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F. F. Seelig [a]
[a] Institut für Physikalische und Theoretische Chemie, Universität Tübingen, Federal Republic of Germany
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SYNTHESIS AND PROPERTIES OF A NEW KIND OF ONE-DIMENSIONAL CONDUCTORS
15. EXTENDED HÜCKEL CALCULATIONS ON THE ENERGY BAND STRUCTURES OF TRIPLY BRIDGED POLYMERS

F. F. SEELIG
Institut für Physikalische und Theoretische Chemie,
Universität Tübingen, Federal Republic of Germany
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The structural principle of previous papers of this series, namely coordination polymers of the type $(MX_4L)_\infty$, in which unities MX_4 are linearly bridged by ligands L to one-dimensional chains, is extended to the type $(M_2L_6)_\infty$. Here each transition metal atom **M** is triply bridged by ligands **L**. EH calculations are **executed** on two samples: $Fe_2^{(III)}$(pyrazolate)$_6$ and $Fe_2^{(0)}(CO)_6$. These calculations yield partly filled energy bands, but the structures seem to be sensitive to Peierls distortions. The influence of irreversible doping is discussed.

1. INTRODUCTION

The joint efforts of the Tübingen group on one-dimensional conductors[1-14] concentrated up to now on a type of coordination polymer depicted in Fig. 1, in which unities MX_4 were simply bridged by a bidentate, non-chelating ligand L containing one or two crossed π-systems.

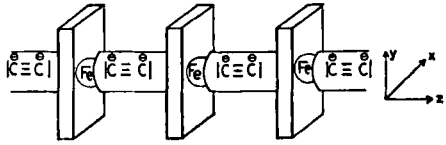

FIGURE 1 Type $(MX_4L)_\infty$, here M=Fe, X_4=Tetrazaporphin, L=C_2

In MX_4L the octahedral coordination of M is preserved, but the symmetry is D_{4h} for the marginal k_z-values 0 and π/c, and only C_{4v} else. Extended Hückel calculations of Fe^{II}-tetrazaporphin-acetylene, Fe^{II}-TAP-$C_2^{2\ominus}$, showed[2] that the a_2-,b_1- and b_2-bands were extremely narrow because there was no contribution from $L=C_2^{2\ominus}$, whereas the a_1-bands with contributions from the local σ-system of L and the e-bands with the crossed local π-system of L were broader. The most astonishing result was that - contrary to naive prejudices about π-systems - the a_1-bands were particularly broad suggesting a kind of σ-conjugation.

The role of X_4 which was in this case the tetragonal 16-membered ring system of TAP was partly to contribute to the conjugation, partly to stabilize the linear chain ...MLML... The two coordination sites of L had to show strictly into opposite directions.

2. THE CONSTRUCTION PRINCIPLE OF TRIPLY BRIDGED COORDINATION POLYMERS

At early stages other principles of coordination polymers were designed and tried to be synthesized. If the coordination octahedron of M is placed in such a way that the polymer axis z is identical with one of the C_3 axes, an angle α of arc $\cos(1/\sqrt{3}) = 54.7356^\circ$ is formed with the z-axis. The supplementary angle of 125.2644° fits best with the angle of 126° formed by the lone pair of one N and the N-N-bond of pyrazole, if it is assumed to be a regular pentagon. Other possibilities like o-diisonitriles were considered, but led to big preparative obstacles. Analogous six-membered rings seem to be not so suitable, because then the corresponding angle of 120° is a bit too small, but may be tolerable, too. The structure is depicted in Fig. 2. The elementary cell consists of M_2L_6, because an identical situation is reached only after another triple of Ls.

