Graphite Lamellar Compounds. A New Route to Transition Metal Intercalates

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Summary Potassium–graphite (C_8K) reacts with transition metal salts [$Ti(Pr^iO)_4$, $MnCl_2{\cdot}4H_2O$, $FeCl_3$, $CoCl_2{\cdot}6H_2O$, $CuCl_2{\cdot}2H_2O$, or $ZnCl_2$] dissolved in tetrahydrofuran to give the corresponding transition metal lamellar compounds of graphite; the insertion of the metal atoms between the carbon layers is established by *X*-ray diffraction methods and the formation of different insertion stages has been observed.

GRAPHITE has a characteristic stacked structure which enables the insertion of many reagents such as mineral acids, metals, metal halides, or oxides between its carbon layers.[1] Recently we found that potassium–graphite can act both as a metallating agent towards weakly acidic substrates[2] and as a reducing agent towards sulphones[3] and $\alpha\beta$-unsaturated carbonyl compounds.[4]

We now report a new convenient method for preparing transition metal lamellar compounds of graphite[5] by utilizing the reducing properties of potassium–graphite (C_8K) towards transition metal salts [see equation (1),

$$nC_8K + MX_n \xrightarrow{\text{THF}} C_{8n}M + nKX \qquad (1)$$

where MX_n = $Ti(Pr^iO)_4$, $MnCl_2{\cdot}4H_2O$, $FeCl_3$,$CoCl_2{\cdot}6H_2O$, $CuCl_2{\cdot}2H_2O$, or $ZnCl_2$, and THF = tetrahydrofuran].

The nature of the salt and the solvent appear to be the determining factors in the intercalation process. Tetrahydrofuran is generally the best solvent for this reaction for soluble anhydrous salts ($FeCl_3$ and $ZnCl_2$), as well as for the hydrated $MnCl_2{\cdot}4H_2O$, $CoCl_2{\cdot}6H_2O$, and $CuCl_2{\cdot}2H_2O$, although the water molecules can partially destroy C_8K. No intercalation occurred using anhydrous $MnCl_2$, $CoCl_2$, or $CuCl_2$ dissolved in hexamethylphosphoric triamide (HMPT).†

In a typical experimental procedure, potassium–graphite (C_8K) (40 mmol) was prepared under argon by adding potassium (1·60 g; Carlo Erba RPE 99·95%) in small pieces to graphite (3·85 g, Roth, impurities < 500 p.p.m.) with stirring, and, heating at 200 °C (external oil-bath) for 15 min. The bronze coloured potassium–graphite was allowed to cool to room temperature and then covered with anhydrous THF (20 ml). A green solution of $CuCl_2{\cdot}2H_2O$ (24 mmol) in THF (100 ml) was then added during 20 min. An exothermic reaction took place with immediate decolorisation. The mixture was stirred for 5 h, and the copper–graphite was filtered off, washed with 0·5% aqueous HCl (50 ml), H_2O (300 ml), MeOH (50 ml), and ether (50 ml), and finally dried *in vacuo* (0·01 mmHg) at 100 °C for 10 h in the presence of P_2O_5. The amount of Cu in the intercalation compound was 11·9% by gravimetric determination.

By a similar procedure‡ Ti–graphite§ (Ti 7·9%), Mn–graphite¶ (Mn 15·2%), Fe–graphite (Fe 12·5%), Co–graphite (Co 12·1%), and Zn–graphite (Zn 7·0%) were obtained.

We have found by *X*-ray diffraction methods that transition metal lamellar compounds of graphite of different stages are formed.** These were identified by (00*l*) reflections which indicate stacking sequences similar to those found for potassium–graphite compounds of stages 1—5.[6] The stacking sequence for the *n*th stage compound is obtained by insertion of intercalated layers in every *n*th graphite interlayer space. The stages found in the reaction products are listed in the Table together with the repeat distances.

Table. Stages and repeat distances (nm) for transition metal lamellar compounds of graphite

Stage	Ti	Mn	Fe	Co	Cu	Zn
1	2·224	2·206	—	2·202	2·200	2·232
2	—	1·824	1·790	1·828	1·816	—
3	—	1·237	1·249	1·233	1·241	1·244
4	3·128	—	—	—	3·129	3·120
5	—	—	1·896	1·904	1·893	—

The thicknesses of the filled layers, obtained from repeat distances, based on the graphite stacking sequences from the data of Rudorff and Schulze[6] for potassium–graphite, are 0·55—0·58 nm, in agreement with the values reported by Vol'pin *et al.*[5] for manganese, iron, cobalt, and copper compounds of stages 1 and 2. Transition metal lamellar compounds of stage 3 and higher have been previously observed for Fe–graphite using high-resolution electron microscopy.[7]

The (*hkl*) reflections can be indexed assuming a hexagonal cell with $a = 0{\cdot}246$ nm which corresponds to the *a*-axis of graphite. This may indicate that the metal atoms are randomly located over the centres of carbon hexagons without stacking correlation between different intercalate layers.

In all cases the diffraction patterns showed the presence of different solid phases in the reaction products. Graphite is always present. Copper oxide and metallic zinc were also observed, respectively, in copper and zinc insertion products.

No attempt was made to assess the relative proportions of the different stages.

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† Anhydrous $MnCl_2$, $CoCl_2$, and $CuCl_2$ are only slightly soluble in THF.

‡ *Ca.* 20% excess of MX_n with respect to the stoicheiometric amount was used.

§ In the case of Ti–graphite the reaction was quenched with MeOH, and the product was filtered off and washed with MeOH (300 ml).

¶ A THF : HMPT (9 : 1) mixture was used in order to dissolve the salt completely.

** The diffraction patterns were recorded using Cu-K_α, Cr-K_α, and Fe-K_α radiations both with a Debye–Scherrer camera (diameter 114·6 mm) and with a one-circle diffractometer.

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