Graphite–Ferric Chloride–Dinitrogen Pentoxide: A Doubly-filled Intercalation Compound

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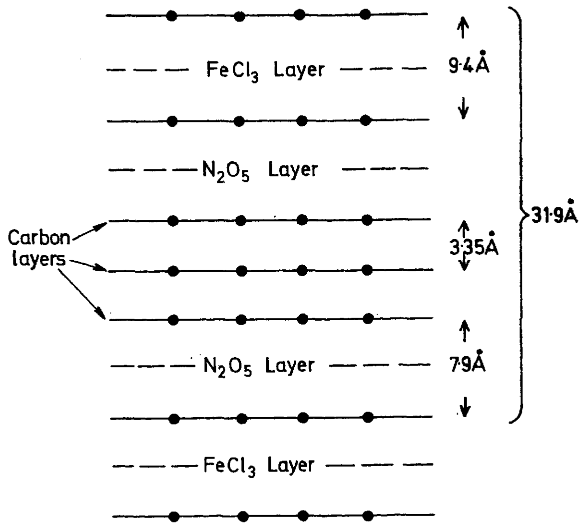
Summary A doubly-filled graphite-ferric chloride-dinitrogen pentoxide intercalation complex of empirical formula $C_{31}\cdot FeCl_3\cdot(N_2O_5)_{1\cdot7}$ has been prepared in which a fourth stage graphite–ferric chloride complex is independently interleaved by a second stage graphite–dinitrogen pentoxide complex.

THE fact that different graphite intercalation complexes have different thermal stability fields raises the possibility of formation of mixed layer complexes. For example, the reaction of a second, or higher, stage intercalation complex of high thermal stability with a different intercalatable species at low temperature could possibly lead to such a mixed-layer complex.

This possibility has been realized in the reaction between graphite–ferric chloride and dinitrogen pentoxide. In the present case a fourth stage graphite–ferric chloride complex was treated with dinitrogen pentoxide at 0°.

The graphite–ferric chloride complex was prepared by heating purified Ceylon graphite (ash content 0·5%) with anhydrous ferric chloride in sealed, evacuated glass tubes at 350°. Excess of unchanged ferric chloride was sublimed from the intercalated graphite by heating, *in vacuo*, at 300°. The product analysed at $C_{31}\cdot FeCl_3$ which formulation corresponds to a fourth stage complex. The Mössbauer spectrum consisted of a single absorption line with an isomer-shift parameter similar to that previously reported.[1]



The *X*-ray powder diffraction pattern showed sharp lines indicating a well ordered product.

The intercalation by dinitrogen pentoxide of the graphite–ferric chloride complex was achieved by condensing dinitrogen pentoxide onto the graphite complex at 0°.

The reaction mixture was held at this temperature for 24 h after which the excess N_2O_5 was pumped off at 20°. The N_2O_5 content of the double complex was estimated from weight-loss measurements at 150°. Removal of N_2O_5 at this temperature is rapid and causes obvious exfoliation of the graphite. The residual $FeCl_3$ content was analysed for in the same manner as before, that is, by converting the graphite complex finally into Fe_2O_3. Complexes formed in this way analysed at $C_{31}{\cdot}FeCl_3{\cdot}(N_2O_5)_{1{\cdot}7}$. Thus, the carbon to ferric chloride ratio remains unaltered during the further intercalation process. The carbon to N_2O_5 ratio is 18:1 which roughly corresponds to a second stage complex.[2]

The Mössbauer spectrum of the $C_{31}{\cdot}FeCl_3{\cdot}(N_2O_5)_{1{\cdot}7}$ was identical with that of the parent graphite–ferric chloride complex. Thus, the environment of the iron remains unaltered during the further intercalation process. Presumably the introduced N_2O_5 enters previously unfilled inter-carbon layer spaces.

With this observed formulation the most ordered possible structure is that shown in the Figure. The repeat distance along the *c*-axis for such a structure is about 31·9 Å. This dimension is based on an observed inter-carbon layer separation distance of 7·8 Å for $C_9{\cdot}N_2O_5$[2] and 9·4 Å for C_8FeCl_3.[3] The *X*-ray powder diffraction pattern of the graphite–ferric chloride complex is completely altered following reaction with N_2O_5. The diffraction pattern of the double complex shows broad peaks for (000 *l*) reflections indicative of dimensional disorder along the c-axis.

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[1] A. G. Freeman, *Chem. Comm.*, 1968 193.

[2] H. Fuzellier and A. Herold, *Compt. rend.*, 1968, **267**, 607.

[3] J. M. Cowley and J. A. Ibers, *Acta Cryst.*, 1956, **9**, 421.