

Note

Transmetallation of nickel(II) ion in a nickel(II) azamacrocyclic complex with gold(III) ion

Hyochoon Bang ^{a,*1}, Eun Ja Lee ^b, Eun Young Lee ^b, Junghun Suh ^b,
Myunghyun Paik Suh ^{b,*2}

^a Department of Chemistry, Duksung Women's University, Seoul 132-714, South Korea

^b School of Chemistry and Center for Molecular Catalysis, Seoul National University, Seoul 151-742, South Korea

Received 27 January 2000; accepted 16 June 2000

Abstract

The Ni(II) macrocyclic complex $[\text{Ni}(\text{L})]^{2+}$ ($\text{L} = 1,8\text{-dimethyl-}1,3,6,8,10,13\text{-hexaazacyclotetradecane}$) reacts with AuCl_4^- in MeCN, and the Ni(II) ion in the macrocyclic complex is exchanged with Au(III) ion. The kinetic study on the transmetallation reaction shows that the rate is inhibited by acid and Cl^- , which is explained in mechanistic terms. © 2000 Elsevier Science S.A. All rights reserved.

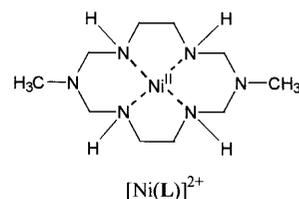
Keywords: Transmetallation; Nickel complexes; Gold complexes; Azamacrocyclic complexes

1. Introduction

The complexes of polyazamacrocyclic ligands with central metal ions with d^8 electronic configuration, such as Ni(II), have been actively studied [1–8]. However, Au(III) macrocyclic complexes have been rarely reported since the first Au(III)–cyclam complexes were reported by Kimura's group [9]. The Au(III) ion has been seldom used as a metal template for the synthesis of macrocyclic complexes [10,11]. Recently, we have synthesized Au(III) complexes of the hexaazamacrocyclic ligand, 1,8-bis(hydroxyethyl)-1,3,6,8,10,13-hexaazacyclotetradecane, by the one-pot metal template synthesis [12].

We have been interested in the possibility of metal exchange reaction for some Ni(II) macrocyclic complexes with Au(III) ion. We have discovered that the Au(III) ion can substitute the Ni(II) ion in the Ni(II)

macrocyclic complex, while other metal ions cannot. In search of factors that facilitate the transmetallation reaction as well as mechanistic information, we carried out a kinetic study for the substitution reaction of Ni(II) with Au(III) in the Ni(II) complex of 1,8-dimethyl-1,3,6,8,10,13-hexaazacyclotetradecane (L) in MeCN.



2. Experimental

2.1. Materials

MeCN was purified according to the literature [13]. $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ and $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ were recrystallized from EtOH and MeCN, respectively, to remove the

¹*Corresponding author. Tel.: +82-2-901 8356; fax: +82-2-901 8469; e-mail: hcbang@center.duksung.ac.kr

²*Corresponding author. Tel.: +82-2-886 8516; fax: +82-2-889 0749; e-mail: mpsuh@plaza.snu.ac.kr

lattice water. $[\text{Ni}^{\text{II}}(\text{L})](\text{ClO}_4)_2$ (**1**) was prepared by the metal-template Schiff-base condensation as reported previously [2b].

2.2. Synthesis of $[\text{Au}^{\text{III}}(\text{L}^-)]\text{Cl}_2$ (**2**)

$[\text{Ni}^{\text{II}}(\text{L})](\text{ClO}_4)_2$ (**1**) (50 mg, 1.02×10^{-4} mol) was dissolved in MeCN (5 ml), and then HAuCl_4 (80 mg, 2.03×10^{-4} mol) in MeCN (3 ml) was added. After the color of the mixture changed to dark brown, the solution was slowly evaporated at room temperature to induce the precipitation. The brown precipitate formed was filtered, washed with MeOH, and dried in vacuo. Yield: 80%. Anal. Calc. for $\text{AuC}_{10}\text{H}_{25}\text{N}_6\text{Cl}_2$: C, 24.16; H, 5.06; N, 16.90. Found: C, 24.58; H, 5.96; N, 16.51%. Λ_{M} (in MeCN): $218 \Omega^{-1} \text{cm}^{-1} \text{M}^{-1}$.

