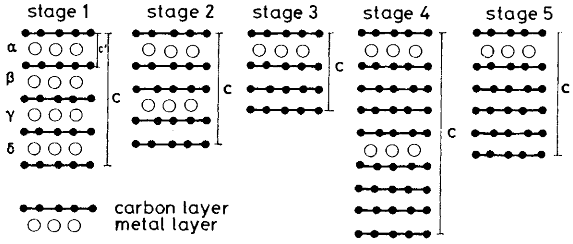
Graphite Lamellar Compounds. Structure of Transition-metal Intercalates

By **Dario Braga, Alberto Ripamonti,* Diego Savoia, Claudio Trombini,** and **Achille Umani-Ronchi,** Istituto Chimico ' G. Ciamician,' Università di Bologna, Via Selmi 2, Bologna, Italy

X-Ray diffraction studies from compounds obtained by reaction of transition-metal salts, dissolved in tetrahydrofuran, with potassium–graphite (C_8K), show that titanium, manganese, iron, cobalt, copper, and zinc intercalate in graphite. It has been established that lamellar compounds of stages 1—5 (*i.e.* with intercalated transition metal layers separated by 1—5 graphite layers respectively) are formed. The introduction of the metal layers leads approximately to the same increase in interlayer spacing for all stages. Values ranging from 0.56 to 0.58 nm were found for the thicknesses of the filled layers.

THE weak bonding interactions between carbon layers in graphite make possible the formation of lamellar compounds, resulting from the inclusion of guest species[1] between the layers. These lamellar compounds of graphite are referred to as discrete stages in which groups of n carbon layers are separated by a layer of intercalated guest.

Rüdorff and Schulze[2] found the first five stages of intercalations in potassium and rubidium graphites. In the first stage ($n = 1$) alkali-metal layers are separated by one graphite layer, and so on until in the fifth stage ($n = 5$) only one space in every five is filled by the guest. The stacking sequences shown in the Figure for stages 1—5 with potassium–graphites were deduced from the *X*-ray diffraction powder patterns.



Recently Nixon and Parry[3] carried out a more detailed structural analysis of potassium–graphite obtained from highly oriented graphite samples derived by stress recrystallization of well oriented pyrolytic graphite.[4] They established that it is possible to form ordered compounds of stages 4, 3, and 2 in succession from the same sample.

Vol'pin *et al.*[5] prepared graphite compounds with chromium, manganese, iron, cobalt, nickel, copper, tungsten, and molybdenum by a two-step sequence, consisting of the preliminary insertion of metal salts in a sealed ampoule, followed by reduction with hydrogen, metal hydrides, sodium in ammonia, or aromatic radical anions.

Iron, copper, and cobalt compounds of stages 1 and 2, the manganese compound of stage 1, and the nickel compound of stage 2 were described. Values of 0.56—0.58 nm were found, for the thicknesses of the filled layers. A much smaller filled-layer thickness (0.37—0.40 nm) was found for molybdenum compounds of stages 2, 3, and 4. However, a detailed study of the *X*-ray diffraction patterns of these compounds was not reported.

We prepared transition metal lamellar compounds of graphite (TMLCG) by reaction of potassium–graphite (C_8K) with transition-metal salts dissolved in tetrahydrofuran (thf)[6] following equation (1). The nature of

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

the salt plays an important role in this reaction, since it must be completely dissolved in order for intercalation to occur. On the other hand, the choice of the solvent seems critical. Thus no intercalation occurred using anhydrous $MnCl_2$, $CoCl_2$, or $CuCl_2$ dissolved in hexamethylphosphorotriamide and $TiCl_4$ in benzene.

X-Ray studies showed that titanium, manganese, iron, cobalt, copper, and zinc give rise to lamellar compounds of graphite by this convenient new method.[6] In this paper the crystallographic analysis of these compounds is described in greater detail.

EXPERIMENTAL

Materials.—Graphite was supplied from Roth (impurities <500 p.p.m.); potassium (99.5%), $Ti(OPr^i)_4$ (24—25% TiO_2), $CuCl_2 \cdot 2H_2O$ (98%), $CoCl_2 \cdot 6H_2O$ (99%), and $MnCl_2 \cdot 4H_2O$ (98%) from Carlo Erba; $ZnCl_2$ (98%) and $FeCl_3$ (99%) from Merck. Oriented pyrolytic graphite was supplied from La Carbone Lorraine, Paris.

