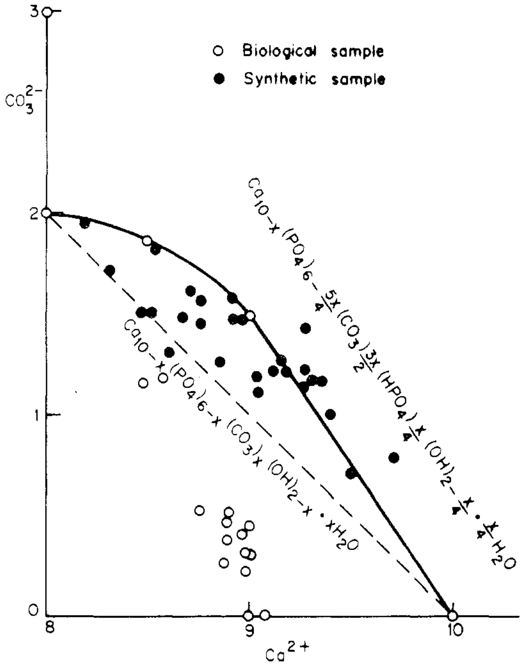


Figure 9. Theoretical domain for the Ca^{2+}/CO_3^{2-} ratio and values obtained in synthetic and biological samples.

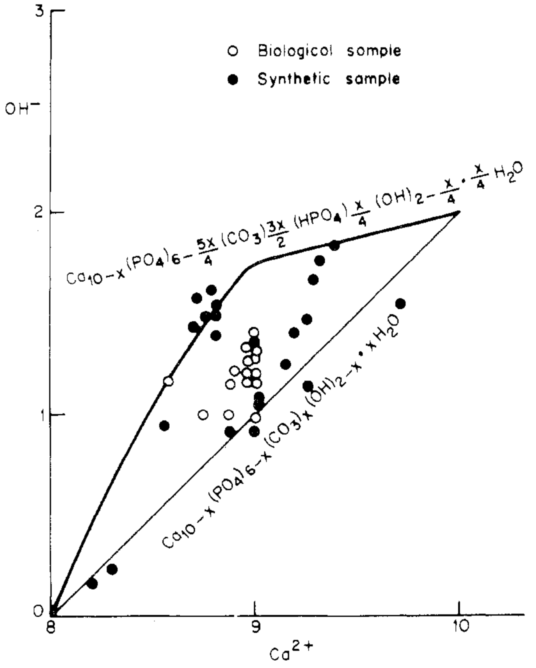


Figure 10. Theoretical domain for the Ca^{2+}/OH^- ratio and values obtained in synthetic and biological samples.

precluded when the value of x increases from 1 to 2.

The theoretical domain of the Ca^{2+}/PO_4^{3-}, Ca^{2+}/CO_3^{2-}, and Ca^{2+}/OH^- ratios predicted by our model are shown in Figures 8–10. The experimental values of these ratios for synthetic[4] and biological carbonate apatites are also shown on these figures. It can be observed that experimental values are collected by an enclosing curve as Bonel et al. reported.[4] For the case of biological carbonate apatites the Ca^{2+}/PO_4^{3-} and Ca^{2+}/CO_3^{2-} ratios occupy different regions inside the same domains. This fact can be explained because synthetic samples are formed in CO_3^{2-}-saturated media and, therefore, at least the first generation of CO_3^{2-} substitutions has to take place. This is not the case for biological samples whose characteristic ratios cannot be included in the representation given by Bonel et al.

Acknowledgment. The authors are indebted to Dr. L. Cifuentes of the Urolithiasis Laboratory, Fundación Jiménez Díaz, Madrid, for providing us with the biological carbonate apatites.

Registry No. Carbonate apatite, 12286-89-4.

References and Notes

(1) P. F. González-Díaz and A. Hidalgo, *Opt. Pur. Apl.*, **8**, 51 (1975).
(2) R. Z. Legeros, Ph.D. Thesis, New York University, 1967.
(3) J. C. Elliot, Ph.D. Thesis, London, 1964.
(4) G. Bonel, J. C. Labarthe, and C. Vignoles, "Physico-chimie et Cristallographie des apatites d'interet biologique, Paris, 10–15 September 1973", Editions du Centre National de la Recherche Scientifique, Paris, 1975.
(5) P. F. González-Díaz and A. Hidalgo, *Spectrochim. Acta, Part A*, **32**, 631 (1976).
(6) P. F. González-Díaz, Ph.D. Thesis, University of Complutense, Madrid, 1974.
(7) A. Hidalgo and P. F. González-Díaz, *C. R. Hebd. Seances Acad. Sci., Ser. B*, **280**, 563 (1975).
(8) J. A. Pople, G. A. Segal, and D. P. Santry, *J. Chem. Phys.*, **43**, S136, S129 (1965).

