
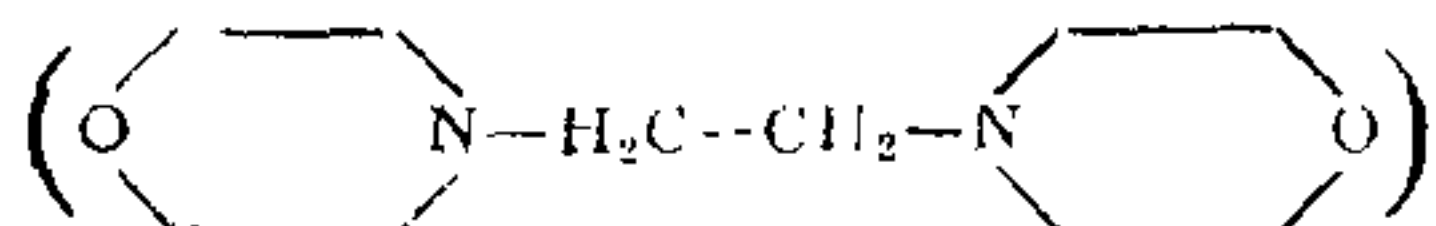


CO-ORDINATION COMPLEXES OF  
MORPHOLINE AND  
DIMORPHOLINOETHANE

MORPHOLINE  and  
dimorpholinoethane



have different types of co-ordination possibilities to metal ions, namely either through nitrogen or oxygen or through both. Over the last two years we have prepared many complexes of the two ligands with various metal halides, nitrates and perchlorates. The complexes were generally prepared by the addition of excess of morpholine or dimorpholinoethane to alcoholic solutions of the respective almost anhydrous metal salts, washing the precipitated complexes first with ethyl alcohol and then with ethyl ether. The following complexes of morpholine (M) were successfully isolated using the above technique:  $ZnCl_2 \cdot 2M$ ,  $CdCl_2 \cdot 2M$ ,  $HgCl_2 \cdot 2M$ ,  $CoCl_2 \cdot 2M$ ,  $CuCl_2 \cdot 2M$ ,  $Cu(NO_3)_2 \cdot M$ ,  $Cu(NO_3)_2 \cdot 2M$ ,  $Cu(ClO_4)_2 \cdot M$ . While our work was in progress Ahuja<sup>1</sup> has very recently reported the isolation and spectral features of the complexes of morpholine with halides of divalent Mn, Co, Cu, Zn and Cd. We have carried out in addition to spectral studies, measurements of electrical conductance and magnetic susceptibility which will be reported in detail later. The nickel complex,  $NiM_4Cl_2$ , could not be isolated by direct methods. However, it was prepared by us for the first time by the displacement of pyridine from  $Nipy_4Cl_2$  with morpholine. Its structural features are being studied.

Dimorpholinoethane gave crystalline 1:1 complexes with  $CoCl_2$ ,  $NiCl_2$ ,  $CuCl_2$ ,  $Cu(NO_3)_2$ ,  $Cu(ClO_4)_2$ ,  $ZnCl_2$ ,  $CdCl_2$  and  $HgCl_2$  when it was added to the alcoholic solutions of the almost anhydrous metal salts. The complexes are being characterised by X-Ray, spectral, electrical conductance and magnetic susceptibility measurements.

Phase equilibrium studies at 30° C. of systems involving morpholine hydrochloride, (MHCl), water and  $CuCl_2$ ,  $ZnCl_2$  or  $CdCl_2$  have established the formation of the following compounds:  $CuCl_2 \cdot 2MHCl$ ,  $ZnCl_2 \cdot 2MHCl$ ,  $2CdCl_2 \cdot MHCl$ ,  $CdCl_2 \cdot MHCl$ . The X-Ray structural investigation of morpholine (at low temperature), morpholine complexes and morpholinium compounds has been taken up.

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Madras, December 5, 1967.

