Synthesis and Properties of a New Kind of One-Dimensional Conductors
2. Extended Hückel Calculations on the Energy Band Structure

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The co-ordination polymer of tetrazaporphin (TAP) with a transition metal, say Fe^{II}, in its center and acetylide anion, $C_2^{2\ominus}$, as an axial bidentate bridging ligand is taken as a model substance for the new type of one-dimensional conductors introduced in the preceding communication of this series. Although the monomer shows D_{4h} symmetry, this is reduced to C_{4v} for arbitrary k_z-values of the Bloch functions of the first Brillouin zone. From the irreducible representations a_1, a_2, b_1, b_2, and e only a_1 and e have contributions from all components, namely $TAP^{2\ominus}$, $Fe^{2\oplus}$ and $C_2^{2\ominus}$, so that for these races broad energy bands can be expected. The a_2, b_1, and b_2 MOs of the TAP-Fe^{II} subunits are separated fairly well and have no counterparts in the $C_2^{2\ominus}$ bridges so that very narrow bands should arise. This is confirmed by an EH calculation. Unexpectedly the a_1 bonds which have contributions from the σ-MOs of $C_2^{2\ominus}$ are broader than the e-bands which contain the two crossed π-MO systems of $C_2^{2\ominus}$. The quantitative results of the nearly self-consistent iterative EH calculation indicate overlap of the energy bands near the Fermi level and fulfill thus one necessary condition for metal-like electrical conductivity.

1. Introduction

In the first contribution of this series [1] we exposed the idea and the general structural principle of a new kind of one-dimensional conductors which consisted essentially of three parts:

1) an octahedral transition metal M surrounded tetragonally by
2) four equal ligands X_4 or a tetragonal ring system, and its two axial positions occupied by
3) a linear bidentate, but non-chelating ligand L with one or two crossed longitudinal π-systems.

These units are continued infinitely in one dimension as depicted in Figure 1. Because of the high and independent variability of the 3 components this type should show a great flexibility and should cover a broad range of preparative realizations. The following theoretical treatment is given for tetrazaporphin (TAP) (cf. Figure 2). Experimental efforts toward a realization of phthalocyanine compounds are published elsewhere [2]. Simple group theoretical considerations of the subunit which is repeated infinitely in the z-direction show the following general and qualitative features: the symmetry is D_{4h} with a partition of AOs of M and local MOs of TAP and $C_2^{2\ominus}$ as given in Table 1. The symmetry of the irreducible representations with respect to symmetry planes in the x, y-plane is depicted in Figure 3.

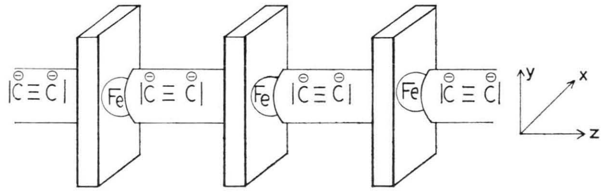

Fig. 1. Structural principle of the proposed new kind of one-dimensional conductors MX_4L: here $M = Fe^{II}$, X_4 = tetrazaporphin (TAP), $L = C_2^{2\ominus}$.

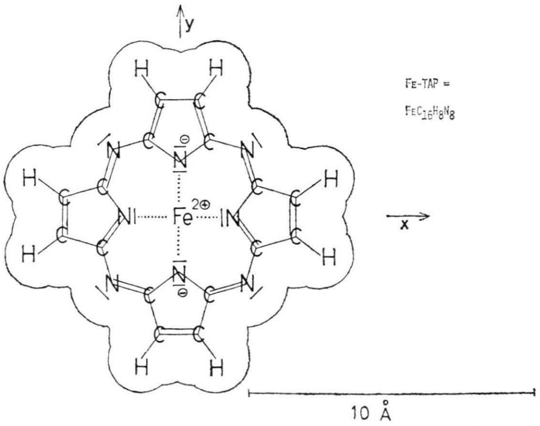

Fig. 2. Geometry of Fe-TAP in the x, y-plane with approximate van-der-Waals-boundaries.

