

Transition Metal Cluster Chalcogenide Ligated by Multiple Redox Active Organometallic Centers: $[\text{Ni}_6(\mu_3\text{-Se})_2(\mu_4\text{-Se})_3(\text{dppf})_3]\text{Br}_2$ and Its Electrocatalysis

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One of the current trends in molecular material science concerns the preparation and the study of materials combining several physical properties in a synergistic way.¹ Organic/inorganic hybrids, in which organic- or organo-metallic- moieties having a special physicochemical property are incorporated into a transition-metal cluster, may exhibit certain coupling phenomena between the *d*-electrons of inorganic transition-metal networks and the mobile π -electrons of the organic conjugated networks.^{2,3} Such coupling effects should provide us with rich opportunities to design and study molecular systems exhibiting special material characteristics, such as superconductivity,⁴ magnetism,⁵ electrical conductivity,⁶ optical properties,³ electrochromism,⁷ and catalytic activity.⁸

On the other hand, there is a considerable interest in the chemistry of multi-metallocenyl assemblies, particularly multi-ferrocenyl assemblies.^{1,9} Such compounds can be viewed as excellent candidates for multielectron reservoir systems, electron-transfer mediators, redox active materials for the modification of electrodes, ion sensors and/or materials for electronic devices.¹⁰ In this respect, if one hybridizes the multi-ferrocenyl moieties onto a transition-metal cluster, the electrical and magnetic properties of both components will be probably combined in a synergistic way, leading to new properties applicable to the material science. However, the chemistry of the transition-metal clusters into which organic and/or organometallic moieties are incorporated, would be difficult to achieve a true advance mainly due to the poorly settled synthetic methods for such molecular assemblies. It is nearly impossible to prepare inorganic clusters having special functionalities in a bond-by-bond fashion. One of the most plausible strategies for constructing such systems with their unique architecture will involve one-pot spontaneous self-assembly of components with required functionalities already in place. Such a strategy has been popularly utilized in organic chemistry¹¹ and supramolecular inorganic chemistry.¹²

As an example of the related synthetic efforts, $[\text{Ni}_6(\mu_3\text{-Se})_2(\mu_4\text{-Se})_3(\text{dppf})_3]\text{Br}_2 \cdot 3/2\text{CHCl}_3$ (**1**) was obtained by the self-assembly reaction of $\text{Ni}(\text{dppf})\text{Br}_2$ with Li_2Se in the presence of $\text{Li}[\text{PhNC}(\text{O})\text{Me}]$ in THF. The first example of

the $[\text{Ni}_6(\mu_3\text{-Se})_2(\mu_4\text{-Se})_3]$ cluster was prepared by the reaction of $(\text{NBu}_3)[\text{NiCl}_3(\text{PPh}_3)]$ with $\text{Se}(\text{SiMe}_3)_2$ and the similar reaction of $[\text{NiCl}_2(\text{PPh}_3)_2]$ with $\text{Se}(\text{SiMe}_3)_2$ produced $[\text{Ni}_{12}\text{Se}_{11}\text{Cl}][\text{NiCl}_3(\text{PPh}_3)]_2$.¹³ The structure of the cluster **1**¹⁴ is shown in Figure 1. The production of **1** from the present reaction is ascribed to the directional-bonding influence of the dppf ligand.¹⁵ During the course of the reaction, the fixed distance between the two phosphine atom of the ferrocene bridge may force the selective construction of the present prismatic structure. The existence of $\text{Li}[\text{PhNC}(\text{O})\text{Me}]$ was essential for an effective reaction. Without this anion it takes more than 14 days for the production of **1** to be detected by TLC. It is known that the addition of the $[\text{PhNC}(\text{O})\text{Me}]^-$ ion suppresses the formation of an intractable polymer by complexing to the metal center and the more reactive anion temporarily displaces the less reactive bromide of the nickel before the attack of selenide, leading to the easy production of the cluster.¹⁶ **1** is soluble in THF and CHCl_3 , moderately soluble in hexane and sparingly soluble in polar solvents. It appears to be stable on exposure to moisture and air. X-ray

