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Metal−Metal *d*−*d* Interaction through the Discrete Stacking of Mononuclear M(II) Complexes (M = Pt, Pd, and Cu) within an Organic-Pillared Coordination Cage

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Stacking of planar transition-metal complexes via *d*−*d* interaction between the metal centers promises unique optical, electroconductive, and magnetic properties.[1] Some planar metal complexes, such as $Pt(CN)_4^{2-}$ and $Pt(NH_3)_4^{2+}/PtCl_4^{2-}$, assemble into infinitely stacked linear polymers in solid state. Unless bridged by organic ligands, however, common planar metal complexes interact very weakly at the metal centers and seldom form metal−metal bonds via discrete/infinite stacking.[2,3] Here, we report that simple and rather classical metal complexes, $M^{II}(acac)_2$ (M = Pt, Pd, or Cu; acac = acetylacetonato), which have been never shown to form an intermolecular M−M bond,[4] exhibit characteristic metal−metal interaction through accommodation within a coordination cage (Figure 1). The cage we employ here (**1**) has an organic-pillared framework with a large box-shaped hydrophobic cavity, which is ideal to bind two planar molecules as previously reported.[5,6] We show that the M−M interaction is clearly demonstrated by spectroscopies, crystallographic analysis (for M = Pt(II)), and electron spin−spin coupling (for M = Cu(II)).

From cage **1** and $Pt(acac)_2$ (**2a**), inclusion complex $\mathbf{1}\supset(\mathbf{2a})_2$ was quantitatively obtained by a very simple procedure. Complex **2a** (4 molar equiv) was suspended in a D_2O solution of **1** (10 mM), and the mixture was stirred at room temperature for 30 min. After the removal of excess **2** by filtration, ^1H NMR analysis of the clear solution revealed the quantitative formation of $\mathbf{1}\supset(\mathbf{2a})_2$ complex. Highly upfield-shifted signals of **2a** were observed at 3.80 and 0.47 ppm, indicating the enclathration of **2a** within **1** (Figure 2b). The host−guest ratio (1:2) was estimated by the integral ratio of **1** and **2a**. CSI−MS measurement also showed the formation of $\mathbf{1}\supset(\mathbf{2a})_2$ very clearly. Intense signals were observed at *m*/*z* 642.9, 740.2, and 904.4, which correspond to $[\mathbf{1}\supset(\mathbf{2a})_2 - 6{\cdot}NO_3^- + 6{\cdot}DMF]^{6+}$, $[\mathbf{1}\supset(\mathbf{2a})_2 - 5{\cdot}NO_3^- + 3{\cdot}DMF]^{5+}$, and $[\mathbf{1}\supset(\mathbf{2a})_2 - 4{\cdot}NO_3^- + DMF]^{4+}$, respectively. The $\mathbf{1}\supset(\mathbf{2a})_2$ host−guest complex was shown to be stable because guest dissociation from cage **1** under the CSI−MS conditions was hardly observed.

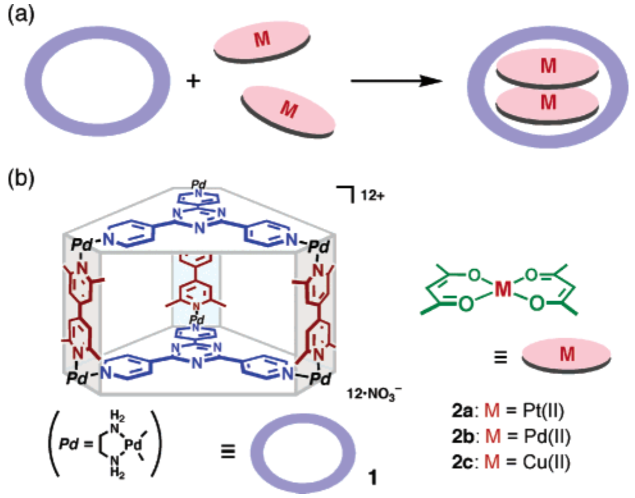

Figure 1. (a) Discrete stacking of planar metal complexes within a cage. (b) Chemical structures of organic-pillared coordination cage **1** and $M^{II}(acac)_2$ complexes **2**.

