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 course[5]. 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 lanthanide[1].

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 compositions[2]. 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 *Cyclo*hexylphosphine

The problem of the tetra-co-ordination of nickel(II) has recently been the object of much interest[1–3] 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 $\mathrm{Ni}X_2\mathrm{2P}R_3$. 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 compound[4] $\mathrm{NiBr_2 2P}Et_3$, 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 *bis*dimethylglyoxime[5].

Issleib *et al.*[6], examining the co-ordinating power of tri*cyclo*hexylphosphine ($\mathrm{P}Cy_3$; Cy = *cyclo*hexyl), mentioned the compound $\mathrm{NiBr_2 2P}Cy_3$ 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: $\mathrm{NiBr_2 2P}Cy_3$, $\mathrm{NiCl_2 2P}Cy_3$, $\mathrm{Ni(SCN)_2 2P}Cy_3$. 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: $\mathrm{NiBr_2 2P}Cy_3$: triclinic; *a*, $9{\cdot}98_2$; *b*, $10{\cdot}2_8$; *c*, $10{\cdot}7_4$; α, 112° 44′; β, 109° 41′; γ, 90° 41′; *z*, 1; space group $P\bar{1}$; observed density, 1·34; calculated, 1·37. $\mathrm{Ni(SCN)_2P}Cy_3$: monoclinic; *a*, $9{\cdot}63_7$; *b*, $13{\cdot}3_8$; *c*, $17{\cdot}8_3$; β, 117° 52′; *z*, 2; space group, $P2_1/c$; observed density, $1{\cdot}19_7$; 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.

Table 1. PROPERTIES AND CHARACTERISTICS OF NiX_22PCy_3 COMPOUNDS

Compound	$Ni(SCN)_22PCy_3$	$NiCl_22PCy_3$	$NiBr_22PCy_3$
Colour	Orange-yellow	Red	Olive-green
Melting point (deg. C.)	230	227	204
Analysis (per cent, calculated values in brackets) C	61·6 (62·0)	62·6 (62·5)	55·1 (55·5)
H	8·8 (9·0)	9·3 (9·6)	8·6 (8·5)
Ni	7·9 (8·0)	—	7·4 (7·5)
Magnetic moment*	Diamagnetic	Diamagnetic	Diamagnetic
Dipole moment* (in benzene)	~0	~0	1·9

* Magnetic moments were measured on the powdered solids by means of a Sucksmith balance. Dipole moments were measured in benzene solution. The compounds are all monomeric in freezing benzene.

Table 2. FREQUENCIES AND MOLAR EXTINCTION COEFFICIENTS OF THE ABSORPTION MAXIMA OF COMPOUNDS NiX_22PCy_3

Band		$X = SCN$	$X = Cl$	$X = Br$
I	ν(cm.$^{-1}$)	33,500	36,000	35,700
	ε	15,000	4,000	9,000
II	ν(cm.$^{-1}$)			27,000
	ε	—	—	(< 1,000)
III	ν(cm.$^{-1}$)	26,300	25,600	23,300
	ε	12,500	10,000	6,000
IV	ν(cm.$^{-1}$)	(22,000)	20,000–19,000–18,000	18,000–17,000–16,500
	ε	(~500)	~500	~500
V	ν(cm.$^{-1}$)	11,500	11,700	11,500
	ε	1,500	200	1,500

Absorption spectra in benzene were taken between 40,000 and 10,000 cm.$^{-1}$. In Table 2 frequencies and molar extinction coefficients of the absorption maxima are summarized.

The diamagnetism of the three compounds rules out any simple relationship between magnetic properties and colour in this series. A comparison with the series containing phenylphosphine[1] is of interest. In this series, there is a transition from blue-green paramagnetic forms (X = Br, Cl) to a red diamagnetic one (X = SCN); in the former series diamagnetism is already attained with the bromide. This behaviour can be interpreted, from the point of view of ligand field theory, as an enhancement of the field along the P—P axis in going from the aromatic to the saturated phosphines. When the field along the P—P axis is weak it is necessary to reach a stronger field along the X—X axis (X = SCN) in order to stabilize the singlet in its ground-state. There seems to be some sort of additive effect for the fields along the two symmetry axes. It may well be that for weak fields the steric arrangement of the ligands becomes a distorted tetrahedron (as Venanzi[1] seems to find in the case of the aromatic phosphines).

The X-ray results found for $NiBr_22PCy_3$ do not agree with the dipole moment of 1·9 Debyes. It is true that this value (obtained making an allowance of 25 per cent P_E for the atomic polarization) refers to steric arrangement of the molecule in solution, where the situation may be different[2,8] from the solid state; nevertheless, the problem of the dipole moment of this compound requires further investigation.

Our X-ray determinations do not exclude as yet the possibility of a co-ordination along the z-axis as well, but analogy with the ethyl phosphine case seems to rule out such a possibility except perhaps for the SCN^- compound, where the nitrogen atom also has co-ordinating power.

The main features of the absorption spectra have been tentatively interpreted as follows. The band around 35,000 cm.$^{-1}$ is attributed to a charge transfer process involving the P—Ni bond electrons. The bands between 23,000 and 26,000 cm.$^{-1}$ are the same type of charge transfer bands for the Ni—X bonds. The weaker bands in the visible region are the well recognized g—g forbidden transitions between d-levels of the central ion. These bands show evidence of structure (see values for band IV in Table 2) which could arise from the overlapping of different electronic transitions in this region. The bromide band at 27,000 cm.$^{-1}$ is probably also of this type. It is interesting to note that the extinction coefficient of these bands is much higher than is usually found in cases of higher symmetry[9]. We are investigating the details of these spectra from the point of view of ligand field theory.

A full account of this study will be published elsewhere.

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Gas Phase Oxidation of Hydrocarbons: Endothermic Nature of the Initial Stage of Reaction

IT is generally agreed that the oxidation of hydrocarbons occurs by steps such as:

$$RH + O_2 \longrightarrow R\cdot + HO_2\cdot + Q' \qquad (1)$$

$$\begin{tikzcd} & RO_2\cdot - Q'' \qquad (2) \\ R\cdot + O_2 \arrow[ur, "+M"] \arrow[dr] & \\ & R' + HO_2\cdot - Q''' \qquad (3) \end{tikzcd}$$

$$R\cdot,\ RO_2\cdot,\ R' \longrightarrow \text{further reactions finally leading to oxides of carbon and water}$$

The initial stage of oxidation as depicted by (1) is endothermic, while (2) and (3), and also many subsequent reactions, are exothermic. Experimentally, however, no evidence seems to have been furnished which would demonstrate the endothermic nature of the initial stage of hydrocarbon oxidation. What is well known is that the reactions are exothermic: cool flames readily appear in the early stages of oxidation of numerous hydrocarbons, particularly n-alkanes (excepting methane and