

m.y. reported by Greenhalgh and Jeffery⁵ relates not to a biotite "hand-picked from the rock", as stated by Wetherill, but to a biotite "hand-picked from the brannerite". The two minerals occur intergrown in nests and may well have been re-constituted contemporaneously.

If these interpretations are correct, the brannerite mineralization is completely lacking in stratigraphical definition and contributes no information about Cambrian chronology. The dating of the base of the Cambrian System at about 600 ± 20 m.y., founded on other evidence, remains unassailed.

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³ Davidson, C. F., *Liverpool and Manchester Geol. J.*, **2**, 311 (1960); *Nature*, **183**, 768 (1959).

⁴ Campana, B., and King, D., "Regional Geology and Mineral Resources of the Olary Province" (Dept. of Mines, Adelaide, 1958).

⁵ Greenhalgh, D., and Jeffery, P. M., *Geochim. Cosmochim. Acta*, **16**, 39 (1959).

⁶ Davidson, C. F., *Econ. Geol.*, **55**, 383 (1960).

CHEMISTRY

A Molecular Complex of Benzene and Hexafluorobenzene

In the course of experiments using mixtures of benzene and hexafluorobenzene, it was observed that a solid was formed on mixing these two substances although this frequently disappeared before the mixing process was complete. This observation has been followed up by the investigation of the freezing points, obtained from cooling curves, of mixtures of known composition of benzene and hexafluorobenzene.

The freezing-point diagram shows two eutectic points occurring at mole fractions of 0.15 and 0.85 of hexafluorobenzene, and melting at about 0.5°C . and -5.5°C . respectively. The diagram shows a maximum melting point of 23.7°C . corresponding to a mixture containing equimolar quantities of the two substances. Benzene and hexafluorobenzene have similar melting points (5.4°C . and 5.0°C . respectively). This clearly demonstrates the formation of a 1:1 molecular complex of the two compounds. Less-complete freezing-point diagrams have been obtained for the systems hexafluorobenzene and fluorobenzene, and pentafluorobenzene and benzene. The first of these shows evidence of the formation of a 1:1 complex of hexafluorobenzene and fluorobenzene melting at about -3°C ., that is, above the melting point of fluorobenzene but below that of hexafluorobenzene. No solid complex appears to be formed between pentafluorobenzene and benzene. The complexes seem to be similar to that formed as a low-melting white solid on mixing aniline and hexafluorobenzene¹.

These complexes may be regarded as examples of the Lewis base-Lewis acid (electron donor-acceptor) or charge-transfer type, of which those between picric acid and a number of aromatic compounds, and between, for example, benzene and *sym*-trinitrobenzene², are familiar examples. Fluorine atoms show a strong negative inductive effect which is

reflected by the observation that the ionization potentials of polyfluorobenzenes are higher than that of benzene³, and by the behaviour of polyfluorobenzenes in chemical reactions. In showing a negative inductive effect, the fluorine atom resembles the nitro group, and it is likely that the conditions in polynitrobenzenes which favour the formation of complexes will also occur in polyfluorobenzenes. The substitution of groups showing a positive inductive effect in the 'basic' partners of the complexes should increase the stability of the complexes with hexafluorobenzene. A complex, melting at 34° , has been prepared from hexafluorobenzene and mesitylene. This complex, unlike that between hexafluorobenzene and benzene, is sufficiently stable to allow its crystallization from ether. A similar complex, melting at 56°C ., has been obtained between hexafluorobenzene and 2-methylnaphthalene, and this also is sufficiently stable to allow its crystallization from ether.

Complexes of this type are generally characterized by a charge transfer spectrum. In the expectation that a transfer spectrum such as that observed (in the region 2800-3400 Å.) in the case of the complex between benzene and *sym*-trinitrobenzene would be found, a preliminary investigation has been made of the spectra of neat mixtures of benzene and hexafluorobenzene. No absorption band has been found in the region 2900-4000 Å., where the two liquids do not themselves absorb light. The spectra of mixtures of the two compounds have been measured in the region 2300-3000 Å. using ethanol and hexane as solvents. No absorption bands were observed other than those due to benzene and hexafluorobenzene, but it is probable that the concentrations used were too small to allow the formation of significant concentrations of the complex.

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Structure of the 1:1-Adducts of Cupric β -Diketone Chelates with Heterocyclic Bases

In a recent communication, Traill¹ raises the question of the structure of the 1:1-adducts formed by cupric β -diketone chelates with heterocyclic bases in organic solvents². The same question has been raised privately by others, and it seemed, therefore, that we should seek some further evidence in support of the 5:co-ordinated structure (I) originally proposed as against the 4:co-ordinated structure (II) suggested by Traill.

The original attribution of structure I to these adducts was essentially intuitive, and as their low stability makes isolation improbable, a definitive structure determination seems unattainable. We believe, however, that the weight of available evidence strongly favours structure (I).

(1) The stability of acetylacetonates and related compounds is largely due to chelation. If reaction