Tetrahydrofuran was anhydrous and oxygen free after distillation over sodium–benzophenone ketyl.

All reactions were performed under an argon atmosphere.

Preparation of Potassium–Graphite (C_8K).—In a 500-ml three-necked flask equipped with argon inlet, condenser, and magnetic stirrer graphite (3.85 g, 320 mg-atom) was heated at *ca.* 200 °C with an oil-bath. Potassium (1.60 g, 40 mg-atom) was then added with stirring. The molten potassium immediately intercalates into the graphite, which swells and becomes bronze-coloured.

X-Ray analysis reveals that the product corresponds to the first stage of intercalation of potassium in graphite, C_8K, as described by Rüdorff and Schulze.[2] The C_8K was cooled to room temperature and covered with thf (20 ml); this suspension is stable under argon for a few days.

Preparation of Cobalt–Graphite.—The dark blue solution, obtained by dissolving $CoCl_2 \cdot 6H_2O$ (5.70 g, 24 mmol) in thf (130 ml), was added dropwise during 60 min to a suspension of C_8K (40 mmol) in thf (20 ml). An exothermic reaction immediately occurred accompanied by rapid decolorisation. The reaction was stirred for 10 h; the cobalt–graphite was then filtered off, washed with boiling

TABLE 1

X-Ray data of transition-metal lamellar compounds of graphite

Ti				Mn				Fe			
$d_{obs.}$	$I_{obs.}$	*hkl*	*n*	$d_{obs.}$	$I_{obs.}$	*hkl*	*n*	$d_{obs.}$	$I_{obs.}$	*hkl*	*n*
0.520	w	006	4	0.551	w	004	1	0.621	vw	002	3
0.312	s	0010	4	0.456	s	004	2	0.316	m	004	3
0.278	w	008	1	0.310	m	004	3	0.298	vw	006	2
0.221	m	0014	4	0.302	w	006	2	0.248	m	005	3
0.213	s	100		0.276	m	008	1	0.237	vw	008	5
				0.247	s	005	3	0.224	vw	008	2
				0.237	vw	008	2	0.213	m	100	

Co				Cu				Zn			
$d_{obs.}$	$I_{obs.}$	*hkl*	*n*	$d_{obs.}$	$I_{obs.}$	*hkl*	*n*	$d_{obs.}$	$I_{obs.}$	*hkl*	*n*
0.619	vw	002	3	0.908	vw	002	2	0.558	w	004	1
0.549	w	004	1	0.787	m	004	4	0.312	m	004	3
0.457	s	004	2	0.554	m	004	1			0010	4
0.412	m	003	3	0.518	w	006	4	0.279	m	008	1
0.316	w	004	3	0.455	s	004	2	0.261	s	0012	4
0.276	m	008	1	0.409	w	003	3	0.248	s	005	3
0.238	w	008	5	0.315	vs	004	3				Zn
0.214	w	100				0010	4	0.231	w		Zn
						006	5	0.214	w	100	
				0.302	w	006	2	0.209	m		Zn
				0.276	s	008	1				
				0.247	m	005	3				
				0.237	w	008	5				
				0.214	m	100					

v = Very, w = weak, m = medium, s = strong.

water (1 l), methanol (100 ml), and ether (50 ml), and dried *in vacuo* (0.01 mmHg *) at 100 °C for 10 h in the presence of P_2O_5. Washing the product with diluted aqueous HCl partially extracts the intercalated metal (Found: C, 75.7. $C_{16}Co$ requires C, 76.5%).

The other transition-metal lamellar compounds of graphite were prepared by the same procedure.

Copper–graphite. A green solution of $CuCl_2 \cdot 2H_2O$ (4.10 g, 22 mmol) in thf (100 ml) was added to C_8K (40 mmol) to give Cu–graphite (Found: C, 79.7. $C_{16}Cu$ requires C, 75.1%).

Iron–graphite. A brown solution of $FeCl_3$ (3.60 g, 22 mmol) in thf (130 ml) was added to C_8K (60 mmol) to give Fe–graphite (Found: C, 84.4. $C_{24}Fe$ requires C, 83.8%).

