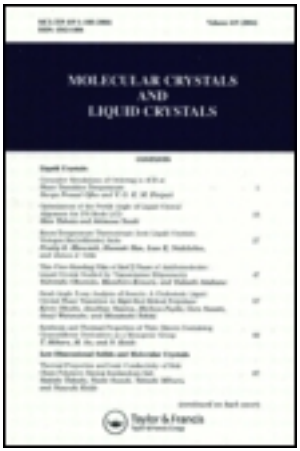

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A Review of: "Crystalline Molecular Complexes and Compounds, by Frank H. Herbstein"

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Book Review

Crystalline Molecular Complexes and Compounds, by Frank H. Herbstein, Oxford University Press, 2005; xxviii + 1273 pp; $249.50, cloth bound.

In the early days of the study of organic metals and charge-transfer complexes, the key crystallographic reference to the existing literature was Frank Herbstein's excellent review article on π-molecular compounds in perspectives in structural chemistry (Wiley, 1979). The present two-volume work can be looked on as an update and significant expansion of that work. It is the 18th volume in the International Union of Crystallography book series.

The books are divided into six parts involving 18 chapters: part 1, Some Preliminaries; part 2, Moieties with Molecules; part 3, Host–Guest Inclusion Compounds; part 4, Packing Complexes; part 5, Molecular Compounds with Localized Interactions; and part 6, Molecular Compounds with Delocalized Interactions. Part 6 is a significant elaboration of the work in the 1971 book. The titles of the various parts reveal the author's classification of the considerable variety of materials under discussion. The intended audience includes chemists, physicists, biologists, and technologists. There is clearly sufficient material to hold the interest of this diverse group of scientists, and they are indebted to Professor Herbstein for the detail that he brings to the various topics under discussion.

Herbstein readily admits that this work is not comprehensive, yet it has almost 4000 references. Readers of the earlier work will not be surprised at the heavy reliance on phase diagrams and will appreciate the substantial use of the Cambridge Structural Database. Just as the earlier work was introduced by a quote from Lewis Carroll's *Through the Looking Glass*, the present work introduced each chapter with an apt quote from either a literary or scientific source. A summary is also given at the beginning of each chapter.

Herbstein gives a classification scheme for binary adducts of type A.....B in terms of interactions A....A, A....B, and B....B. There is an interesting historical introduction to his topics. He traces gas

hydrates to Priestly (1777–1778), Davy (1811), and Faraday (1823). The first mixed-stack donor–acceptor compounds (picrates of aromatic hydrocarbons) are traced to von Fritzsche (1858). In a work of this length and breadth, one can rightly be concerned about whether the literature search is current, yet a significant number of citations are later than 2000.

Not surprisingly in a work of this breadth, a number of errors in structures and in some discussions may be found. These would include guayacanin (p. 398), TMDTDM-TTF (pp. 641, 643), BEDT-TTF (p. 658), DTDS (p. 663), and $TCVPDM^{-}$ (p. 1051).

The discussion of polarization energies (p. 941 ff.) is too simple. The value obtained for solid-state ionization energy can depend on the metal substrate used as well as the morphology of the material on that substrate.

The discussion of the determination of degree of charge transfer in chapter 13 is a valuable one. The shortcomings of attempts to use bond lengths are well discussed. The use of vibrational spectroscopy has numerous shortcomings, as pointed out. Major mistakes have been made; a well-known example of such a case is DBTTF-TCNQ.

The discussion of donors based on phenazine in section 15.9.5 misses some relevant points. Any phase containing the N-methylphenazinium cation is ill defined because of the organic chemistry that occurs with the synthesis and subsequent processing of this moiety. Because of their low oxidation potentials, the products of interaction of dihydrophenazine donors with TCNQ or similar acceptors are likely to be ionic and not near a neutral-ionic transition.

This work will prove valuable to both researchers and beginning students seeking to learn about the classes of materials discussed herein for the foreseeable future.

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