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Halogen-Bridged Mixed-Valence Linear-Chain Complexes: Molecular Orbital Model of Electron Localization

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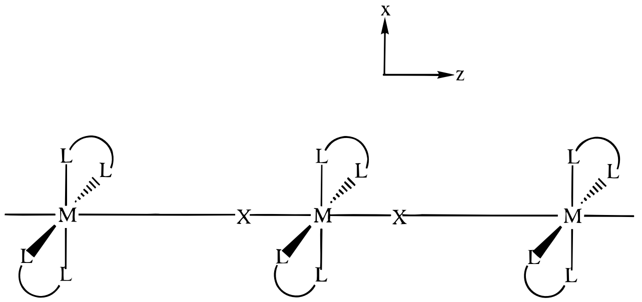
A simple tight-binding model is used to study electronic distributions and Peierls distortions in a series of mixed-valence linear-chain complexes $[M^{II}(LL)_2][M^{IV}(LL)_2X_2]$ (M = Ni, Pd, Pt; X = Cl, Br, I; LL = 1,2-diaminoethane, 1,3-diaminopropane). The calculated values of Peierls distortions for complexes with known structure are in good agreement with the experimental data. For the whole series, the model is employed as a qualitative tool to analyze structural and electronic properties. It is shown that charge disproportionation occurs in the related dimers. Thus, our quantum chemical calculations as well as previous phenomenological approaches indicate that, in metal−halogen chains, one deals with the interplay of local and cooperative effects.

Introduction

Various kinds of halogen-bridged one-dimensional $M^{II}-M^{IV}$ mixed-valence complexes of Ni, Pd, and Pt have attracted much interest regarding the chemistry and physics of low-dimensional compounds.[1,2] One important example of such chain complexes is Wolffram's red salt (WRS), $[Pt^{II}(C_2H_5NH_2)_4][Pt^{IV}(C_2H_5NH_2)_4Cl_2]Cl_4{\cdot}4H_2O$. Many complexes of the WRS kind $[ML_4][ML_4X_2]Y_4$ have been synthesized, whose chain structure is presented schematicallty as follows:



L is a neutral equatorial ligand such as NH_3, CH_3NH_2, or $C_2H_5NH_2$. Additionally, bidentate ligands LL such as 1,2-diaminoethane (en), 1,2-diaminopropane (pn), and 1,3-diaminopropane (tn) can also form complexes of this structural type.[3] Y is a counterion such as ClO_4^-, BF_4^-, or a halide.

The electronic and vibrational spectral properties of the WRS type complexes have been well documented.[2,3] Moreover, the above mentioned complexes exhibit a considerable variety of semiconducting properties correlated with the wavenumber of the symmetric $X-M^{IV}-X$ stretching vibration.[3,4] It has been clearly demonstrated that these properties are determined by the oxidation states of the metallic ions.[5,6] The latter are strongly related to the metal−halogen distances. The ratio ρ between $M^{IV}-X$ and $M^{II}-X$ distances is a key parameter measuring the distribution of electronic densities over metallic sites. As the bridging ligand changes from Cl to I, ρ approaches unity while the oxidation states become nearly trivalent. Conversely, in series of complexes with a given counterion, the $M^{II}-M^{IV}$ distance is primarily determined by equatorial amines but is less sensitive to the nature of bridging halogen.[6,7] The counterion clearly influences the chain parameters participating in hydrogen bonding and contributing to steric effects.[7,8]

The displacement of halogen atoms from the central position results in a mixed-valence state for metallic ions in the initially homogeneous chain of M^{III} ions. Similar desymmetrizing distortions in mixed-valence clusters lead to delocalization−localization transitions of "excess" electron distributions. The two-site Piepho−Krausz−Schatz (PKS) vibronic model has been applied to the unit cell of a platinum chain.[9,10] Theoretical studies based on model Hamiltonians and quantum chemical calculations have been conducted to identify the driving force which induces the off-center displacement of the halogen along the chain direction.[11−14] The main result from these studies is