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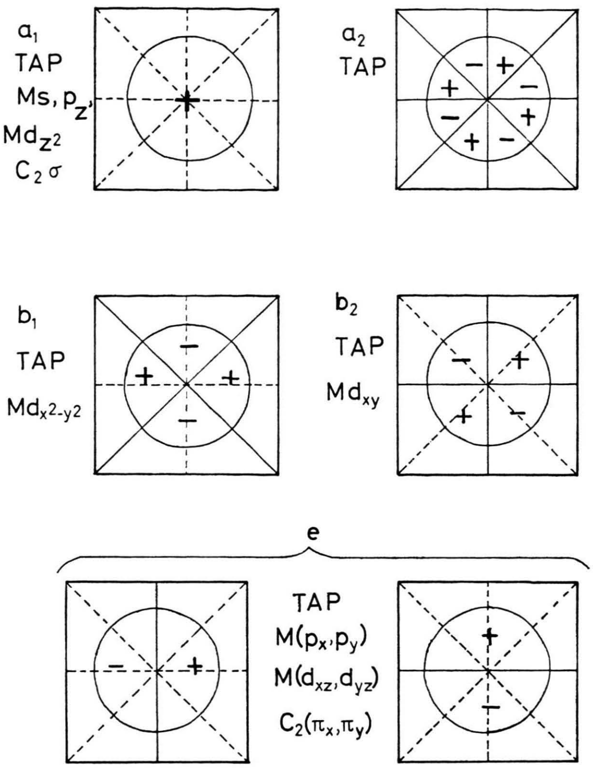

Fig. 3. Symmetries of the irreducible representations of the group C_{4v} in the x, y-plane.

Table 1. Symmetries of AOs and local MOs.

Irreducible representation		AOs and local MOs		
D_{4h}	C_{4v}	$TAP(D_{4h})$	M	$C_2{}^{2\ominus}(D_{\infty h})$
a_{1g}	a_1	$a_{1g}\ \sigma$	$s,\ d_z{}^2$	$\sigma_g{}^+$
a_{2u}		$a_{2u}\ \pi$	p_z	$\sigma_u{}^+$
a_{2g}	a_2	$a_{2g}\ \sigma$	—	—
a_{1u}		$a_{1u}\ \pi$	—	—
b_{1g}	b_1	$b_{1g}\ \sigma$	$d_{x^2-y^2}$	—
b_{2u}		$b_{2u}\ \pi$	—	—
b_{2g}	b_2	$b_{2g}\ \sigma$	d_{xy}	—
b_{1u}		$b_{1u}\ \pi$	—	—
e_g	e	$e_g\ \pi$	$(d_{xz},\ d_{yz})$	$(\pi_{xg},\ \pi_{yg})$
e_u		$e_u\ \sigma$	$(p_x,\ p_y)$	$(\pi_{xu},\ \pi_{yu})$

In the polymer crystal the maximal symmetry D_{4h} survives only in the marginal k_z-values of the reciprocal space 0 and π/c (where c is the length of the elementary cell in the z-direction, which is here 4.46 Å). These k_z-values are at the same time expected to correspond to the band edges. For all other intermediate k_z-values the two planes of symmetry perpendicular to the z-axis are lost and the symmetry is reduced to C_{4v}. It is essential that there are no longer global σ- or π-crystal orbitals (COs), but each race of C_{4v} is a mixture of local σ-and π-MOs of TAP, whereas the σ-MOs of $C_2{}^{2\ominus}$ are melted down into a_1 and the π-MOs of $C_2{}^{2\ominus}$ contribute to e. There are no a_2, b_1, and b_2 counterparts in $C_2{}^{2\ominus}$ so that it can be expected that the local MOs of TAP with these symmetries behave like those of isolated molecules, i.e., yield very narrow energy bands in the solid state. From the σ-core of TAP the lone pairs on the ligand N-atoms near Fe are the most important components for the macroscopic conjugation which can hardly be expressed in conventional terms of classical π-conjugation here.

2. Method of Calculation

Although many descriptions of the EH method exist in the literature for isolated molecules and a general MO description for crystals is given by Ladik [3], too, a short repetition will clarify notations used later on.