2.3. Kinetic measurements

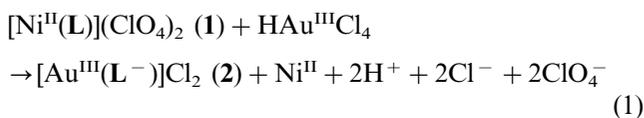
Reaction rates were measured at 25°C with a Shimadzu UV-260 spectrophotometer by following the absorbance change at 318 nm, which corresponds to the maximum absorption of the product $[\text{Au}^{\text{III}}(\text{L}^-)]\text{Cl}_2$ (**2**) formed from the reaction of HAuCl_4 and $[\text{Ni}^{\text{II}}(\text{L})](\text{ClO}_4)_2$ (**1**). Reaction mixtures were made in MeCN with the total ionic strength being maintained at 0.023 M with NaClO_4 . Water associated with concentrated HClO_4 or the hydrated form of $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ was introduced to the reaction mixture, but its total content was negligible. The initial concentration of HAuCl_4 ($[\text{HAuCl}_4]_0$) was 2.7×10^{-5} M, whereas that of **1** ($[\text{1}]_0$) was $(0.6 \sim 8.0) \times 10^{-3}$ M. Under these conditions, pseudo-first-order kinetic behavior was observed for the formation of **2**.

Caution! Perchlorate salts of metal complexes with organic ligands and perchloric acid are potentially explosive. Handle in only small amounts and with great care.

3. Results and discussion

3.1. Properties of $[\text{Au}^{\text{III}}(\text{L}^-)]\text{Cl}_2$ (**2**)

Complex **2** was prepared by substituting the Ni(II) ion in $[\text{Ni}^{\text{II}}(\text{L})]^{2+}$ with the Au(III) ion as in Eq. (1):



The resulting dark brown precipitate was stable in the air. It is insoluble in water, but slightly soluble in EtOH and CH_3CN . The infrared spectrum of complex **2** showed ν_{NH} of the secondary amines of the macrocyclic ligand L at 3150 and 3200 cm^{-1} (split), while the reactant (complex **1**) showed ν_{NH} at 3200 cm^{-1} . The peak at 1200 ~ 1100 cm^{-1} , which is a characteristic peak for the anion ClO_4^-

of $[\text{Ni}^{\text{II}}(\text{L})](\text{ClO}_4)_2$ (**1**), disappeared for the product. This indicates that the counter anion of the product was replaced with Cl^- . The electronic absorption spectrum of the brown product measured in MeCN showed a maximum absorption at 318 nm ($\epsilon = 12\,000 \text{ M}^{-1} \text{cm}^{-1}$). The peaks for the product in the visible range were not observed because of their overlapping with an intense absorption at 318 nm. In the case of complex **1**, the absorption maximum for the d–d transition appeared at 449 nm ($\epsilon = 56 \text{ M}^{-1} \text{cm}^{-1}$) [2b]. The large ϵ value at $\lambda = 318$ nm for the product must be attributed to the charge transfer from L^- to Au(III). This result is comparable with Kimura's Au(III) macrocyclic complex [9]. A deprotonated form of the compound was characterized by elemental analysis and the molar conductance value corresponded to a 1:2 electrolyte.

3.2. Kinetic study for transmetallation

Kinetic data were obtained in MeCN at 25°C by following absorbance increases at 318 nm. At this wavelength, the molar extinction coefficient of the product was $12\,000 \text{ M}^{-1} \text{cm}^{-1}$. The ionic strength was maintained at 0.023 M. The data were measured with $(2.10 \pm 0.07) \times 10^{-2}$ M NaClO_4 and $(0.28 \sim 6.48) \times 10^{-4}$ M HClO_4 .

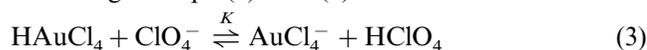
Under the conditions of $[\text{1}]_0 \gg [\text{HAuCl}_4]_0$, pseudo-first-order kinetic behavior was observed for the formation of **2**. The pseudo-first-order rate constants (k_o) measured at various concentrations of $[\text{1}]_0$ in the presence of 1.55×10^{-4} M HClO_4 are illustrated in Fig. 1. The values of k_o were proportional to $[\text{1}]_0$ with proportionality constant k_{bi} . The rate was first-order with respect to both $[\text{HAuCl}_4]_0$ and $[\text{1}]_0$. The overall rate law can be expressed as Eq. (2):

$$\text{rate} = \frac{d[\text{2}]}{dt} = k_o[\text{HAuCl}_4]_0 = k_{\text{bi}}[\text{1}]_0[\text{HAuCl}_4]_0 \quad (2)$$

We examined the effects of the H^+ and Cl^- ion on the reaction rate, by using HClO_4 and tetrabutylammonium chloride (TBAC). Addition of HClO_4 inhibited the reaction (Fig. 2). Addition of low concentrations of TBAC reduced the rate in comparison with the reaction carried out in the absence of TBAC. When $[\text{TBAC}]_0$ was greater than 3×10^{-4} M, however, the reaction became considerably faster than when carried out in the absence of TBAC (Fig. 3).