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known as the Peierls theorem,[15] which states that, for a strictly 1D system, the equidistant nuclear configuration of solids with a partially filled energy band is unstable with respect to a static deformation of wave vector $\mathbf{G} = 2\mathbf{k}_F$. Such a deformation leads to an enlargement of the unit cell and introduces a gap into the single-particle energy spectrum at the new Brillouin-zone boundaries. Corresponding phonons are coupled with band electrons at the Fermi surface, thereby lowering their energy below the energy gap.[16] The deformation proceeds until limited by the increase of elastic energy which within the harmonic approximation is quadratic in the distortion.[17] The Peierls distortion can be considered as the extended system analogue of the molecular Jahn−Teller effect.[18] However, numerous studies of mixed-valence linear-chain complexes based on the Peierls−Hubbard Hamiltonian do not include the features of electronic and molecular structures of real compounds. A tight-binding scheme was used[11] to elucidate some of the behavior characteristics of the mixed-valence chain complex $[Pt^{II}(NH_3)_4][Pt^{IV}(NH_3)_4Cl_2]^{4+}$. In particular, the stability of the band formed mainly from the d_{z^2} orbital of Pt^{III} (d^7) and the p_z orbital of the bridging halogen against distortions was studied. *Ab-initio* calculations were also performed for a $Pt_2Br_6(NH_3)_4$ crystal.[14] It was shown that if one neglects the equatorial ligands, the dimerization in the metal−halogen chain cannot be reproduced.

Since many new compounds of this type have been synthesized and structurally characterized, it is possible to make a comparative analysis of valence disproportionation in compounds with different metals and bridging halogen atoms. We will be concerned here with two families of compounds with en and tn as equatorial bidentate ligands, respectively. Metal-alternated mixed-valence complexes have also been reported in the literature,[5a,6,19−21] but they will not be studied here.

Description of the Model: The Tight-Binding Scheme

As in a previous study,[11] we will use the extended Hückel band structure calculations which were found quite reliable to address organic and inorganic structural problems.[22,23] Recently, we showed that the simple Hückel type model containing only metal d states and ligand p states can describe localization−delocalization transitions in dimeric and trimeric mixed-valence iron−oxygen clusters.[24,25] As was shown earlier,[11] the d_{z^2} band in chain complexes undergoes the most significant changes under axial distortions of bridging ligands. This is why we limit the metal basis set to nd functions ($n = 3-5$ for Ni, Pd, and Pt, respectively). Also, only the n'p functions ($n' = 3-5$ for Cl, Br, and I, respectively) were taken into account for halogen atoms since corresponding n's functions lie much lower in energy. The diagonal matrix elements and orbitals exponents are presented in Table 1; a modified Wolfsberg−Helmoltz formula[26] was used to calculate off-diagonal matrix elements.

Table 1. Atomic Parameters[a]

μ	ζ_μ	ζ_ν	$H_{\mu\nu}$ (eV)
Ni 3d[b]	6.785 (0.6462)	2.359 (0.5504)	−10.05
Pd 4d[c]	5.983 (0.5535)	2.613 (0.6701)	−10.51
Pt 5d[d]	6.013 (0.6333)	2.696 (0.5512)	−11.26
Cl 3p	1.733		−14.20
Br 4p	2.131		−13.10
I 5p	2.322		−12.70
C 2s	1.625		−21.40
C 2p	1.625		−11.40
N 2s	1.950		−26.00
N 2p	1.950		−13.40
H 1s	1.300		−13.60

[a] The values for the d orbitals are given as a linear combination of two Slater type functions, and each is followed in parentheses by the weighting coefficient. [b] Reference 27. [c] Reference 28. [d] Reference 29.

Table 2. Geometrical Parameters[a,b]

	LL = en	LL = tn
$M^{II}-M^{IV}$ (Å)	5.35	5.60
M−N (Å)	2.06, 2.03	2.06, 2.03
N−M−N (deg)	82.0	82.0

[a] LL molecules are arranged such that the chain has C_2 site symmetry. [b] Note that the metal−equatorial ligand nitrogen bonds are not exactly the same in length.

The metal−metal and metal−nitrogen distances as well as the N−M−N angles employed in our calculations are summarized in Table 2. Our goal was to qualitatively describe the valency disproportionation in series of chains with different metals and halogens. Therefore, we neglected the influence of counterions which was shown to modulate metal−metal distances.[8] Since the X-ray structures of calculated complexes were not all available, we took the average parameters for en and pn complexes with known structures.[6] As mentioned previously, within the bare chains the metal−metal distances are mainly determined by the nature of equatorial ligands. Thus, we assume that these values will not undergo significant changes for any other combination of metal, halogen, and ligand. Our simplifications concerning the geometry are rather crude, but they allow us to study within the same approximations the series of compounds including those which are not experimentally characterized. The geometries of the equatorial ligands were optimized through *ab-initio* SCF type calculations. Then, molecular orbitals were constructed separately using the extended Hückel method. Six of them were selected on the basis of their energies. Moreover, only the metal−halogen and metal−nitrogen nearest neighbor interactions were taken into account and interactions with metal *n*d functions were limited to 2p nitrogen functions. Direct metal−metal bondings were neglected in agreement with the relatively high metal−metal experimental distance.

