Metal–Metal Bond Formed in Tetrakis(2-pyridonato)Copper(II)–Platinum(II)/Palladium(II) Complexes

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New tetrakis(2-pyridonato)copper(II)–palladium(II)/platinum(II) complexes, [CuPd(2-pyrd)$_4$(py)] (**1**), [CuPt(2-pyrd)$_4$(py)] (**2**), [CuPd(2-pyrd)$_4$(H$_2$O)] (**3**), and [CuPt(2-pyrd)$_4$(H$_2$O)] (**4**) (2-pyrd = 2-pyridone, py = pyridine), were prepared, and the metal–metal bonds between Pt^{II}/Pd^{II} and Cu^{II} atoms were evidenced on the basis of X-ray structural and ESR spectroscopic methods, which were also supported from the DFT calculations.

Recently, assembled metal complexes containing a metal–metal interaction/bond have attracted great attention from the viewpoint of crystal engineering, nanoscientific, electrochemical, magnetochemical, and photochemical interests.[1] Ito et al. have synthesized $[\{Pt(phpy)_2\}_2\{Ag(acetone)\}_2]_n{}^{2n+}$ and $[\{Pt(phpy)_2\}_2\text{-}\{Cd(cyclen)\}](ClO_4)_2$ (Hphpy = 2-phenylpyridine) and demonstrated that the occupied d_{z^2} orbital of a d^8 transition-metal ion with a square-planar geometry acts as an electron donor to another metal ion.[2] However, the metal ions employed in their studies were not transition-metal ions such as Cu^{II} ion but a main element such as Cd^{II} and Ag^{I} ions. Lippert et al. have previously reported a metal–metal bond between Pt^{II} and Cu^{II} ions,[3] and their bonds have been explained in terms of a Pt→Cu dative bond between the filled d_{z^2} orbital of Pt^{II} and the half filled $d_{x^2-y^2}$ orbital of Cu^{II}. To our knowledge, there is no report in which the metal–metal bond between d_{z^2} orbitals of Pt^{II} and Cu^{II} atoms was demonstrated experimentally. We have previously designed "metalland" complexes to prepare dinuclear complexes leading to a short meta–metal distance.[4] Here we report the experimental and theoretical evidence on the formation of the metal–metal interaction/bond between the occupied d_{z^2} orbital of Pd^{II}/Pt^{II} ion and the singly occupied d_{z^2} orbital of Cu^{II} ion using a lantern-type ligand, 2-pyridone (2-pyrd).

Among four tetrakis(2-pyridonato)Cu^{II}–Pd^{II}/Pt^{II} complexes, [CuPd(2-pyrd)$_4$(py)] (**1**) and [CuPt(2-pyrd)$_4$(py)] (**2**) were synthesized from [CuPd(2-pyrd)$_4$(H$_2$O)] (**3**) and [CuPt(2-pyrd)$_4$(H$_2$O)] (**4**), respectively, by counter change reaction. Complex **3** was prepared by adding an aqueous solution of CuCl$_2$ into a mixture of $\{(C_2H_5)_4N\}_2PdCl_4$ and 4 equiv of 2-pyrdH which had been deprotonated with 10% $(C_2H_5)_4NOH$ in H$_2$O. In the synthesis of complex **4**, K$_2$PtCl$_4$ and H$_2$PtCl$_6$ were used as starting materials of Pt^{II} ion, and a method similar to the case of the Pd complex was conducted.[9] Structural characterizations were carried out by elemental analysis and electronic absorption, IR, and ESR spectroscopy. The two complexes among them, **1** and **2** were obtained as a single crystal suitable for X-ray structure analysis.[5,9] The structure of **2**, which is isomorphous with **1**, revealed the dinuclear metal complex coordinated by four deprotonated 2-pyridonato molecules, as shown in Figure 1 as representative. Both of the Pt and Cu atoms were tetrakis-coordinated by four deprotonated 2-pyridonato ligands through the four nitrogens and four oxygens in a square-planar geometry. One axial site of Cu was occupied by a pyridine molecule, and another was linked to Pt with a short distance of Cu–Pt (2.534(1) Å), which is significantly shorter than the sum (2.68 Å) of metallic bond radii of Pt^{II} (1.39 Å) and Cu^{II} (1.28 Å) atoms,[6] which is shorter than the Pd–Cu distance (2.5582(6) Å) in complex **1**, although that of Pd^{II} (1.38 Å) is 0.01 Å shorter than Pt^{II}. The Cu–N(py) bond, 2.095(8) Å, is also short as compared with the normal Cu–N$_{ax}$(py) bond lengths (2.113–2.183 Å).[7] Considering the longer equatorial Cu–O bond length of av. 2.048 Å (Cu–O1 = 1.954(6), Cu–O2 = 2.123(7), Cu–O3 = 1.949(7), and Cu–O4 = 2.163(7) Å) as compared with those reported hitherto (Cu–O$_{eq}$ 1.896–1.951 Å),[7] the coordination geometry around the Cu atom for **2** may be defined as an axially contracted square-pyramid. The geometry around the Pt^{II} atom (Pt–N1(2-pyrd) = 2.019(6), Pt–N2 = 2.036(8), Pt–N3 = 2.011(6), and Pt–N4 = 2.049(8) Å) was normal square-planar. The above finding is in contrast to the case of complex **1**: The coordination structure around the Cu atom for **1** is axially elongated square-pyramidal that is coordinated with an average equatorial Cu–O bond length of 2.003 Å and axial Cu–N(py) bond length of 2.160(4) Å, which is in the range of those reported hitherto.[7] These facts suggest the existence of appropriate metal–metal interaction/bond between the Cu^{II} and Pt^{II} atoms.