Contribution from the Departments of Chemistry,
University of Karlsruhe, 75 Karlsruhe, West Germany,
and Ames Laboratory—ERDA,
Iowa State University, Ames, Iowa 50011

Rare Earth Metal-Metal Halide Systems.
19. Structural Characterization of the Reduced Holmium Chloride Ho_5Cl_{11}

U. Löchner,[1a] H. Bärnighausen,*[1a] and J. D. Corbett[1b]

Received January 26, 1977 AIC70068C

In recent years numerous rare earth metal–metal halide phase diagrams have been investigated, many of which contain one or more intermediate phases between the trihalide and the pure dihalide.[2] Once the structures of the salt-like dihalides became well understood,[3,4] gradually more insight has been gained into the structures of the intermediate phases in these systems.[5,6] In 1975 the condensed holmium–holmium(III) chloride system[2b] was described which featured a single reduced phase of analytical composition $HoCl_{2.14}$, the very narrow range between its peritectic melting point at 551 °C and the eutectic (with $HoCl_3$) at 543 °C contributing to the difficulty of the preparation. In the course of subsequent single crystal work on reduced rare earth halides, especially on Dy_5Cl_{11},[5] the holmium phase has now been structurally identified as the isostructural Ho_5Cl_{11}, that is, with the correct composition $HoCl_{2.20}$.

Experimental Section

The work utilized powder diffraction data secured photographically on an IRDAB (Stockholm) Guinier camera of 100 mm diameter with monochromatized Cu $K\alpha_1$ radiation, λ 1.540 562 Å. The diffraction intensities were measured on a Zeiss-Jena Schnellphotometer G III. Intensity readings from a scale $S = \log 1/D$ from 0 to ∞ were corrected for individual background, and the lightest background was set to zero and the primary beam line intensity to ∞. I_0 values given in Table I (supplementary material) are photometer readings scaled to I_c.

Results and Discussion

The reduced holmium phase has the composition Ho_5Cl_{11} and is isomorphous with the monoclinic Dy_5Cl_{11}. The structure was identified using powder Guinier photographs collected during the original phase diagram work.[2b] As shown in Table I, 75 observed lines in the diffraction pattern can now be completely indexed with good agreement between observed and calculated[7] intensities. From these, 29 sharp and clearly resolved reflections were chosen for the final lattice constant

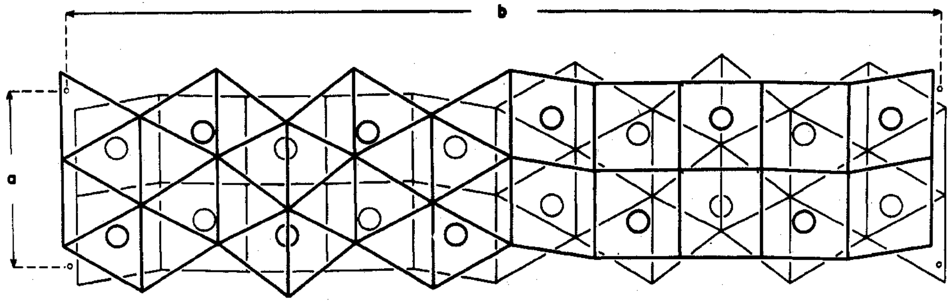


Figure 1. Schematic representation of the crystal structure of Ho_5Cl_{11} (from ref 5). The holmium atoms are drawn as light and bold circles at $z \approx 0$ and $z \approx {}^1/_2$. The chlorine atoms are located at the intersection points of the somewhat puckered nets at $z \approx {}^3/_4$ and $z \approx {}^1/_4$.

refinement,[8] yielding the unit cell $a = 7.078$ (2) Å, $b = 34.57$ (2) Å, $c = 6.603$ (3) Å, and $\beta = 90.19$ (5)°. The numbers in parentheses are estimated errors obtained by tripling numerical standard deviations. The actual space group is $P2_1/m$ (No. 11) but to a very good approximation the structure can be described with the space group *Pnma* (No. 62) which is a minimal supergroup of $P2_1/m$. There are 4 formula units per unit cell and the calculated density is 4.994 g cm^{-3}. The crystal structure (Figure 1) can be understood as a one-dimensional superstructure of the fluorite type built from five basic fluorite units with four additional anions per unit cell. In order to accommodate these anions, half of the primitive cubic anion packing is transformed into a closest packing. The superimposed anion layers of these two packings lead to a vernier-like[9] picture.