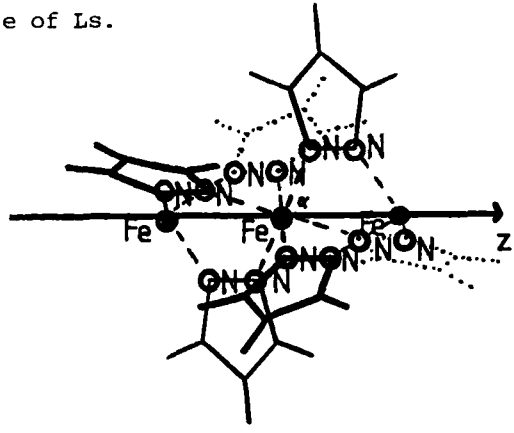

FIGURE 2 Type $(M_2L_6)_\infty$ here $M=Fe^{3\oplus}$, $L=\text{pyrazolate}^{\ominus}$

In this type of structures the former principle of one atom: one coordination site is conserved, however L is now angled rather than straight. But in transition metal carbonyls, i.e. $Fe_2(CO)_9$, CO-ligands can bind to two metal atoms simultaneously, which is true for the inner group $(CO)_3$. An extrapolation of this structure would yield $Fe_n(CO)_{3n}$ or $(Fe_2(CO)_6)_\infty$, although this compound is unknown in the series of iron carbonyls. The advantage of one carbon binding to two irons is that very short bonds are formed which in turn should express itself in relatively broad energy bands. In addition, by means of the unusual short Fe-Fe distance a certain amount of direct interaction of the metal atoms via their dz^2-orbitals can be expected as is the case with the Pt atoms in KCP of Krogmann[15].

3. RESULTS FOR FE^{III}-PYRAZOLATE

All EH calculations were performed with the program already described[2], only slight adaptations being done to the particular problem. The unit cell contains $Fe_2(C_3H_3N_2)_6$. Since each C or N is made up of 2s, 2px, 2py, 2pz, each H of 1s, and each Fe of 4s, 4px, 4py, 4pz, $3dz^2$, 3dxz, 3dyz, 3dxy, $3dx^2-y^2$ atomic orbitals, there is a total of 156 AOs. Only for the marginal k_z-values 0 and π/c computations were done, where the symmetry is D_{3d}, if one Fe is the centre of the unit cell. Thus the irreducible representations a_{1g}, a_{2g}, e_g, a_{1u} a_{2u} e_u are used which contain 22, 5, 2 x 27, 5, 20, 2 x 25, symmetry basis functions for $k_z=0$ and 21, 5, 2 x 26, 5, 21, 2 x 26 for $k_z=\pi/c$, respectively. In the latter case by means of the special symmetry only pairs of degenerate a_{1g}/a_{2u}, a_{2g}/a_{1u}, e_g/e_u band limits are formed so that as a total result all energy bands form double bands with together 2 electron pairs per unit cell for $a_1 = a_{1g} + a_{2u}$ and $a_2 = a_{2g} + a_{1u}$ and 4 electron pairs per unit cell for $e = e_g + e_u$. Since the unit cell contains 83 electron pairs it is impossible to get completely filled double bands in any case. The attempt to lead the iterative process to selfconsistence with respect to charge and ionisation potential did not succeed, so an average over one oscillation cycle had to be taken. In most cases the boundaries of the double bands were formed by $k_z=0$, $k_z=\pi/c$ being the degenerate level of both half bands, i.e. the half bands were adjacent rather than overlapping, but in some cases the degenerate π/c-level was the upper or lower limit so that the half bands overlapped each other strongly. The result is depicted in Fig. 3. If (according to the lower symmetry C_{3v} for arbitrary k_z-values) the a_{1g} and a_{2u} double bands are designated a_1, a_{2g} and a_{1u} are called a_2, and e_g and e_u form e, there