In the next section, we will study and compare the stabilities of ideal symmetric chains against halogen displacements involving dimerization of the lattice unit. The total energies for a given wave vector are approximated as a sum of one-electron energies. Then, the energy per unit cell is calculated using numerical integration within the Brillouin zone. The usual Mulliken definition for atomic charge is used to examine the charge redistribution process.

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Table 3. Calculated Equilibrium Displacements ΔR_{eq}, Energy Barriers ΔE, and Electronic Charges Z on Metal Centers[a] for Chain Compounds with LL = en

		Cl	Br	I
Ni	ΔR_{eq} (Å)	0.38	0.32	0.24
	ΔE (eV)	0.049	0.053	0.035
	Z	8.24, 6.53 (7.37)	8.16, 6.66 (7.39)	8.05, 6.79 (7.41)
Pd	ΔR_{eq} (Å)	0.37	0.28	0.17
	ΔE (eV)	0.12	0.096	0.040
	Z	8.29, 6.70 (7.46)	8.18, 6.90 (7.51)	8.03, 7.08 (7.55)
Pt	ΔR_{eq} (Å)	0.31	0.22	0.14
	ΔE (eV)	0.12	0.076	0.028
	Z	8.43, 7.09 (7.74)	8.29, 7.34 (7.80)	8.15, 7.52 (7.82)

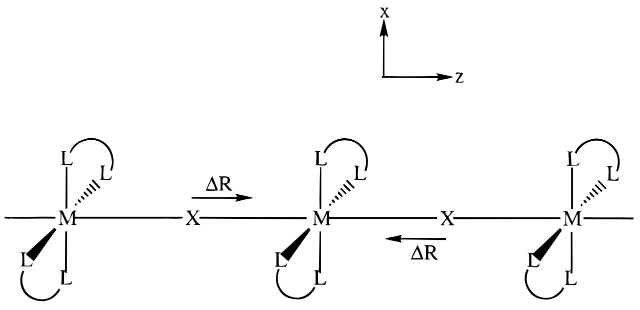
[a] The charge for $\Delta R = 0$ ("ideal chain" geometry) is given in parentheses to stress charge disproportionation.

Table 4. Calculated Equilibrium Displacements ΔR_{eq}, Energy Barriers ΔE, and Electronic Charges Z on Metal Centers for Chain Compounds with LL = tn

		Cl	Br	I
Ni	ΔR_{eq} (Å)	0.36	0.39	0.34
	ΔE (eV)	0.016	0.049	0.051
	Z	8.23, 6.51 (7.36)	8.22, 6.57 (7.37)	8.16, 6.65 (7.38)
Pd	ΔR_{eq} (Å)	0.40	0.38	0.28
	ΔE (eV)	0.10	0.15	0.14
	Z	8.31, 6.65 (7.45)	8.27, 6.79 (7.49)	8.22, 6.88 (7.52)
Pt	ΔR_{eq} (Å)	0.40	0.32	0.25
	ΔE (eV)	0.13	0.15	0.095
	Z	8.49, 7.02 (7.73)	8.42, 7.21 (7.78)	8.33, 7.35 (7.81)

Results and Discussion

Since we were dealing with three different metallic atoms, three different halogen ions, and two different equatorial bidentate ligands, eighteen halogen-bridged chain compounds were studied. Within the framework of our approximations, we were also concerned with the stability of the hypothetical corresponding dimers of general formula $[X-M(LL)_2-X-M(LL)_2-X]^{3+}$. For the sake of simplicity, we neglected the displacements of the metal atoms and considered only the stretching distortions of metal−halogen bonds. Therefore, the C_2 symmetry of chains and dimers was retained throughout the calculations. We also supposed that upon electron trapping the two M−X distances for a given metallic center are exactly the same in length. So, only one parameter, namely ΔR, is needed to describe the stretching distortion. ΔR_{eq} refers to the estimated equilibrium geometry.