3.2.1. Effect of HClO_4

As the rate data measured in MeCN, HClO_4 and NaClO_4 may be regarded as a weak acid and its conjugate base, respectively, which act as a buffer system. In this buffer solution, HAuCl_4 may be partially neutralized according to Eqs. (3) and (4):



$$K = \frac{[\text{AuCl}_4^-][\text{HClO}_4]}{[\text{HAuCl}_4][\text{ClO}_4^-]} \quad (4)$$

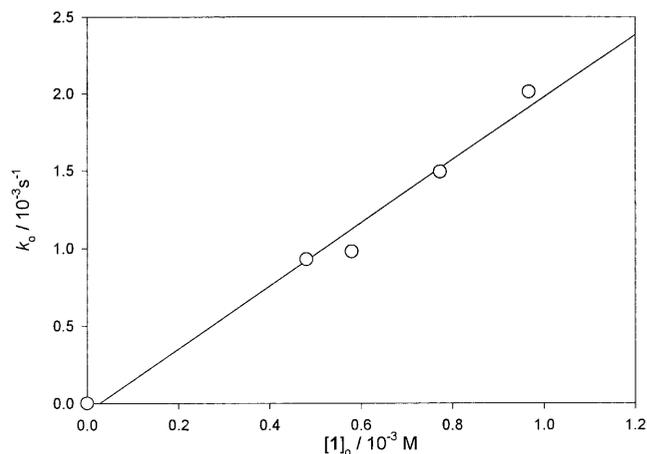


Fig. 1. The plot of k_o against $[1]_o$ for the reaction of **1** with AuCl_4^- in the presence of 1.55×10^{-4} M HClO_4 in MeCN at 25°C . The slope of the solid line is k_{bi} .

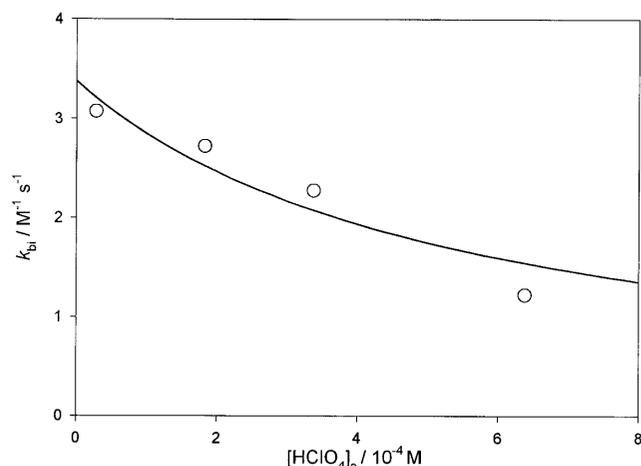


Fig. 2. Plot of k_{bi} against $[\text{HClO}_4]_o$ for the reaction of **1** with AuCl_4^- in MeCN at 25°C . The solid line was drawn to fit the curve with Eq. (7).

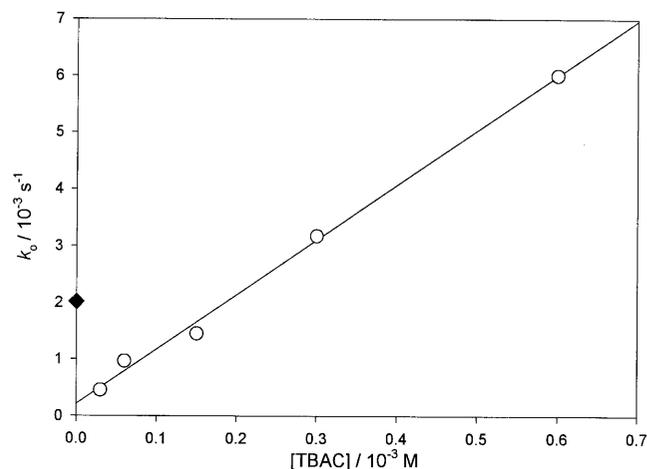


Fig. 3. Values of k_o measured in the absence (◆) or presence (○) of TBAC for the reaction of **1** with AuCl_4^- in the presence of 1.0×10^{-4} HClO_4 and 2.9×10^{-5} M HAuCl_4 in MeCN at 25°C .