are 11 filled a_1 double bands, 3 a_2 double and 14 e quadruple bands, all other bands being separated from these by a big gap. But since these add up to 84 bands, whereas only 83 electron pairs exist, the highest band, 14 e, is only filled 3/4. At first sight this result could suggest a fairly good electrical conductivity, however the EH crystal orbitals are found in a strongly simplified one electron model that does not consider electron repulsions and exchange effects explicitly, but only in an averaged way. So comparing this situation with the similar one of near degeneracy of weak ligand field complexes which lead to singly occupied high spin states, one can expect that the upper two bands of the 14 e quadruple band are filled exactly half with electrons forming the highest total spin and multiplicity possible. In this case only terms in the Hamiltonian exerting directly on the spin would allow transitions between the singly occupied levels. But since those operators are of some influence only in the case of strong magnetic fields (vd. EPR), no substantial contribution to electrical conductivity can be expected from the mere fact that the 14 e band is not completely filled. The consideration would be different, if the 11 a_1 or 3 a_2 bands would strongly overlap with 14 e.

Another interesting result of the EH calculation is the fact that even the a_2-bands are relatively broad although they do not contain contributions from the d-orbitals of the iron atoms, i.e. the strong vicinity of the local π-systems of the different pyrazole rings near the metal atoms lead to the broadening of these energy bands.

Quite another point is the possibility of a Peierls instability. In our computations an equal Fe-Fe-distance was assumed. If by means of a Peierls distortion longer and shorter Fe-Fe-distances would alter then the found degeneracy of adjacent bands at $k_z=\pi/c$ would disappear and the double and quadruple bands would separate to single and double bands with gaps in between, growing with the distance alteration.

Attempts of Strähle and co-workers to synthesize Fe^{III}-(pyrazolate)$_3$ resulted at the moment in Fe^{II}-(pyrazolate)$_2$, which is a black-brown powder without measurable conductivity, but they did not succeed to gain single crystals suitable for X-ray studies so that the identity of their product with the assumed structure is not yet confirmed.

