

and the normal state of the molecule is represented by the symmetrical resonance hybrid of the twenty structures, making nearly equal contributions. The formal charge of the chromium atom for these structures is  $3-$ . To be compatible with the electroneutrality principle, the structure would have to involve ionic character of the bonds great enough to neutralize two of the three negative charges. The amount of ionic character required is 22%, close to the value, 19%, that corresponds to the difference in electronegativity of chromium and carbon. It is accordingly likely that other structures, with a smaller amount of double-bond character, do not contribute, and that the six chromium-carbon bonds in the molecule are to be assigned 50% double-bond character.

The discussion of the bond length can be made with reasonable confidence. Whitaker & Jeffery (1967) pointed out that I had assigned the values 1.21, 1.22, and 1.23 Å, respectively to  $\text{Ni}^{\text{IV}}$ ,  $\text{Co}^{\text{III}}$ , and  $\text{Fe}^{\text{II}}$  as the octahedral covalent radii for  $d^2sp^3$  bonds, with three unshared electron pairs for each atom (Pauling, 1939, p. 169). The electronic structure of the chromium atom with oxidation number 0 and forming six covalent bonds is isoelectronic with that of these atoms, permitting the linear extrapolation of the values to the value 1.25 Å to be made with confidence. With the single-bond radius 0.77 Å for carbon, this leads to 2.02 Å for the chromium-carbon single bond length corresponding to such a structure.

The equation  $D(n) = D(1) - 0.60 \text{ \AA} \log n$  (Pauling, 1960, p. 400) gives the correction  $-0.104 \text{ \AA}$  for 50% double-bond character, and accordingly leads to an expected bond length about 1.91 Å in chromium hexacarbonyl, in satisfactory agreement with the observed bond length. There exists an uncertainty of about 0.03 Å in the correction for double-bond character, but the conclusion is nevertheless justified that the observed bond length in this molecule has very nearly the value expected from valence-bond theory.

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**Crystalline americium trihydroxide.** By W. O. MILLIGAN and M. L. BEASLEY, *Baylor University, Waco, Texas, U.S.A.* and M. H. LLOYD and R. G. HAIRE, *Oak Ridge National Laboratory\*, Oak Ridge, Tennessee, U.S.A.*

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Aging of amorphous precipitated hydrous americium gel under water yields rod-like or scroll-like particles of hexagonal  $\text{Am}(\text{OH})_3$  ( $a = 6.426 \pm 0.002$ ,  $c = 3.745 \pm 0.002 \text{ \AA}$ ) isostructural with  $\text{Nd}(\text{OH})_3$  ( $a = 6.422 \pm 0.002$ ,  $c = 3.742 \pm 0.002 \text{ \AA}$ ).

The addition of alkali to a trivalent americium salt solution yields a gelatinous precipitate, which, when washed and dried rapidly at room temperature, exhibits an amorphous type electron diffraction pattern, and which has been shown by electron microscopy to consist of particles about 15–20 Å in diameter (Milligan, Chetham-Strode & Keller, 1963).

In view of the fact that hydrous neodymia is amorphous under like conditions, becoming crystalline to form  $\text{Nd}(\text{OH})_3$  on aging under water after several hours, it was suggested

(Milligan & Dwight, 1965) that hydrous americium might exhibit a similar behavior. Such results would be of interest in providing additional information concerning the expected similarity of the lanthanides and the actinides.

A sample of hydrous americium gel was prepared from highly pure  $\text{Am}(\text{NO}_3)_3$ . Isotopic analysis by mass spectrometry established the americium to be  $^{241}\text{Am}$  with < 5 ppm of other isotopes, and cation impurities were determined to be less than 0.5%, the principal impurity being ~0.2% cerium. The gel was prepared by the addition of 0.06 M americium nitrate solution that was 2.2 M in  $\text{HNO}_3$  to a threefold excess of 10M  $\text{NH}_4\text{OH}$ . The precipitate was

\* Operated by Union Carbide Corporation for the U.S. Atomic Energy Commission.

