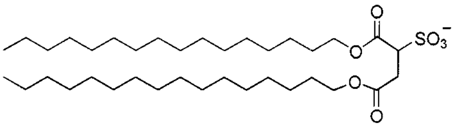
Molecular Dispersion of Chains in the Mixed-Valence Complexes $[M(en)_2][MCl_2(en)_2]$ (M: Pt, Pd, Ni) and Anionic Amphiphiles in Organic Media**

Nobuo Kimizuka,* Sang Ho Lee, and Toyoki Kunitake

Controlled manipulation of inorganic nanostructures under the influence of organic molecular assemblies is an important area of current research in nanochemistry.[1, 2] Though there are many artificially built inorganic nanostructures known to date[1] they are normally insoluble and exist only as basic structural motifs in solid materials. The linear halogen-bridged platinum complexes $[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$ (en = ethylenediamine) represent one of the pseudo one-dimensional inorganic systems that have been extensively characterized in crystalline samples.[4] These one-dimensional chains exist only in the crystalline state, and dissolution in water results in dissociation into single molecular complexes. We recently devised an approach to isolate and to solubilize one-dimensional platinum complexes into organic media by transforming them into lipophilic supramolecular assemblies.[3] The introduction of anionic lipid **1** as a counterion enabled the one-dimensional complex $[Pt(en)_2][PtCl_2(en)_2]$ to become soluble in organic media through the formation of mesoscopic supramolecular assemblies.[3] Herein we describe a generalization of our approach by the use of mixed valent palladium and heterometallic complexes. The morphology of the aggregates, spectral characteristics, and thermal stability of these assemblies in chloroform are discussed.



1

Ternary supramolecular complexes were prepared by mixing aqueous solutions of mixed-valence complexes $[Pd(en)_2][PdCl_2(en)_2](ClO_4)_4$, $[Pd(en)_2][PtCl_2(en)_2](ClO_4)_4$, and $[Ni(en)_2][PtCl_2(en)_2](ClO_4)_4$ (12.7 mM, 1 mL), with the aqueous bilayer membrane **1** (in the Na^+ form, 12.7 mM, 4 mL) at room temperature. The highly colored precipitates of $[Pd(en)_2][PdCl_2(en)_2](\mathbf{1})_4$ (dark green), $[Pd(en)_2][PtCl_2(en)_2](\mathbf{1})_4$ (yellow), and $[Ni(en)_2][PtCl_2(en)_2](\mathbf{1})_4$ (red) that formed immediately were washed with deionized water (5 mL, × 3) and ethanol (3 mL, × 2), and then dried in vacuo. The stoichiometry of these complexes was confirmed by elemental analysis. The observed colors are different from those of the corresponding ethylenediamine complexes and are ascribed to intervalence electron transfer transitions ($M^{II} \rightarrow M^{IV}$) within chloro-bridged complexes.[4, 5] Therefore, it is apparent that the mixed-valence structures are maintained in the lipid complexes. These ternary complexes are readily dispersed in chloroform by ultrasonication, without any loss of color from the solids. The maintenance of the absorption arising from intervalence electron transfer in chloroform has been also observed for the platinum complex $[Pt(en)_2][PtCl_2(en)_2](\mathbf{1})_4$,[3] and thus the complexation of polyions with anionic amphiphiles provides a general route for solubilizing halogen-bridged mixed-valence complexes in organic media.

Figure 1 shows transmission electron micrographs of solutions of $[Pd(en)_2][PdCl_2(en)_2](\mathbf{1})_4$ (a), $[Pd(en)_2][PtCl_2(en)_2](\mathbf{1})_4$ (b), and $[Ni(en)_2][PtCl_2(en)_2](\mathbf{1})_4$ (c) in chloroform. These samples are not stained, and the dark images are ascribed to metal components in the mixed-valent complexes. The palladium complex displayed rodlike structures with widths of 60–120 nm and lengths of 2.5–17 μm (a), while the heterometallic complex of $[Pd(en)_2][PtCl_2(en)_2](\mathbf{1})_4$ showed only irregular nanostructures (b). Fragmented tapes are seen for $[Ni(en)_2][PtCl_2(en)_2](\mathbf{1})_4$ (c), which resembles that observed for the platinum complex $[Pt(en)_2][PtCl_2(en)_2](\mathbf{1})_4$.[3] It is noteworthy that changes in the metal species remarkably influence the aggregate morphology.