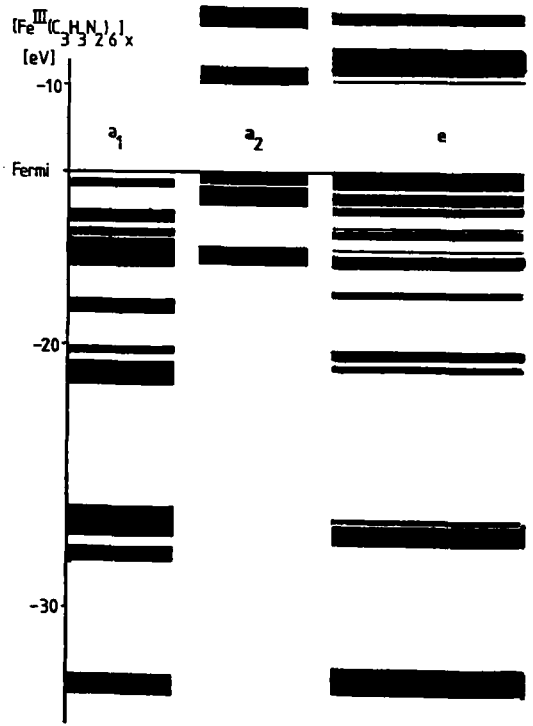

FIGURE 3 Energy band structure of $Fe_2^{(III)}(pyrazolate)_6$

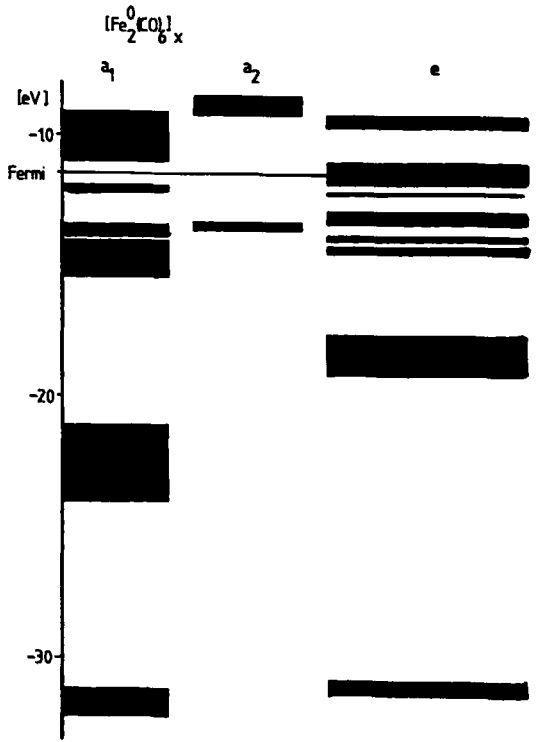

FIGURE 4 Energy band structure of $Fe_2^{(0)}(CO)_6$

4. RESULTS FOR HYPOTHETICAL $|FE_2(CO)_6)|_\infty$

In this case the unit cell contains 66 AOs splitting in D_{3d} symmetry for $k_z=0$ into 10 a_{1g}, 2 a_{2g}, 2 x 12 e_g, 2 a_{1u}, 8 a_{2u}, 2 x 10 e_u symmetry basis functions that are occupied by 38 electron pairs. Again a degeneracy between a_{1g}/a_{2u}, a_{2g}/a_{1u}, e_g/e_u is observed at $k_z=\pi/c$ leading again to double and quadruple bands. Of these 5 a_1 and 1 a_2 double bands are occupied, but the 7th e quadruple band is crossed by the Fermi level. Thus either electron pairs 37 and 38 fill quadruple band 7 e in a high spin way, occupying each individual energy level only with one electron rather than with a pair, or only the lower two bands of 7 e are occupied, but then the border of the upper two empty bands is strongly endangered by the Peierls instability which would distort the formerly equal Fe-Fe-distances and cause the formation of an energy gap between completely filled and completely empty bands. Both situations are not very favourable to high conductivity.

The quantitative results for $|Fe_2(CO)_6|_\infty$ in which now self-consistence could be achieved are depicted in Fig. 4. Contrary to Fe_2 pyrazolate$_3$ there is no broad gap near the Fermi level.

5. SPECULATIONS ON THE EFFECT OF IRREVERSIBLE DOPING

It is well known from vast fields in literature that doping can increase the conductivity of poor semi-conductors by several orders of magnitude. Doping is performed in most cases by partial oxidation by J_2, AsF_5, SbF_5, seldom by reduction by alkali metals because these substances are extremely unstable on air. But it is known, too, that this kind of "external" doping is more or less reversible, i.e. the conductors are unstable, especially in the case of oxidation by J_2.

On the other hand the nowadays "classical" doped semiconductors like n-type or p-type Ge, Si etc. are doped "internally" by controlled contamination of the otherwise extremely pure crystals with As or Ga at the very stage of production. If doping is very weak the doping atoms imitate the host atoms leaving the crystal structure completely unaffected and adding some extra electrons or holes, respectively, to the otherwise filled valence and unfilled conduction bands. It is this situation of avoiding even exactly half-filled bands that causes that dramatic increase in conductivity.

Thus it can be supposed that by introducing alien atoms in an odd rate at the stage of synthesis rather than withdrawing or adding electrons at a later stage results in an

irreversible doping with at least the same effect.

6. CONCLUSIONS

The new type $|M_2L_6|_\infty$ introduced here as opposed to the formerly discussed type $|MX_4L|_\infty$ dispenses with the somewhat passive component X_4 and adds further synthetic flexibility, because L that is angled here allows for much more realizations than the formerly strictly linear L. The hypothetical ligand CO could be replaced by isonitriles CNR, instead of pyrazole other heterocyclic systems are conceivable. The possibility of non-conducting high spin configurations at exactly half-filled bands cannot be settled in the frame of EH calculations, the appearance of double bands seems to make the structures especially sensitive to Peierls distortions. This effect could be overcome by irreversible doping by adding alien atoms at the very stage of synthesis rather than by later diffusion.

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