

Effect of Water upon the Polymorphic Transitions in Anhydrous Sodium Sulphate

THE polymorphism of anhydrous sodium sulphate is well known¹⁻⁴ and the latent heats associated with its two transitions (orthorhombic form V to the orthorhombic form III at 177° C., and III to the hexagonal form I at 241° C.) have recently been determined by J. P. Coughlin⁵.

In the course of an investigation of the thermal properties of this material, we measured its heat capacity over a range of temperatures from 37° to 320° C. using a water calorimeter and partially encapsulated samples. Under these conditions, we were able to observe only the upper transition at approximately 238° C., and we determined the corresponding heat of transition as approximately 23 kcal./mole (making a correction for the heat of solution of the amount of salt dissolved). This value is considerably larger than the value 16.80 kcal./mole obtained by Coughlin⁵ for the upper (III-I) transition, and it is actually closer to the sum of this value plus that of the lower (V-III) transition (7.40 kcal./mole), namely, 24.20 kcal./mole.

Thus, it appeared that in presence of water the high-temperature hexagonal form I is inverted directly into the low-temperature form V. This is unusual since the transition V-III is normally irreversible and the salt remains in the metastable form III, when once heated over the transition temperature.

We were able to observe the complete inversion of samples brought to the form I (above 250° C.) by water-quenching the heated samples on a hot-stage X-ray diffractometer. Fig. 1 shows the powder

patterns obtained on (a) the metastable form III, (b) the hexagonal form I at 305° C. and (c) the low-temperature form V after water-quenching from 300° to 78° C. Comparison of the powder pattern c with that of the original form V shows complete identity and thus confirms that water acts as a mineralizer making the V-III transition reversible.

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Complexes of Nickel(II) with 2-Pyridinaldoxime

THE complexing properties of 2-pyridinaldoxime (I) would be expected to follow from those of 2,2'-bipyridine (II) and dimethylglyoxime (III) since this new ligand incorporates in its structure the functional groups of both the latter substances. In the course of synthesizing and characterizing the nickel(II) complexes of pyridinaldoxime (HPO) it has become apparent that some very unusual deviations from the expected behaviour occur. By analogy with the nickel(II) complexes of 2,2'-bipyridine¹, two complexes containing molecular pyridinaldoxime should form: *bis*(pyridinaldoxime)nickel(II) and *tris*(pyridinaldoxime)nickel(II). In addition, a third complex, containing one molecule of pyridinaldoxime co-ordinated to each nickel(II) atom, might also be expected to exist. The first two complexes, [Ni(HPO)₂]⁺⁺ and [Ni(HPO)₃]⁺⁺, have been prepared as the chloride and iodide salts, respectively. The *bis* complex is prepared by mixing 1 mole of nickel chloride 6-hydrate with 2 moles of the ligand in hot absolute ethanol. The compound is precipitated as fine green crystals. The *tris* complex may be isolated as fine tan crystals by mixing 3 moles of ligand with 1 mole of nickel(II) chloride in aqueous solution, followed by the addition of solid potassium iodide. The colour changes occurring in aqueous solutions indicate that the *bis*-pyridinaldoxime complex is considerably less subject to disproportionation, and consequent formation of the *tris* complex, than is true of the corresponding 2,2'-bipyridine complex. Both the *bis* and *tris* complexes containing the neutral pyridinaldoxime molecule are paramagnetic, having corrected effective magnetic moments of 3.16 and 3.12 Bohr magnetons, respectively. It may be concluded that these compounds are normal representatives of the classes of nickel(II) complexes formed by the aromatic heterocyclic diamines and other related ligands.

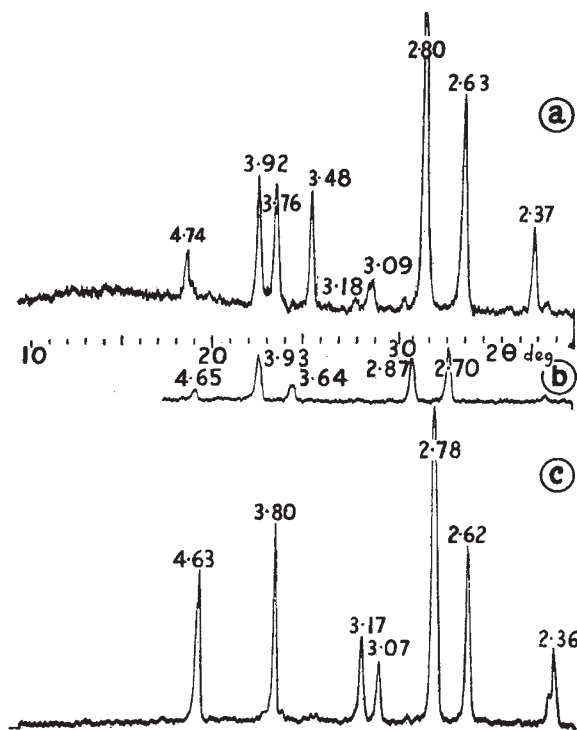


Fig. 1. (a) Sodium sulphate (III), before heating; (b) sodium sulphate (I) at 305° C.; (c) sodium sulphate (V), after water quench

