The Nature of the Bonding in Graphite Intercalation Compounds

By A. G. FREEMAN

(*Department of Chemistry, Victoria University of Wellington, Wellington, New Zealand*)

IN an attempt to understand the bonding involved in intercalation compounds of graphite with metal halides, we have examined the Mössbauer spectra of a range of graphite–ferric chloride and graphite–ferric chloride–aluminium chloride compounds. Previous work had indicated that species of the type $C_n^+Cl,FeCl_2,3$—$4FeCl_3$,[1] or $C_n^+(FeCl_4)_m^-,FeCl_3$[2] are present in these compounds. The Mössbauer spectra of such species as $FeCl_2$, $FeCl_3$, and $(FeCl_4)^-$ are readily differentiated and so this approach promised to yield valuable information concerning the bonding.

The intercalation compounds were prepared following the methods of Rudorff and Schulz[3] and of Croft.[4] Graphite and anhydrous ferric chloride were heated in sealed tubes, under chlorine or nitrogen atmosphere, between 250° and 350°, to give a series of compounds with $FeCl_3$ content ranging from 5—35%. Similar methods were used to produce graphite–ferric chloride–aluminium chloride compounds with $FeCl_3/AlCl_3$ ratio ranging from 0·2—0·5. The preparations were freed from excess metal halide by either washing with 2N-HCl, or by sublimation in a stream of chlorine gas at about 250°. The samples were analysed by decomposition to the respective oxide following the method used by Croft.[4]

The Mössbauer spectra were recorded on a spectrometer which has been fully described[5] using a ^{57}Co in Pd source. Powdered sodium nitroprusside dihydrate was used as the velocity calibrant. The spectra were analysed statistically using an Elliot 503 computer with programs developed by Dr. A. Hudson.

The spectra of all compounds produced, and of anhydrous $FeCl_3$ which was used as a reference standard, are essentially the same. They show a single absorption peak at approximately 0·6 mm./sec. The peaks due to iron in the graphite matrix show a slight, but significant, shift to higher velocity, relative to anhydrous $FeCl_3$ (Table). The peak shape is essentially the same for all compounds.

This evidence indicates that such species as $FeCl_2$ and $(FeCl_4)^-$, which have previously been suggested to account for the stability of these compounds, are not present in large proportion, if at all. The spectrum for $FeCl_2$ consists of a well separated quadrupole split doublet,[6] whereas the spectra for $(FeCl_4)^-$, in a number of compounds that have been studied, show a single line at lower velocity (0·40 mm./sec.).[7]

TABLE

Compound	Isomer shift (mm./sec.)	Width at half height (mm./sec.)
$FeCl_3$ (anhydrous) at 298° K	0·55 ± 0·20	0·40 ± 0·05
Graphite–$FeCl_3$ at 298° K (all preps.)	0·61 ± 0·02	0·40 ± 0·05
Graphite–$FeCl_3$–$AlCl_3$ at 298° K (all preps.)	0·62 ± 0·02	0·40 ± 0·05

That the peak due to intercalated iron is shifted to higher velocity, with respect to anhydrous $FeCl_3$, may be taken as evidence for a donation of graphite π-electrons into the iron d-shell. This suggestion was originally made by Croft.[7] It appears that all the intercalated iron atoms take an active part in stabilizing the structure rather than only a proportion, with the rest acting as inert "spacers" as suggested by Dzurus and Hennig.[1]

Although we only present evidence for the condition of the iron atom in the intercalated molecule it is probable that the chlorine atoms also play an important part in determining the stability of these compounds. In particular, donation of graphite π-electrons into the empty d-shells of chlorine is highly likely. This type of electron transfer has been postulated to account for the stability of molecular compounds of carbon tetrabromide with aromatic ring systems.[8] The transfer of graphite π-electrons into the chloride d-shells may be of greater importance in bonding such molecules as $AlCl_3$ or $SnCl_4$ than in $FeCl_3$. On this basis we may represent the bonding in graphite–ferric chloride as $C_n^{\delta-}$ $(FeCl_3)^{\delta-}$ which indicates that graphite π-electrons are transferred into both the Fe and Cl d-shells.

(*Received, December 19th*, 1967; *Com.* 1358.)

[1] M. L. Dzurus and G. R. Hennig, *J. Amer. Chem. Soc.*, 1957, **79**, 1051.
[2] A. R. Ubbelohde and F. A. Lewis, "Graphite and its Crystal Compounds," Oxford University Press, 1960.
[3] W. Rüdorff and H. Schulz, *Z. anorg. Chem.*, 1940, **245**, 121.
[4] R. C. Croft, *Austral. J. Chem.*, 1956, **9**, 206.
[5] J. Vickerman and H. J. Whitfield, *New Zealand, J. Sci.*, 1967, **10**, 782.
[6] K. Ono, A. Ito, and T. Fujita, *J. Phys. Soc. Japan*, 1964, **19**, 2119.
[7] G. M. Bancroft, A. G. Maddock, W. K. Ong, and R. H. Prince, *J. Chem. Soc.* (*A*), 1966, 723.
[8] F. J. Streiter and D. H. Templeton, *J. Chem. Phys.*, 1962, **37**, 161.