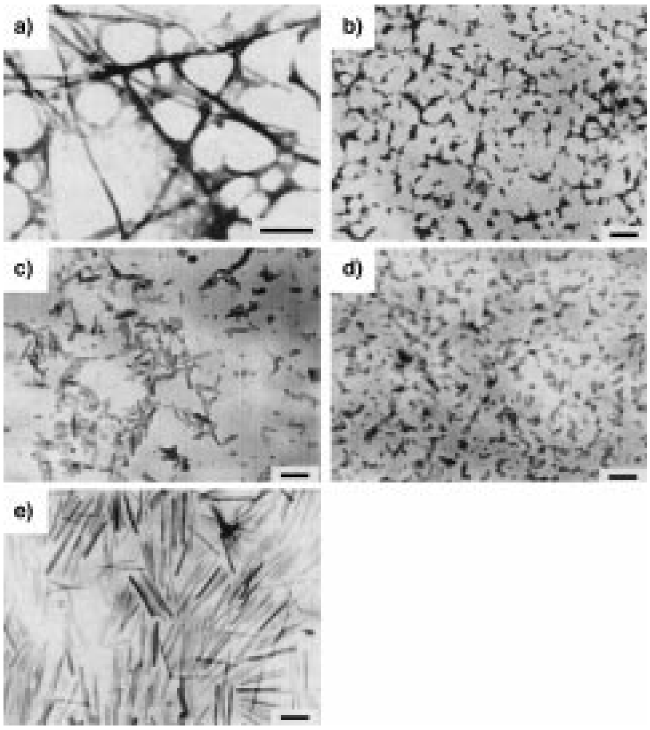


Figure 1. Transmission electron micrographs of solutions of the following complexes in chloroform: a) $[Pd^{II}(en)_2][Pd^{IV}(en)_2(Cl)_2](\mathbf{1})_4$, b) $[Pd^{II}(en)_2][Pt^{IV}(en)_2(Cl)_2](\mathbf{1})_4$, c) $[Ni^{II}(en)_2][Pt^{IV}(en)_2(Cl)_2](\mathbf{1})_4$, d) $[Pd^{II}(en)_2][Pd^{IV}(en)_2(Cl)_2](\mathbf{1})_4$ heated at 60 °C, e) $[Pd^{II}(en)_2][Pt^{IV}(en)_2(Cl)_2](\mathbf{1})_4$ after cooling the 60 °C sample. The scale bars represent 100 nm. Samples are not stained.

Figure 2 shows the UV/Vis spectra obtained for the four complexes. These colored dispersions were stable over a period of one month. The absorption maxima of these

---

[*] Dr. N. Kimizuka, Dr. S. H. Lee, Prof. T. Kunitake
Department of Chemistry and Biochemistry
Graduate School of Engineering, Kyushu University
Hakozaki 6-10-1, Fukuoka 812-8581 (Japan)
Fax: (+81) 92-6423611
E-mail: kimitcm@mbox.nc.kyushu-u.ac.jp

[**] This work was partly supported by a Grant-in-Aid for COE Research "Design and Control of Advanced Molecular Assembly Systems" from the Ministry of Education, Science, Sports, and Culture, Japan (No. 08CE2005). S.H.L. thanks the Korea Science and Engineering Foundation (KOSEF).

