

A more detailed account of some of this work was presented by A. W. Norris to the Sixth International Ceramic Congress, and will be published in due course⁵. We are indebted to Dr. A. T. Green, director of research, for permission to publish this communication.

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CHEMISTRY

Structural Chemistry of Promethium

THE physico-chemical properties of promethium and its compounds are generally predicted from knowledge of the properties of other lanthanides. However, since promethium lies between neodymium and samarium—two elements which show sensible differences in structural behaviour in some of their compounds—an experimental examination of promethium compounds is indicated. This will also throw light on general lanthanide chemistry.

Lanthanide sesquioxides exist in three crystal structures: hexagonal *A*; an ill-defined *B*; and cubic, nearly fluoritic, *C*, the crystal habit depending on the temperature and the atomic number of the lanthanide¹.

Normally, sesquioxides up to and including neodymium exist in form *A*, and those from samarium onwards in form *C*. This behaviour is also reflected in the different capacity of sesquioxides for dissolving, in the solid state, in the fluorite lattice of some dioxides (of cerium, praseodymium, thorium) to give anomalous mixed crystals: sesquioxides up to and including those of neodymium dissolve partially in the fluorite lattice, while those of samarium onwards dissolve in all compositions². Nothing is known regarding the sesquioxide of promethium.

Direct investigations on promethium sesquioxide are not practicable because of the difficulties in obtaining sufficient quantities of the compound. We therefore employed a method using the radioisotope promethium-147, carrier-free.

Measurements of radioactivity were carried out systematically over a large range of temperatures to determine the distribution of promethium sesquioxide between two non-soluble solid phases: one with a fluorite lattice and the other with an *A* structure. These were solid solutions of cerium, praseodymium and thorium dioxides saturated with sesquioxides, and sesquioxides in the *A*-form saturated with dioxides respectively. The two solid phases were separated by dissolving the *A* phase only with suitable solvents.

In all the experiments the promethium sesquioxide accumulated in the cubic phase (*C* form); reversal seemed to occur only at very high temperatures. We therefore infer that over a large range of temperatures promethium sesquioxide has a nearly fluoritic structure.

This type of investigation could also be used to study the changes of structure with temperature in the solid state of dioxides with fluorite-type structures. Details of this work will be published elsewhere.

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Tetra-co-ordination of Nickel(II)—Some Complexes with Cyclohexylphosphine

THE problem of the tetra-co-ordination of nickel(II) has recently been the object of much interest¹⁻³ owing to the peculiar situation of this ion in the field of co-ordination chemistry, and because of the many opportunities for testing theoretical predictions on the structural, magnetic and optical properties of transition metal complexes. Of particular interest are the complexes of the type $NiX_2 \cdot 2PR_3$. These seem to be clear examples of pure tetra-co-ordination around nickel(II). We had previously examined by X-rays the crystal structure of the red diamagnetic compound⁴ $NiBr_2 \cdot 2PEt_3$, and found it to be trans-planar as expected. We did not detect any co-ordination along the other axis (unpublished work), as occurs in other cases, for example, in nickel bisdimethylglyoxime⁵.

Issleib *et al.*⁶, examining the co-ordinating power of tricyclohexylphosphine (PCy_3 ; $Cy = cyclohexyl$), mentioned the compound $NiBr_2 \cdot 2PCy_3$ and described it as an olive-green substance. Since the ligand field around the nickel ion should not be greatly different from that in the analogous complexes containing aliphatic phosphine, this compound was obviously of interest. The green or blue colour has, in fact, been found only among the paramagnetic forms of the nickel-phosphine series^{1,7}. Although ligand field theory does not justify any simple relationship between colour and magnetic properties, or structure, many regularities have been observed at one time or another and the relationship is often mentioned as an empirical rule.

It seemed of interest to investigate this class of compounds also, with the aim of collecting more experimental data in order to throw further light on the general problem.

We prepared the following compounds: $NiBr_2 \cdot 2PCy_3$, $NiCl_2 \cdot 2PCy_3$, $Ni(SCN)_2 \cdot 2PCy_3$. Attempts to prepare the nitrate and the perchlorate did not give samples of sufficient purity, although green precipitates, consisting mainly of the phosphine complexes, were obtained. Analyses and characteristics of the compounds are shown in Table 1.

Single crystals of bromide and thiocyanate have been examined by X-rays with the following results: $NiBr_2 \cdot 2PCy_3$: triclinic; a , 9.98₂; b , 10.2₈; c , 10.7₄; α , 112° 44'; β , 109° 41'; γ , 90° 41'; z , 1; space group $P\bar{1}$; observed density, 1.34; calculated, 1.37. $Ni(SCN)_2 \cdot 2PCy_3$: monoclinic; a , 9.63₃; b , 13.3₈; c , 17.8₃; β , 117° 52'; z , 2; space group, $P2_1/c$; observed density, 1.19₇; calculated, 1.208.

In both cases the nickel atoms lie at centres of symmetry of the crystal, thus showing a trans-planar arrangement of the four ligands.