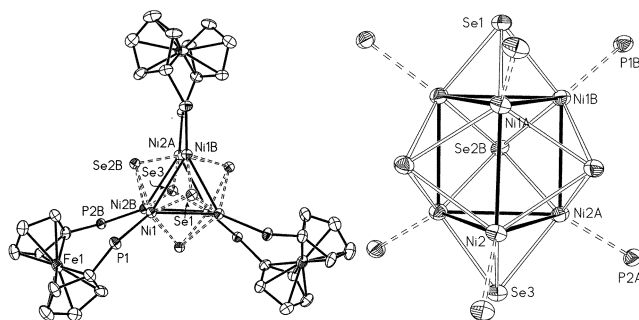


Figure 1. Crystal structure of **1** drawn with 30% probability ellipsoids. Selected distances (Å): Ni1-P1, 2.196(2); Ni1-Se1, 2.269(1); Ni1-Se2, 2.375(1); Ni1-Se2B, 2.399(1); Ni1-Ni1A, 2.695(1); Ni1-Ni2B, 2.635(1); Ni2-P2, 2.210(2); Ni2-Se3, 2.276(1); Ni2-Se2, 2.369(1); Ni2-Se2A, 2.408(1); Ni2-Ni2A, 2.712(1). Selected angles (°): P1-Ni1-Se1, 99.65(7); P1-Ni1-Se2, 111.00(8); P1-Ni1-Se2B, 123.35(8); P1-Ni1-Ni1B, 140.66(7); Se1-Ni1-Ni1B, 53.58(3); Se2-Ni1-Ni1B, 104.76(4); Ni2B-Ni1-Ni1B, 89.76(3); Ni2B-Ni1-Ni1A, 90.60(3); Ni1B-Ni1-Ni1A, 60.0; Ni2B-Ni2-Ni2A, 60.0; Ni1B-Se1-Ni1, 72.84(6); Ni2-Se2-Ni1A, 67.11(4); Ni1-Se2-Ni1A, 68.72(5); Ni2-Se3-Ni2A, 73.16(6).

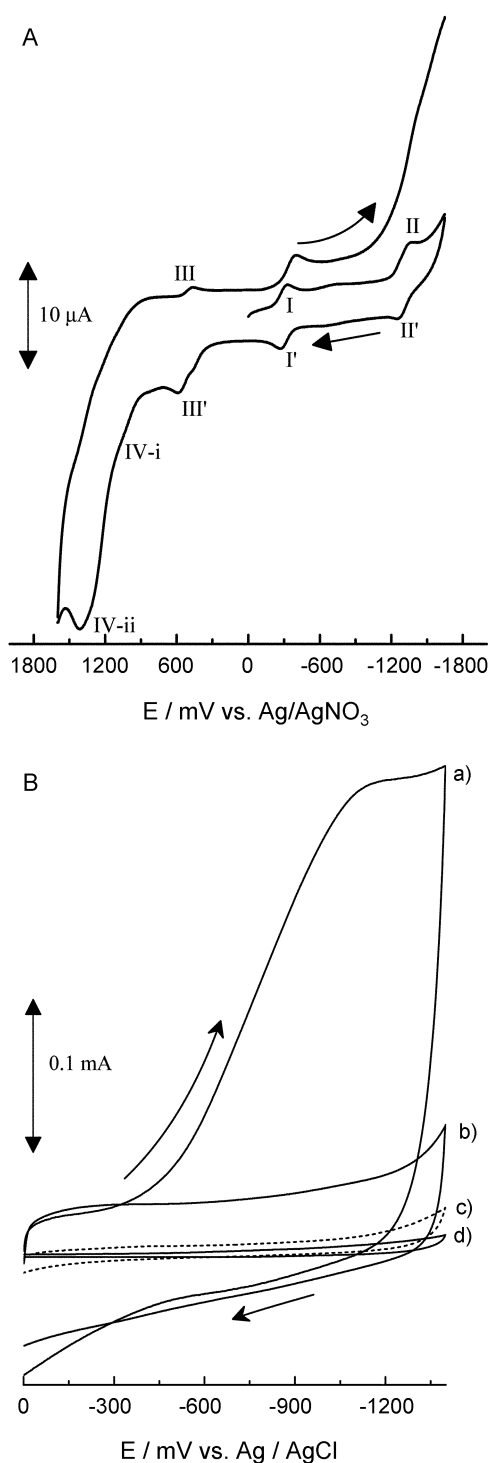


Figure 2. (A) CVs recorded for the cluster in a CH₂Cl₂ solution containing 0.1 M TBAP (Scan rate: 100 mV/s). (B) CVs recorded for the cluster modified electrode in (a) CO₂ and (b) N₂ saturated - 0.1 M KCl solutions, and CVs for the bare electrodes in (c) CO₂ and (d) N₂ saturated - 0.1 M KCl solutions.

quality crystals¹⁴ were grown by the slow successive diffusion of *n*-hexane into a solution of **1** in CHCl₃. The crystal structure of the [Ni₆Se₅]²⁺ cluster is depicted in Figure 1.

