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Band structure of linear organometallic chains

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Abstract

A band structure of the infinite linear organometallic chain, which is considered to be the limiting case of linear metal (Cr, Co and Ni) complexes with ligands, has been investigated using the tight-binding calculation including both σ and π electrons. From the band structures, we predict the electronic properties of the organometallic chain. A linear Ni chain has a direct semiconductor gap with a narrow bandwidth for the highest occupied band, whose molecular orbital is localised on the ligand strands. On the other hand, a linear Cr or Co chain exhibits a metallic character that is dependent on the delocalised 3d orbitals.

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In recent years, there has been considerable interest in the use of extended linear structures, in which one species of elements catenate into linear chains, as a starting material for quantum nanowires [1]. It is well known that organic conducting polymers, polyacetylene and the related π-conjugated polymers possess relatively higher mobilities as compared to the other organic polymers [2]. As inorganic polymers, both polysilane and polystannane have high mobility due to the delocalised σ electrons along the polymer chain [3,4]. The applications of linear organometallic salts of tetracyanoplatinate, $Pt(CN)_4^{2-}$ (Krogmann's salt), as a one-dimensional (1D) conducting material have been studied extensively [5]. These salts have a crystal structure that contains planar platinum complexes stacked together to form parallel linear chains. When partially oxidized, these salts exhibit a metallic character with anisotropic electrical conduction. Recently, there has been considerable interest in the applications of porphyrinatometal salts with transition metals (Co and Ni) as a 1D conducting material [6,7]. These salts contain porphyrin or phthalocyanine in the form of metal-over-metal columnar stacks and possess high and anisotropic conductivities. The band structures of the salts were calculated using the tight-binding calculation [8,9]. The calculated band structure of porphyrinatonickel exhibits semiconductor properties in which the highest occupied (HO) band is formed by the atomic orbitals of the ligands. On the other hand, the band structure of porphyrinatocobalt possesses a HO band formed by a half-filled Co $3d_z^2$ band with a narrow bandwidth. These porphyrinatometal salts have a metal–metal bond length that is greater than 3.0 Å.

Peng et al. have synthesized linear metal string complexes with transition metals (Cr, Co and Ni) and ligands containing pyridine rings and amides [10]. They have extensively examined the crystal structures and the magnetic properties in detail and have observed that the bond lengths of these complexes are small – less than 2.5 Å – as compared to those of porphyrinatometal salts [6,7]. They have also investigated a theoretical model of an infinite linear Cr chain [11]. Such a linear metal chain will make it easy to prepare an anisotropic electrical conductor. Band structures of a Ni or Co chain are of interest in connection with the Cr chain. In order to investigate the electronic properties of a linear Ni or Co chain, we performed tight-binding calculations. In particular, we examined electrical conduction from the calculated band structures of the metal chain and the effect of the ligand strands on the delocalisation of the 3d electrons on the central metal chain.

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Table 1
Parameters for the bondlength

Bond	Length (Å)
Cr–Cr	2.25
Cr–N	2.05
Co–Co	2.23
Co–N	2.30
Ni–Ni	2.30
Ni–N	1.90
C–C (pyridine)	1.38
C–N (pyridine)	1.37
C–N (amide)	1.37
C–H	1.10

We adopt the tight-binding calculation including both the π-type and σ-type electrons (extended Hückel approximation in the quantum chemical terminology [12]) using the YAeHMOP program [13]. The atomic parameters (H_{ii} = orbital energy, ζ = Slater exponent) for the approximation are provided in our previous paper [14]. It has been reported that a so-called counterintuitive orbital mixing is induced when using the approximation especially in the calculations of transition metal complexes [15]. Therefore, a modified Wolfsberg–Helmholz formula was employed for the off diagonal matrix elements H_{ij} as follows:

$$H_{ij} = 1/2KS_{ij}(H_{ii} + H_{jj})$$

$$K = k + \Delta^2 + \Delta^4(1 - k); \quad k = 1.75$$

$$\Delta = (H_{ii} - H_{jj})/(H_{ii} + H_{jj})$$

with the usual notation [15]. Twenty representative wave vectors (k) were chosen from 0 to π/a (a is the unit cell length) with regular intervals, and neighbouring unit cells as far as the fifth nearest cells were considered. The geometrical representations of linear metal chains are described in Fig. 1. We refer to each of these models as a Ni chain, Co chain, and Cr chain. There are six metal atoms and four ligands in a unit cell, as shown in Fig. 1(a). One ligand contains three pyridine rings and three amides in the unit cell, and the M–N bond (M: Cr, Co and Ni) is staggered by 15° against the nearest M–N bond; here, an N atom combines directly with the next M atom. As a result, the ligand combines with the next one in the nearest unit cell. Finally, we can obtain a helix structure of four infinite ligand strands that surround the infinite central linear metal chain, as shown in Fig. 1(b). The symmetry of the unit cell is C_{4v}–$4/m$. The bond length and angles are determined by referring to the crystal structures of the ligands [16–18] and other typical organic compounds [19]. We assumed that the bond lengths between the nearest metal atoms in the Ni, Co and Cr chains are equivalent by referring to the experimental results of neutral linear metal string complexes [10]. The bond lengths are described in Table 1. Some bond angles and dihedral angles are distorted from the crystal structures of the ligands by determining the helix structures of the ligand strands.

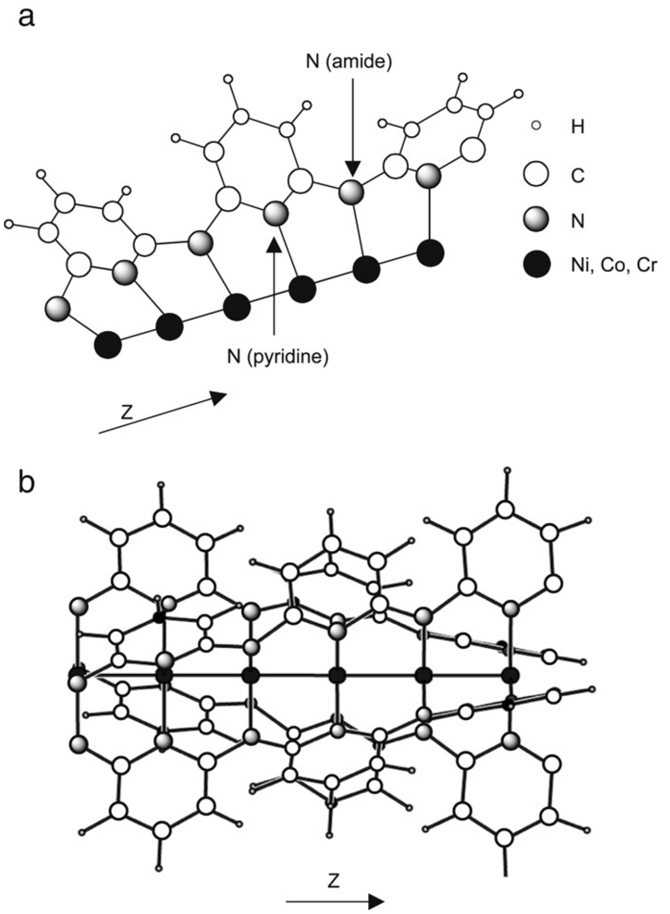

Fig. 1. Chemical structures of (a) one ligand with six metal atoms and (b) a unit cell of the linear transition metal chains.

Fig. 2(a) shows the band structure of the Ni chain. The Ni chain exhibits semiconductor properties with a bandgap of 1.52 eV, which is comparable to the calculated band structure of porphyrinatonickel [8]. As described in Fig. 2(b), the highest occupied molecular orbital (HOMO) (k = 0), next HOMO (HOMO-1) (k = 0) and HOMO-2 (k = 0) mainly consist of 2p orbitals of the ligand strands. HOMO-3 (k = 0), which is located at −11.77 eV, contains Ni $3d_z^2$ orbitals with an alternate arrangement of the phase. If p-type doping is performed in the chain, localised positive charges are simply derived at the ligands and the central linear chain does not participate in electrical conduction. The width of the lowest unoccupied (LU) band is narrow, and the molecular orbital (LUMO) (k = 0) contains Ni $3d_{x^2-y^2}$ orbitals and N $2p_z$ orbitals that exhibit an antibonding character with Ni $3d_{x^2-y^2}$ orbitals. It is considered that n-type doping may be also ineffective for electrical conduction.

Fig. 3(a) shows the band structure of the Co chain. A delocalised band of the Co $3d_z^2$ orbital traverses the Fermi level at −11.30 eV, which suggests that the chain exhibits a metallic character. The Co $3d_z^2$ electrons are extensively delocalised in contrast to those of porphyrinatocobalt [9]. This is because for a given internuclear distance, the Co $3d_z^2$ orbital of the Co chain overlaps with the next $3d_z^2$ orbital to a greater extent than that of porphyrinatocobalt. On the other hand, there are some localised bands near the Fermi level. Molecular orbitals of the localised bands consist of p orbitals of the pyridine ring. These band structures suggest that the electronic properties of the chain undergo a slight change in the oxidized or reduced state due