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Molecular-Orbital Calculation on the Neutral Mixed-Valent Platinum Complex $[Pt^{II}Cl_2(en)][Pt^{IV}Cl_4(en)]$

Tokutaro Komatsu [a] & Norimichi Kojima [a]

[a] Department of Basic Sciences, Graduate School of Arts & Sciences, University of Tokyo, Komaba 3-8-1, Meguro-ku, Tokyo, 153-8902, Japan

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Molecular-Orbital Calculation on the Neutral Mixed-Valent Platinum Complex $[Pt^{II}Cl_2(en)][Pt^{IV}Cl_4(en)]$

TOKUTARO KOMATSU and NORIMICHI KOJIMA

Department of Basic Sciences, Graduate School of Arts & Sciences, University of Tokyo, Komaba 3–8–1, Meguro-ku, Tokyo 153–8902, Japan

The character of the photo-induced metastable state is investigated via molecular-orbital calculation. The anisotropic g-factor and the hyperfine coupling constants are simulated based on the extended-Hückel calculation. The most plausible environment around the metastable Pt^{III} is found to be a spin-soliton like state, whose spin-orbital mainly comprises one platinum and one chlorine atoms. The vibration mode of the elemental unit of the complex is calculated for both high- and low-temperature structures employing a density-functional method.

Keywords: mixed-valent complex; platinum complex; non-linear excitation; extended Hückel calculation; density-functional method

INTORODUCTION

One-dimensional halogen-bridged mixed-valence platinum complexes have extensively been studied to clarify the nature of the mixed-valent electronic state. In these systems, the strong electron-phonon coupling stabilizes the alternation of the Pt^{II} and Pt^{IV} sites, via the relaxation of the bridging halogen atom. The mismatch of the valence alternation in these complexes can be regarded as non-linear excitations such as kink-solitons and polarons.

In $[Pt^{II}Cl_2(en)][Pt^{IV}Cl_4(en)]$ (en=ethylenediamine, abbreviated as PEC), the non-linear excitation produced by a UV-VIS irradiation

has been studied by optical[1] and ESR[2] measurements. The observation of ESR signal revealed that the non-linear excitation is such as spin-soliton or polaron, which contain paramagnetic Pt^{III}. The non-linear excitation has a long lifetime below 200 K, where a freezing of the puckering motion of the ethylene group has been confirmed by X-ray[3] and NMR[4] measurements. In addition, the degree of the zigzag distortion of $Pt^{II}..Cl..Pt^{IV}$ chain increases at 200 K.

To clarify the character of the metastable state, we simulated the anisotropic g-factor and the hyperfine coupling constants based on the extended-Hückel calculation. Also the electronic state and the vibration mode are analyzed by a density-functional method, using Gaussian 98[5]. The origin of the persistent non-linear excitation is discussed based on the low-temperature and the high-temperature crystal structure.

RESULTS

Extended-Hückel Calculation

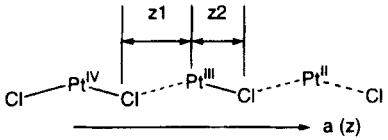
The model structure for the ESR-parameter simulation is shown in Fig. 1. The parameters are summarized in Tab. 1. For the intuitive comprehension of the orbital character, the z direction is assigned to the chain axis. The x and y axes roughly correspond to the c- and b-axes, respectively. Since the only difference between the Pt^{II} and Pt^{IV} sites is the z-coordination of the bridging chlorine atom, the Pt^{III} site is modeled by regarding the z-coordination as the adjustable parameter. Following spin-orbit coupling constants (ζ) and isotropic and anisotropic hyperfine coupling constants (A_F and $A_{d,p}$) are used: $\zeta(Pt)=1000$, $\zeta(Cl)=586$ cm^{-1}, $A_F(Pt)=2000$, $A_{d,p}(Pt)=10$, $A_F(Cl)=167.2$, $A_p(Cl)=5.1$ mT. Figure 2 shows the angular dependence of the best simulation of the g-factor, as well as the observed ones. The z-coordinate of the best model structure is given in Figure 1.