CVs recorded for **1** in a CH₂Cl₂ solution shows four redox

processes at +1.0/+1.5 V, +0.25/+0.75 V, -0.25 V/-0.60, -1.15/-1.50, respectively (Figure 2A). Figure 2B shows the CVs recorded for the electrode modified by **1** in a 0.1 M KCl solution under an atmosphere of N₂ and CO₂ and for the bare electrode under the same condition. The catalytic peak for the electroreduction of CO₂ was observed for the electrode modified with dropping the solution of **1** in CH₂Cl₂ on the GCE surface. The redox peak of **1** recorded in a 0.1 M KCl solution with a bare GCE was so small compared with the catalytic reduction peak of CO₂ that it was difficult to observe in the CVs as shown in Figure 2B. While a small cathodic peak at -1.38 V appeared at the bare electrode in a 0.1 M KCl solution saturated with CO₂, a large cathodic one (*I*_{pc} = 300 μA) (Figure 2B(c)) was observed at the electrode modified by **1** in the same solution. In addition, the cathodic peak was shifted to a more positive potential by *ca.* 0.28 V and was therefore observed at -1.10 V. The enhanced current and the shifting of the potential should be attributed to the catalytic activity of **1** towards the electroreduction of CO₂. Since increasing the CO₂ concentration in the atmosphere is a major global concern, the electrochemical and the photoelectrochemical reduction of CO₂ have become one of topics of considerable interest which have been extensively studied.¹⁷ Thus, this cluster could be used as the electrode material for the electrocatalytic reduction reaction of CO₂. In conclusion, the nickel cluster selenide **1**, which is the first example of utilizing the catalytic reduction of CO₂ with a transition metal cluster chalcogenide ligated by multiple redox-active organometallic centers, was prepared by the one-pot self-assembly method, and shows catalytic activity for the reduction of CO₂ at the GCE electrode. The extension of the present synthetic protocol *via* the variation of the reaction parameters has the potential to provide large variety of such transition metal cluster chalcogenides ligated by multiple organometallic centers, thereby opening an intensifying research area in fields ranging from the catalytic reactions of organic substrates to the preparations of new types of multielectron redox catalysts. Further investigation on the detailed redox mechanism of the cluster film on electrodes will be undertaken.

Experimental Section

Chemicals. Anhydrous methylene chloride, CH₂Cl₂ (Aldrich Co., Sure/SealTM) was used as solvent as received and without further purification. Tetrabutylammonium perchlorate (TBAP; Fluaka, USA) was used as supporting electrolyte, which was recrystallized twice from ethanol followed by drying at 110 °C in a vacuum oven at a reduced pressure for over 24 hours before use. Other reagents and solvents were purchased from Aldrich Co.

Synthesis of [Ni₆(μ₃-Se)₂(μ₄-Se)₃(dppf)₃]Br₂·3/2CHCl₃ (1**).** To a solution of acetanilide (0.27 g, 2.0 mmol) in tetrahydrofuran (10 mL) was added *n*-BuLi (1.6 M, 1.4 mL, 2.2 mmol) and stirred for 30 min. at room temperature. To this solution, Ni(dppf)Br₂ (1.60 g, 2.0 mmol) and a solution

of Li_2Se prepared from Se (0.13 g, 2.0 mmol) and lithium triethylborohydride (1.0 M, 4.3 mL, 4.3 mmol) in tetrahydrofuran (20 mL) were added and stirred for 24 h at room temperature. Dichloromethane was poured into the reaction mixture, which was washed with brine and dried over MgSO_4 . The solvent was removed under reduced pressure. The residue was chromatographed on a silica gel column; a consecutive elution of ethyl acetate and mixed eluent of dichloromethane-methanol (20 : 1) gave 0.53 g (62% yield) of **1** as black solids. Black crystals suitable for X-ray crystallography were obtained by diffusing *n*-hexane into the solution of **1** in CHCl_3 . Anal. Calcd. For $\text{C}_{102}\text{H}_{84}\text{Br}_2\text{Fe}_3\text{-Ni}_6\text{P}_6\text{Se}_5$: C, 47.66; H, 3.26. Found: C, 47.73; H, 3.25.