Kinetic data were obtained with 2.75×10^{-5} M of $[\text{HAuCl}_4]_o$, which is considerably smaller than $[\text{NaClO}_4]_o$ (the initially added concentration of NaClO_4 ; 2.17×10^{-3} M) or $[\text{HClO}_4]_o$ (the initially added concentration of HClO_4 ; $2.76 \times 10^{-4} \sim 6.38 \times 10^{-4}$ M). Under these conditions, $[\text{AuCl}_4^-]$ can be approximated as Eq. (5), which can be derived from Eq. (4) and the mass balance of gold element, $[\text{HAuCl}_4]_o = [\text{HAuCl}_4] + [\text{AuCl}_4^-]$. The ratio $[\text{HClO}_4]/[\text{ClO}_4^-]$ corresponds to $[\text{H}^+]/K_a$, where K_a stands for the ionization constant of HClO_4 in MeCN. Since $[\text{HAuCl}_4]_o \ll [\text{NaClO}_4]_o$ or $[\text{HClO}_4]_o$, $[\text{HClO}_4]$ and $[\text{ClO}_4^-]$ can be taken as $[\text{HClO}_4]_o$ and $[\text{NaClO}_4]_o$, respectively.

$$[\text{AuCl}_4^-] = \frac{[\text{HAuCl}_4]_o}{1 + \frac{[\text{HClO}_4]}{K[\text{ClO}_4^-]}} \quad (5)$$

If we consider the case in the absence of HClO_4 as the limiting case, the following relationship (Eq. (6)) could be established, where k_{bi}^{lim} is the k_{bi} value measured in the absence of added HClO_4 .

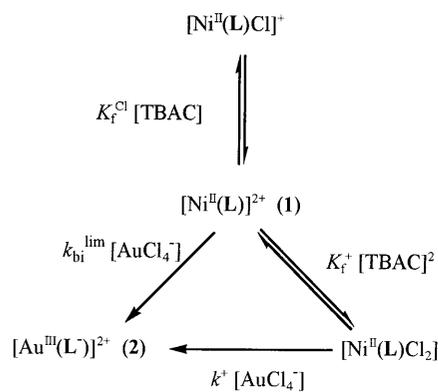
$$k_{bi}^{\text{lim}} [\text{AuCl}_4^-] = k_{bi} [\text{HAuCl}_4]_o \quad (6)$$

From Eqs. (5) and (6), we can deduce the relationship between k_{bi} and $[\text{HClO}_4]_o$ as Eq. (7). If AuCl_4^- , instead of HAuCl_4 , is the reactive species, the inhibitory action of HClO_4 can be explained with Eq. (7). Here, the K° , which is same as the $K[\text{ClO}_4^-]$ term of Eq. (5), is the value of $[\text{HClO}_4]_o$ at which k_{bi} is half of k_{bi}^{lim} .

$$k_{bi} = \frac{k_{bi}^{\text{lim}}}{1 + \frac{[\text{HClO}_4]_o}{K^\circ}} \quad (7)$$

The k_{bi} values were measured at several $[\text{HClO}_4]_o$ concentrations. The dependence of k_{bi} on $[\text{HClO}_4]_o$ is illustrated in Fig. 2. The curve indicated in Fig. 2 was obtained by fitting the experimental data to Eq. (7). The values of k_{bi}^{lim} and K° used for the construction of the curve are $3.37 \text{ M}^{-1} \text{ s}^{-1}$ and 5.38×10^{-4} M, respectively. From K° , K is calculated as 19.6, indicating that HAuCl_4 is slightly more acidic than HClO_4 in MeCN.

The inhibitory action of HClO_4 suggests that HClO_4 masks the reactive species involved in the formation of **2**. A likely reactant to be masked is AuCl_4^- . HClO_4 may protonate AuCl_4^- to form HAuCl_4 as indicated in Eq. (3). It is also possible that HAuCl_4 may form an adduct with ClO_4^- in MeCN. HAuCl_4 may be much less reactive than AuCl_4^- toward **1**, presumably due to reduced electrostatic affinity toward cationic complex **1**.



Scheme 1.