The band structure of the frontier orbitals is calculated for an

isolated chain, as the transverse interaction was negligibly small. The calculated energy dispersion along the chain direction is given in Figure 3, for both RT and 195 K. The band parameters are listed in Table 2.

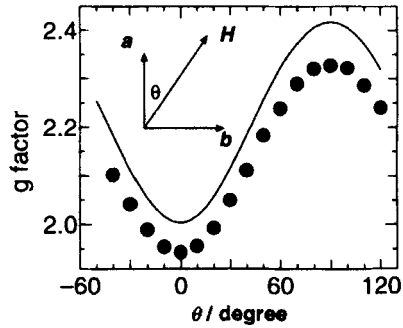
TABLE 1 The ESR parameters of $[Pt^{II}Cl_2(en)][Pt^{IV}Cl_4(en)]$ with the magnetic field parallel and perpendicular to the one-dimensional chain. . The experimental values are taken from Ref [2]. The hyperfine coupling constants are calculated for ^{195}Pt and ^{35}Cl. and given in mT.

	g//	g⊥	A_{Pt}//	$A\perp_{Pt}$	$A//_{Cl}$	$A\perp_{Cl}$
obs.	1.94	2.34	----	41.6 mT	6.5 mT	~0 mT
calcd.	2.003	2.418	62 mT	40.5 mT	1.77 mT	>0.25 mT



z1 = 0.28
z2 = 0.22

FIGURE 1 The model structure that gave the best simulation of the ESR parameters. The z-coordinates are given for doubled a-axis. For Pt^{IV} and Pt^{II}, they are z1 = z2 = 0.212 and z1 = z2 = 0.288, respectively.



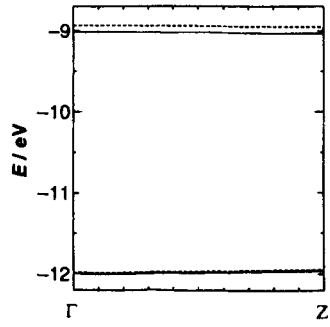


FIGURE 2(left) The angular dependence of the calculated g factor (solid line). Experimental values taken from Ref [2] are plotted with closed circles.

FIGURE 3(right) The energy dispersion of the HOMO and LUMO bands. Solid and dotted lines indicate those at RT and 195 K, respectively.

TABLE 2 The calculated band parameters. Energies are given in eV.

temperature	Eg	HOMO band width	LUMO band width
RT	2.93	0.04	0.02
195 K	2.99	0.04	0.02

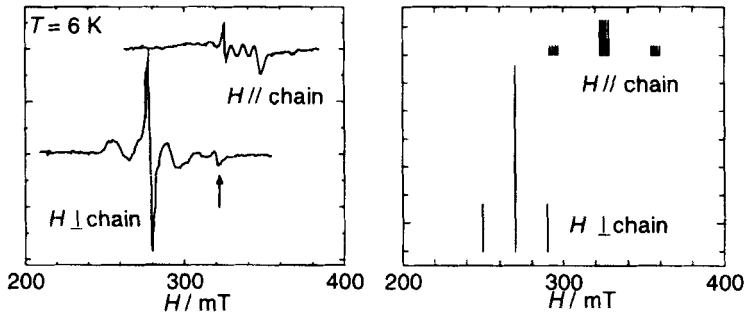


FIGURE 4 The observed (left) and simulated (right) ESR spectra of $[Pt^{II}Cl_2(en)][Pt^{IV}Cl_4(en)]$ [1]. The arrow indicates the signal of the quartz tube used as a sample holder.