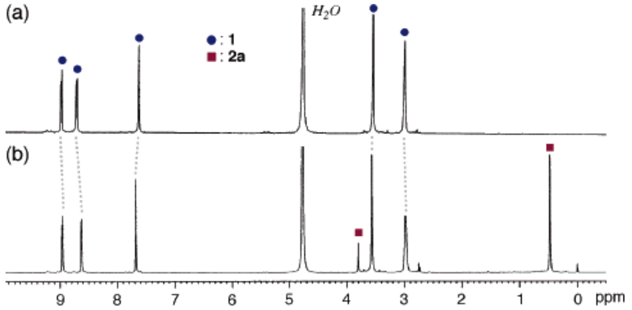

Figure 2. NMR spectra (500 MHz, D_2O, rt) of (a) **1** and (b) $\mathbf{1}\supset(\mathbf{2a})_2$.

Pt(II)−Pt(II) interaction in $\mathbf{1}\supset(\mathbf{2a})_2$ was displayed by X-ray crystallographic analysis (Figure 3). Orange-colored single crystals suitable for X-ray analysis grew by the slow evaporation of water from an aqueous solution of $\mathbf{1}\supset(\mathbf{2a})_2$ at room temperature for 3 days.[7] The crystal structure reveals the stacking of two molecules of **2a** in such a way that two Pt(II) metals exist on the C_2 symmetry axis of the stacked dimer. The Pt(II)−Pt(II) distance is 3.32 Å, being characteristic to typical Pt(II)−Pt(II) *d*−*d* interaction (ca. <3.5 Å).[1−3] Around the Pt(II)−Pt(II) axis, the two $Pt(acac)_2$ molecules are twisted by 24.8° to reduce the steric repulsion between the methyl groups. Cage **1** itself is also twisted by 23.5° to maximize the host−guest interaction.

UV−vis measurement of powdered $\mathbf{1}\supset(\mathbf{2a})_2$ also evidenced Pt(II)−Pt(II) interaction. The spectrum showed absorption band around 500 nm (Figure 4), which is featured by *d*−*d* interaction of Pt(II) complexes.[1−3] For **1** and **2a**, no absorption was observed above 450 nm. The orange color of the complex turned almost colorless when the complex was dissolved in water, suggesting that the Pt(II)−Pt(II) interaction became weaker in solution. However, ^{195}Pt NMR of $\mathbf{1}\supset(\mathbf{2a})_2$ showed a broad signal at −280 ppm, which was considerably downfield-shifted ($\Delta\delta = 130$ ppm) compared with that of free **2a**.[8,9] This indicated that the Pt(II)−Pt(II) interaction still remained to some extent even in solution.[2,3]

We also examined the accommodation of analogous $Pd(acac)_2$ (**2b**) by cage **1**. Again, $\mathbf{1}\supset(\mathbf{2b})_2$ complex was obtained quantita-

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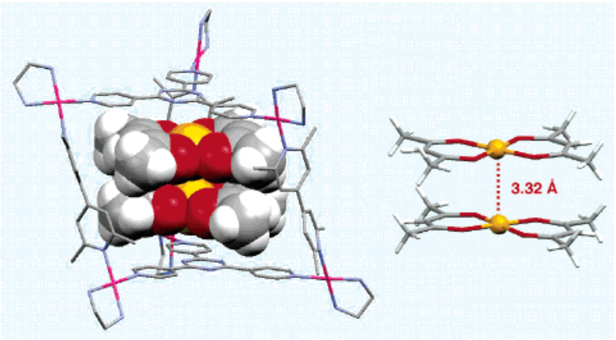

Figure 3. X-ray structure of $\mathbf{1}\supset(\mathbf{2a})_2$ (left) and selected structure of **2a** (yellow = Pt, red = oxygen) within **1** (right).