3.2.2. Effect of TBAC

The kinetic data were also measured in the presence of TBAC ($3 \times 10^{-5} \sim 6 \times 10^{-4}$ M). Here, $[\text{I}]_0$, $[\text{HClO}_4]_0$ and $[\text{HAuCl}_4]_0$ were 1.00×10^{-3} , 1.55×10^{-4} , and 2.90×10^{-5} M, respectively. The values of k_o measured at various $[\text{TBAC}]_0$ are illustrated in Fig. 3. As revealed by Fig. 3, addition of 0.30×10^{-4} M TBAC reduced k_o from $2.01 \times 10^{-3} \text{ s}^{-1}$ to $0.449 \times 10^{-3} \text{ s}^{-1}$. When TBAC was added further, however, k_o was proportional to $[\text{TBAC}]_0$. The line of Fig. 3 is drawn with the proportionality constant of $10.3 \text{ M}^{-1} \text{ s}^{-1}$.

Both the inhibitory and the accelerating effects of TBAC are consistent with the mechanism described in Scheme 1. The rate expression for Scheme 1 is derived as Eq. (8) under the condition of $[\text{I}]_0 \gg [\text{HClO}_4]_0$.

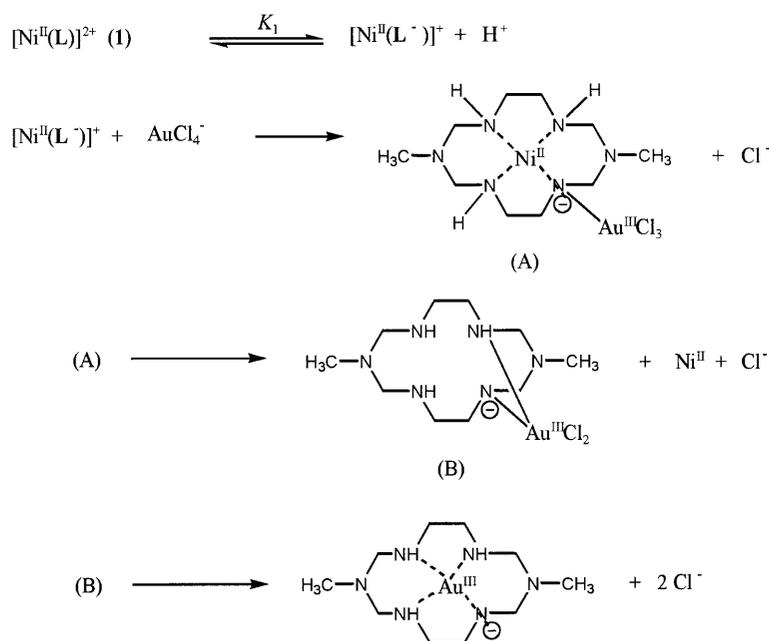
$$k_{\text{bi}} = \frac{k_{\text{bi}}^{\text{lim}} + k^+ K_f^+ [\text{TBAC}]^2}{1 + K_f^{\text{Cl}} [\text{TBAC}] + K_f^+ [\text{TBAC}]^2} \quad (8)$$

If the Ni(II) complex of L exists primarily as the monochloro species ($[\text{Ni}^{\text{II}}(\text{L})]^{2+} \cdot \text{Cl}^-$), then $K_f^{\text{Cl}} [\text{TBAC}] \gg 1 + K_f^+ [\text{TBAC}]^2$ and Eq. (8) becomes Eq. (9). The decrease in k_o at low $[\text{TBAC}]$ and the linear dependence of $k_{\text{bi}}^{\text{lim}}$ on $[\text{TBAC}]$ illustrated in Fig. 3 is predicted by Eq. (9). If $k_{\text{bi}}^{\text{lim}} \gg k^+ K_f^+ [\text{TBAC}]^2$ at low concentrations ($< 3 \times 10^{-5}$ M) of TBAC, Eq. (9) predicts that k_{bi} is suppressed in the presence of TBAC. When $k_{\text{bi}}^{\text{lim}} \ll k^+ K_f^+ [\text{TBAC}]^2$, Eq. (9) predicts k_{bi} is proportional to $[\text{TBAC}]$.

$$k_{\text{bi}} = \frac{k_{\text{bi}}^{\text{lim}}}{K_f^{\text{Cl}} [\text{TBAC}]} + \frac{k^+ K_f^+ [\text{TBAC}]}{K_f^{\text{Cl}}} \quad (9)$$

