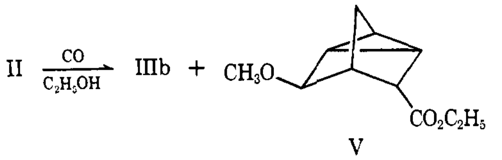
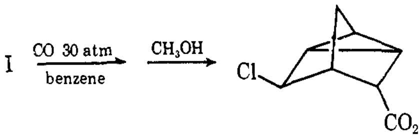
reaction with the hydrogen chloride liberated during the carbonylation. When II was carbonylated in ethanol a mixture of IIIb (7%) and 3-*endo*-carboethoxy-5-*exo*-methoxynortricyclene, V (93%), was obtained.[9]



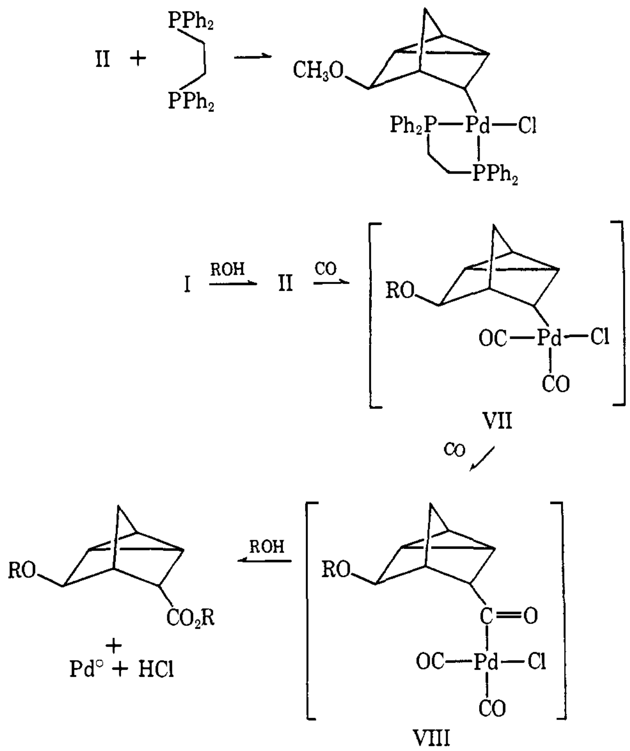
V

Carbonylation of I in benzene gave a product resulting from an initial *trans* addition of Cl–Pd to the coordinated double bond. The acid chloride which was obtained was converted to the methyl ester, 3-*endo*-carbomethoxy-5-*exo*-chloronortricyclene (VI).



VI

These results are in general agreement with the proposed mechanism (eq 1). Reaction of II with carbon monoxide forms the σ-bonded complex VII[10] which undergoes an alkyl–acyl rearrangement *with retention* to VIII.



Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

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have found that II can be carbonylated in methanol to give IIIa even when the solution is saturated with dry hydrogen chloride.

(9) The total conversion of II to IIIb and V was ~90%. The stereochemistry of V is based on nmr data.

(10) Formulation of the alkyl intermediate VII as shown is reasonable if analogy is made to the bridge cleavage reaction of II by 1,2-bis(diphenylphosphino)ethane which produces a stable complex containing the nortricyclene ring system.[6]

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Received January 9, 1970

Gadolinium Sesquichloride, an Unusual Example of Metal-Metal Bonding[1]

Sir:

Among the results of numerous studies[2,3] of rare earth metal-metal halide systems carried out in this laboratory, perhaps the most unexpected was the discovery of a lower gadolinium chloride.[4] The composition of the compound was concluded to be $GdCl_{1.58 \pm 0.06}$, with the range based on estimated upper and lower limits for the amount of $GdCl_3$ impurity which could have been detected in powder patterns of different compositions. Subsequent magnetic measurements[5] found only the paramagnetism of the $4f^7$ metal cores with evidence for an antiferromagnetic ordering near 50°K.

