Electronic Supplementary Information

Predominance of Covalency in Water-Vapor-Responsive MMX-Type Chain Complexes Revealed by ^{129}I Mössbauer Spectroscopy

Hiroaki Iguchi,[*,a,b] *Shinji Kitao,*[c] *Makoto Seto,*[c] *Shinya Takaishi,*[a,b] *and Masahiro Yamashita,*[*a,b]

[a]Department of Chemistry, Graduate School of Science, Tohoku University, 6-3 Aramaki-aza-aoba, Aoba-ku, Sendai 980-8578, Japan

[b]Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Agency (JST), 4-1-8 Kawaguchi, Saitama 332-0012, Japan

[c]Research Reactor Institute, Kyoto University, Kumatori, Sennan, Osaka 590-0494, Japan

Analysis of ^{129}I Mössbauer Spectra.

In the Mössbauer spectroscopy, the energy of γ-ray is controlled by changing the relative velocity of the source. The difference between the nuclear transition energy of the source and that of the absorber is called isomer shift (IS) and is customary denoted by the relative velocity to ZnTe source. IS is known to be expressed by the following empirical equation:[S1]

$$\mathrm{IS} = -9.2h_\mathrm{s} + 1.5h_\mathrm{p} - 0.54 \quad (1)$$

where h_s and h_p are the hole numbers of the s and p shells, respectively. In this study, since the s electron of iodide ion does not contribute to the Pt–I bond, we can assume that the $h_\mathrm{s} \approx 0$. Therefore, the charge on the ^{129}I calculated from IS (ρ_IS) is given by the following equation.

$$\rho_\mathrm{IS} = h_\mathrm{p} - 1 = \frac{\mathrm{IS} + 0.54}{1.5} - 1 \quad (2)$$

The other parameter available from Mössbauer spectroscopy is the quadrupole coupling constant (QCC), which is a direct measure of the electric field gradient (EFG) at the iodine nucleus. The QCC is related to the electric quadrupole hyperfine interaction between the nucleus and the electrons. Because the nuclear spins of the excited state (I_e) and the ground state (I_g) of ^{129}I are 5/2 and 7/2, respectively, and the selection rule is $\Delta I = 1$, $\Delta m_I = 0, \pm 1$, totally eight transitions are allowed. The following equation has been known for nuclear quadrupole resonance data:[S1]

$$U_\mathrm{p} = h_z - (h_x + h_y)/2 = -\mathrm{QCC}/2293\ MHz \quad (3)$$

where U_p is the difference between the populations of iodine 5p$_z$ orbitals and the 5p$_x$ and 5p$_y$ orbitals, and is sometimes referred to as the p-electron imbalance, and h_n ($n = x, y, z$) is the hole number of the p_n orbitals. All QCC values shown in this paper are customarily converted to the equivalent ^{127}I values. The s electron has no effect on the QCC value because the electron density is spherically symmetrical. In this study, an iodine atom has σ-bonding character but no π-bonding character, indicating that $h_x = h_y = 0$ is valid. Therefore the charge on the ^{129}I calculated from QCC (ρ_{QCC}) is given by the following equation.

$$\rho_{\mathrm{QCC}} = h_z - 1 = U_{\mathrm{p}} - 1 = -\{1 + \mathrm{QCC}/2293\} \quad (4)$$

Validity of the High ρ_{IS} under the Predominance of Covalent Interaction.

The existence of covalent interaction means that the s electron of iodide ion somewhat contributes to the Pt–I bond and our assumption that $h_{\mathrm{s}} \approx 0$ is not correct. However, as is clear from equation 1, if IS is constant and $h_{\mathrm{s}} > 0$, the h_{p} should be larger than that calculated on the assumption that $h_{\mathrm{s}} \approx 0$. Hence, the true ρ_{IS} ($= h_{\mathrm{s}} + h_{\mathrm{p}} - 1$) of each complex should be smaller than the ρ_{IS} in Table 1. In other words, the ρ_{IS} is underestimated by the assumption that $h_{\mathrm{s}} \approx 0$. Therefore, the small ρ_{IS} in MMX chains with binary countercations are effective even if h_{s} is larger than 0.

Relationship between QCC and IS.

It has been known that a linear relationship exists between the IS and QCC values for the series of the iodide anion (I^-), iodine (I^0), and the iodine cation (I^+).[S1] Kobayashi et al. reported that iodide ions in MMX chains follow this linear IS–QCC relationship.[S2] They also found that dta and pop systems seem to follow different IS–QCC relationships as shown in the linear approximation (dashed and solid lines) in Figure S1. However, the present complexes, which are shown in red solid circles in Figure S1, do not follow the IS–QCC relationship in the pop system. These smaller absolute QCC values should be derived from the arrangement of the negative- and positive-charged layer as discussed in main manuscript and Figure 4. Especially, the IS–QCC relationships of **1·4H$_2$O**, **1** and **2** are close to the guide shown as the dashed line in Figure S1. This indicates that the electric field gradient (EFG) at the iodine nucleus is close to that in the series of dta system, whereas **1·4H$_2$O**, **1** and **2** did not form ACP state, which is common state in the dta system. This strongly supports the fact that the charge on the iodide ion should be calculated from IS but not from QCC.

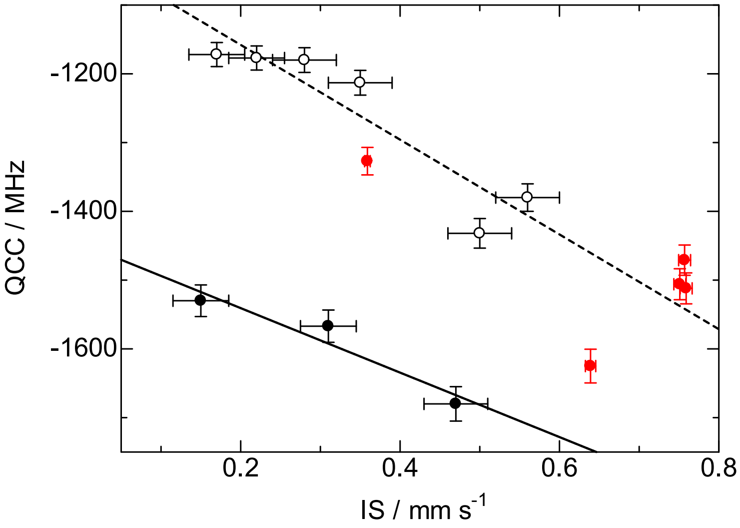

Figure S1. IS-QCC correlation diagram of MMX chains based on Table 1 in the main text. reported dta system, pop system and the pop system with binary countercations (**1·4H$_2$O, 2·4H$_2$O** and their dehydrated complexes) are shown in black open circle, black solid circle, and red solid circle, respectively. Solid and dashed lines represent guides for the pop and dta systems, respectively.

Reference in the Electronic Supplementary Information

(S1) R. V. Parish, in *Mössbauer Spectroscopy Applied to Inorganic Chemistry*, *Vol. 2*, ed. G. J. Long, Plenum, New York, 1984, ch. 9.

(S2) A. Kobayashi, S. Kitao, M. Seto, R. Ikeda, H. Kitagawa, *Inorg. Chem.*, 2009, **48**, 8044–8049