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The Adduct of 1,2-Diiodotetrafluorobenzene and *trans*-Diiodobis(1,2-dimethoxyethane)nickel(II): an Inclusion System with a Transition Metal Complex as Guest in a Novel Host System – 1,2-Diiodotetrafluorobenzene

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Intercalation systems with inorganic compounds [1] or complex ions [2] as guests have been reported. In these intercalates, however, respective examples of which are the (graphite)(CrO_3) [2] and $(RNH_3)_2(CuCl_4)$ [3] systems, the guest and/or the host consist of two dimensional macromolecular layers [3–6] and often there is considerable bonding between the guest and host subsystems [4]. Recently the preparation of channel inclusion systems with ferrocene of ferrocene and nickelocene as guests in a thiourea lattice have been reported [7] and structurally characterised by X-ray crystallography [8]. To our knowledge no inclusion systems incorporating molecular transition metal complexes, other than the above pseudo-organic systems, as guests have been discovered [9].

We now wish to report that the adduct, formed by the reaction of *trans*-diiodobis(1,2-dimethoxyethane)nickel(II) (*A*) and 1,2-diiodotetrafluorobenzene (ditfb) in 1,2-dimethoxyethane (dme), formulated as $NiI_2(dme)_2(ditfb)_2$ [10] (B) is an inclusion compound.

The evidence in support of our conclusion and against the alternative possibility that *B* may be a charge transfer (CT) complex is outlined below.

(a) In the ultra-violet and visible regions the spectrum of *B* shows no absorptions other than those attributable to *A* and ditfb.

(b) The ^{19}F nmr spectrum of the adduct in dme solution shows no shift or broadening when compared to that of ditfb, at the same total concentration, in dme.

(c) On dissolving *A* in dme/ethanol with 1,3,5-trinitrobenzene, picric acid or chloranil no characterisable adducts formed.

(d) Thermogravimetric analyses of *A* and *B* indicate that *B* loses dme at a higher temperature than does *A* and that *B* loses dme only after some ditfb has been lost. To within experimental error *A* commences to lose ditfb at the same temperature as ditfb itself sublimes.

(e) *B* is less susceptible to water vapour in the atmosphere than is *A* (water readily replaces the dme ligands in the nickel complex).

(f) The trends in the elemental analysis for nickel in adducts *B* formed in reaction systems with varying reactant molar ratios (ditfb/*A*) indicate that as the reactant ratio increases from 1 the product becomes deficient in $NiI_2(dme)_2$. A typical experiment with the reactant ratio ditfb/*A* at 3 and with the solution saturated in *A* gave $(NiI_2(dme)_2)_{0.9}(ditfb)_2$.

The absence of a CT interaction is shown by a [11], b[12], and c[13] whilst d[14], e[14, 15], and f[15] demonstrate behaviour characteristic of inclusion systems and indicate that the transition metal complex is the guest. This conclusion is intuitively acceptable as for an inclusion compound of formula XY_2 in which X and Y are of similar size (as are *A* and ditfb) X would most probably be the guest.

The possibility that the system *B* consists of *A* with ditfb as solvate molecules must be discounted. Whilst transition metal complexes may crystallise with organic molecules of solvation, in all such cases, to our knowledge, the latter are much smaller than the complex and also usually derive from the solvent. In *B, A* and ditfb are of approximately the same size and the solvent system from which *B* is formed is dme.

Further, our attempts to discover other similar systems to *B* by using different substituted fluorobenzenes, including 1,2-dibromotetrafluorobenzene and iodopentafluorobenzene have all failed – if *B* contained *A* with ditfb as solvate, success at such attempts would be expected.

We speculate that the structure of the new system consists of an open arrangement of ditfb molecules [16] held together by intermolecular electrostatic forces between the 1,2-iodine atoms of one ditfb molecule and the 4,5-fluorine atoms on an adjacent molecule the plane of which is perpendicular to the first (Fig. 1) [17]. These intermolecular forces between ditfb molecules will arise naturally from the effects of charge polarisation across ditfb which will leave the iodine atoms positively charged and the fluorine atoms, if not all certainly those in the 4,5-positions, negatively charged (μ(ditfb) = 1.96 D) [18].

The two-dimensional layer is envisaged as being made up of the unit shown (Fig. 1) repeating in its plane. The three dimensional structure will consist of layers, identical to those shown in Fig. 1, stacked such that a second layer ditfb molecule, with its plane parallel to that of the first layer, lies directly above the void in the first layer. With another layer eclipsed by the second layer but below the first an almost cubic void results. These layers will be held together in the same manner as the molecules within the layers.

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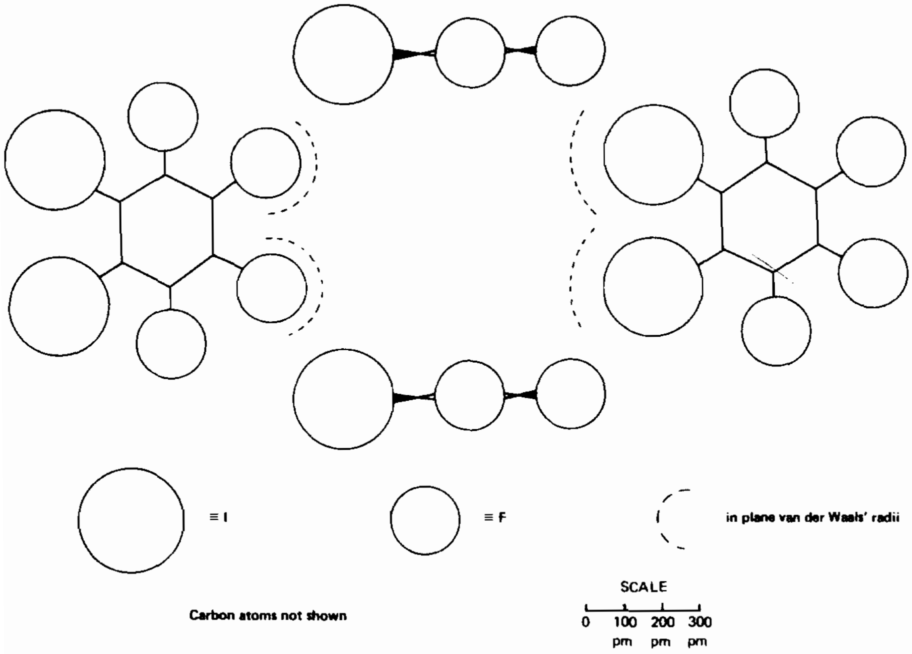

