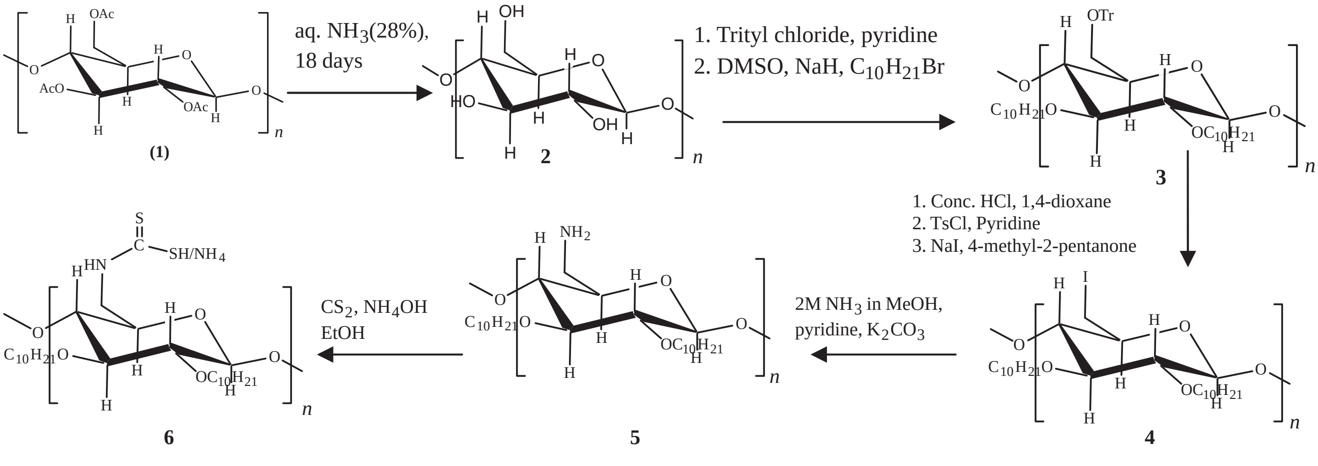
Regioselective Synthesis of Lipophilic Dithiocarbamate Derivatives of Cellulose to Prepare a Novel Solvent Extraction Reagent for Selective Extraction of PGM Ions and Cu(II)

Rabindra Prasad Dhakal,*[1] Katsutoshi Inoue,[2] Keisuke Ohto,[2] and Yoshinari Baba[1]
[1]*Department of Applied Chemistry, University of Miyazaki, 1-1 Gakuen Kibandai Nishi, Miyazaki 889-2192*
[2]*Department of Applied Chemistry, Saga University, Honjo-1, Saga 840-8502*

(Received June 29, 2006; CL-060734; E-mail: dhakalrabi@cc.miyazaki-u.ac.jp)

Regenerated cellulose from cellulose triacetate was regioselectively converted into its lipophilic amino and dithiocarbamate derivatives to prepare novel solvent extraction reagents with series of substitutions and deoxy substitution reaction. The 6-deoxydithiocarbamate-2,3-didecyl cellulose prepared in this work significantly demonstrated the high lipophilicity coupled with high selectivity for PGM ions and also to the Cu(II) over Ni(II) and Zn(II) in liquid–liquid extraction.