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THERMAL DEHYDRATION OF  
SYNTHETIC HYDROXYLAPATITE

HYDROXYLAPATITE (written as HA for brevity),  $3Ca_3(PO_4)_2 \cdot Ca(OH)_2$ , is the inorganic constituent of animal bones and teeth. It is isomorphic with the naturally occurring fluorapatite,  $3Ca_3(PO_4)_2 \cdot CaF_2$ . Because of its ability to undergo both cationic and anionic exchange reactions, it has been the subject of extensive physico-chemical investigations.<sup>1</sup> Since the earlier work<sup>2-5</sup> could not establish the exact nature of water bound up with samples of HA obtained by precipitation from aqueous solutions, it was decided to carry out thermal dehydration studies in air on such samples under atmospheric pressure.

The various aspects of preparation of HA by precipitation from aqueous solutions containing  $Ca^{2+}$  and  $PO_4^{3-}$  have earlier been investigated in detail.<sup>6,7</sup> A sample of HA was prepared using the method of Collin.<sup>8</sup> All chemicals used were either of A.R. (B.D.H.) or of extra pure (E. Merck) grade. Stoichiometric quantities of diammonium hydrogen phosphate and calcium nitrate solutions required to form HA were mixed by adding the former to the latter at a slow rate. Throughout the addition the medium of precipitation was kept well stirred and maintained at a pH of 12 by adding ethylenediamine. Since the presence of carbon dioxide leads to the formation of carbonate-apatite, water free from it was used to prepare the solutions. In addition, air free from carbon dioxide was bubbled through the solutions during precipitation. To improve crystallinity of the precipitate, it was aged by keeping in contact with the mother liquor overnight after refluxing for about 30 min. Later it was filtered and washed till the washings were neutral. It was finally washed with acetone and dried in air. The sample was analysed by the method of Washburn and Shear.<sup>9</sup> The experimental Ca/P ratio (1.697) was found to be in agreement with the theoretical value (1.667)

A convenient weight of the sample was heated in a silica crucible to different increasing temperatures at intervals of about 50° C. upto about 1000° C. At each temperature the heating was continued till constancy of weight was attained. Figure 1 represents the loss of water