The relatively large difference between the x-ray and the analytical stoichiometries, Cl/Ho = 2.20 vs. 2.14, deserves some comment since typical analyses normally give ratios which are accurate to within ±0.02 or less. Since there is no evidence in the powder diffraction patterns for a range of composition for $HoCl_{2.20}$ the low analytical results must have been caused by inclusion of a small amount of either the metal or a still lower phase. In either case, the small amount necessary to account for the difference would hardly be evident in the x-ray powder films and impossible to detect on solution of a sample for analysis since fairly strong acetic acid has to be used in order to avoid precipitation of quite stable hydrolysis products. Although sheets rather than chunks of metal were used in most equilibrations small amounts of metal could have been scraped from the substrate in an attempt to recover all of the material. Finely divided holmium might also be produced by either a disproportionation equilibrium under small temperature gradients or, better, by accidental excursions of the sample above the peritectic decomposition temperature (551 °C) since the region for effective equilibration above the eutectic is only 8° wide. Magnetic evidence for traces of finely divided metal has been found for a $GdCl_{1.5}$ sample,[10] a comparable situation where there is only a 31° wide region for equilibration below the decomposition point of the sesquichloride (632 °C).

On the other hand, very recent experiences have made it increasingly clear that many of the earlier rare earth metal–metal halide studies in which only a dihalide or less-reduced phase has been achieved during equilibration of the molten trichloride with excess metal represented only metastable equilibrium. It now appears that very small amounts of more reduced monochloride or other phases form and effectively block the surface of the metal toward further reaction, as recently demonstrated during the synthesis of ScCl.[11] Simultaneously the synthesis of GdCl, TbCl, and still others has been reported.[12] The fact that earlier equilibrations in the $HoCl_3$–Ho system with chunks of metal yielded Cl/Ho ratios around 2.18 and ratios around 2.14 were obtained only on extended equilibrations using small amounts of $HoCl_3$ and packets of holmium foil to ensure complete reduction is consistent with either contamination by metal or by monochloride, but the latter now seems more likely. Further studies of this system are necessary to show this conclusively, however.

Acknowledgment. This work was supported in part by the U.S. Energy Research and Development Administration, Division of Physical Research.

Registry No. Ho_5Cl_{11}, 63039-66-7.

Supplementary Material Available: Table I, the observed and calculated distances and intensities for Ho_5Cl_{11} (1 page). Ordering information is given on any current masthead page.

References and Notes

(1) (a) University of Karlsruhe. (b) Iowa State University.
(2) (a) J. D. Corbett, *Rev. Chim. Miner.*, **10**, 239 (1973); (b) U. Löchner and J. D. Corbett, *Inorg. Chem.*, **14**, 426 (1975).
(3) H. Bärnighausen, H. P. Beck, and H.-W. Grüninger, *Proc. Rare Earth Res. Conf., 9th*, **1**, 74 (1974).
(4) H. Bärnighausen, "The Crystal Chemistry of the Salt-Like Rare Earth Dihalides", to be submitted for publication.
(5) H. Bärnighausen, *Proc. Rare Earth Res. Conf., 12th*, **1**, 404 (1976).
(6) H. Bärnighausen and J. M. Haschke, *Inorg. Chem.*, submitted for publication.
(7) C. M. Clark, D. K. Smith, and G. G. Johnson, "A FORTRAN IV Program for Calculating X-Ray Powder Diffraction Patterns, Version 5", Pennsylvania State University, 1973. Positional and thermal parameters were taken from Dy_5Cl_{11}, ref 5, p 408.
(8) K. Krogmann, "An ALGOL Least-Squares Program for Refinement of Lattice Dimensions", University of Karlsruhe, 1971.
(9) B. G. Hyde, A. N. Bagshaw, S. Andersson, and M. O'Keeffe, *Annu. Rev. Mater. Sci.*, **4**, 43 (1974); see especially p 82.
(10) J. D. Greiner, J. F. Smith, J. D. Corbett, and F. J. Jelinek, *J. Inorg. Nucl. Chem.*, **28**, 971 (1966).
(11) K. R. Poeppelmeier and J. D. Corbett, *Inorg. Chem.*, **16**, 294 (1977).
(12) A. Simon, H. Mattausch, and N. Holzer, *Angew. Chem.*, **88**, 685 (1976).

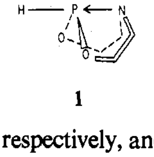
Contribution from Gilman Hall and the Ames Laboratory
of the ERDA, Iowa State University, Ames, Iowa 50011

Unusual Phosphorus Basicity of $P(OCH_2CH_2)_3N$ and the Molecular Structure of $H_3BP(OCH_2CH_2)_3N$

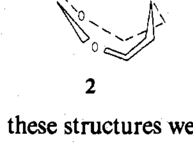
J. C. Clardy,[1] D. S. Milbrath, and J. G. Verkade*

Received March 16, 1977 AIC70207Q

In two recent communications we showed that spectral (NMR and IR) and chemical properties of the new polycyclic species **1**[2a] and **2**[2b] were consistent with a tricyclic and bicyclic



1



2

configuration, respectively, and these structures were confirmed