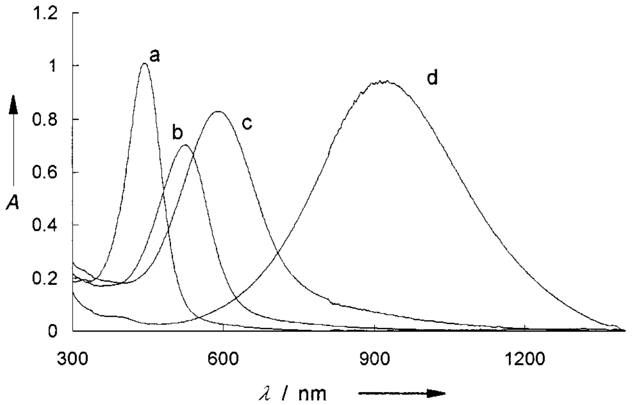


Figure 2. UV/Vis spectra of solutions of the following complexes in chloroform ($[M^{II}] = [M^{IV}] = 0.3$ mM, 1 mm cell, 20 °C): a) $[Pd^{II}(en)_2][Pt^{IV}(en)_2(Cl)_2](\mathbf{1})_4$, b) $[Ni^{II}(en)_2][Pt^{IV}(en)_2(Cl)_2](\mathbf{1})_4$, c) $[Pt^{II}(en)_2][Pt^{IV}(en)_2(Cl)_2](\mathbf{1})_4$, d) $[Pd^{II}(en)_2][Pd^{IV}(en)_2(Cl)_2](\mathbf{1})_4$.

solutions are located at $\lambda_{max} = 443$ nm (2.80 eV, $\varepsilon = 33733\,M^{-1}cm^{-1}$, a), 524 nm (2.37 eV, $\varepsilon = 21833\,M^{-1}cm^{-1}$, b), 590 nm (2.10 eV, $\varepsilon = 27667\,M^{-1}cm^{-1}$, c), and 910 nm (1.36 eV, $\varepsilon = 31567\,M^{-1}cm^{-1}$, d). These absorption bands are not present for the component ethylenediamine complexes, and are ascribed to intervalence electron transfer transitions along the chloro-bridged chains. These absorption peaks are apparently dependent on the combination of the mixed-valent metal ions, which indicates that the electronic structure in these supramolecular assemblies is tunable. The series of charge-transfer bands are in the same order as that reported for the corresponding perchlorates in the crystalline state (reflectance spectra:[4, 5] Pd/Pt: 385 nm (3.22 eV), Ni/Pt: 440 nm (2.82 eV), Pt/Pt: 456 nm (2.72 eV), Pd/Pd: 605 nm (2.05 eV)), but are considerablely red shifted. The intervalence electron transfer absorption energy of halogen-bridged mixed-valent Pt complexes is known to decrease with increasing distances between Pt^{II} and Pt^{IV} centers.[4, 6] As these lipid complexes display identical colors both in the powdery state and in chloroform solution the observed red shifts in solution must reflect lengthened metal(II) – metal(IV) distances in the one-dimensional chains, which probably arise from the presence of large organic counterions.

As the aggregate diameters observed by electron microscopy (Figure 1) are much larger than the molecular length of **1**, the observed structures must be comprised of aggregates of the unit supramolecular polyion complex, which is schematically shown in Figure 3. Long alkyl chains of **1** act as solvophilic moieties in this structural unit, while the polyion complex moiety serves as a solvophobic moiety, and this combination gives rise to an amphiphilic supramolecular structure in organic media.[7]

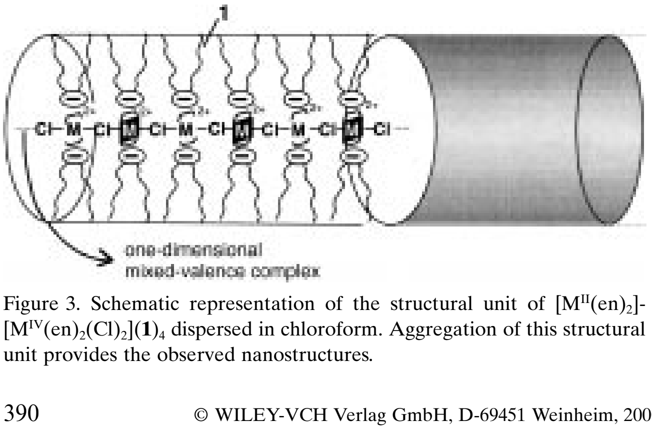


Figure 3. Schematic representation of the structural unit of $[M^{II}(en)_2][M^{IV}(en)_2(Cl)_2](\mathbf{1})_4$ dispersed in chloroform. Aggregation of this structural unit provides the observed nanostructures.

