both $\partial n/\partial M'$ and τ^*, and the calculated $N_{z'}$ increased from *ca.* 2.0 to *ca.* 2.7.

The room-temperature data confirm the hypothesis[13] that hafnium (or zirconium) is more extensively aggregated as hydrolysis progresses, such that the possibility of monomers exists only at very high acidity.

The changes in series c and d upon heating were much larger and are best seen in Figures 3 and 4 where $1/N_{z'}$ values are plotted for solutions 0.05 *M* in total hafnium *vs.* time for each of four temperatures. For the plots shown z' was arbitrarily taken to be 0.50. The solutions of series c and d were returned to room temperature in order to see if they would exhibit any slight tendency to return to the room-temperature values of turbidity. No such tendency was observed. Perhaps a better test would have been to take the 75° solutions back to 60° and look for a reduction in turbidity. Such an experiment was not performed.

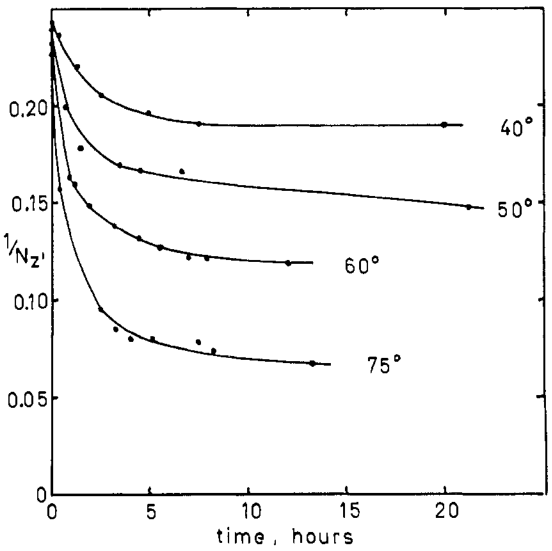

Figure 3.—Reciprocal of degree of aggregation *vs.* time for series c; [Hf] = 0.05 *M*.

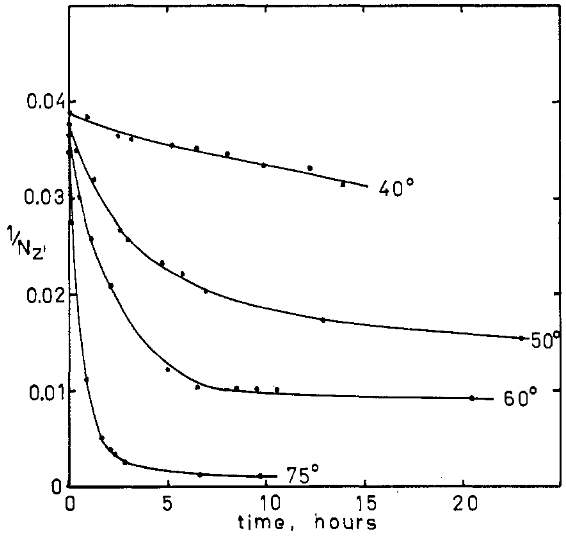

Figure 4.—Reciprocal of degree of aggregation *vs.* time for series d; [Hf] = 0.05 *M*.

It would be tempting to state unequivocally that solutions of $HfOCl_2$ in NaCl-supporting electrolyte exhibit an average degree of aggregation of 20; see Figure 2. However it is clear from Figures 3 and 4 that the degrees of aggregation of such solutions are strong functions of both time and temperature of storage, even though it is not possible to say whether or not the equilibrium itself is a function of temperature. As a tentative hypothesis we propose that such solutions are tending toward a single equilibrium which consists of hafnium oxide as a heterogeneous phase and a small residual concentration of monomeric hafnium solute cation in very strong acid, which acid is built up as the oxide precipitates: $Hf(OH)_2^{2+} + 2H_2O \rightleftarrows Hf(OH)_4 + 2H^+$.

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A Magnetic Study of a Chlorapatite of Manganese, $Ba_5(MnO_4)_3Cl$

By L. H. Brixner and J. F. Weiher

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Despite the fact that there is evidence of the existence of manganates(V) in the literature as early as 1864 by Rosenstiehl[1] and later by Auger[2] and Sackur,[3] it was not until 1946 when Lux[4] recognized the presence of manganese in its pentavalent state and correctly formulated the first pure manganate(V) as $Na_3MnO_4 \cdot 10H_2O$. Although many other manganates(V) have since been prepared by Scholder[5] and Klemm,[6] the pentavalent state of Mn is still considered an "unusual" valence state which should be well supported by experimental evidence. An analytical determination of the oxidation state of manganese would be arbitrary since an equimolar mixture of Mn^{4+} and Mn^{6+} would indicate the same results as Mn^{5+}. In the present note, we wish to give magnetic measurements as evidence for the existence of Mn^{5+} in the new compound $Ba_5(MnO_4)_3Cl$.

Experimental Section

$Ba_5(MnO_4)_3Cl$ was prepared by the "flux-reaction technique" (where the flux serves both as such and as the constituent com-

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(1) J. Rosenstiehl, *J. Pharm.*, [3] **46**, 344 (1864).

(2) V. Auger and M. Billy, *Compt. Rend.*, **138**, 500 (1904).

(3) O. Sackur, *Ber.*, **43**, 381 (1910).

(4) H. Lux, *Z. Naturforsch.*, **1**, 281 (1946).

(5) R. Scholder, *Z. Angew. Chem.*, **16**, 461 (1954).

