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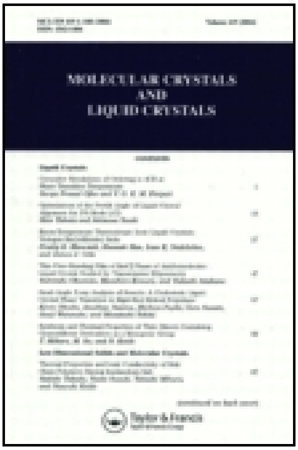

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# Charge Ordering and Lattice Modulation in Quasi-One-Dimensional Halogen-Bridged Binuclear Metal Complexes

Makoto Kuwabara [a] & Kenji Yonemitsu [a]

[a] Institute for Molecular Science, Okazaki, 444-8585, Japan

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# Charge Ordering and Lattice Modulation in Quasi-One-Dimensional Halogen-Bridged Binuclear Metal Complexes

MAKOTO KUWABARA and KENJI YONEMITSU

*Institute for Molecular Science, Okazaki 444–8585, Japan*

Ground state phase diagrams of the MMX chains are studied in a one-dimensional dimerized 3/4-filled model by exactly diagonalizing 12-site clusters. Experimentally observed phases are reproduced by changing relative strengths of an electron-lattice coupling, the inter-dimer transfer integral, and an elastic constant whose variation is roughly estimated from the interatomic spacing, the species of the halogen ions and the presence/absence of counter ions.

*Keywords:* MMX chain; dimerization; Peierls-Hubbard model

## INTRODUCTION

Competition between electron-lattice (e-l) couplings and electron-electron (e-e) interactions as well as the band filling play essential roles in manifestation of a variety of phases with spin-charge-lattice orders in many quasi-one-dimensional molecular conductors. The halogen-bridged metal complexes (MX and MMX chains) are linear chains consisting of transition-metal (M) ions bridged by halogen (X) ions and have strong e-e interactions and e-l couplings. The MX chains have a half-filled M $d_{z^2}$-band and have two kinds of ground states depending on the constituent elements [1-6]; the Mott insulator state due to strong on-site repulsion $U$ and the CDW state with lattice distortion due to the Peierls instability. Meanwhile the MMX chains possess M dimers and have a 3/4-filled M $d_{z^2}$-band, which makes the transport, magnetic and structural properties more

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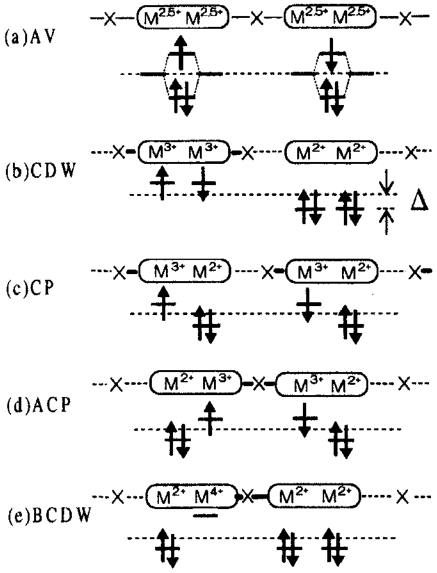

Figure 1: Schematic electronic and lattice structures of the MMX chains.

fascinating [7-14]. So far it is generally expected that there are four possible electronic states; an averaged-valence (AV) state, a charge-density-wave (CDW) state, a charge-polarization (CP) state, and an alternate-charge-polarization (ACP) state [7, 11]. These are schematically shown in Fig. 1(a-d). Recently we have found another possibility (Fig. 1(e)), which we call a bond-charge-density-wave (BCDW) state [15, 16].

Recent experiments indicate realization of above mentioned various phases. It is determined by the X-ray diffraction method that the phase of $K_4[Pt_2(pop)_4Br]3H_2O$ (pop=$P_2O_5H_2^{2-}$) is the CDW state [8]. The Raman spectra show that $Li_4[Pt_2(pop)_4I]4H_2O$ is the AV state [12]. The optical absorption experiments imply the phase of $\{(CH_3(CH_2)_7)_2NH_2\}_4[Pt_2(pop)_4I]$ to be the CP state [17]. $Pt_2(dta)_4I$ (dta=$CH_3CS_2$) is metallic above 300K and characterized by the AV state. At least below 80K, it is suggested to be the ACP state [11].

Here we study ground state phase diagrams of the MMX chains to investigate the effects of e-e and e-l interactions on the formation

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of the ordered states.