The calculated metal−halogen distances and metal charges in symmetric and equilibrium geometries are summarized in Tables 3 and 4. For all complexes, we find a Peierls-distorted version of the symmetric chain. The band formed mainly from the d_{z^2} orbital of M^{III} (d^7) and the p_z orbital of the bridging halogen is half-filled, and under distortion, this band splits into a filled valence band (mainly M^{II} in character) and an empty conduction band (mainly M^{IV} in character).[11] The dependence of the total energy per unit cell on ΔR is a two-minimum curve (Figure 1). For any set of metal and equatorial ligand, the ΔR_{eq} value changes in the order Cl > Br > I (i.e., ρ increases, approaching unity), in agreement with the experimental observations. For some complexes with known structures, our simple model gives metal−halogen distances close to the experimental ones. Indeed, X-ray and EXAFS studies give $\Delta R = 0.38$ Å for $[Pt^{II}(en)_2][Pt^{IV}(en)_2Cl_2]^{4+}$,[6] $\Delta R = 0.20$ Å for $[Pt^{II}(en)_2][Pt^{IV}(en)_2I_2]^{4+}$,[30] 0.35 Å for $[Pd^{II}(en)_2][Pd^{IV}(en)_2Cl_2]^{4+}$, 0.22 Å for $[Pd^{II}(en)_2][Pd^{IV}(en)_2Br_2]^{4+}$,[6] and 0.30 Å for $[Ni^{II}(en)_2][Ni^{IV}(en)_2Cl_2]^{4+}$.[5c]

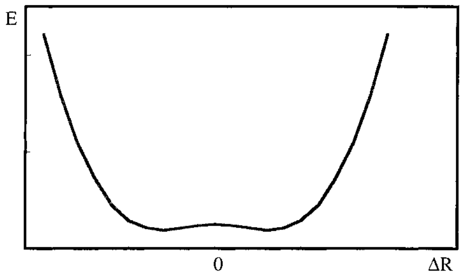


Figure 1. Total energy (eV) per $[ML_4][ML_4X_2]^{4+}$ unit as a function of ΔR (Å).

The lack of structural information did not allow us to compare the variation of ΔR_{eq} in the Ni, Pd, Pt sequence with experimental data. Apart from the case of $[Ni^{II}(tn)_2][Ni^{IV}(tn)_2Cl_2]^{4+}$, the order Ni > Pd > Pt was found. In terms of orbital interactions, this behavior correlates with the increasing intersite interactions as orbitals are constructed from high quantum numbers. The smaller the intersite coupling, the greater the gain of energy due to distortion. According to the phenomenological theory of mixed-valence chain compounds, distortion leads to electron localization. However, the conductivity and intervalence band measurements suggest that the degree of delocalization changes in the order Ni > Pd > Pt. But the simple correlation between the delocalization properties and ΔR_{eq} may not be valid, since a large number of wave vector dependent levels are taken into account. If we consider the energy barrier ΔE between the two "localized" geometries (the activation barrier for electron transfer), in almost all cases, the lowest values are obtained for Ni compounds (see Tables 3 and 4). The small stabilization energy of distorted Ni chains may be related to the existence of undimerized isomers.[5c,31] Both the geometric parameters and energetic factors must be taken into account to properly depict the physical properties of mixed-valence systems.

Our model can also be used to evaluate the charges on the different atoms and ligands of the unit cell. Let us consider the studied halogen-bridged chain compounds as a regular sequence of M^{IV} ions with two "excess" electrons per unit cell. In the process of geometry relaxation, only part of this "excess" charge density is redistributed. This phenomenon was described elsewhere[24,25] for Fe(II)−Fe(III) mixed-valence clusters. Similar conclusions can be drawn for systems with two "excess" electrons: the usual terminology "electron localization−delocalization" is somehow approximate. Nevertheless, the charge value at $\Delta R = 0$ is very close to the mean value of charges at the equilibrium geometry (estimated for $\Delta R = \Delta R_{eq}$), indicating that the bridging halogen is not involved in charge reorganization. Moreover, the charge disproportionation decreases as the size of the bridging halogen increases, which is in perfect agreement with experimental data.

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Table 5. Calculated Equilibrium Displacements ΔR_{eq}, Energy Barriers ΔE, and Electronic Charges Z on Metal Centers for Dimeric Complexes with LL = en

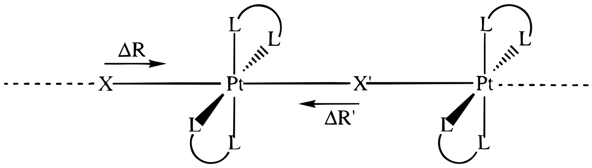
		Cl	Br	I
Ni	ΔR_{eq} (Å)	0.40	0.34	0.29
	Z	8.27, 6.51 (7.37)	8.23, 6.60 (7.40)	8.16, 6.70 (7.42)
Pd	ΔR_{eq} (Å)	0.39	0.31	0.23
	Z	8.32, 6.68 (7.47)	8.27, 6.83 (7.53)	8.21, 6.95 (7.57)
Pt	ΔR_{eq} (Å)	0.33	0.26	0.18
	Z	8.49, 7.06 (7.75)	8.42, 7.26 (7.82)	8.30, 7.45 (7.87)