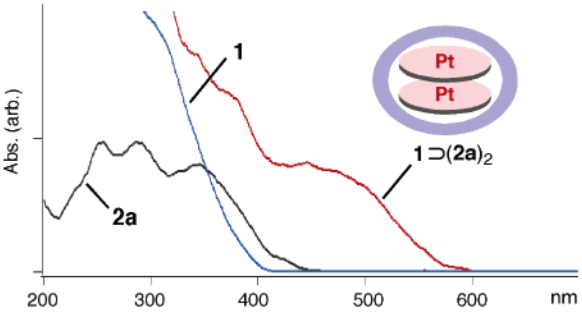

Figure 4. UV−vis spectra of **1**, **2a**, and $\mathbf{1}\supset(\mathbf{2a})_2$ in solid state.

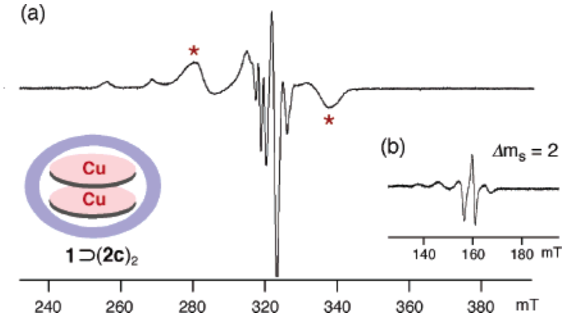

Figure 5. ESR spectra (H_2O, 103 K, MnO as external standard) of (a) $\mathbf{1}\supset(\mathbf{2c})_2$ and (b) the forbidden transition.

tively, and it exhibited a new absorption band around 450 nm in solid state, which is attributed to Pd(II)−Pd(II) interaction.[2,9]

For a d^9 square-planar metal complex, $Cu(acac)_2$ (**2c**), we expected spin−spin interaction between two Cu(II) centers by spontaneous stacking of **2c** within **1**. In fact, the treatment of **2c** with an aqueous solution of **1** gave $\mathbf{1}\supset(\mathbf{2c})_2$ complex, and broad signals in ESR at low temperature (labeled by the asterisks (*) in Figure 5a) grew up with the formation of $\mathbf{1}\supset(\mathbf{2c})_2$ complex.[9] The broad signals are attributed to the d−d interaction between the copper centers of $\mathbf{1}\supset(\mathbf{2c})_2$ in $S = 1$ state, and the large splitting of ca. 60 mT is due to the spin−spin interaction. The presence of a triplet species ($S = 1$ state) is confirmed by observing $\Delta m_s = 2$ (forbidden transition) signal at 160 mT (half of 320 mT for $\Delta m_s = 1$ transition) (Figure 5b). The splitting of 60 mT gives an averaged interspin distance of 3.6 Å.[10−12] A sharply split signal around 325 mT is assigned as a doublet radical ($S = {}^1\!/_2$), which suggests the presence of $\mathbf{1}\supset\mathbf{2c}$ as a minor component.[9] It should be noted that the estimated Cu(II)−Cu(II) distance is longer than the Pt(II)−Pt(II) distance determined by X-ray analysis. This comes from the different fashion of d−d interaction between the two cases. Whereas the Pt(II)−Pt(II) interaction involves the bonding overlap of linearly disposed d_{z^2} and p_z orbitals, the Cu(II)−Cu(II) interaction involves nonbonding stacking of two $d_{x^2-y^2}$ orbitals.

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Supporting Information Available: Experimental details and spectroscopic data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Krogmann, K. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 35−42. (b) Thomas, T. W.; Underhill, A. E. *Chem. Soc. Rev.* **1972**, *1*, 99−120. (c) Gilemann, G.; Yersin, H. *Structure and Bonding*; Springer-Verlag: New York, 1985; Vol. 62, pp 87−153. (d) Palmans, R.; MacQueen, D. B.; Pierpont, C. G.; Frank, A. J. *J. Am. Chem. Soc.* **1996**, *118*, 12647−12653.

(2) (a) Lai, S.-W.; Cheung, T.-C.; Chan, M. C.-W.; Cheung, K.-K.; Peng, S.-M.; Che, C.-M. *Inorg. Chem.* **2000**, *39*, 255−262. (b) Lu, W.; Chan, M. C. W.; Zhu, N.; Che, C.-M.; Li, C.; Hui, Z. *J. Am. Chem. Soc.* **2004**, *126*, 7639−7651.