For a crystal of one-dimensional polymer chains which are thought to be isolated in the x- and y-direction and infinite in the z-direction COs are formulated as Bloch functions depending on the chosen k_z-value ($0 \leqq k_z \leqq \pi/c$)

$$\psi_j(\boldsymbol{x}, k_z) = \sum_r \varphi_r(\boldsymbol{x}, k_z)\, C_{rj}(k_z)\,, \tag{1}$$

$$\varphi_r(\boldsymbol{x}, k_z) = \sum_{p=-\infty}^{+\infty} e^{ik_z pc}\, \varphi_r(\boldsymbol{x}_p) \tag{2}$$

(p = integers including 0)
with position vectors

$$\boldsymbol{x} = (x, y, z)\,, \tag{3}$$

$$\boldsymbol{x}_p = (x, y, z - p\,c)\,. \tag{4}$$

That means that each CO is a linear combination of basis functions in much the same way as a MO is comprised of AOs, but each basis function here is the superposition of the local AOs of the p-th cell modulated by a sinoidal factor. $\varphi_r(\boldsymbol{x}, k_z)$ and $\psi_j(\boldsymbol{x}, k_z)$ are complex save at the boundaries of the first Brillouin zone, $k_z = 0$ and $k_z = \pi/c$, where $e^{ik_z pc}$ becomes $+1$ and $+1$ or -1 for even or odd p, respectively. (Strictly speaking the boundaries of the first Brillouin zone are $-\pi/c$ and π/c, but the latter is symmetric at $k_z = 0$.)

If all different ψ_j and φ_z form row vectors $\boldsymbol{\psi}'$ and $\boldsymbol{\varphi}'$ and all coefficients C_{rj} form a square matrix $\mathscr{C}$, application of some one-electron Hamiltonian $\mathbf{H}$ to $\boldsymbol{\psi}' = \boldsymbol{\varphi}'\mathscr{C}$ yields the matrix notation of the Schrödinger equation

$$\mathscr{H}(k_z)\,\mathscr{C}(k_z) = \mathscr{S}(k_z)\,\mathscr{C}(k_z)\,\mathscr{E}(k_z) \tag{5}$$

with (the argument k_z dropped further on)

$$H_{rs} = \int \varphi_r^* \,\mathscr{H} \varphi_s \,\mathrm{d}v\,, \tag{6}$$

$$S_{rs} = \int \varphi_r^* \varphi_s \,\mathrm{d}v\,, \tag{7}$$

where $\mathscr{H}$ and $\mathscr{S}$ are complex hermitian and $\mathscr{E}$ is the real diagonal matrix of the CO energies (eigenvalues) which on varying k_z from 0 to π/c broaden to energy bands each. Typically in the EH method $\mathscr{S}$ is exactly calculated for Slater type orbitals (STOs), but $\mathscr{H}$ is approximated semi-empirically by setting the diagonal elements equal to the valence orbitals ionisation potentials (in dependence on the formal charge in case of the iterative method [4]) and putting

$$H_{ij} = \tfrac{1}{2}(H_{ii} + H_{jj}) \cdot K \cdot S_{ij} \tag{8}$$

for the off-diagonal elements [5]. (In our calculations was $K = 1.75$.)

Since even for arbitrary k_z the symmetry is still high and since relatively many basis functions (121 for $\mathrm{Fe^{II}TAPC_2}^{2\ominus}$) enter, it seemed worthwhile to utilize this high symmetry to transform to symmetry adapted basis functions yielding $\mathscr{S}$ and $\mathscr{H}$ in blocks along the diagonal, each block comprising functions belonging to the same irreducible representation. The necessary real orthogonal matrix $\mathscr{T}$ was constructed individually for each molecule. Denoting $\mathscr{T}'$ the transpose of $\mathscr{T}$ and noting that $\mathscr{T}\mathscr{T}' = \mathbf{1}$ we get

$$(\mathscr{T}'\mathscr{H}\mathscr{T})(\mathscr{T}'\mathscr{C}) = (\mathscr{T}'\mathscr{S}\mathscr{T})(\mathscr{T}'\mathscr{C})\,\mathscr{E}$$
$$\mathscr{H}_\mathrm{B}\mathscr{C}_\mathrm{B} = \mathscr{S}_\mathrm{B}\mathscr{C}_\mathrm{B}\,\mathscr{E} \tag{9}$$

with

$$\mathscr{T}'\mathscr{H}\mathscr{T} = \mathscr{H}_\mathrm{B}\,, \quad (\mathscr{S}_\mathrm{B} \text{ analogously}) \tag{10}$$

$$\mathscr{T}'\mathscr{C} = \mathscr{C}_\mathrm{B}\,. \tag{11}$$

Again $\mathscr{H}_\mathrm{B}$ and $\mathscr{S}_\mathrm{B}$ are complex hermitian, but they as well as $\mathscr{C}_\mathrm{B}$ decompose to much smaller submatrices.