## MODEL AND METHOD

We use a one-dimensional dimerized 3/4-filled model for the M $d_{z^2}$ band with $2N$ sites;

$$\begin{aligned} H &= -\sum_{i,\sigma}^{N} t_i (c^\dagger_{a,i,\sigma} c_{b,i,\sigma} + \text{h.c.}) - \sum_{i,\sigma} t_{i,i+1} (c^\dagger_{b,i,\sigma} c_{a,i+1,\sigma} + \text{h.c.}) \\ &- \beta \sum_i (y_{a,i} n_{a,i} + y_{b,i} n_{b,i}) + U \sum_i (n_{a,i,\uparrow} n_{a,i,\uparrow} + n_{b,i,\downarrow} n_{b,i,\downarrow}) \\ &+ \frac{K_{\mathrm{MX}}}{2} \sum_i (y^2_{a,i} + y^2_{b,i}) + \frac{K_{\mathrm{MXM}}}{2} \sum_i (y_{b,i} + y_{a,i+1})^2, \end{aligned} \tag{1}$$

where $c^\dagger_{a,i,\sigma}$ ($c^\dagger_{b,i,\sigma}$) creates an electron with spin $\sigma$ at site $a$ ($b$) in the $i$-th dimer, $n_{a,i,\sigma} = c^\dagger_{a,i,\sigma} c_{a,i,\sigma}$ and $n_{a,i} = \sum_\sigma n_{a,i,\sigma}$. The unit cell consists of two M sites $a$ and $b$, forming a dimer, and an X site. The intradimer transfer integral is denoted by $t_i = t_{\mathrm{MM}}$, and the interdimer transfer integral through the X $p_z$ orbital by $t_{i,i+1} = t_{\mathrm{MXM}} - \alpha(y_{b,i} + y_{a,i+1})$, where $y_{a,i}(y_{b,i})$ is the bond length relative to that in the undistorted phase between the M site $a$ ($b$) in the $i$-th unit cell and its neighboring X site. The strengths of the site diagonal and off-diagonal e-l interactions are denoted by $\beta$ and $\alpha$, respectively. $U$ is the on-site repulsion. $K_{\mathrm{MX}}$ denotes the elastic constant between M and X, and $K_{\mathrm{MXM}}$ the interdimer elastic constant.

We exactly diagonalize the 12-site cluster with the periodic boundary condition. The electronic ground state is self-consistently determined with the static lattice distortion.

## RESULTS AND DISCUSSIONS

First, we consider the situation where counter ions force the uniform configuration of the dimers so that only the displacements of X are allowed. This corresponds to $K_{\mathrm{MXM}} = \infty$, and reduces the possible phases to AV, CDW and CP ones. In Fig. 2(a), we show a phase diagram in the space spanned by $t_{\mathrm{MXM}}$, $\beta$ and $U$. The site-diagonal e-l coupling $\beta$ brings about the Peierls transition, which favors the CDW or CP phase, whereas the on-site repulsion $U$ suppresses dou-

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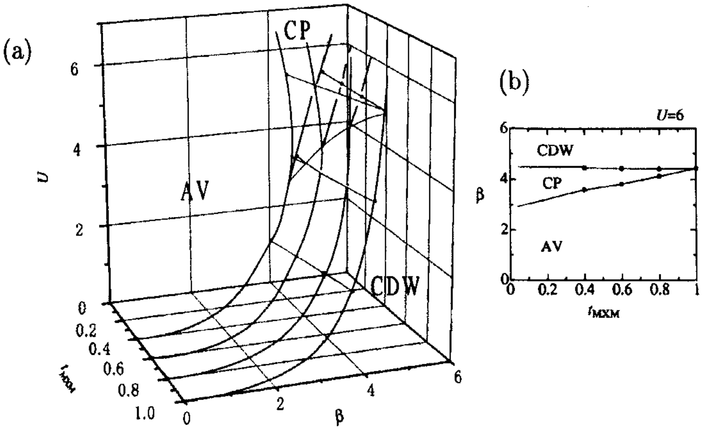

Figure 2: Ground state phase diagram (a) in the $t_{\mathrm{MXM}}$-$\beta$-$U$ space, and (b) in the $t_{\mathrm{MXM}}$-$\beta$ plane for $t_{\mathrm{MM}} = 1$, $\alpha = 0$, $K_{\mathrm{MX}} = 6$ and $K_{\mathrm{MXM}} = \infty$.

