Preparation, Mössbauer Spectra, and Structure of Intercalation **Compounds of Boron Nitride with Metal Halides**

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Evidence has been obtained which confirms that boron nitride forms intercalation compounds with a number of metal halides (FeCl₃, CuCl, Hg₂l₂, and AsCl₃). The Mössbauer spectrum of the iron(III) chloride compound shows that the intercalated iron nucleus lies in a strong electrical-field gradient, and that the d-electron population has been reduced compared to that of high-spin iron(III) in free iron(III) chloride. It is suggested that bonding, in these compounds, is due to electron transfer from the intercalated molecule to the BN layers, and that the intercalated molecules are isolated from each other.

CROFT¹ has reported that boron nitride forms intercalation compounds with a variety of molecules (SbCl₃, AsCl₃, CuCl, FeCl₃, AlCl₃, and N₂H₄). His main line of evidence for intercalation was the obvious exfoliation when particles of these compounds were heated in air. Croft used a black form of boron nitride for this work. Rüdorff and Stumpp² could find no evidence of intercalation in an attempted preparation of the BN-FeCl_a compound. These workers used a white form of boron nitride and they attributed Croft's success to the unusual, and uncharacterised, black form which he used. However, the procedure used by Rüdorff and Stumpp to prepare their boron nitride would almost certainly lead to a product of small particle size, and, probably, of low crystallinity. Under these circumstances it would be difficult to prepare intercalation compounds.

We have attempted to reproduce Croft's results, by using white boron nitride, in order to gain an insight into the bonding and structure of these compounds.

EXPERIMENTAL

In all cases B.D.H. Reagent grade materials were used. The boron nitride had the following quoted analytical figures: B, 43.9, N, 55.6, B_2O_3 , <0.05, and C, <0.01%.

duct was analysed, when possible, by fusion with sodium peroxide in a covered nickel crucible and application of standard analytical procedures to the aqueous extract.

The following halides showed evidence of intercalation with boron nitride: FeCl₃ (280-450°, heated up to 5 days) 7% intercalated, CuCl (450°, 22 hr.) 2% , CuCl_2 (400°, 20 hr.) 2%, Hg_2I_2 (280°, 2 hr.) not analysed, $AsCl_3$ (120°, 24 hr.) not analysed. The iron and copper halide compounds were a characteristic buff or pink colour. The colour of the Hg₂I₂ and AsCl₃ compounds was masked by the presence of free Hg_2I_2 or As_2O_3 . These compounds were not analysed because of these insoluble impurities. Throughout this work chemical analyses tend to give a low impression of the amount of intercalated species. This is due to leaching of the intercalate from the BN layers during the purification process, and is a consequence of the small particle size of the BN used.

In addition, intercalation was attempted with the following halides and halogens, but without any indications of reaction: AlCl₃ (200–250°, up to 5 days), Hg_2Cl_2 (450°, 65 hr.), PCl₃ (95°, 16 hr.), SCl₂ (25°, 16 hr.), SbCl₃ (250°, 24 hr.), BiCl₃ (500°, 120 hr.), BiOCl (530°, 120 hr.), HgCl₂ $(320^{\circ}, 120 \text{ hr.}), \text{ Cl}_2 (-35^{\circ}, 10 \text{ hr.}), \text{ Br}_2 (-80, 25, 60^{\circ}, \text{ up to})$ 48 hr.), I₂ (25, 180°, up to 48 hr.), ICl (25, 90°, up to 48 hr.), and SnCl₄ (168°, 48 hr.).

X-Ray powder diffraction patterns of products were

					Тав	LE 1					
B	N	FeCl _a	-BN	CuCl	-BN	CuCl	-BN	Hg_2I_2	$_2$ -BN	AsCl	-BN
d (Å)	I/I_{0}	d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0
		$17.8 \\ 11.6$	4 4					6.81	12		-
		8.93	1	6.41	12	4.91	0	6.15	9	5.16	5
		7.89	32 17	4·23 3·45	8 35	4·21 3·44	$\frac{8}{20}$	3.91	30	4.08	9
3.33	100	3.33	100	3.32	100	3.32	100	3.30	100	3.33	100
		2.51	9	2.99	45	2.98	46	2.45	12	2.59	5
		2.36	4	$2 \cdot 68$	21	2.67	23	$2 \cdot 22$	9		
2.17	15	2.17	29	2.17	17	2.17	3	$2 \cdot 16$	25		
2.06	6	2.06	8	$2 \cdot 12$	16	2.11	18	2.06	4		
1.817	10	1.817	10	2.07	6	2.06	1	2.03	30		
1.665	7	1.665	7	2.02	12	2.02	10				
1.322	4	1.519	4	1.73	11	1.73	10	1.76	15		
1.253	10	1.253	10								
1.173	9	1.173	9								

Intercalation was attempted in each case by mixing boron nitride and an excess of the appropriate reagent in glass tubes; these were then sealed under a dry air or nitrogen. The conditions of reactions are given below.