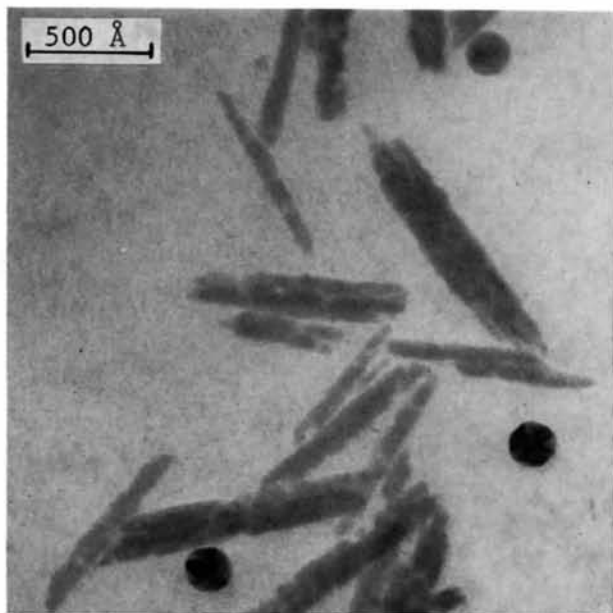


Fig.1. Electron micrograph of Am(OH)<sub>3</sub>. Magnification 320,000 diameters. The three dense particles are colloidal gold used as a focusing aid.

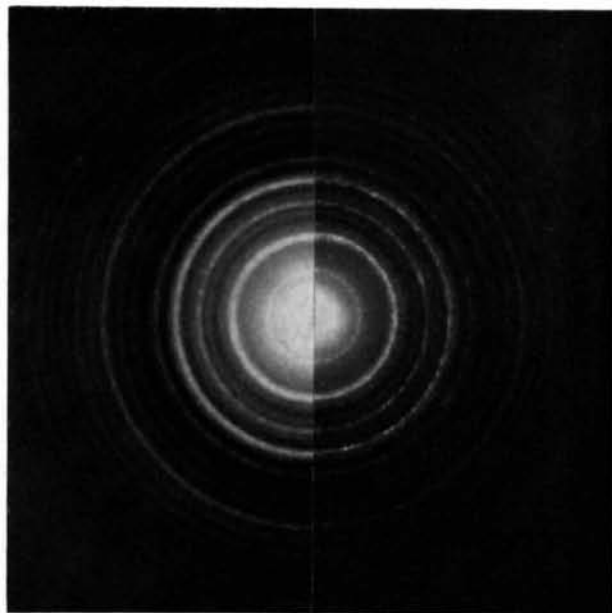


Fig.2. Electron diffraction patterns of (right) Am(OH)<sub>3</sub> and (left) Nd(OH)<sub>3</sub>.

Table 1. Observed and calculated interplanar spacings for Am(OH)<sub>3</sub>

$a = 6.426 \pm 0.002 \text{ \AA}$ , $c = 3.745 \pm 0.002 \text{ \AA}$											
<i>h</i>	<i>k</i>	<i>l</i>	Obs.	Calc.	<i>I</i> / <i>I</i> <sub>0</sub>	<i>h</i>	<i>k</i>	<i>l</i>	Obs.	Calc.	<i>I</i> / <i>I</i> <sub>0</sub>
1	0	0	5.565	5.565	4	1	0	2	1.774	1.775	1
1	1	0	3.217	3.213	10	1	1	2	1.619	1.618	1
1	0	1	3.105	3.107	10	2	2	0	1.605	1.606	2
2	0	0	2.783	2.783	1	3	1	0	1.545	1.544	1
1	1	1	2.441	2.439	1	3	1	1	1.425	1.427	1
2	0	1	2.236	2.234	7	2	1	2	1.397	1.399	0.5
2	1	0	2.102	2.104	3	3	0	2	1.320	1.318	2
3	0	0	1.850	1.855	8	3	2	0	1.278	1.277	2
2	1	1	1.832	1.834	7	4	1	0	1.214	1.214	1