The thermal stability of these supramolecular assemblies in chloroform was subsequently investigated. In the case of a solution of $[Pd(en)_2][PdCl_2(en)_2](\mathbf{1})_4$ in chloroform (2.5×10^{-5} M) a temperature change from 5 to 55 °C resulted in a decrease in absorbance by approximately 35 %, and this was accompanied by a blue shift in the spectrum to 878 nm (Figure 4a). The initial intensity of the absorption was recovered upon cooling the solution to 5 °C. An electron micrograph of $[Pd(en)_2][PdCl_2(en)_2](\mathbf{1})_4$, which was prepared by dropping a solution of the aggregate in chloroform at 60 °C onto a carbon-coated copper mesh, was devoid of the rodlike nanostructures. It, instead, consisted of irregular aggregates that resemble that of $[Pd(en)_2][PtCl_2(en)_2](\mathbf{1})_4$ at 20 °C (Figure 1d). Though we can not exclude the possibility that the irregular structure is formed as a result of a rapid evaporation of the warm chloroform, it is more likely that the rodlike nanostructure is destroyed as a consequence of partial dissociation of the linear coordination chain into molecular complexes of $[Pd(en)_2](\mathbf{1})_2$ and $[PdCl_2(en)_2](\mathbf{1})_2$. In accordance with the observed spectral recovery, the rodlike nanostructure was reformed upon cooling the heated solution (data not shown). When the temperature was further raised to 60 °C, however, recovery of absorption after cooling became

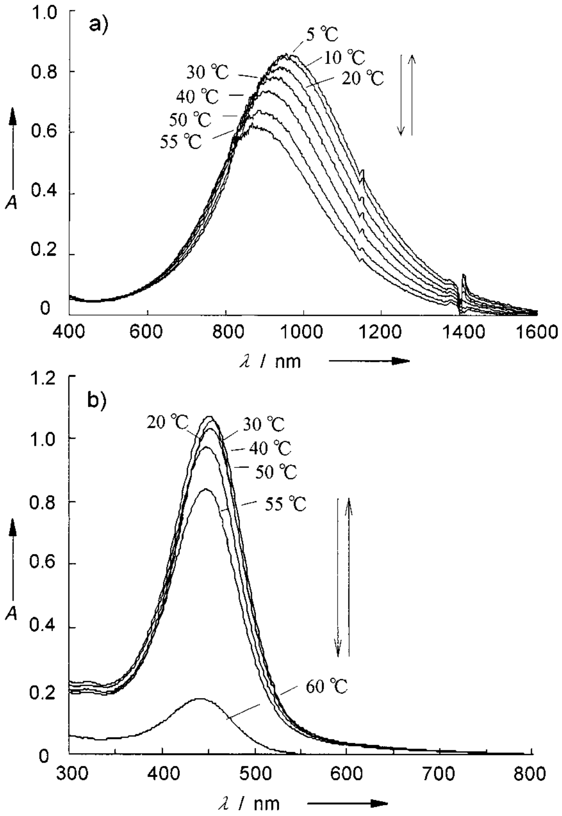


Figure 4. Temperature dependence of the UV/Vis spectra of a) $[Pd^{II}(en)_2][Pd^{IV}(en)_2(Cl)_2](\mathbf{1})_4$, 0.25 mM in chloroform, 1 cm cell, b) $[Pd^{II}(en)_2][Pt^{IV}(en)_2(Cl)_2](\mathbf{1})_4$, 0.4 mM in chloroform, 1 mm cell.