A first diagonalisation, that of $\mathscr{S}_\mathrm{B}$ according to

$$\mathscr{R}_\mathrm{B}^+\,\mathscr{S}_\mathrm{B}\mathscr{R}_\mathrm{B} = \boldsymbol{\lambda}_\mathrm{B} \tag{12}$$

($\mathscr{R}_\mathrm{B}^+$ is the conjugate complex transpose of $\mathscr{R}_\mathrm{B}$) yields the complex unitary matrix $\mathscr{R}_\mathrm{B}$ and the real diagonal matrix $\boldsymbol{\lambda}_\mathrm{B}$.

There are two possibilities for the further treatment. Either we use the *Löwdin symmetric orthogonalization* [6] according to

$$\mathscr{S}_\mathrm{B}^{-1/2} = \mathscr{R}_\mathrm{B}\,\boldsymbol{\lambda}_\mathrm{B}^{+1/2}\,\mathscr{R}_\mathrm{B}^+\,,$$
$$(\mathscr{S}_\mathrm{B}^{1/2} \text{ analogously}) \tag{13}$$

which is complex hermitian and has the properties $\mathscr{S}_\mathrm{B}^{-1/2}\;\mathscr{S}_\mathrm{B}\;\mathscr{S}_\mathrm{B}^{-1/2} = \mathbf{1}$ and $\mathscr{S}_\mathrm{B}^{-1/2}\;\mathscr{S}_\mathrm{B}^{1/2}$ and form

$$(\mathscr{S}_\mathrm{B}^{-1/2}\,\mathscr{H}_\mathrm{B}\,\mathscr{S}_\mathrm{B}^{-1/2})(\mathscr{S}_\mathrm{B}^{1/2}\mathscr{C}_\mathrm{B})$$
$$= (\mathscr{S}_\mathrm{B}^{-1/2}\,\mathscr{S}_\mathrm{B}\,\mathscr{S}_\mathrm{B}^{-1/2})(\mathscr{S}_\mathrm{B}^{1/2}\mathscr{C}_\mathrm{B})\,\mathscr{E}\,, \tag{14}$$

$$\mathscr{H}_u\mathscr{C}_u = \mathscr{C}_u\,\mathscr{E} \tag{15}$$

with

$$\mathscr{S}_\mathrm{B}^{-1/2}\mathscr{H}_\mathrm{B}\,\mathscr{S}_\mathrm{B}^{-1/2} = \mathscr{H}_u \tag{16}$$

and

$$\mathscr{S}_\mathrm{B}^{1/2}\mathscr{C}_\mathrm{B} = \mathscr{C}_u \tag{17}$$

where $\mathscr{H}_u$ is complex hermitian and $\mathscr{C}_u$ complex unitary.

Because of

$$\mathscr{C}_u^+\;\mathscr{H}_u\mathscr{C}_u = \mathscr{E} \tag{18}$$

the eigenvalues $\mathscr{E}$ and matrix of eigenvectors $\mathscr{C}_u$ are found by a second diagonalization procedure and the matrix of very eigenvectors $\mathscr{C}$ back by reversing (11) and (17)

$$\mathscr{C} = \mathscr{T}\mathscr{S}_\mathrm{B}^{-1/2}\mathscr{C}_u\,. \tag{19}$$

Or starting from (12) we use the *canonical orthogonalization* [7] according to

$$\mathscr{S}_\mathrm{C}^{-1/2} = \mathscr{R}_\mathrm{B}\,\boldsymbol{\lambda}_\mathrm{B}^{-1/2}\,, \tag{20}$$

$$\mathscr{S}_\mathrm{C}^{1/2+} = \boldsymbol{\lambda}_\mathrm{B}^{1/2}\,\mathscr{R}_\mathrm{B}^+\,, \tag{21}$$

$$\mathscr{S}_\mathrm{C}^{-1/2+} = \boldsymbol{\lambda}_\mathrm{B}^{-1/2}\,\mathscr{R}_\mathrm{B}^+ \tag{22}$$

which all are complex and have the properties $\mathscr{S}_\mathrm{C}^{-1/2+}\;\mathscr{S}_\mathrm{B}\,\mathscr{S}_\mathrm{C}^{-1/2} = \mathbf{1}$