Table 2. Lattice constants for Am(OH)<sub>3</sub> and Nd(OH)<sub>3</sub>

	<i>a</i>	<i>c</i>	Reference
Am(OH) <sub>3</sub>	6.426 ± 0.002 Å	3.745 ± 0.002 Å	Reported here
Nd(OH) <sub>3</sub>	6.422 ± 0.002	3.742 ± 0.002	Reported here
Nd(OH) <sub>3</sub>	6.421 ± 0.010	3.74 ± 0.02	Roy & McKinstry (1953)
Nd(OH) <sub>3</sub>	6.43 ± 0.02	3.75 ± 0.02	Zachariassen (1948)

filtered and washed by resuspending the filter cake in water and filtering. After eight washings with water, a small amount of water was added to the filter cake; and the mixture was heated at 80°C for about 90 minutes. During this period the filter cake converted to a fluid sol which contained 87 milligrams of americium per milliliter and a residual nitrate concentration of 0.21 mole of nitrate per mole of americium. The sol was aged in this form for several weeks. The sample reported here was removed after five weeks, at which time the sol was diluted with distilled water and a drop (micropipet) was allowed to dry on each of several carbon membranes supported on 400 mesh copper Athene screens. The carbon membranes were prepared by vacuum evaporation on a freshly cleaved mica sheet. The carbon membranes were tested in the electron microscope for detectable impurities or deposits before use. The amount of sample on the entire grid corresponded to about 0.01 μg of americium-241.

Electron micrographs were obtained with a Siemens 'Elmiskop I' at 100 kV with a magnification on the negative of 80,000 diameters. Electron diffraction patterns were obtained in the same instrument at 100 kV, employing evaporated aluminum metal as an internal standard ( $a = 4.0494 \text{ \AA}$ , NBS-ASTM 4-0787). The thickness of the evaporated aluminum film was adjusted so that the intensity of the Debye-Scherrer rings for the standard and the sample were approximately the same. A combined camera and microphotometer constant was derived. The electron diffraction pattern of the pure aluminum standard yielded nine useful calibration lines. The average camera-microphotometer constant was used to calculate *a* from each aluminum reflection, from which was derived an average value of  $a = 4.049 \pm 0.001 \text{ \AA}$ , indicating that the results of the calibration are internally consistent.

A typical electron micrograph for a sample aged under water for two weeks is given in Fig. 1. The rod-like or scroll-like particles are very similar to corresponding samples of Nd(OH)<sub>3</sub> (Milligan & Dwight, 1965). The noticeably 'spotted' appearance of the particles may be the result of some self-radiation damage. Further work is in progress on samples of Am(OH)<sub>3</sub> exposed for various time periods to self-radiation (*a*) under water and (*b*) in the dry state.

In Fig. 2 there are given the electron diffraction patterns for Am(OH)<sub>3</sub> and Nd(OH)<sub>3</sub>. The close similarity is obvious. In Table 1 there are given calculated and observed interplanar spacings for Am(OH)<sub>3</sub>. A comparison with values of the lattice constants for Nd(OH)<sub>3</sub> is given in Table 2. The two hydroxides are clearly isostructural, and the data demonstrate for the first time the preparation of a definite trihydroxide of americium. The lattice constants for Am(OH)<sub>3</sub> are just detectably larger than for Nd(OH)<sub>3</sub>. The new values reported here for Nd(OH)<sub>3</sub> agree within the error limits of the earlier results of Zachariassen (1948) and Roy & McKinstry (1953). The conflicting values of Fricke & Seitz (1947) have been discussed earlier (Roy & McKinstry, 1953; Milligan & Dwight, 1965).

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