Zinc–graphite. A solution of $ZnCl_2$ (3 g, 22 mmol) in thf (120 ml) was added to C_8K (40 mmol) to give Zn–graphite (Found: C, 77.3. $C_{16}Zn$ requires C, 74.6%).

Manganese–graphite. A pale green solution of $MnCl_2 \cdot 4H_2O$ (4.35 g, 22 mmol) in thf (90 ml) and hexamethylphosphorotriamide (10 ml) was added to C_8K (40 mmol) to give Mn–graphite (Found: C, 80.8. $C_{16}Mn$ requires C, 77.8%).

Titanium–graphite. A solution of $Ti(OPr^i)_4$ (3.4 g, 12 mmol) in thf (50 ml) was added to C_8K (40 mmol). After washing the residue with CH_3OH (300 ml), Ti–graphite was obtained (Found: C, 91.5. $C_{32}Ti$ requires C, 88.9%).

Oriented samples of copper intercalation compounds were obtained from well oriented pyrolytic graphite using the same method of preparation.

Crystallographic Analysis.—The diffraction patterns of the powder samples 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. The *X*-ray patterns of the pyrolytic graphite samples were recorded using a Weissenberg camera (diameter 57.28 mm).

RESULTS

Lamellar compounds of different stages were identified by the series of *X*-ray reflections corresponding to the basal plane *d*-spacing. *X*-Ray diffraction patterns of these lamellar compounds prepared from samples of pyrolytic graphite were used to confirm the indexes assignment. Pyrolytic graphite is a polycrystalline material in which the crystallites have an approximatively common *c*-axis orientation. Thus, when the sample is mounted with the graphite layers parallel to the *X*-ray beam, the photographs have the appearance of single-crystal rotation pattern in which the *c* axis of graphite is the rotation axis.

When intercalation occurs the uniaxial texture of the pyrolytic samples is preserved. Thus the crystallites of lamellar compounds of different stages have an approximately common *c*-axis orientation, which allows the unambiguous indexing of the (001) reflections. Indexes, *d*-values, observed intensities, and the stage number *n* are reported in Table 1.

The reaction products were always mixtures of compounds of different stages: stages 1 and 4 were found in Ti–graphite, stages 1, 2, and 3 in Mn–graphite, stages 2 and 3 in Fe–graphite, stages 1, 2, 3, and 5 in Co–graphite, stages 1, 2, 3, 4, and 5 in Cu–graphite, and stages 1, 3, and 4 in Zn–graphite.

TABLE 2

Stages, identity periods *c* (nm), and thicknesses of filled layers *c′* (nm) for the lamellar compounds

	Ti		Mn		Fe	
Stages *n*	*c*	*c′*	*c*	*c′*	*c*	*c′*
1	2.224	0.556	2.206	0.551		
2			1.824	0.577	1.790	0.560
3			1.237	0.567	1.249	0.578
4	3.128	0.560				
5					1.896	0.556

	Co		Cu		Zn	
Stages *n*	*c*	*c′*	*c*	*c′*	*c*	*c′*
1	2.202	0.551	2.202	0.550	2.232	0.558
2	1.828	0.578	1.816	0.573	1.244	0.572
3	1.233	0.563	1.241	0.571		
4			3.129	0.560	3.120	0.550
5	1.904	0.560	1.893	0.553		

---

* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

TABLE 3

Comparison of observed and calculated intensities for stages 1—5 of Cu–graphite *

Cu–graphite		Stage 1		Stage 2		Stage 3		Stage 4		Stage 5	
$d_{obs.}$	$I_{obs.}$	$00l$	I_c	$00l$	I_c	$00l$	I_c	$00l$	I_c	$00l$	I_c
								002	100		
						001	45				
										002	12
0.908	vw			002	60						
0.787	m							004	35		
						002	28			003	10
0.554	m	004	100								
0.518	w							006	28		
0.455	s			004	90					004	20
0.409	w					003	60				
								008	10	005	22
0.315	vs					004	100	0010	87	006	100
0.302	w			006	100						
0.276	s	008	80							007	4
								0012	10		
0.247	m					005	25				
0.237	w			008	2			0014	1		

* I_c includes the weighted contribution from the copper atoms assuming the composition CuC_{16} for the filled layers.