poor (ca. 18% of the initial intensity). This result can be ascribed to the smaller stability of $[Pd^{IV}Cl_2(en)_2]$ at elevated temperatures, with the complex being readily reduced to a $Pd^{II}(en)_2$ species by oxidation of the coordinating chloride ion.[8]

In the case of $[Ni(en)_2][PtCl_2(en)_2](\mathbf{1})_4$ in chloroform (3×10^{-4} M), the recovery of intervalence electron transfer absorption after heating was inferior to that observed for $[Pd(en)_2][PdCl_2(en)_2](\mathbf{1})_4$. Only approximately 50% of the initial intensity was recovered after cooling the 60 °C solution to room temperature,. However, reversible thermochromism was observed for $[Pd(en)_2][PtCl_2(en)_2](\mathbf{1})_4$ in chloroform (4×10^{-4} M). When a solution of this complex was heated to 60 °C (Figure 4b), the UV absorption decreased to 17% of the initial intensity without changing the peak position. The original intensity was restored upon cooling to room temperature, and this reversible change was possible even after three thermal cycles. Figure 1e shows an electron micrograph of $[Pd(en)_2][PtCl_2(en)_2](\mathbf{1})_4$ after cooling. Rectangular nanocrystals (length: ca. 1400–2000 nm, width: ca. 80–200 nm) are abundant. These nanostructures are more developed than those before the heat treatment (Figure 1b). It is clear that this regular supramolecular structure is formed by self-assembly of thermally dissociated component complexes.

In conclusion, it is established that formation of amphiphilic supramolecular assemblies is a general route to stabilize one-dimensional, halogen-bridged mixed-valent complexes in organic media. The combination of metal ions significantly alters their spectral properties and morphologies, which gives rise to a wide spectrum of one-dimensional electronic systems in the solution phase. These new findings offer a new basis for research on molecular wires.

Experimental Section

The synthesis of sodium dihexadecyl sulfosuccinate (Na-**1**) was described previously.[9] Ethylenediamine complexes and chloro-bridged mixed-valence complexes were prepared according to the literature.[10] Elemental analyses (calcd (found)): $[Pd(en)_2][Pt(en)_2Cl_2](\mathbf{1})_4$ ($C_{152}H_{308}N_8O_{28}S_4Cl_2PdPt$): C 57.11 (56.80), H 9.71 (9.68), N 3.51 (3.45); $[Ni(en)_2][PtCl_2(en)_2](\mathbf{1})_4$ ($C_{152}H_{308}N_8O_{28}S_4Cl_2NiPt$): C 57.97 (57.31), H 9.86 (9.81), N 3.56 (3.45); $[Pt(en)_2][PtCl_2(en)_2](\mathbf{1})_4$ ($C_{152}H_{308}N_8O_{28}S_4Cl_2Pt_2$): C 55.57 (55.06), H 9.45 (9.38), N 3.41 (3.32); $[Pd(en)_2][Pd(en)_2Cl_2](\mathbf{1})_4$ ($C_{152}H_{308}N_8O_{28}S_4Cl_2Pd_2$): C 58.74 (58.11), H 9.99 (10.09), N 3.61 (3.52). UV/Vis absorption spectra were obtained using a JASCO V-570 spectrophotometer. Transmission electron microscopy (TEM) was conducted on a Hitachi H-600 instrument. Samples were readily dispersed in chloroform (0.3 mM) by ultrasonication (Branson Sonifier Model 185) for 0.5–1 min at 0 °C, and were dropped on a carbon-coated Cu grid. The Cu meshes were subjected to TEM observation with an acceleration voltage of 75 kV and magnifications of 5000–20000.

Received: June 23, 1999 [Z13616]

---

[1] G. A. Ozin, *Adv. Mater.* **1992**, *4*, 612–649.

[2] N. Kimizuka, T. Kunitake, *Adv. Mater.* **1996**, *8*, 89–91.