(3) Pt(II)−Pt(II) interaction between Pt-containing molecular cleft and a planar Pt complex: Goshe, A. J.; Steele, I. M.; Bosnich, B. *J. Am. Chem. Soc.* **2003**, *125*, 444−451.

(4) (a) Onuma, S.; Horioka, K.; Inoue, H.; Shibata, S. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2679−2680. (b) Knyazeva, A. N.; Shugam, E. A.; Shkol'nikova, L. M. *Zh. Strukt. Khim.* **1970**, *11*, 938−939.

(5) (a) Yoshizawa, M.; Nakagawa, J.; Kumazawa, K.; Nagao, M.; Kawano, M.; Ozeki, T.; Fujita, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 1810−1813. (b) Yoshizawa, M.; Nagao, M.; Kumazawa, K.; Fujita, M. *J. Organomet. Chem.* **2005**, in press.

(6) Recent reviews for self-assembled cages: (a) Lützen, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 1000−1002. (b) Vriezema, D. M.; Aragonès, M. C.; Elemans, J. A. A.; Cornelissen, J. J. L. M.; Rowan, A. E.; Nolte, R. J. M. *Chem. Rev.* **2005**, *105*, 1445−1456.

(7) X-ray crystal data of $\mathbf{1}\supset(\mathbf{2})_2$: $C_{110}H_{148}N_{42}O_{89}Pd_6Pt_2$, $M = 4511.28$, crystal dimensions $0.30 \times 0.20 \times 0.20$ mm^3, monoclinic space group $P2_1/c$, $a = 18.682(3)$ Å, $b = 36.535(6)$ Å, $c = 26.576(4)$ Å, $\beta = 108.157(3)°$, $V = 17236(5)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.738$ g cm^{-3}, $F(000) = 8984$, radiation, λ(Mo Kα) = 0.71073 Å, $T = 80(2)$ K, reflections collected/unique 194260/41116 ($R_{\mathrm{int}} = 0.3143$). The structure was solved by direct methods (SHELXL-97) and refined by full-matrix least-squares methods on F^2 with 1753 parameters. $R_1 = 0.1496$ ($I > 2\theta(I)$), $wR_2 = 0.2894$, GOF 1.025; max/min residual density 3.518/−8.602 e Å^{-3}. CCDC reference number 270934.

(8) A control experiment was done with pyrazine-pillared cage **1′** (Kumazawa, K.; Biradha, K.; Kusukawa, T.; Okano, T.; Fujita, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 3909−3913). In contrast to $\mathbf{1}\supset(\mathbf{2a})_2$, $\mathbf{1'}\supset\mathbf{2a}$ complex showed an upfield-shifted signal in ^{195}Pt NMR compared with free **2a**. Thus, significant downfield shift in $\mathbf{1}\supset(\mathbf{2a})_2$ is due not to the influence of the cage but to the Pt(II)−Pt(II) interaction.

(9) See Supporting Information.

(10) Point dipole approximation was applied:

$$D = \pi \frac{3}{2}\left(\frac{\mu_0}{4\pi}\right)\frac{(g\beta)^2}{R^3} = (2.80 \times 10^3)\frac{1}{R^3}$$

where D (mT) is the splitting of the dipole interaction and R (Å) is the averaged interspin distance.

(11) Tanaka, K.; Tengeiji, A.; Kato, T.; Toyama, N.; Shionoya, M. *Science* **2003**, *299*, 1212−1213.

(12) This loose stacking and the twisted orientation of the two ligands by ca. 25° lead to the ferromagnetic coupling between the two $d_{x^2-y^2}$ orbitals of the Cu(II) centers, in contrast to the diamagnetic spin-singlet ground state in dicopper acetate monohydrate, where Cu(II)−Cu(II) distance is only 2.6 Å. See: (a) Brown, G. M.; Chidambaram, R. *Acta. Crystallogr.* **1973**, *B29*, 2393−2403. (b) Meester, P.; Fletcher, S. R.; Skapski, A. C. *J. Chem. Soc., Dalton* **1973**, 2575−2578.

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