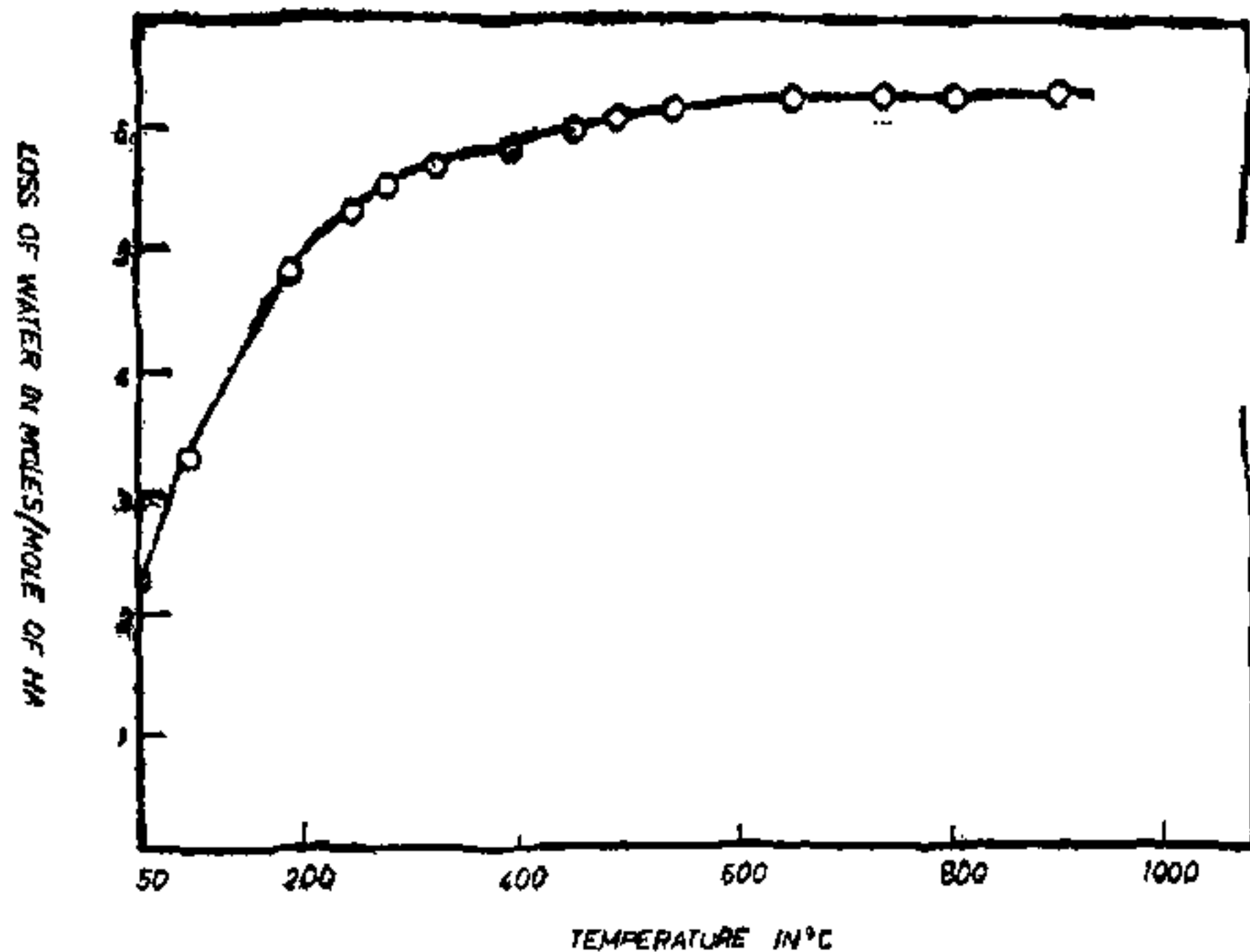


FIG. 1. Loss of water of synthetic HA, as function of temperature.

in moles per mole of HA as a function of temperature. The uniform loss of water as indicated by the curve suggests the absence of any hydrate<sup>10</sup> within the temperature range investigated. Further, from the lack of discontinuity in the curve it can be concluded that the water of constitution amounting to one mole per mole of HA was not given out upto 1000° C. Thus the water given out was supposed to be of zeolitic type on the basis of the similarity of the dehydration curve of synthetic HA with that of zeolites.<sup>11</sup> The trapping of water within the bulk of HA is facilitated by its large surface area consequent upon its well-established colloidal nature in aqueous solutions.<sup>12</sup>

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Varanasi, September 18, 1967.

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## A COMPOSITE DOLERITE DYKE FROM TIRUPATI, SOUTH INDIA

THE composite dolerite dyke is exposed 8 km. south of Tirupati by the right side of the Tirupati-Rayalacheruvu Road near the village Ramapuram. It is coarse-grained 10 to 12 m. wide and 30 to 35 m. long as measured on an erosion surface in the low levels of the region. The dyke is highly altered (Fig. 2), contains 42% of pyroxene and hornblende, 46% of altered and unaltered plagioclase ( $An_{50-55}$ ) and 12% of iron ores, biotite and other accessory minerals.

The dolerite dyke has intruded into granite and has developed one weak plane near its centre parallel to its borders (Smellie, 1914). Silicic residuum, the extreme end product of differentiation of doleritic magma has been injected into the dyke along the plane of weakness, making sharp contacts with the dolerite (Fig. 1). It forms a band with a variable width, the maximum being 50 cm. The silicic band is white in colour consisting of quartz and plagioclase ( $An_{5-10}$ ) intergrown together. The intergrowth of the two minerals imparts a typical granophyric texture to the band (Fig. 3). It consists of a little of ferromagnesian minerals seldom exceeding 10% in the whole band. The occurrence of interstitial granophyre in the differentiated dolerite dykes is common; but its occurrence as a separate band in the form of composite intrusion (Thomas and Baily, 1924; Tyrrell, 1929) is rare and not reported from India.

Most of the silicic band shows granophyric texture. The texture may be developed by a primary process (Vogt, 1930; Hughes, 1960; Dunham, 1965) such as simultaneous crystallization of quartz and feldspar or by a secondary process (Walker and Poldervaart, 1949; Black, 1954; Govindarajulu and Asadulla Sharief, 1967) such as diffusion and deuteric replacement. Evidences suggest that the granophyric texture of the silicic band in this composite intrusion,