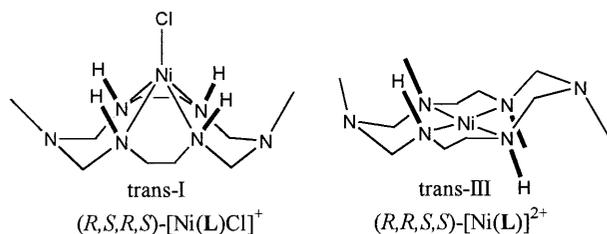
3.3. Proposed mechanism

As described in Scheme 1, four- and six-coordinate Ni(II) species, $[\text{Ni}^{\text{II}}(\text{L})]^{2+}$ and $[\text{Ni}^{\text{II}}(\text{L})\text{Cl}_2]$, are able to react with AuCl_4^- , but five-coordinate Ni(II) species $[\text{Ni}^{\text{II}}(\text{L})\text{Cl}]^+$ do not react with AuCl_4^- . Although the detailed process from $[\text{Ni}^{\text{II}}(\text{L})]^{2+}$ or $[\text{Ni}^{\text{II}}(\text{L})\text{Cl}_2]$ to $[\text{Au}^{\text{III}}(\text{L})]^{2+}$ in Scheme 1 cannot be proposed by the rate law, a plausible mechanism is suggested in Scheme 2. Since $[\text{Ni}^{\text{II}}(\text{L})]^{2+}$ and $[\text{Ni}^{\text{II}}(\text{L})\text{Cl}_2]$ species have a *trans*-III structure, where two hydrogen atoms in secondary amines orient to a side opposite to that of the other two, which is the most stable form thermodynamically [14], the approach of AuCl_4^- to the Ni(II) complex is easy as described in Scheme 2. However, the five-coordinate $[\text{Ni}^{\text{II}}(\text{L})\text{Cl}]^+$ has a *trans*-I structure



Scheme 2.

where all four hydrogen atoms of secondary amines orient toward the same direction and the Ni(II) ion is located out of square-coordination plane toward the same direction of the protons. The access of AuCl_4^- to the deprotonated secondary amine may be difficult because of the steric hindrances.



Acknowledgements

This work was supported by the Non-directed Research Fund, Korea Research Foundation, 1996.

References

- [1] M.P. Suh, *Adv. Inorg. Chem.* 44 (1996) 93.
- [2] (a) M.P. Suh, W. Shin, H. Kim, C.H. Koo, *Inorg. Chem.* 26 (1987) 1846. (b) M.P. Suh, S. Kang, *Inorg. Chem.* 27 (1988) 2544. (c) M.P. Suh, W. Shin, S. Kang, M.S. Lah, T.M. Chung, *Inorg. Chem.* 28 (1989) 1602. (d) M.P. Suh, S. Kang, V. Goedken, S. Park, *Inorg. Chem.* 30 (1991) 365. (e) M.P. Suh, B.Y. Shim, T. Yoon, *Inorg. Chem.* 33 (1994) 5509.
- [3] C.L. Schmid, M. Neuburger, M. Zehnder, T.A. Kaden, *Helv. Chim. Acta* 80 (1997) 241.
- [4] L. Fabbri, M. Licchelli, P. Pallavicini, L. Parodi, *Angew. Chem., Int. Ed.* 37 (1998) 800.
- [5] B. Korybut-Daszkiewicz, P. Gluzinski, J. Krajewski, A. Kemme, *Mishnev, Eur. J. Inorg. Chem.* (1999) 263.
- [6] M.A. Donnelly, M. Zimmer, *Inorg. Chem.* 38 (1999) 1650.
- [7] A. McAuley, S. Subramanian, *Inorg. Chem.* 38 (1999) 5078.
- [8] J. Elmes, M. Basato, G. Valle, *Inorg. Chim. Acta* 293 (1999) 14.
- [9] E. Kimura, Y. Kurogi, T. Takahashi, *Inorg. Chem.* 30 (1991) 4117.
- [10] J.H. Kim, G.W. Everette, Jr., *Inorg. Chem.* 18 (1979) 3145.
- [11] J.H. Kim, G.W. Everette, Jr., *Inorg. Chem.* 20 (1981) 853.
- [12] M.P. Suh, I.S. Kim, B.Y. Shim, D. Hong, T. Yoon, *Inorg. Chem.* 35 (1996) 3595.
- [13] D.D. Perrin, W.L.F. Armarego, *Purification of Laboratory Chemicals*, 3rd ed., Pergamon, Oxford, UK, 1988.
- [14] R.D. Hancock, *Acc. Chem. Res.* 23 (1990) 253.