and

$$\mathscr{S}_\mathrm{C}^{-1/2}\;\mathscr{S}_\mathrm{C}^{1/2+} = \mathscr{S}_\mathrm{C}^{1/2+}\;\mathscr{S}_\mathrm{C}^{-1/2} = \mathbf{1}$$

and form

$$(\mathscr{S}_\mathrm{C}^{-1/2+}\mathscr{H}_\mathrm{B}\,\mathscr{S}_\mathrm{C}^{-1/2})(\mathscr{S}_\mathrm{C}^{1/2+}\,\mathscr{C}_\mathrm{B})$$
$$= (\mathscr{S}_\mathrm{C}^{-1/2+}\;\mathscr{S}_\mathrm{B}\,\mathscr{S}_\mathrm{C}^{-1/2})(\mathscr{S}_\mathrm{C}^{1/2+}\mathscr{C}_\mathrm{B})\,\mathscr{E} \tag{23}$$

$$\mathscr{H}_\mathrm{C}\mathscr{C}_\mathrm{C} = \mathscr{C}_\mathrm{C}\,\mathscr{E} \tag{24}$$

with

$$\mathscr{S}_\mathrm{C}^{-1/2+}\;\mathscr{H}_\mathrm{B}\,\mathscr{C}_\mathrm{C}^{-1/2} = \mathscr{H}_\mathrm{C} \tag{25}$$

and

$$\mathscr{S}_\mathrm{C}^{1/2+}\;\mathscr{C}_\mathrm{B} = \mathscr{C}_\mathrm{C}\,, \tag{26}$$

where again $\mathscr{H}_\mathrm{C}$ is complex hermitian and $\mathscr{C}_\mathrm{C}$ is complex unitary and both retain this block structure. The real diagonal matrix $\mathscr{E}$ of eigenvalues and the matrix of eigenvectors, $\mathscr{C}_\mathrm{C}$, are again gained by a second diagonalization procedure. But here the very eigenvectors are achieved by the back transformations of (11) and (26)

$$\mathscr{C} = \mathscr{T}\mathscr{S}_\mathrm{C}^{-1/2}\mathscr{C}_\mathrm{C}\,. \tag{27}$$

3. Computer Programs and Computational Results

An isolated molecule version of an iterative EH program including d-orbitals exists in the literature which was written by P. Dibout, Rennes, France, and can be got from the Quantum Chemistry Program Exchange as program No. 256 (EHT-SPD). This was used as a basis, but was heavily changed incorporating the transition from MOs to COs with the complications of having complex instead of real matrices which caused severe problems of storage and needed different diagonalization procedures. Another feature is the block diagonalization by using $\mathscr{T}$. The main part that was retained essentially concerns the evaluation of overlap integrals. Since the appearance of complex matrices added some difficulties and the matrices remain real at the boundaries of k_z, 0 and π/c, two different versions of the program were written: one special form only for $k_z = 0$ and π/c and a general one for arbitrary k_z. Iterative EH calculations with self-consistence between formal charge distribution and valence orbital ionization potentials were performed only with the real version. The real version uses the somewhat more convenient symmetric orthogonalization technique as in the original QCPE program. In the complex version for some cases with maximal imaginary part (near $k_z = \pi/2c$) problems arose when the first diagonalization (12) produced some very small or even slightly negative λ's because of almost singular $\mathscr{S}$. Here only the canonical orthogonalization could be used because in this method these pathological λ's and corresponding eigenvectors can be canceled, the matrices $\mathscr{S}_\mathrm{C}^{-1/2}$ and $\mathscr{S}_\mathrm{C}^{-1/2+}$ becoming rectangular rather than square in this case. Therefore in the complex program only the canonical variant was used. Severe problems arose on trying to get self-consistence because the energies of the bands with strong contribution of d-orbitals are only slightly split and these COs have a tendency to be either all occupied or all empty causing heavy oscillations in the charge of the transition metal. If convergence could not be achieved the potential was averaged. The fixed mean value of potentials for $k_z = 0$ and $k_z = \pi/c$ was used for the calculation of COs and energy bands (k_z in steps of $\pi/6c$) with the general complex program. Because of the non-orthogonality of the basis functions the elements of $\mathscr{C}$ cannot be used directly for the interpretation of the results with respect to the contribution of the basis functions, especially the d-orbitals of M. Defining for the basis function φ_r in the CO ψ_j in the special case of real functions

$$q_{rj} = C_{rj} \sum_s S_{rs}\, C_{sj}\,. \tag{28}$$

$100\,q_{rj}$ can be interpreted as the percentage of basis function φ_r in CO ψ_j (although some terms can become slightly negative) because

$$\sum_r q_{rj} = \sum_{r,s} C'_{jr} S_{rs}\, C_{sj} = 1 \tag{29}$$

which is the normalization condition of ψ_j as expressed by (1). If the summation in (28) is performed appropriately the definition applies to the original basis functions as well as to the symmetry adapted ones.

