seems even closer than might be hoped or expected. The two shortest Cl-Cl distances tabulated earlier, 3.22 and 3.34 Å, are not particularly noteworthy when it is observed that a 3.26-Å distance occurs more frequently in $GdCl_3$.[17]

The extreme contrast between the coordination geometry of gadolinium in the present structure and that in the only reference state, the metal itself, means that only a very qualitative interpretation can be given to the observed metal-metal distances. The average metal-metal distance in the 12-coordinate metal is 3.604 Å, from which Pauling[19] has derived a "single bond" value of 3.264 Å. Considering the marked difference in environment and the limited transferability of such a "standard" metal radius, the short Gd(1)-Gd(4), distance, 3.349 Å, may be taken to be substantially the same as the "single bond" distance. Distances to the apical Gd(2) and Gd(3) atoms, 3.71-3.78 Å, correspond to Pauling bond orders of ~0.15 although for obvious reasons this must be taken as only a qualitative bench mark. The repeat distance in the chain, 3.896 Å, probably corresponds to a negligible interaction; the closest approach of metal ions in $GdCl_3$ (where the bonding electrons are presumably lacking) is the c dimension, 4.106 Å.[17]

The strength expected for the metal chains oriented parallel to the needle axis and the relatively lower cohesion between these chains gives a reasonable explanation for the inevitable fraying which resulted on all attempts to cut crystals normal to the long dimension. In this light the earlier conclusion[3] that the material is not a metallic conductor was undoubtedly not meaningful since it would have been substantially impossible to attain electrical contact at opposite ends of an appreciable number of individual chains using the VTVM probes in the drybox. AC loss measurements are also not useful for a one-dimensional case. Any potential Pauli paramagnetism in the metallic possibility could not be discerned magnetically because of the large $4f^7$ core contribution.[4] However, the plethora of "good" orbitals available in the metal[20] would intuitively make a delocalized conducting state seem very probable.

A band calculation would be an obviously appropriate way to interpret the bonding in these chains and the high symmetry found is an encouraging factor. Meanwhile, a simple heuristic device which accounts for the bonding is to assign one pair of electrons to the short Gd(1)-Gd(4) bond (z axis) and the remaining two electron pairs (per repeat unit) to the two approximately planar, four-center systems generated from a linear combination of either d_{xz} or d_{yz} orbitals on Gd(1) and Gd(4) and d_{xy} orbitals on Gd(2) and Gd(3), these overlapping more or less in the Gd(1)-Gd(2 or 3′)-Gd(4)-Gd(2′ or 3) faces in Figure 3.

There is very little known regarding other sesquihalides, and the structure and bonding in Gd_2Cl_3 may be completely unique. The Sc-$ScCl_3$ and Sc-$ScBr_3$ systems are now known to contain sesquihalide phases which are isostructural with one another but evidently not with Gd_2Cl_3.[21,22] They exhibit an extremely acicular crystal habit and a color which are reminiscent of Gd_2Cl_3. The sesquibromide shows a weak, temperature-dependent paramagnetism and in bulk appears to be an insulator (which again probably proves nothing if the conduction is unidirectional). Interestingly both scandium and gadolinium also form metallic iodides, namely, $ScI_{2.15}$[21] and GdI_2.[3] This behavior, like the chains found in Gd_2Cl_3, doubtlessly requires substantial radial extension of the bonding orbitals.

Registry No. $[Gd_4{}^{6+}(Cl^-)_6]_n$, 37209-68-0.

Acknowledgments. The crystals used in this structure determination were prepared by Doug Adolphson, who was prevented from following up on the structure by a call to military service. J. E. Benson was particularly helpful in data-taking aspects of the study.

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