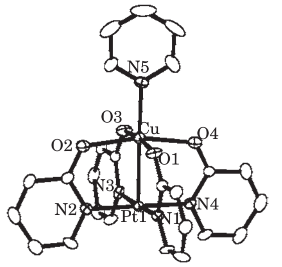


Figure 1. ORTEP drawing of [CuPt(2-pyrd)$_4$(py)] (**2**). 50% ellipsoids are shown on selected atom.

In order to confirm the metal–metal interaction/bond for these complexes **1** and **2**, the X-band ESR spectra were measured and compared with those of complexes **3** and **4**. Their frozen solution ESR spectra in DMSO at 77 K are shown together in Figure 2. These spectra were all unique; that of complex **2** was unusual, although the $g_{//}$ and $|A_{//}|$ values for complexes **1**, **3**, and **4** largely deviated from those of typical square-pyramidal structure;[8] 2.42 and 9.2 mT, 2.42 and 10.0 mT, and 2.44 and 8.3 mT for **1**, **3**, and **4**, respectively. Complex **2** ($g_{\parallel} = 2.03$,

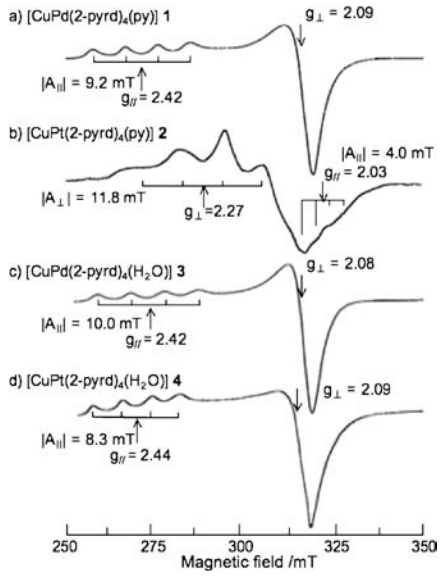
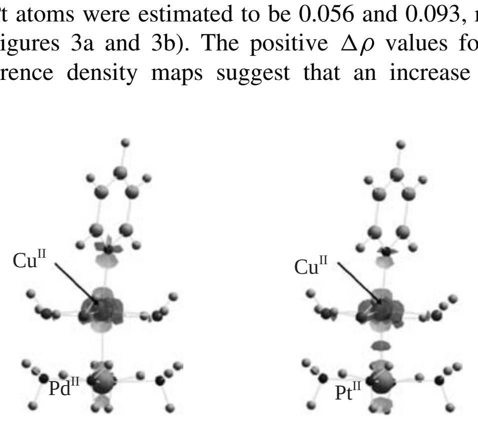


Figure 2. Frozen solution ESR spectra of complexes **1**–**4**.

$|A_{\parallel}| = 4.0\,\text{mT}$, $g_{\perp} = 2.27$, $|A_{\perp}| = 11.8\,\text{mT}$) exhibited a spectral pattern characteristic of d_{z^2}-ground state ($g_{//} < g_{\perp}$), as was expected from the above structural feature. The small $|A_{\parallel}|$ values for complexes **1** (9.2 mT), **3** (10.0 mT), and **4** (8.3 mT) and that (4.8 mT) for complex **2** with a d_{z^2} ground state suggest that the coordination of the axial ligand (H_2O or py) to the Cu^{II} ion became strengthened in the order of **3** $<$ **1** $<$ **4** $\ll$ **2**; the energy level of d_{z^2} orbital is raised in this order (**3** $<$ **1** for Pd series and **4** $<$ **2** for Pt series, respectively). The d_{z^2} ground state found in complex **2** suggests stronger coordinations of the lone-paired orbital of pyridine nitrogen and occupied d_{z^2} orbital of Pt^{II} to the Cu atom, suggesting the metal–metal bond between Pt^{II} and Cu^{II} atoms.