The band scheme of $\mathrm{Fe^{II}TAPC_2^{2\ominus}}$ is shown in Fig. 4 and shows that the Fermi energy allows the $13a_1$ band to be filled with electrons only roughly half suggesting good electrical conductivity. The percentage of basis functions in the frontier a_1- and e-CO's is given in Table 2 for $k_z = 0$ and in Table 3 for $k_z = \pi/c$. The wave function of $13a_1$ for $k_z = 0$ and $k_z = \pi/c$ at the z-axis is depicted in Fig. 5.

For comparison the polymer $\mathrm{Fe^{II}TAPN^{\ominus}}$ was computed in much the same way with $c = 3.36$ Å. The analogous dimer compound $(\mathrm{Fe^{II,\,III}\text{-}TTP})_2\mathrm{N}$ is experimentally known [8] (TTP = tetraphenylporphin) with an extremely short axial Fe-N-distance of 1.66 Å [9] which is so short that the two Fe-atoms are pulled out of the TTP-planes and which can explain the impossibility to synthesize the corresponding polymer. In the hypothetical polymer $\mathrm{Fe^{II}TAPN^{\ominus}}$ the Fe-N-Fe distance was therefore increased to the normal van-der-Waals distance of two touching TTP-molecules. The corresponding band scheme is given in Figure 6.

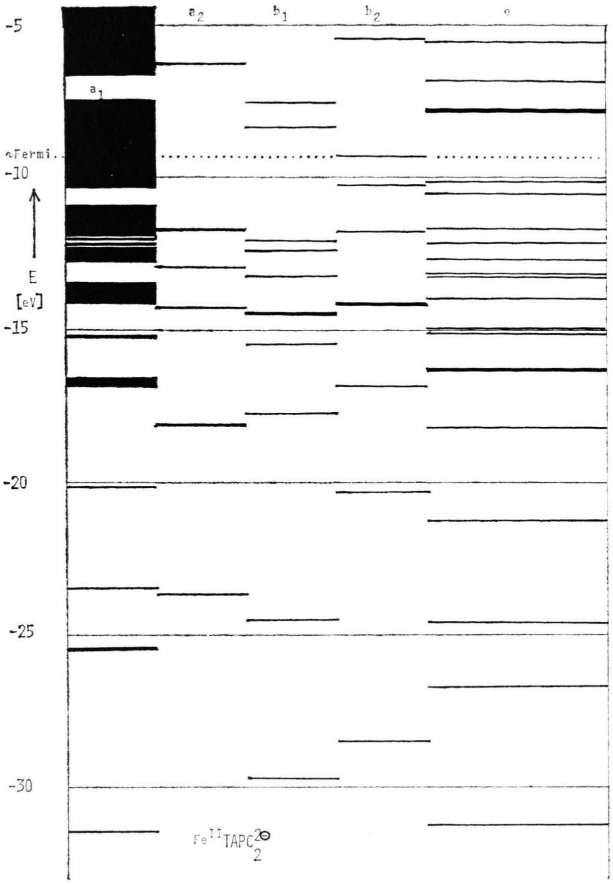

Fig. 4. Energy band scheme of $Fe^{II}TAPC_2^{2\ominus}$.