Molecular-Vibration

The molecular vibration is calculated on one unit of $[Pt^{II}Cl_2(en)][Pt^{IV}Cl_4(en)]$. CEP-121G basis set and B3LYP hybrid functional is applied on the molecular structure obtained by x-ray structure analysis[3]. The vibronic mode that can be related to the intervalence charge transfer from Pt^{II} to Pt^{IV} is listed in Table 3.

TABLE 3 The vibration-modes including the axial displacement of the bridging Cl atoms.

	Cl ------- Pt^{IV} ------ Cl --------- Pt^{II} --------- Cl →z1 →z2 →z3 →z4 →z5		
mode	temperature	frequency(cm^{-1})	(z1, z2, z3, z4, z5)
1	RT	27.1	(0.14, 0.15, 0.16, -0.13, -0.23)
	195 K	28.6	(0.14, 0.15, 0.16, -0.14, -0.25)
2	RT	343.9	(-0.62, -0.03, 0.73, -0.01, 0.05)
	195 K	349.0	(-0.62, -0.03, 0.72, -0.01, 0.05)
3	RT	414.7	(0.57, -0.16, 0.43, 0.0, 0.0)
	195 K	419.8	(0.56, -0.16, 0.43, 0.0, 0.0)

DISCUSSION

Simulation of ESR Parameters

No parameter sets for polaron-type configuration, in which the coordination around Pt^{III} is symmetric, could provide even a qualitative reproduction of the experimental ESR parameters. Hence, the Pt^{III} site is deduced to have an asymmetric soliton-type configuration. Among various parameter sets, those given in Figure 1 gave the most plausible g-factors and hyperfine-splitting pattern, as shown in Figs. 2 and 4. Although the simulated hyperfine splitting due to chlorine atom is rather small, the other ESR parameters are successfully emulated.

For the structure in Figure 1, the singly-occupied molecular orbital is mainly constituted by the d_{z2} orbital of Pt^{III} and p_z of the Cl atom that the shortest bond length with the Pt^{III} atom.

Band Calculation

The energy gap (E_g) between the HOMO- and LUMO bands is a direct one situated at the Z-point. The band structures are almost the same for RT and 195 K, except for the slight increase of E_g at 195 K. The magnitude of E_g is larger than the experimental value (2.11 eV) obtained by the UV-VIS spectra measurement [1]. At Z-point, the dominant orbital characters of HOMO and LUMO are $d_{z2}(Pt^{II})$-$p_z(Cl)$ antibonding and $d_{z2}(Pt^{IV})$-$p_z(Cl)$ antibonding, respectively. Thus, the lowest-energy optical transition corresponds to the charge transfer from Pt^{II} to Pt^{IV}. The dispersions of both bands are negligible. Therefore, PEC can be regarded as a simple ionic crystal at the ground state, where electron-transfer interaction is not significant.

Molecular-Vibration

The modes 1 and 2 correspond to the axial compression of Pt^{II} site and the axial elongation of the Pt^{IV} one, respectively. Considering the coordination environment of Pt^{II} and Pt^{IV}, the mode 1 can couple to the oxidation of Pt^{II}. Conversely, the mode 2 corresponds to the reduction

of Pt^{IV}. For both modes, a slight shift of the frequency is obtained for different temperatures, *i.e.*, the vibronic modes are stiffened at 195 K. Even though the difference is small, this result may pour light on the origin of the persistent metastable state. Since the hopping of charge along the chain is inevitable to the recombination of two Pt^{III} sites, the stiffening of the vibronic mode should affect the relaxation rate.

CONCLUSION

The ESR parameters of the metastable state in PEC were simulated for trinuclear model complex, varying the position of the bridging chlorine atom. The best qualitative simulation was obtained from a spin-soliton configuration. The band calculation showed that the lowest optical excitation corresponds to the charge transfer from Pt^{II} to Pt^{IV}. The molecular-vibration revealed that the vibronic-mode frequency is raised below 200 K, which may contribute to sustain the lifetime of the metastable state by inhibiting the charge transfer along the chain.

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