Table 6. Calculated Equilibrium Displacements ΔR_{eq}, Energy Barriers ΔE, and Electronic Charges Z on Metal Centers for Dimeric Complexes with LL = tn

		Cl	Br	I
Ni	ΔR_{eq} (Å)	0.39	0.41	0.36
	Z	8.26, 6.48 (7.36)	8.25, 6.55 (7.38)	8.23, 6.61 (7.39)
Pd	ΔR_{eq} (Å)	0.48	0.41	0.30
	Z	8.34, 6.64 (7.45)	8.32, 6.77 (7.50)	8.29, 6.84 (7.53)
Pt	ΔR_{eq} (Å)	0.41	0.35	0.29
	Z	8.52, 7.01 (7.74)	8.49, 7.17 (7.80)	8.45, 7.29 (7.85)

To clarify the origin of charge disproportionation, we also studied the related hypothetical dimer compounds of general formula $[X{-}M(LL)_2{-}X{-}M(LL)_2{-}X]^{3+}$. The charge of the dimers corresponds to two trivalent metallic ions. Other dimeric elementary units could have been chosen to reproduce the chain primitive cell; however, a center of symmetry is required to start with a symmetric complex which might undergo charge redistribution. Few examples of two-electron difference dimeric mixed-valence complexes are known in the literature.[32,33] Surprisingly, the symmetric geometry of all complexes was found unstable against asymmetric displacements of axial ligands. The potential surface has again two minima (Figure 1). Tables 5 and 6 summarize the ΔR_{eq} values and associated charges estimated within the same framework of approximations. Besides the similarities of ΔR_{eq} evolutions, one should note that these values are close to the ones calculated for the infinite-chain compounds. It follows that disproportionation is apparently settled down in a dimer and is not significantly sensitive to the collective effect of electron–phonon interaction. This may be the reason that using a two-site approach yields a reasonable description of spectral properties for infinite mixed-valence chains.[8] It has already been noted[13a] that only the electron–phonon interaction leading to the Peierls instability cannot explain all the properties of the CDW (charge density wave) state in metal–halogen chains. The intersite electron–electron interaction must be considered. In our case, we also need some kind of intersite interaction to construct the CDW state from vibronically disproportionated dimers. There is no doubt that more sophisticated quantum calculations taking into account interelectronic interaction would be useful to elucidate the driving forces of charge disproportionation.

Mixed-valence mixed-halogen systems $[Pt^{II}(en)_2][Pt^{IV}(en)_2X_{2-z}X'_z]^{4+}$ ($0 \leq z \leq 1$) have been repored.[34–37] The structure of these systems is still questioned, but most recent NMR experiments suggest the presence of X–Pt–X′ units randomly distributed along the chain.[37] Within the framework of our model, calculations were performed for regular alternating-halogen chains $[Pt^{II}(en)_2][Pt^{IV}(en)_2XX']^{4+}$ whose unit cell is shown in the following diagram:



The values of bridging atom displacements (ΔR, $\Delta R'$) (Å) for the different halogen couples are as follows. Cl, Br: 0.26, 0.21. Cl, I: 0.18, 0.11. Br, I: 0.18, 0.14. One can see that the dissymmetry in bridging ligands leads to smaller displacements from central positions than for single halogen chains. The alternation of halogens lifts the degeneracy at the edge of Brillouin zone, and instead of first-order Peierls distortion, the system undergoes second-order Peierls distortion.[38]

Conclusion

Using the tight-binding model, we were able to provide new insights into the intramolecular electron transfer and accompanying distortions in infinite-chain mixed-valence compounds. The results agree with the Peierls theorem, which states that a one-dimensional system with a less than half-filled band undergoes a distortion increasing the lattice unit cell. In spite of its approximate character, the model provides information which cannot be found in phenomenological theories. The relation between structure and delocalization properties is not straightforward when real electron band structure is considered. Even though the calculated absolute energies cannot be used in physical arguments, the qualitative influence of bridging ligand displacements on intercenter and vibronic interactions is taken into account. An interesting question arises as to whether charge disproportionation already exists in a dimer due to the relation between electronic and vibronic interactions and does not require the fulfillment of the Peierls theorem conditions.

The model can be extended to systems with alternating metal centers. In particular, elucidation of the effect on the band gap and the bandwidths may require more extensive theoretical work.

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