Fig. 1. Possible structure of the 1,2-diiodotetrafluorobenzene (ditfb) host system.

The repulsive forces between the 3,6-F atoms on different ditfb molecules will be negligible as the charge density on these atoms, assuming a steady gradation of charge density across the molecule, will be very small. Assuming van der Waals contacts between the non-bonded atoms in the system and with the proviso that cages may stretch slightly on clathration [19, 20] the void is seen to be of sufficient capacity (edge ≅750–850 pm) to accept the $NiI_2(dme)_2$ molecule (the elevation and plan views of which are shown in Fig. 2 and which has the approximate dimensions including van der Waals radii of 950 × 850 × 600 pm), possibly with its longest axis lying diagonally in the cage.

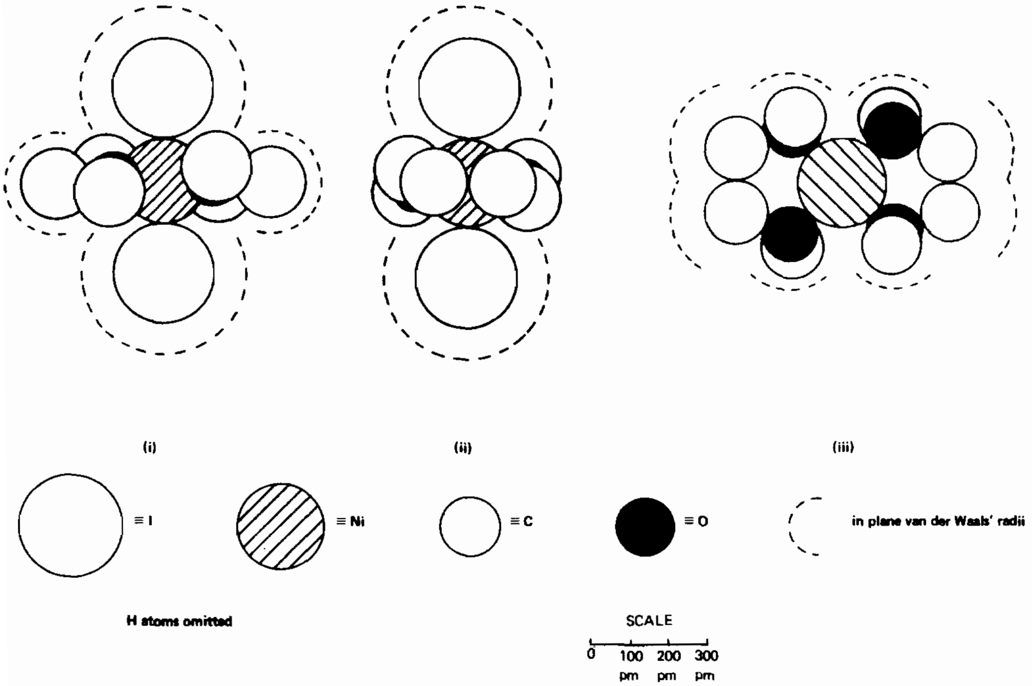

Fig. 2. i) and ii) $NiI_2(dme)_2$ in elevation, iii) plan view of $NiI_2(dme)_2$ (iodine atoms omitted).

Interestingly, the above structure may be *described* as arising from a cubic close-packed array of the almost spherical *A* molecules with ditfb molecules occupying all the tetrahedral sites. Although this is a very concise description of the general form of system *B*, in reality it will be an extremely expanded system (with radius ratio ≅1) in which the ditfb rather than the nickel complex *A* molecules are in contact.

The above is a further argument against the adduct being a solvate as it illustrates very clearly the way in which *A* molecules would be separated from each other and the possibility of strong inter-ditfb interactions.

This novel inclusion system is potentially useful for the study of isolated molecules of transition metal complexes. For instance the magnetic moment, μ, of *A* at 20 ° is 3.20 B.M.No. which is typical of octahedral complexes of Ni(II) whereas for *B*, μ is 2.82 B.M.No., the spin-only value for octahedral Ni(II) systems.

Another potential use is the possible separation of 1,2- and 1,4-diiodotetrafluorobenzene and the *cis*- and *trans*-isomers of neutral octahedral transition metal complexes of about 800 pm diameter.

We are currently extending this work and that on the thiourea systems [7, 8]. As part of this program we wish to report that we have isolated and characterised the analogues of *B* with Mn(II), Fe(II) and Co(II). The magnetic behaviour of the $CoI_2(dme)_2$/ditfb adduct in comparison to that of $CoI_2(dme)_2$ parallels the behaviour of *B* and *A*.

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