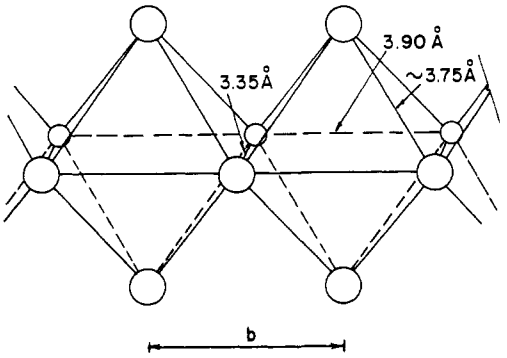

Figure 1. The configuration of the metal chains in Gd_2Cl_3.

± 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

Table I. Final Positions and Temperature Factors from Isotropic Refinement of Gd_8Cl_{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 $x + 1/2, 1/2, z$.

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.

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 $(Gd_4^{6+})_n(Cl^-)_{6n}$ 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.

(8) L. Pauling, "The Nature of the Chemical Bond," 2nd ed, Cornell University Press, Ithaca, N. Y., 1960, p 403.
(9) B. Morosin, *J. Chem. Phys.*, **49**, 3007 (1968).
(10) J. O. Dimmock and A. F. Freeman, *Phys. Rev. Lett.*, **13**, 750 (1964).
(11) J. C. Slater, *J. Chem. Phys.*, **41**, 3199 (1964).
(12) B. C. McCollum and J. D. Corbett, *Chem. Commun.*, 1666 (1968).

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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.

(1) See, for example, *Methods Enzymol.*, **11**, Section V (1967).
(2) L. K. Ramachandran and B. Witkop, *ibid.*, **11**, 283 (1967).

The ideal system for testing the NBS method for its capabilities under favorable (but not uncommon) circumstances would be with a protein which contained only one of the susceptible amino acids. This is the case for rabbit thymus lysine-rich histone (mol wt 21,000), which contains a single tyrosyl residue, but no tryptophan, histidine, or sulfur-containing amino acids.[3] As reported previously,[4] NBS cleaves the lysine-rich histone at its single tyrosyl residue, producing two components which are separable on Sephadex G-100. The yields of the two components (N_1 and N_2) were not quantitative and they were unequal on a molar basis, and therefore it seemed that the cleavage was similar to that in more complicated proteins. Now, however, we are able to recover both fragments in nearly quantitative yields (Table I).

Table I. Representative Yields of NBS Fragments of Rabbit Thymus Lysine-Rich Histone

Applied with sucrose Yield, %		Applied without sucrose Yield, %	
N_1	N_2	N_1	N_2
44[a]	91[a]	99	91
49	84	97[a]	97[a]

[a] Yields calculated for Figure 1.

The large discrepancy in the yields of the two fragments which was observed previously can be eliminated by omitting sucrose from the sample applied to the G-100 column. The dramatic effect this has on yield and chromatographic pattern can be seen in Table I and Figure 1.

The manufacturer (Pharmacia Fine Chemicals, Inc.) recommends that application of samples to columns of Sephadex G-100 be accomplished with the aid of an inert substance such as sucrose so that the sample may be applied as a dense solution beneath a layer of eluent, thus facilitating the application and preventing disturbance of the resin. The use of sucrose, however, has an unsatisfactory effect on the chromatography of fraction N_1, which is highly basic.[3,4]

When the products of NBS cleavage are chromatographed with sucrose included in the application mixture, fraction N_1 shows a large tail which underlies the peak containing the other peptide fraction (N_2). If the amount of N_1 recovered is calculated just from the symmetrical portion of the first peak, its yield is very much less than that of N_2. When the area under the tailing portion of the chromatogram is summed with N_1, the yields of N_1 and N_2 become very nearly equal. Amino acid analysis of the tailing portion has confirmed that these regions are largely N_1. The reason for this effect of sucrose is as yet unexplained, although it may be related to the high lysine content of N_1 and the acidic solvent used for chromatography. Perhaps a weak reversible three-way binding of peptide–sucrose–Sephadex occurs causing transient retention of the peptide and dissociation occurs progressively as the peptide and sucrose are gradually separated on the column. In any case when sucrose is not used both peaks are symmetrical and give nearly quantitative yields.

(3) M. Bustin, S. C. Rall, R. H. Stellwagen, and R. D. Cole, *Science*, 163, 391 (1969).
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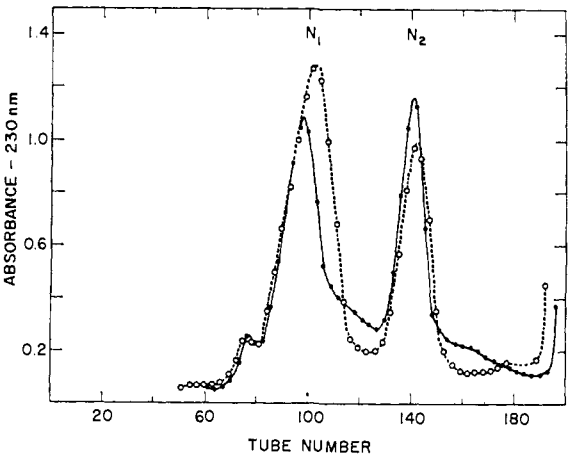

Figure 1. Chromatography of the NBS reaction mixture of a rabbit thymus lysine-rich histone on a column (2 × 190 cm) of Sephadex G-100 (particle size 40–120 μ). In each case 3.3×10^{-6} mol of starting material was treated with NBS, applied to the column, and eluted with 0.02 *N* HCl at 3 ml per tube. Yields when applied with sucrose: tubes 85–110, 44%; tubes 129–152, 91%. Yields when applied without sucrose: tubes 85–117, 97%; tubes 129–153, 97%: —●—, absorbance when applied with sucrose; --○--, absorbance when applied without sucrose.

The nearly quantitative cleavage of tyrosine by NBS in lysine-rich histone points out how useful this method can be when applied to proteins or peptides which contain only one of the residues susceptible to NBS oxidation. Thus, NBS offers an excellent alternative to enzymatic or other chemical methods, such as cyanogen bromide, for structural studies on peptides and proteins.

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Neighboring Boron in a Concerted Electrophilic Displacement

Sir:

Direct bonding interaction between the attacking and leaving groups has been postulated to be a general feature of electrophilic displacements with retention at tetrahedral carbon.[1,2] The methyl-bridged aluminum compound $Al_2Me_5NPh_2$ (**1**), which has been characterized by X-ray diffraction,[3] is a reasonable model for the transition state (**2**) of a typical electrophilic displacement, mercurideboronation.[2a,4]

It is difficult to obtain experimental evidence for the three-center electron-pair bond (represented by the dashed-line triangle) and the boron–oxygen–mercury

(1) S. Winstein, T. G. Traylor, and C. S. Garner, *J. Amer. Chem. Soc.*, 77, 3741 (1955).
(2) Reviews: (a) D. S. Matteson, *Organometal. Chem. Rev.*, *A*, 4, 263 (1969); (b) F. R. Jensen and B. Rickborn, "Electrophilic Substitution of Organomercurials," McGraw-Hill Book Co., New York, N. Y., 1968; (c) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965.
(3) V. R. Magnuson and G. D. Stucky, *J. Amer. Chem. Soc.*, 91, 2544, (1969).
(4) D. S. Matteson and E. Krämer, *ibid.*, 90, 7261 (1968).