Instrumentation. CV and chronocoulometric curves were recorded using a KOSENTECH KST-PI (Korea) and BAS-50 (Bioanalytical Systems, West Lafayette, IN, USA) electrochemical analyzers equipped with a conventional cell. Pt and GCE (each of them were 3 mm in diameter) as working and Pt-wire as a counter electrodes were used. For the CPC experiment, Pt-mesh was used as working and Pt-wire as a counter electrode and they were separated from each other by a capillary. Before each experimental run, Pt or GCE were pretreated with polishing the surface with 0.3 and 0.05 Micron α -alumina, respectively. The applied potentials for the first (peak I and I' in Figure 2A) and second (peak II and II' in Figure 2A) cathodic processes were -0.49 V and -1.5 V respectively, whereas, that of the first (peak III' in Figure 2A) and second (peak IV-i + IV-ii in Figure 2A) anodic processes were $+0.5$ and $+1.45$ V respectively. For the CC experiments, the experimental setup is similar to CV. The potential windows for the CC experiments for the first (peak I and I' in Figure 2A) and second (peak II and II' in Figure 2A) cathodic processes were (-0.25 & -0.60) V and (-1.15 & -1.50) V respectively. On the other hand, the potential windows for the first (peak III' in Figure 2A) and second (peak IV-i + IV-ii in Figure 2A) anodic processes were ($+0.25$ & $+0.75$) V and ($+1.0$ & 1.50) V respectively. For all the experiments, Ag/AgNO_3 in acetonitrile was used as reference electrode. The ESCA analysis was performed using a VG Scientific Escalab 250 XPS spectrometer with monochromated Al K_{α} source with charge compensation at KBSI (Busan). Rotating ring-disc electrode (RRDE) experiments were performed using a PINE, Model AFRDE5 Bi-Potentiostat connecting with a KOSENTECH-8 channel Data Acquisition System DA-1 and a PC and an EG&G (Princeton Applied Research) Model 636 Ring-Disk Electrode System.

Working solution. The working solution for the voltammetric measurements was 0.1 mM of the metal cluster in CH_2Cl_2 containing 0.1 M TBAP. In case of CPC, 0.05 mM of the metal cluster in 0.1 M TBAP was used and subjected to bulk electrolysis at a Pt-mesh electrode. Before each run, nitrogen gas was purged through the solution for twenty minutes and a continuous stream of nitrogen gas-flow was maintained above the surface of the working solution. All the voltammetric measurements were performed at room temperature and pressure.

[Ni-Se-dppf] modified GCE electrode preparations for CO_2 reduction. For the preparation of the [Ni-Se-dppf] modified GCE, 20 μL of the 0.1 mM [Ni-Se-dppf] cluster solution in CH_2Cl_2 was carefully transferred to the clean GCE surface and the solvent was allowed to evaporate at room temperature. The modified electrode was kept at 60°C for at least four hours to remove the rest of the organic solvent from the electrode surface before use. For the RRDE experiment, the glassy carbon disk (area 0.459 cm^2) was modified by the metal cluster in a similar way above, whereas, the glassy carbon ring electrode remained unmodified.

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- 148.
14. Crystal data for **1**: $C_{102}H_{84}Br_2Fe_3Ni_6P_6Se_5 \cdot 3/2CHCl_3$, $M=2748.93$, Rhombohedral, space group $R\bar{3}$ (no. 148), $a = 21.621(9)$ Å, $c = 83.919(7)$ Å, $\alpha = \beta = 90$, $\gamma = 120^\circ$, $V = 33974(4)$ Å³, $Z = 12$, $F(000) = 18396$, $D_c = 1.822$ Mg/m³, $T = 123(2)$ K, μ (Mo-K α) = 4.109 mm⁻¹, $R1 = 0.075$ for 91731 observed reflections ($I > 2.00\sigma(I)$), $wR2 = 0.230$ (all data). Large positive (4.929 eÅ⁻³) and negative (-4.030 eÅ⁻³) difference Fourier peaks located at short distances from Br1 were attributed to ghosts of the heavy Br atom. Large Su max value was due to the increase of temperature factor from the strong vibration of Br3 and Br4. CCDC 255801.
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