In all cases graphite was found in the reaction products. Copper oxide and metallic zinc were also observed in copper and zinc lamellar compounds, respectively.

The presence of different solid phases precludes an unambiguous assignment of indexes to the (*hkl*) reflections. However, the strongest reflections can be indexed in the hexagonal system with $a = 0.246$ nm, which is the dimension of the two-dimensional hexagonal cell of the carbon layers. This may indicate that the metal atoms are randomly located over the centres of carbon hexagons in adjacent graphite layers. The small number of strong (*hkl*) reflections for each stage, and the uncertainties mentioned above, preclude the determination of the graphite layer stacking sequences. Therefore we have not been able to establish the effective repeat distances for the different stages; the *c*-values given in Table 2 were calculated assuming the stacking sequences shown in the Figure.

The thicknesses of the filled layers, c', were obtained from $c' = c - 0.335n$ for $n = 3$ and 5, $c' = c/2 - 0.335n$ for $n = 2$ and 4, and $c' = c/4$ for $n = 1$.

The intensities of the (00*l*) reflections based on the carbon contribution and the weighted contribution from the metal atoms with zero temperature factor were calculated for each stage of the copper–graphite compounds. The comparison between observed and calculated intensities, given in Table 3, shows that the strongest calculated reflections correspond to those effectively observed but the calculated intensities do not always follow the sequence of observed intensities in detail. This can be explained assuming a disordered structure or a composition which does not follow, within each intercalated layer, the stoicheiometry of the reaction.

DISCUSSION

X-Ray diffraction data provide clear evidence that potassium–graphite, C_8K, reacts with transition-metal salts dissolved in tetrahydrofuran to give lamellar graphite compounds with intercalated metal-atom layers.

The reaction products are mixtures of insertion compounds of different stages. The composition of the reaction products corresponds fairly well to that expected from the stoicheiometry of the reaction. Because of the presence of stages with $n > 1$ the concentration of the metal atoms within each intercalated layer must be greater than the ratio M : C determined by equation (1).

Table 2 shows that the introduction of the metal layer leads approximately to the same increase in interlayer spacing for all stages. The thicknesses of the filled layers are 0.55—0.58 nm, in agreement with the data reported by Vol'pin *et al.* for the intercalated compounds of cobalt, manganese, iron, and copper of stages 1 and 2.[5] Graphite lamellar compounds with $n \geqslant 3$, containing metal atoms of the first transition series, have not been previously reported.

The thicknesses of the filled layers have almost the values expected for a pure van der Waals interaction. The small shortening observed for these compounds could be due (especially for zinc and titanium compounds) to a weak bonding interaction.

Since transition-metal lamellar compounds of graphite could be of interest as catalysts, further work is in progress in order to intercalate other metals and to obtain better insight into the nature of the interactions between transition-metal atoms and carbon layers.

[8/1953 *Received*, 9*th November*, 1978]

REFERENCES

[1] A. K. Holliday, G. Hughes, and S. M. Walker, in 'Comprehensive Inorganic Chemistry,' eds. J. C. Bailar, *et al.*, vol. 1, Pergamon Press, Oxford, 1976, p. 1250.

[2] W. Rüdorff and E. Schulze, *Z. anorg. Chem.*, 1954, **227**, 156.

[3] D. E. Nixon and G. S. Parry, *J. Phys.* (*D*), 1968, **1**, 291.

[4] A. W. Moore, A. R. Ubbelohde, and D. A. Young, *Proc. Roy. Soc.*, 1964, **A280**, 153.

[5] M. E. Vol'pin, N. Y. Novikov, N. D. Lapkina, V. I. Kasatochkin, Y. T. Struchkov, M. E. Kazakov, R. A. Stukan, V. A. Povitskij, Y. S. Karimov, and A. V. Zvarikina, *J. Amer. Chem. Soc.*, 1975, **97**, 3366.

[6] D. Braga, A. Ripamonti, D. Savoia, C. Trombini, and A. Umani-Ronchi, *J.C.S. Chem. Comm.*, 1978, 927.