[3] N. Kimizuka, N. Oda, T. Kunitake, *Chem. Lett.* **1998**, 695–696.

[4] H. Okamoto, M. Yamashita, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2023–2039, and references therein.

[5] Y. Wada, T. Mitani, M. Yamashita, T. Koda, *J. Phys. Soc. Jpn.* **1985**, *54*, 3143–3153.

[6] H. Okamoto, T. Mitani, K. Toriumi, M. Yamashita, *Mater. Sci. Eng. B* **1992**, *13*, L9-L14.

[7] Amphiphilicity directed supramolecular assembly in organic media: N. Kimizuka, T. Kawasaki, K. Hirata, T. Kunitake, *J. Am. Chem. Soc.* **1995**, *117*, 6360–6361.

[8] F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 4th ed., Wiley, New York, **1980**, chap. 22.

[9] T. Kunitake, Y. Okahata, *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1877–1879.

[10] F. Basolo, J. C. Bailar, B. R. Tarr, *J. Am. Chem. Soc.* **1950**, *72*, 2433–2438.

The First Organoxenon(IV) Compound: Pentafluorophenyldifluoroxenonium(IV) Tetrafluoroborate**

Hermann-Josef Frohn,* Nicolas LeBlond, Karel Lutar, and Boris Žemva

The preparative chemistry of the noble gases is based on their binary fluorides. Of the compounds derived from the three known xenon fluorides XeF_2, XeF_4, and XeF_6, relatively few Xe^{IV} species have been prepared to date.[1] The bonding systems that have been observed are limited to $Xe^{IV}{-}F$ and $Xe^{IV}{-}O$ compounds (XeF_4, $[XeF_3]^+$, $[XeF_5]^-$, $XeOF_2$, $[XeOF_3]^-$, $Xe(OTeF_5)_4$, $XeF_3(OIOF_4)$). Important aspects of the reactivity of the parent compound XeF_4 are its fluoride-donor and -acceptor and oxidative-fluorinating abilities. The latter is intermediate to those of the other xenon fluorides: $XeF_6 > XeF_4 > XeF_2$. The fluoride-donor ability of XeF_4 is much lower than that of either XeF_2 or XeF_6.

Since 1989 an increasing number of organoxenon(II) compounds have been prepared, mainly in the form of cationic xenonium compounds [OrgXe][X] (Org = aryl,[2] alkenyl,[3] and alkynyl[4]) but also as molecular species such as C_6F_5XeCl.[5] In most cases the $Xe^{II}{-}C$ bond formation occurs through nucleophilic substitution with organoboranes [xenodeborylation: Eq. (1)] and in some specific cases through electrophilic substitution on electron-poor aromatic compounds [xenonylation: Eq. (2)].[6]

$$XeF_2 + Org{-}BX_2 \rightarrow [Org{-}Xe][BF_2X_2] \qquad (1)$$

$$X{-}Xe{-}Y + C_6H_x(CF_3,F)_{6-x} \rightarrow [(C_6H_{x-1}(CF_3,F)_{5-x})Xe][X] + HY \qquad (2)$$

We have now been able to apply an optimized form of the xenodeborylation procedure successfully to XeF_4. Because of

---

[*] Prof. Dr. H.-J. Frohn, Dr. N. LeBlond
Fachgebiet Anorganische Chemie der Universität
47048 Duisburg (Germany)
Fax: (+49) 203-379-2231
E-mail: frohn@uni-duisburg.de

Dr. K. Lutar, B. Žemva
Jožef Stefan Institute
1001 Ljubljana (Republic of Slovenia)

[**] The preliminary investigations for this work were supported by the German–Slovenian Joint Project "Versuche zur ersten Synthese von Xenon(IV)-Kohlenstoff Verbindungen". We acknowledge the National Science and Engineering Council of Canada (postdoctoral fellowship for N.L.), the Fonds der Chemischen Industrie, and the Ministry of Science and Technology of the Republic of Slovenia for financial support.