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STRUCTURAL CONSIDERATIONS IN THE DESIGN AND SYNTHESIS OF POLYME--ETC(U)
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The purpose of this research project was to study synthetically, theoretically and experimentally the effects of molecular forces on crystal structure; and, in particular on the structure of transition-metal ligand complex "polymers."

In compounds where hydrogen bonding can occur, the crystal structure tends to be dominated by the requirement that the number of such bonds must be maximized. We made a preliminary investigation to see if this fact could be utilized to control the crystal structure of compounds to which had been added certain specific hydrogen-bonding "labels." Studies were made of the effect on the solubility in a variety of solvents of a number of complementary pairs of H-bonding compounds e.g. uracil or thymine with 2-6 diaminopyridine and adenine. No clear evidence was found of the expected pairing. Further investigation is needed to determine the role of impurities and moisture in the materials.

A detailed study was made of a number of transition metal complexes of bis - benzoquinonedioximato $(bqd)_2$ ligand systems. The Ni, Pd and Pt

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complexes form stacked arrays in the crystal some of which give evidence of one-dimensional conductive behavior and others not. A structural determination(1) was made of $Pt(bqd)_2$ which revealed a strikingly short Pt-Pt distance, shorter than in the isostructural α-$Pd(bqd)_2$. This is interpreted as being due to enhanced backbonding from Pt to the (bqd) ligand. The Pd compound is known to exist in two forms, the α- and β-forms. Of these only the α- form exhibits a strong electronic anisotropy. A determination(2) was made of the structure of the β- modification. This revealed that the (bqd) planes were stacked at an angle inclined to the stacking direction. In this case the β-$Pd(bqd)_2$ is thus isostructural with $Ni(bqd)_2$.

This shows that where the ligand-ligand interaction is strong, stacking occurs with the molecular planes inclined to the stacking axis. This gives the highest density. Where the metal-metal interaction is strong as in the $Pt(bqd)_2$ the perpendicular stacking arrangement with the metal atoms in contact with one another is favored. In $Pd(bqd)_2$ obviously the free energy difference between these two is small and either α- or β- forms can be prepared depending on the conditions of crystalization. This illustrates once more the delicate balance between the competing forces in the determination of the structure of these compounds.

In order to study further the effects of electron withdrawing or donating groups on the ability of transition-metal complexes to form linear conductive systems the Bis-1, 10-phenanthroline macrocycle (Fig 1) was prepared. A detailed crystal and molecular structure determination of it was made(3) which revealed that the hole in the center was large enough to accommodate Ni but not Pt. Studies were made of the pK_a- values of the mono- and dications. Work has continued with the preparation of a larger sulphur-bridged macrocycle able to accommodate Pt.

Finally, as an outgrowth of the work initiated under this program a joint U. S. - Japan cooperative research program has been started and is being funded by the National Science Foundation. This program is entitled "The Development of the Design of Molecular Structures." As part of this a U. S. - Japan seminar on the "Design of Molecular Systems for Electronic Devices" will be held in Okazaki, Japan November 26 - 29, 1980.

Publications:

1. "Crystal and Molecular Structure of the Linear Metal-Chain Semiconductor Bis (1,2-benzoquinonedioximato) platinum(II), $Pt(bqd)_2$"
   M. Megnamisi-Belombe, Journal of Solid State Chemistry 27, 389-396 (1979).
2. "Structure of a β-Bis(1,2-benzoquinone dioximato) palladium(II), β-$Pd(bqd)_2$"
   H. Endres and M. Magnamisi-Belombe, W. A. Little and C. R. Wolfe, in Acta Cryst (1979) B35, 169-171.
3. "Crystal and Molecular Structure of a Hexaazamacrocycle"
   H. Endres and M. Hunziker, J. Cryst and Mol. Structure, (in press) (1979).
4. "Dimeric Dibromo(2,3-butanedione dioximato)copper(II)"
   H. Endres, in Acta Cryst (1978) B34, 3736-3739.
5. "The Crystal and Molecular Structure of Bis(oxamide oximato) nickel(II)Dihydrate"
   H. Endres, in Acta Cryst, B35, 625 (1979).

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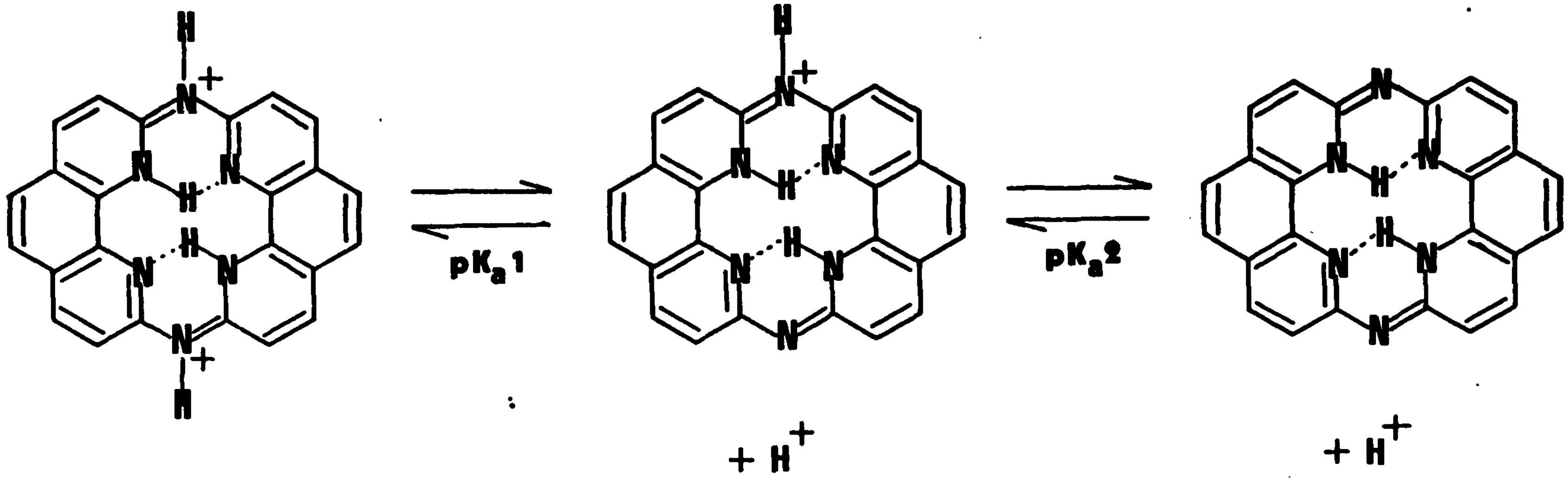

Fig 1. Illustration of structure and protonation of Hexaazamacrocycle.