proximately pure monomer 2 is greatly dependent on the value of r_1.

The values obtained for the function when $r_2 = 0.5$ precisely are shown in Fig. 3. These composition distributions are of little practical significance since r_2 values only slightly greater or less than 0.5 result in functions of the form shown in Figs. 1 and 2, respectively.

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The Dimeric Nature and Crystallographic Unit Cell of Ammonium 6-Molybdochromiate[1]

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Elsewhere in this issue[3] a detailed argument, based on chemical evidence, is presented concerning the formulas and structures of the isomorphous heteropoly 6-molybdate anions of trivalent Cr, Fe, Co and Al. The formula therein proposed for these anions is $[(XO_6Mo_6O_{15})_n]^{-3n}$, where X represents the trivalent atom and n is an undetermined integer which is probably small.

The structural argument[3] makes it clear that a monomeric formula is extremely improbable. The crystallographic evidence described below shows that there are two empirical formulas per simplest crystallographic unit cell in the ammonium salt of the chromic complex. Therefore, $n = 2$; and the correct formula for the compound is $(NH_4)_6[(CrO_6Mo_6O_{15})_2]\cdot 20H_2O$.

Isomorphism of this Cr compound with the corresponding Fe, Co and Al compounds was previously strongly indicated by chemical evidence[3] and mixed crystal formation.[4] It is further supported by our observation that the powder X-ray patterns of the four salts are extremely similar.[1]

The results described below lend further strong support to the structure which was postulated previously[3] for these anions, because the unit cell is of appropriate size and shape to contain that specific structure.

Experimental

Samples of the ammonium salts of the Cr, Fe, Co and Al complexes were prepared[1,3] and analyzed.

Anal. Calcd. for $(NH_4)_6[(CrO_6Mo_6O_{15})_2]\cdot 20H_2O$: Mo, 48.1; Cr, 4.35; N, 3.52. Found: Mo, 48.2; Cr, 4.39; N, 3.68. The analytical results for the other salts were equally satisfactory.

Pycnometer densities of powdered samples of the salts were found to be: (av. in g./cc.) Cr cpd., 2.866; Fe cpd., 2.874; Co cpd., 2.878; and Al cpd., 2.767.

The pure Fe and Al compounds were obtained only as microcrystalline precipitates. Bigger crystals of the Cr and Co compounds may be grown, and a number of attempts were made to obtain material suitable for complete single crystal work. However, these crystals tend to develop well in two crystallographic directions while the development in the third direction is less satisfactory. The net result of this circumstance is that one of the crystallographic angles (β^*) could be determined only by indirect calculation. Doubt is not cast on the value obtained for the volume and content of the unit cell, however, because this volume was calculated from appropriate simultaneous equations[5] which do not utilize β^*

$$V = \frac{d_{100}d_{010}c_0}{\sin \gamma^*} \quad \text{and} \quad V = \frac{d_{001}d_{010}a_0}{\sin \alpha^*}$$

In appearance, the crystals of the chromic compound are small, flat rhombs. They proved to be triclinic. Rotation and zero and first layer line X-ray diffraction photographs were taken about the short diagonal of the rhombic platey face, about the long diagonal of this face, and about one of the edges. The results are summarized in Table I.

Although the simplest crystallographic unit cell contains two empirical formulas, it was found more convenient, for purposes of crystallographic calculation, to consider a body-centered triclinic unit cell containing four empirical formulas. The results given below in Table I are in terms of this larger body-centered cell rather than the smallest crystallographic unit cell.

TABLE I

CRYSTALLOGRAPHIC DATA FOR AMMONIUM 6-MOLYBDOCHROMIATE

Crystal system, triclinic; space group, $I\bar{1}$

a_0 = 12.0 Å. = periodicity of acute bisectrix

c_0 = 10.8 Å. = periodicity of obtuse bisectrix

D_{100} = D of acute bisectrix = 11.8 Å.

D_{010} = D of platey direction = 21.2 Å.

D_{001} = D of obtuse bisectrix = 10.7 Å.

α^* = 85°32′ = angle between 010 and 001

β^* = approx. 90° = angle between 100 and 001[6]

γ^* = 77°04′ = angle between 010 and 100

Av. vol. of body-centered unit cell = 2760 ± 15 Å.^{3}

Mol. wt. of body-centered unit cell = 4765

No. of empirical formula units per body-centered cell = 3.98

No. of empirical formula units per simplest crystallographic unit cell = 1.99

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[1] Abstracted from portions of a thesis, presented by Murry L. Block to the Graduate School of Boston University in partial fulfillment of the requirements for the A.M. degree in chemistry.

[2] Addressee for reprint requests.

[3] L. C. W. Baker, G. Foster, W. Tan, F. Scholnick and T. P. McCutcheon, THIS JOURNAL, **77**, 2136 (1955).

[4] G. A. Barbieri, *Atti. Acad. Lincei*, [5], **23i**, 338 (1914).

[5] C. W. Wolfe, *Am. Mineralogist*, **26**, 134 (1941).

[6] The value of β^* was calculated by using the relationship

$$V^* = a^*b^*c^* \times \sqrt{1 - \cos^2\alpha^* - \cos^2\beta^* - \cos^2\gamma^* + 2\cos\alpha^*\cos\beta^*\cos\gamma^*}$$

wherein

$$V^* = \frac{1}{V},\ a^* = \frac{1}{d_{100}},\ b^* = \frac{1}{d_{010}},\ \text{and}\ c^* = \frac{1}{d_{001}}.$$

Body-centered unit cell volumes below 2750.5 Å.^{3} give imaginary values for β^*. When the volume employed is 2750.53 Å.^{3}, $\beta^* = 90°00'$. The largest cell volume ever indicated by any of the experimental measurements was 2767 Å.^{3}, for which β^* may be either 82°47′ or 95°14′. The best experimental results and the majority of the results give values for β^* which are very much closer to 90°.

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