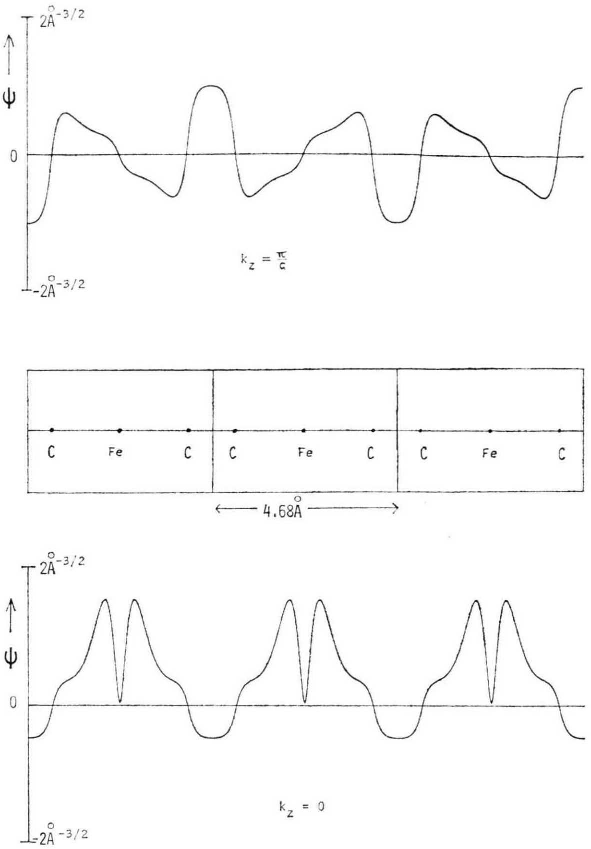

Fig. 5. Partly filled CO $13a_1$ along the z-axis for $k_z = 0$ (equal phase in adjacent unit cells) and for $k_z = \pi/c$ (alternating phase in adjacent unit cells).

Table 2. Percentages of basis functions in frontier a_1- and e-CO's of $Fe^{II}TAPC_2^{2\ominus}$ for $k_z = 0$.

Basis function	CO energy [eV] $12a_1$	$13a_1$	$14a_1$	$15e$	$16e$	$17e$
	−10.9465	−10.3212	− 5.7125	−10.5208	−10.1206	− 7.8449
H	—	0.02	—	—	—	0
sC_H	—	0.01	—	—	—	0
sC_N	—	0	—	—	—	0
sN_B	—	0.02	—	—	—	0
sN_L	—	0.07	—	—	—	0.04
sFe	—	0.99	—	—	—	—
sC_A	21.79	0.55	0.34	—	—	—
x, yC_H	—	0.20	—	—	—	0.10
x, yC_N	—	0.25	—	—	—	− 0.06
x, yN_B	—	0.05	—	—	—	0.03
x, yN_L	—	2.26	—	—	—	1.47
x, yFe	—	—	—	1.51	0.48	− 0.02
x, yC_A	—	—	—	15.40	14.18	98.43
zC_H	4.63	—	7.49	19.87	16.03	—
zC_N	1.28	—	48.90	10.13	18.66	—
zN_B	12.83	—	22.32	1.52	8.68	—
zN_L	29.40	—	20.37	—	—	—
zFe	9.95	—	− 0.01	—	—	—
zC_A	20.12	26.37	0.57	—	—	—
z^2Fe	—	69.20	—	—	—	—
xz, yzFe	—	—	—	51.57	41.96	—

C_H = C atoms connected with H, C_N = C atoms adjacent to N, N_B = N atoms bridging 5-membered rings, N_L = ligand N atoms at Fe, C_A = acetylene C atoms; x, y and z = p-orbitals; z^2, xz, yz = d-orbitals.

Table 3. Percentages of basis functions in frontier a_1- and e-CO's of $\mathrm{Fe^{II}TAPC_2}^{2\ominus}$ for $k_z = \pi/c$.

Basis function	CO energy [eV] $12a_1$	$13a_1$	$14a_1$	$15e$	$16e$	$17e$
	−11.9289	− 7.4564	− 6.6372	−10.5592	−10.1394	− 7.7373
H	—	—	− 0.02	—	—	—
$s\mathrm{C_H}$	—	—	− 0.01	—	—	—
$s\mathrm{C_N}$	—	—	− 0.02	—	—	—
$s\mathrm{N_B}$	—	—	0.02	—	—	—
$s\mathrm{N_L}$	—	—	0.99	—	—	—
$s\mathrm{Fe}$	—	—	2.12	—	—	—
$s\mathrm{C_A}$	0.31	0.15	15.59	—	—	—
$x, y\mathrm{C_H}$	—	—	0.92	—	—	—
$x, y\mathrm{C_N}$	—	—	− 0.22	—	—	—
$x, y\mathrm{N_B}$	—	—	0.30	—	—	—
$x, y\mathrm{N_L}$	—	—	15.84	—	—	—
$x, y\mathrm{Fe}$	—	—	—	—	—	—
$x, y\mathrm{C_A}$	—	—	—	3.53	1.06	92.22
$z\mathrm{C_H}$	0.64	1.23	—	15.75	13.89	1.27
$z\mathrm{C_N}$	0.01	4.12	—	20.16	15.26	0.76
$z\mathrm{N_B}$	41.58	3.07	—	10.57	18.64	0.33
$z\mathrm{N_L}$	55.16	0	—	1.53	8.84	− 0.02
$z\mathrm{Fe}$	0.63	12.29	—	—	—	—
$z\mathrm{C_A}$	1.67	79.14	18.29	—	—	—
$z^2\mathrm{Fe}$	—	—	46.22	—	—	—
$xz, yz\mathrm{Fe}$	—	—	—	48.47	42.32	5.44