ble occupancy and thus the CDW phase. The CP phase is realized for large $U$ and small $t_{\mathrm{MXM}}$. The relative stability between the CP and CDW phases is mainly ascribed to the competition between $U$ and $\beta$. In the CP phase, the kinetic energy gain through the intradimer charge transfer is about $t_{\mathrm{MM}}^2/(2\Delta)$, where $\Delta$ is the deviation of the $d_{z^2}$ level from its position in the AV state. In the CDW phase on the other hand, it is about $t_{\mathrm{MM}}^2/U$. Thus the CP phase is relatively stable for strong $U$ and the CDW for strong $\beta$. As for the kinetic energy gain through the interdimer charge transfer, there is almost no difference. Therefore, the boundary between the CP and CDW phases is almost independent of $t_{\mathrm{MXM}}$ as seen in Fig. 2(b).

The above mentioned tendency in the phase diagram is unchanged by the presence of nearest-neighbor repulsion. Introduction of intradimer repulsion suppresses the CDW phase, resulting in the relative stabilization of the CP phase.

We compare our results with experimental ones by roughly estimating the variation of the relative parameter values from the structural data shown for several compounds in Tab. 1 [8]. Recent experiments suggest that the phases of (i) [8], (ii) [17], (iii) [17] and (iv) [11] are the CDW, CP, AV and ACP phases, respectively. Essential dif-

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| | | $l_{\mathrm{MM}}$[Å] | $l_{\mathrm{MXM}}$[Å] |
|---|---|---|---|
| (i) | $K_4[Pt_2(pop)_4Br]3H_2O$ | 2.781 | 5.357 |
| (ii) | $\{(CH_3(CH_2)_7)_2NH_2\}_4[Pt_2(pop)_4I]$ | 2.849 | 6.458 |
| (iii) | $Li_4[Pt_2(pop)_4I]4H_2O$ | 2.859 | 5.938 |
| (iv) | $Pt_2(dta)_4I$ | 2.677 | 5.956 |

Table 1: Intradimer ($l_{\mathrm{MM}}$) and interdimer ($l_{\mathrm{MXM}}$) distances between the neighboring metal atoms.

ference between (ii) and (iii) is the species of the counter ions, which results in the difference in the interdimer distances ($l_{\mathrm{MXM}}$) without affecting the intradimer distance ($l_{\mathrm{MM}}$) [17]. Therefore, $t_{\mathrm{MXM}}$ is expected to be smaller in (ii) than in (iii) because $l_{\mathrm{MXM}}$ of (ii) is larger than that of (iii). The other parameters, $U$ and $\beta$, would be almost the same. Figure 1(b) shows that the AV phase is changed into the CP phase when $t_{\mathrm{MXM}}$ gets small for intermediate $\beta$. This is consistent with the experimental result.

In the compound (i) the halogen ion is different from the others. When estimating the transfer integral, we need to take account of the $p_z$ orbitals. The interdimer transfer integral $t_{\mathrm{MXM}}$ is roughly estimated as $t_{\mathrm{MXM}} \sim t_{\mathrm{MX}}^2/|\varepsilon_{\mathrm{X}}|$, where $t_{\mathrm{MX}}$ is the transfer integral between the M $d_{z^2}$ and X $p_z$ orbitals, and $\varepsilon_{\mathrm{X}}$ is the bare level difference between these orbitals. It is generally believed that $|\varepsilon_{\mathrm{X}}|$ of Br is much larger than that of I [11]. Thus, $t_{\mathrm{MXM}}$ of (i) is expected to be small compared with (ii), although $l_{\mathrm{MXM}}$ of (i) is substantially smaller than that of (ii). The shortness of the interdimer distance makes $\beta$ large. Therefore, the essential difference of (i) from the others lies in $\beta$. Our results show that the CDW phase is stable for large $\beta$, which is consistent with the experimental result.

The compound (iv) has no counter ions, so that $K_{\mathrm{MXM}}$ is considered to be quite small. In this case, the ACP phase is stable in a wide parameter space of sufficiently large $\alpha$ [15, 16].

In summary, we have investigated ground state phase diagrams of the MMX chains in the one-dimensional dimerized 3/4-filled model by exactly diagonalizing the 12-site cluster, and found that the experimentally observed variation of the phases is understood by the relative strengths of $\beta$, $t_{\mathrm{MXM}}$ and $K_{\mathrm{MXM}}$ that depend on the interatomic spacing, the species of the halogen ions, and the presence/absence of counter ions.

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