Crystals of the reduced phase produced as before[4] continued to be inadequate for a structural investigation. However, reaction of $GdCl_3$ vapor with the metal at 610° for several days did produce large single crystals. These could not be cut further without the characteristic "fraying,"[4] so data were taken on a relatively large pentagonal prism 70 × 480 μ. The monoclinic cell dimensions are $a = 15.237 \pm 0.004$, $b = 3.896 \pm 0.001$, $c = 10.179 \pm 0.003$ Å, $\beta = 117.66 \pm 0.03°$, and extinctions for only $(h + k)$ odd indicate space groups C2/m, C2, or Cm. A density of 5.14 ± 0.3 g cm^{-3} determined micropycnometrically using $CHCl_3$ compares with 5.23 g cm^{-3} calculated for the final structure Gd_8Cl_{12}. A total of 1378 integrated intensities (1331 observed above the $3\sigma_F$ level) were measured with Mo Kα radiation in two independent octants using an automated, four-circle diffractometer.[6] The raw data were corrected for the usual effects, including absorption using Busing and Levy's[7] method for a general polyhedron. The Patterson map was successfully interpreted in the acentric space group Cm for the positions of four independent metal atoms, while the six chlorine atoms were located by Fourier synthesis maps. Full-matrix least-squares refinement with atomic scattering factors corrected for anomalous dispersion and using all data, unit weights, and isotropic temperature factors gave $R = 0.073$, while the use of anisotropic thermal parameters yielded $R = 0.052$. Atom positions and the isotropic temperature factors are given in Table I. Standard deviations in distances between neighboring metals were ±0.004 Å or less (including the uncertainty in the unit cell dimensions) while those in distances to chlorine were ≤0.02 Å. The final difference map was smooth to better than 1.5 e/Å^3, thereby also confirming unit occupancy of sites. Electron microprobe and emission spectroscopic examinations of single crystals also established the absence of foreign metals, and the 100

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[1] Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 2685.

(2) J. D. Corbett, R. A. Sallach, and D. A. Lokken, Advances in Chemistry Series, No. 71, American Chemical Society, Washington, D. C., 1967, p 56.

(3) P. E. Caro and J. D. Corbett, *J. Less-Common Metals*, **18**, 1 (1969).

(4) J. E. Mee and J. D. Corbett, *Inorg. Chem.*, **4**, 88 (1965).

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(6) D. J. Dahm, J. E. Benson, D. M. Nimrod, D. R. Fitzwater, and R. A. Jacobson, USAEC Report IS-1052, Ames Laboratory, Iowa State University, 1967.

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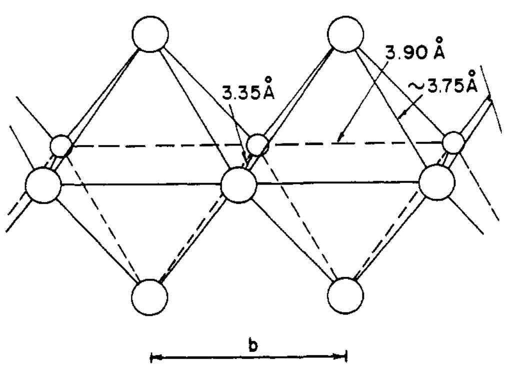

Figure 1. The configuration of the metal chains in Gd$_2$Cl$_3$.

± 0.3% recovery as Gd + Cl[4] supported the absence of substantial amounts of nonmetallic impurities.

The unusual feature of the structure is the occurrence of chains of gadolinium atoms running parallel to the unique (fiber) axis. The configuration of the chains, illustrated in Figure 1, can be described in terms of elongated octahedra sharing opposite edges or, better, pairs of close metal atoms to 3.349 Å joined side to side by pairs of bridging atoms at 3.71–3.79 Å. (The planes containing the two types of atoms make an angle of 91.3°.) The repeat distance in the chain is the *b* dimension, 3.896 Å. For comparison, distances in the 12-coordinate metal distribute equally between 3.636 and 3.573 Å, and Pauling's "single bond" distance is 3.246 Å.[8] The chains appear to dictate the structural arrangement and occur well separated from one another (≥4.48 Å) by sheaths of chlorine atoms (ions) all of which occur on the faces of triangles of metal atoms (ions). Thus four of the six chlorines occur above the side faces of the chain shown in Figure 1 at distances of 2.71–2.83 Å, compared with 2.82 Å as the shortest distance observed in GdCl$_3$.[9] Additional chains translated by *b*/2 occur above and below each chain with the apices bridged by the remaining chlorines to form sheets parallel to the 20$\bar{1}$ planes of the structure. The sheets pack somewhat more loosely, again with relative displacements of *b*/2, to give half of the first type of chlorine atoms a fourth more distant metal neighbor in a "dimer" at 3.10 Å.

