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An X-Ray Study of the Alkaline Earth Hexaammines at 77°K†

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X-Ray diffraction patterns taken at 77°K of the compounds $M(NH_3)_6{}^0$, M = Ca, Sr, Ba, correspond to *bcc* structures with a_0 values of 9.20, 9.45, and 9.77 Å, respectively. No sign of a gross crystal structure change was observed.

In their study of the phase behavior of metal-ammonia solutions Birch and MacDonald (*1*) recorded an observation that has received virtually no comment—viz., thermal anomalies were detected in the warming curves of the alkaline earth metal-ammonia solutions. These anomalies were seen at the following temperatures: Ca/NH_3, 184°K; Sr/NH_3, 175°K; Ba/NH_3, 164°K. The eutectic temperatures for these systems were reported as 186°K, 184°K, and 184°K, respectively, indicating that the anomalies are occurring in the solid state—i.e., below the eutectic temperature—and cannot be associated with the solid-liquid phase behavior. The transitions were also detected in resistivity studies below the eutectic but, interestingly, not at all compositions nor in the solid hexaammines. The authors suggested that the transitions could be explained by a change from a "higher to a lower ammoniate, the transition marking the intersection of their vapor pressure curves".

In view of the relatively unexplored character of these interesting *expanded metal* compounds, it seemed worthwhile to examine these anomalies by low temperature X-ray diffraction. The experimental procedure was as previously described (*2*).

Cagle and Holland (*3*) have reported the results of powder X-ray diffraction investigation of the alkaline earth metal hexaammines at 233°K. Their data indicate that the metal atoms are arranged in a body-centered cubic structure with octahedral orientation of ammonia molecules around each metal atom. The variation of cell constant with composition seen in their work was consistent with vapor pressure studies showing a nonintegral ratio of ammonia-to-metal in the hexaammines (*4*, *5*). The range of lattice constants and the average a_0 value for compositions approximately equal to $NH_3/M = 6$ was given as follows:

	a_0	a_0 (avg.)
Ca ammine	9.05–9.20 Å	9.12 Å
Sr ammine	9.45–9.75 Å	9.57 Å
Ba ammine	9.85–10.10 Å	9.97 Å

The temperatures at which the above X-ray work was performed is higher than the transition temperature reported by Birch and MacDonald. Repeating the X-ray work at 77°K, to determine if the thermal anomalies can be associated with a change in crystal structure, we find that the diffraction data again indexed as body-centered cubic. The diffraction photographs at 77°K do not admit a careful comparison with the intensity data at 233°K, but within the limits of visual observation, no change in the intensities was observed. If the anomalies are associated with a change in the orientation of the ammonia molecules, as in a rotational transition, then an alteration in the intensities would not have been detected. Thus, our work at 77°K indicates that the observations of Birch and MacDonald are not due to a gross crystal structure change.

A further inference of our work at 77°K can be seen from a comparison of the low-temperature lattice constants with the values listed above: Ca

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ammine, $a_0 = 9.20$ Å, Sr ammine, $a_0 = 9.45$ Å; Ba ammine, $a_0 = 9.77$ Å. As expected the lattice constants for Sr and Ba ammines decrease with decreasing temperature. The fact that the lattice constant for Ca ammine apparently *increases* with decreasing temperature is believed to be attributable to the large variation of lattice constant with deviation from stoichiometry. Because the pure hexaammines are solids at room temperature and consequently difficult to prepare as homogeneous samples without heating above the unknown melting point at higher temperatures, our samples were prepared as ammonia-rich homogeneous liquid samples at −33°C and then frozen for the X-ray studies. It appears that the influence of variable composition, mentioned by Holland and Cagle, has completely swamped the expected contraction of cell length with decreasing temperature.

The above observation may be of some consequence. It has been reported that evaporation of ammonia from a solution of the alkaline earth metals yields a blue solid (*6*)! It may be that this blue solid is a strongly ammonia-rich hexaammine and that the blue-to-bronze, nonmetal-to-metal transition observed in the liquid solutions is also seen in the solid state, at least with respect to the alkaline earth metal-ammonia systems. Conductivity versus composition studies would be interesting in this connection.

References

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