To elucidate the experimental results, we performed ab initio density functional theory (DFT) calculations using model complexes derived from the crystal structures of **1** and **2**, $[Cu(H_2O)_4Pd(NH_3)_4(py)]$ (**1′**) and $[Cu(H_2O)_4Pt(NH_3)_4(py)]$ (**2′**), respectively.[9] In the SOMO for **1′** and **2′** (Figures S1a and S1b, respectively), the α-spin density of the Cu atom was distributed on the central Pd and Pt atoms, whose spin densities on the Pd and Pt atoms were estimated to be 0.056 and 0.093, respectively (Figures 3a and 3b). The positive $\Delta\rho$ values found in the difference density maps suggest that an increase in the electron density originated from the formation of metal–metal bond. The natural bond orbital found for the Pt complex, $0.416\phi_{\beta}(Cu^{II}, ds) + 0.910\phi_{\beta}$ (Pt^{II}, d_{z^2}, indicates a strong donor–acceptor interaction from $5d_{z^2}$ on Pt^{II} to the ds hybrid orbital on Cu^{II}. The α spin density induced on the central metal indicates a lack of β electrons due to the movement to the Cu^{II} ion, meaning that the metal–metal interaction is explained by the dative formation from the d_{z^2} orbital of the Pt to the empty ds hybrid orbital of Cu.



$[CuPd(NH_3)_4(H_2O)_4(py)]$ (**1’**) $[CuPt(NH_3)_4(H_2O)_4(py)]$ (**2’**)

Figure 3. Difference spin density maps for complexes **1′** (a) and **2′** (b).

In summary, we succeeded in preparation of unique "metal-land" complexes leading to metal–metal bond formation. The crystal structure of complex **2** revealed the shorter Pt–Cu distance and the axially contracted octahedral structure around the Cu ion. The frozen solution ESR spectra supported this coordination structure and electron configuration, and furthermore the theoretical approach for these complexes showed the permeation of spin density by the formation of metal–metal bond between Pt and Cu atoms.

This work was supported partly by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan and 21st Century COE Program, to which our thanks are due.

References and Notes

1 a) M. Kato, A. Omura, A. Toshikawa, S. Kishi, Y. Sugimoto, *Angew. Chem., Int. Ed.* **2002**, *41*, 3183. b) V. W.-W. Yam, K. M.-C. Wang, N. Zhu, *J. Am. Chem. Soc.* **2002**, *124*, 6506. c) T. J. Wadas, Q.-M. Wang, Y.-j. Kim, C. Flaschenreim, T. N. Blanton, R. Eisenberg, *J. Am. Chem. Soc.* **2004**, *126*, 16841. d) M. Kato, *Bull. Chem. Soc. Jpn.* **2007**, *80*, 287.

2 a) T. Yamaguchi, F. Yamazaki, T. Ito, *J. Am. Chem. Soc.* **1999**, *121*, 7405. b) T. Yamaguchi, F. Yamazaki, T. Ito, *J. Am. Chem. Soc.* **2001**, *123*, 743.

3 a) C. Mealli, F. Pichierri, L. Randaccio, E. Zangrando, M. Krumm, D. Holtenrich, B. Lippert, *Inorg. Chem.* **1995**, *34*, 3418. b) G. Fusch, E. C. Fusch, A. Erxleben, J. Hüttermann, H.-J. Scholl, B. Lippert, *Inorg. Chim. Acta* **1996**, *252*, 167. c) A. Hegmans, E. Zangrando, E. Freisinger, F. Pichierri, L. Randaccio, C. Mealli, M. Gerdan, A. X. Trautwein, B. Lippert, *Chem.—Eur. J.* **1999**, *5*, 3010.

4 a) M. Mizutani, K. Jitsukawa, H. Masuda, Y. Aoyama, H. Einaga, *Chem. Lett.* **1998**, 663. b) M. Mizutani, S. Miwa, N. Fukushima, Y. Funahashi, T. Ozawa, K. Jitsukawa, H. Masuda, *Inorg. Chim. Acta* **2002**, *339*, 543. c) N. Ichieda, T. Kamimura, S. Yamaguchi, Y. Funahashi, T. Ozawa, K. Jitsukawa, H. Masuda, *Adv. Mater. Res.* **2006**, *11–12*, 473. d) Y. Funahashi, T. Kamimura, M. Mizautani, Y. Wasada-Tsutsui, M. Sakai, H. Yashiro, T. Ozawa, K. Jitsukawa, H. Masuda, *Adv. Mater. Res.* **2006**, *11–12*, 273.

5 Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-291008 and CCDC-291009. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.

6 *Kagaku Binran*, 3rd. ed., ed by the Chemical Society of Japan, Maruzen, Tokyo, **1984**, II-718.

7 H.-B. Bürgi, J. D. Dunitz, *Structure Correlation*, **1994**, Vol. 2, pp. 808, 821.

8 *Comprehensive Coordination Chemistry*, ed. by G. Wilkinson, R. D. Gillard, J. A. McCleverty, Pergamon, Oxford, **1987**, Vol. 5, pp. 533–774.

9 Supporting Information is available electronically on the CSJ-Journal web site, http://www.csj.jp/journals/chem-lett/index.html.