(6) W. Klemm, *ibid.*, **16**, 468 (1954).

ponent of the reaction leading to the desired end product) using $BaCl_2$ (Allied Chemical) and MnO_2 (Baker Analyzed). $BaCl_2$ (300 g) was charged into a 250-ml Pt dish and was molten at 1000°. MnO_2 (10 g) was charged into the melt and moist air was bubbled through the melt by way of a 0.5-in. diameter platinum tube, perforated at the bottom. The melt was held at 1000° for 2 hr and at 1200° for 1 hr. After furnace cooling excess halide was leached away with water and the product was filtered, washed, and dried. About half of the reaction product was obtained as intensely colored blue-green crystals of acicular habit; the other half (readily separated by flotation) was Mn_3O_4. Chemical analysis of the manganate gave the following results. *Anal.* Calcd for $Ba_5(MnO_4)_3Cl$: Ba, 63.65; Mn, 15.27; Cl, 3.28. Found: Ba, 64.0; Mn, 15.3; Cl, 3.4. The compound was structurally identified as an apatite and X-ray parameters were found to be $a_h = 10.38$ Å, $c_h = 7.73$ Å.

Results and Discussion

The observed susceptibility for $Ba_5(MnO_4)_3Cl$ was independent of field from 2000 to 8000 Oe at room temperature, 300°K ($10^3\chi_m = 8.82 \pm 0.08$) and at liquid temperature, 77°K ($10^3\chi_m = 29.6 \pm 0.2$).

After correcting the observed susceptibility for temperature-independent diamagnetism, $10^3\chi_m{}^d = -0.348$, estimated from Pascal's constants, the reciprocal paramagnetic susceptibility $[1/(10^3\chi_m + 0.348)]$ is not quite linear with absolute temperature. The effective moment per manganese at 300°K is 2.69 BM and at 77°K is 2.50 BM.

If a small temperature-independent paramagnetic component of about $+0.497 \times 10^{-3}$ per manganese is included in addition to the diamagnetic correction, the corrected susceptibility follows a Curie–Weiss law with a very small Weiss constant. On a per manganese basis, this is

$$\chi_m - (0.381 \times 10^{-3}) = \frac{0.758 \pm 0.001}{T + (0.34 \pm 0.26)}$$

The magnetic moment calculated from the slope of the Curie–Weiss type of susceptibility is 2.46 BM.

For pentavalent tetrahedral manganese, d^2 (^3A), the expected moment is

$$\mu = 2.83\left(1 - \frac{4\lambda}{10Dq}\right) \simeq 2.6 \text{ BM}$$

essentially independent of temperature.

Hexavalent tetrahedral manganese, d^1 (^2E), should exhibit also an essentially temperature-independent moment

$$\mu = 1.73\left(1 - \frac{2\lambda}{10Dq}\right) \simeq 1.6 \text{ BM}$$

whereas quadrivalent tetrahedral manganese, d^3 ($^4T_1$), should exhibit a significantly temperature-dependent moment, estimated to be about $\mu = 3.5$ BM at 300°K and $\mu = 2.5$ BM at 100°K. Thus, on the basis of an equal mixture of Mn^{4+} and Mn^{6+}, the average moment

$$\bar{\mu} = \sqrt{\frac{\mu_1{}^2 + \mu_2{}^2}{2}}$$

to be observed would be about $\mu = 2.72$ BM at 300°K and 2.10 BM at 100°K.

These observed and calculated magnetic moments are summarized in Table I.

TABLE I

MAGNETIC MOMENTS OF TETRAHEDRAL MANGANESE (IN BM)

Temp, °K	Calcd		Obsd	
	Mn^{5+}	$Mn^{4+}:Mn^{6+}$	μ_{eff}	μ_{slope}
300	$\sim 2.6 \pm 0.15$	$\sim 2.7 \pm 0.2$	2.69	2.46
100	$\sim 2.6 \pm 0.15$	$\sim 2.1 \pm 0.2$		2.46
77	$\sim 2.6 \pm 0.15$	<2.1	2.50	2.46

On the basis of the results presented in Table I, it would seem correct to state that the manganese in $Ba_5(MnO_4)_3Cl$ is indeed in the pentavalent state. Klemm[6] prepared the equivalent hydroxy manganate(V), $Ba_5(MnO_4)_3(OH)$, and observed that this compound is more distinctly blue-green than the regular manganate(V), $Ba_3(MnO_4)_2$. We noted the same difference for $Ba_5(MnO_4)_3Cl$. As a final piece of supporting evidence, we observed the absorption spectrum of $Ba_5(MnO_4)_3Cl$ to be very similar to that of a solution of $MnO_4{}^{3-}$ in strong alkali. Similar observations have been made by Johnson.[7]

All of this evidence clearly supports the statement that $Ba_5(MnO_4)_3Cl$ is a novel barium chloromanganate(V) crystallizing in the apatite structure.

(7) P. D. Johnson, J. S. Prener, and J. D. Kingsley, *Science*, **141**, 1179 (1963).

Correspondence

Reactivity Patterns in Inner- and Outer-Sphere Reductions of Halogenopentaamminecobalt(III) Complexes[1]

Sir:

The reductions of halogenopentaamminecobalt(III) complexes by various reducing agents have been extensively investigated. For all of the reducing agents studied the rate constants vary monotonically as the halide is changed from fluoride to iodide. The reactivity order has come to be known as "normal" or "inverse" depending on whether the rate increases or decreases with increasing atomic number of the halogen. The normal reactivity order (F < Cl < Br < I) is observed for the inner-sphere reductions by chromium(II)[2] and pentacyanocobaltate(II);[3] for the outer-

(1) This work was supported by the National Science Foundation under Grant GP-6528.

(2) J. P. Candlin and J. Halpern, *Inorg. Chem.*, **4**, 766 (1965).

(3) J. P. Candlin, J. Halpern, and S. Nakamura, *J. Am. Chem. Soc.*, **85**, 2517 (1963).