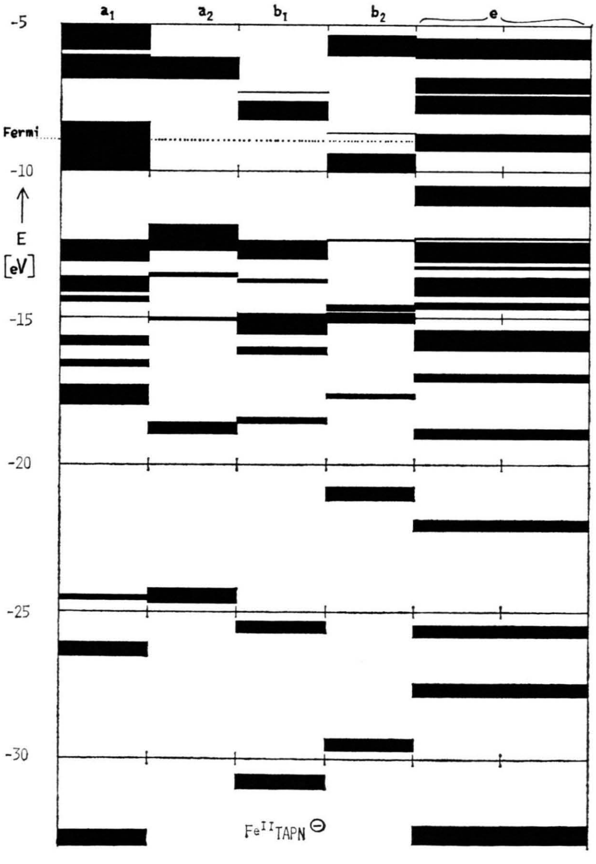

Fig. 6. Energy band scheme of $\mathrm{Fe^{II}TAPN^{\ominus}}$.

4. Discussion

Theoretical considerations were intended to serve as guidelines for the preparative efforts of our joint project on a new kind of one-dimensional conductors from the very beginning. The best method for this purpose would be without question an *ab-initio* calculation, but regarding the great number of basis functions in the fairly big elementary cell this very expensive method is prohibiting at the beginning. The simplest method just allowing for the inclusion of σ-orbitals is the extended Hückel method which was applied here as a rough theoretical means and a more qualitative rather than quantitative backbone for a search for possible realizations of the general idea. We are fully aware of all the limitations of this semi-empirical method and are just proceeding to more sophisticated approximations including explicit Coulomb and exchange interactions like CNDO or MINDO, if compatible with our computer facilities (TR 440).

The results obtained so far with the reported EH calculations were partly expected, like strong interactions and broad energy bands for the a_1- and e-species in any case, and broad energy bands for all races in case of extremely short axial ligands L causing direct interaction of the TAP or TTP components. Other results were quite unexpected especially the fact that the a_1-bonds which arise from the σ-core of L are broader than the e-bands containing the two crossed π-systems of $C_2^{2\ominus}$. Particularly the $13a_1$-CO of Fe^{II}-$TAPC_2^{2\ominus}$ which is only partly filled (because the approximate Fermi level crosses it) is almost purely built up from 69% $d_{z^2}Fe$ and 26% p_zC_A at $k_z=0$, whereas it contains 79% p_zC_A and 12% p_zFe at $k_z=\pi/c$, i.e. this most important CO is extremely concentrated at the center axis ...FeC_2FeC_2... of the one-dimensional polymer and makes virtually no use of the TAP-component.

It should be noted that partial occupation of some energy bands was solely obtained by band overlap and not by odd numbers of electrons per unit cell which could easily be achieved simply by using other transition metals. The wanted effect arose although formally at M a complete nobel gas configuration exists.

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