Table I. Final Positions and Temperature Factors from Isotropic Refinement of Gd$_8$Cl$_{12}$[a]

Atom	*x*	*y*	*z*	*B*
Gd 1	0.0	0.0	0.0	0.78 (5)
Gd 2	0.2737 (3)	0.0	0.7568 (4)	0.72 (5)
Gd 3	0.5463 (3)	0.0	0.3417 (4)	0.64 (5)
Gd 4	0.8207 (1)	0.0	0.1029 (2)	0.60 (4)
Cl 5	0.1786 (16)	0.0	0.9336 (22)	1.41 (28)
Cl 6	0.0712 (12)	0.0	0.5642 (17)	0.70 (20)
Cl 7	0.4582 (14)	0.0	0.7794 (20)	1.15 (26)
Cl 8	0.3590 (13)	0.0	0.3169 (18)	0.80 (22)
Cl 9	0.7532 (15)	0.0	0.5390 (23)	1.42 (28)
Cl 10	0.6405 (12)	0.0	0.1682 (16)	0.53 (18)

[a] Errors in least significant digits are in parentheses. The symmetry related atoms are at $x + {}^1/_2, {}^1/_2, z$.

The structure manifests in a striking way aspects of both metallic and ionic (plus covalent) bonding. Distances within the chains are certainly appropriate for metal–metal bonding, and, with the plethora of "good" bonding orbitals available in gadolinium[10] plus the high symmetry of the chain, a substantial delocalization into a one-dimensional metal seems indicated. In view of the structure and the tendency of the crystal to "fray" at the ends, earlier attempts[4] to deduce the conductivity directly were very likely inadequate. The metal chains are surrounded by chlorine in a geometry and with distances remarkably suitable for Gd^{3+}–Cl$^-$ interactions, suggesting that the metal-binding electrons properly define a larger nonbonding distance mainly "inside" the chains. As pleasing as this $(\mathrm{Gd_4}^{6+})_n(\mathrm{Cl}^-)_{6n}$ formulation may be, some caution is necessary since there is always the ambiguity of ionic *vs.* covalent distances,[11] and, in addition, the reference distances used throughout for comparison come from examples with higher coordination numbers and much more symmetric environments. Notwithstanding, our surprise at a structure with so little precedent and so much information seems well founded; an explanation for its occurrence with gadolinium (or elsewhere) is by no means obvious. To date only scandium is known to give halides of the same stoichiometry (ScX$_{1.5}$, X = Cl, Br)[12] but an adequate single crystal of either has not yet been located.

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Received January 13, 1970

Quantitative Cleavage of a Protein with N-Bromosuccinimide

Sir:

Various nonenzymatic methods for selective cleavage of peptide chains have been described,[1] but with the exception of the cyanogen bromide method few have been applied in practice to structural studies of large peptides and proteins. The reluctance to apply these techniques to proteins may be due to the impression that yields are low and complicated by side reactions. We wish to report the nearly quantitative cleavage of a protein by N-bromosuccinimide (NBS) oxidation of a tyrosyl bond.

In their review,[2] Ramachandran and Witkop report yields for the cleavage of tyrosyl bonds by NBS in the range of 30–65% for proteins and peptides. Yields for tryptophanyl and histidyl bonds are comparable. The review points out a number of complications that are encountered when various combinations of tryptophan, tyrosine, histidine, and half-cystine occur in a peptide or protein. While it is essential to recognize these problems, many large peptides and some proteins contain only a few of these residues in kind or in number and in these cases the cleavage may go much more smoothly. The objective in these cases is more like that in cleaving the relatively rare methionyl peptide bonds with cyanogen bromide.

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(1) See, for example, *Methods Enzymol.*, 11, Section V (1967).

(2) L. K. Ramachandran and B. Witkop, *ibid.*, 11, 283 (1967).