After reaction the tubes were opened and the boron nitride was washed free of excess of reagent with hydrochloric acid followed by distilled water. The purified proobtained with a Philips powder-diffractometer with CuK_{α} radiation. Table 1 gives the X-ray powder diffraction patterns of some of the intercalation products. Reflections which could not be assigned to the starting material, or to

¹ R. C. Croft, Austral. J. Chem., 1956, 9, 206. ² W. Rüdorff and E. Stumpp, Z. Naturforsch., 1958, 13b, 459.

hydrolysis, or breakdown products are assigned to the intercalation compound.

The Mössbauer spectra were obtained on a spectrometer which has been fully described previously.³ A ⁵⁷Co in Cu source was used, and the velocities were calibrated with powdered sodium nitroprusside dihydrate as the reference standard. The Mössbauer parameters are shown in Table 2 with velocities quoted with respect to the centre of the nitroprusside spectrum. The spectra were statistically analysed using an Elliott 503 computer.

DISCUSSION

Evidence of intercalation is strongest with the iron(III) chloride compound. The buff colour of this compound, and also of the copper chloride compounds, seems to be a characteristic of intercalation compounds of BN since it has been noted in BN-alkali-metal intercalation compounds as well.⁴ The amount of iron(III) chloride intercalated is less than that observed by Croft (14%). This difference is probably due to the difference in the particle size of the boron nitride used; Croft's material had a much larger particle size than the material used here and it would be less susceptible to leaching.

With $BN-FeCl_3$ the low-angle X-ray reflections, particularly those due to interplanar spacings of 17.8, 11.6, and 7.89 Å, may be taken as evidence of intercalation. These reflections could be due to the expansion of the interlayer spacing of BN to accommodate the FeCl₃, or to spacings between FeCl₃ molecules within BN layers. By analogy with graphite-FeCl₃ the expected repeat distance along the c axis is approximately 9 Å for a stage (1) compound,⁵ that is, a compound containing alternate layers of BN and FeCl₃. The ratio of $BN: FeCl_3$ for a stage (1) compound would be in the region of 6:1, if we assume one FeCl₃ molecule per two boron nitride hexagons. On this basis, the observed analytical figures would provide for only one pair of layers in fourteen to be completely filled by FeCl_a. This would give a repeat distance of ca. 51 Å [*i.e.*,

 $9 + (13 \times 3.3)$ Å]. However, the Mössbauer spectral evidence, Table 2, indicates that the structure of BN-

TABLE 2

Mössbauer parameters at 298° k

Compound	Isomer shift (mm./sec.)	Quadrupole split (mm./sec.)	<i>W</i> <u>+</u> (mm./sec.)
FeCl ₃ , anhydrous BN-FeCl ₃ (this study) BN-FeCl ₃ (Croft) *	$\begin{array}{c} 0.64 \pm 0.02 \\ 0.55 \pm 0.02 \\ 0.53 \pm 0.03 \end{array}$	$0.93 \pm 0.02 \\ 0.81 \pm 0.03$	$\begin{array}{c} 0.37 \pm 0.02 \\ 0.38 \pm 0.02 \\ 0.39 \pm 0.03 \end{array}$

* This sample was kindly supplied by Dr. R. C. Croft and has been described in ref. 1.

FeCl₃ does not have a close analogy with that of graphite-FeCl₃. Firstly, the isomer shift value of BN-FeCl₃ is slightly lower than that observed for pure FeCl₃. This value indicates that iron remains in the high-spin iron(III) state after intercalation, but that there is a reduction in its *d*-electron population. Thus, there is a net transfer of charge to the boron nitride layers from the iron(III) chloride molecule. The opposite effect is observed in graphite-FeCl₃.^{6,7} Secondly, the spectrum is quadrupole split and the degree of splitting indicates that the iron nucleus lies in a position of fairly low symmetry. In graphite-FeCl₃ compounds the Mössbauer spectrum is single-lined in compounds of high FeCl₃ content. X-Ray and electron-diffraction studies⁸ have shown that the octahedral symmetry of the Cl about the iron is distorted but not destroyed in these compounds.

In graphite compounds of very low iron-content the Mössbauer spectrum does become quadrupole split.⁹ Apparently the octahedral symmetry about the iron is destroyed and this implies that the FeCl₂ molecules exist as discrete entities between the layers. The same interpretation may be applied in the case of BN-FeCl₃ compounds.

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⁷ B. V. Liengme, M. W. Bartlett, J. G. Hooley, and J. R. Sams, *Phys. Letters* (A), 1967, 127.

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 ⁹ P. R. Girardot, M. Schara, and G. D. Smith, Abstracts, American Chemical Society, 156th National Meeting, 1968.

³ J. Vickerman and H. J. Whitfield, New Zealand J. Sci., 1966, 9, 782.
⁴ A. G. Freeman and J. P. Larkindale, unpublished results.
⁵ W. Rüdorff and H. Schulz, Z. anorg. Chem., 1940, 245, 121.
⁶ A. G. Freeman, Chem. Comm., 1968, 193.