Precious metal ions are tremendously used in many industrial processes that obviously draw due attention for its proper recovery from its waste, particularly from spent catalyst and electrolytes as well as electronic and jewellery scraps. On the other hand, cellulose, the most abundant biopolymer in nature that possesses two kinds of hydroxy groups in its pyranose ring, was utilized to increase its selectivities for specific metal groups like PGM (Platinum Group Metal) ions and some others. However, several chemical modifications are needed to prepare a solvent extraction reagent from such a biopolymer as evidenced and inspired by previous works on chitosan.[1] On contrast, the novelty of this study is the cost effective use of available tremendous resources, innovative and regioselective synthetic approach, and preferable stripping process by incineration, among others. Hence, the lipophilic moieties were regioselectively introduced into the secondary positions of the cellulose whereas reactive functional moiety to the primary position as shown in Scheme 1 tends to create stereo electronically free environment for reactive functional groups. The microcrystalline structures of cellulose[2,3] usually pose set back for complete conversion of such polymer, hence, cellulose triacetate (**1**), was taken as a starting material to regenerate the cellulose by mild alkaline hydrolysis for 18 days which is presumed to be turned into amorphous cellulose **2**. By doing so, the degradative hydrolysis (peeling effect of polymer chain) was avoided while using strong alkaline solution, and at the same time, complete regeneration of hydroxy group was achieved. It was then protected regioselectively by trityl group to keep the primary hydroxy group intact for further chemical modification after refluxing dehydration with pyridine repeatedly at elevated temperature.[3,4] We have observed that the tritylation degree was as high as 1.002 with trityl chloride equivalent to a primary hydroxy group where as 1.007 on using monomethoxy trityl chloride as tritylating reagent, as latter is the better protecting group. It was evaluated by elemental analysis (C, 74.42 (obs.); 74.25 (cal.); H, 6.00 (obs.); 5.94 (calc.)), ^{1}H NMR (270 MHZ, $CDCl_3$): δ 7.45–7.24 (m, br), and IR: C–H stretching at 3032 cm^{-1} and bending at 1468 cm^{-1} representing for trityl group that is also on agreement with conventional trends to protect only primary hydroxy group. It was then treated with *n*-bromodecane in presence of dimsyl anion solution[5,6] to get **3** substituting two equivalent of hydroxy groups as revealed by ^{1}H NMR, particularly, δ 1.55–1.26 (m, br), 3.18 (br) for methylene moieties and 0.88 (t) for methyl moieties of decyl groups. Moreover, lacks of O–H stretching band in IR spectroscopy strongly supports the successful conversion. The subsequent deprotection was done by HCl in 1,4-dioxane[7] as other solvents appeared inappropriate to regenerate hydroxy group which was evidenced by O–H stretching band at 3498 cm^{-1} with slight blue shift compared to previous non alkylated products suggesting less hydrogen bonding than before. Moreover, there is no more absorbance for aromatic moieties on ^{1}H NMR suggesting complete regeneration of primary hydroxy group previously occupied by



Scheme 1. Synthetic route to prepare lipophilic cellulose and its dithiocarbamate derivative.

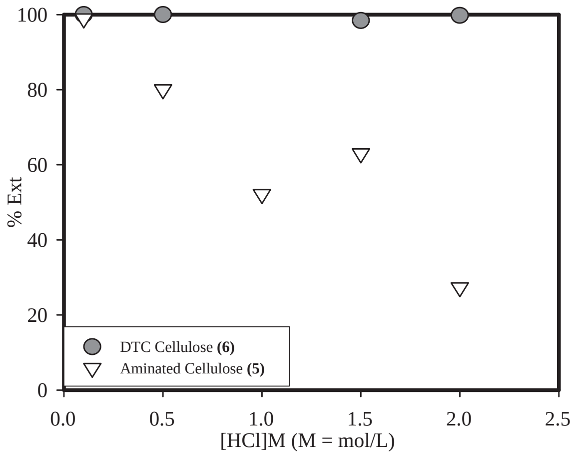


Figure 1. Extraction of Pd^{II} by **5** and **6** using chloroform as diluents HCl concentration. Reagent concentration = 2.00 kg m^{-3}. Diluent = chloroform. Initial metal ion concentration = 1 mM. Aqueous/organic phase ratio = 1:1. Shaking time = 24 h. Temperature = 303 K.

the trityl moieties. It was then preferably substituted by tosyl group to offer complete conversion followed by iodo-substitution[8] to avoid the inevitable hydrolysis of tosyl group going back to hydroxy while using aqueous ammonia solution for amination; hence, the tosylation was appeared a key step for the successful substitution. The tosylation was confirmed by presence of asymmetric stretching at 1365 cm^{-1} and symmetric stretching at 1177 cm^{-1} for $S(=O)_2$ in IR and δ 2.44(s), 7.79(d), and 7.29(d) in ^{1}H NMR representing for tosyl moieties. Moreover, it was soluble in acetone differing to the compound formed and through which it was transformed. It was then converted into **4** which was evaluated by lack of previously observed spectral evidences for tosyl groups and chemical shifts for C^6–methylene group (δ 4.46–4.31 (m, br) which in turn was transformed into amino derivatives as supported by δ 7.40–7.179 (m, br) to offer the reactive site for preparation of dithiocarbamate derivatives.[1] The conversion was confirmed by IR and NMR with stretching band of C=S, C–S, and S–H at 1377, 729, and 2600 cm^{-1} and overtone band at 2100 cm^{-1} to represents $NH_4{}^+$ and chemical shift, δ 7.836–7.766, 7.542–7.44 (m, br, $NH_4{}^+$). The ^{1}H NMR clearly revealed the complete conversion of amino derivative into dithiocarbamate derivative evidenced by lack of resonance band presumed for protonated amino moieties. The cellulose which is insoluble in many conventional solvents was successfully converted into highly lipophilic compounds as revealed by its solubility trends whereby it was found soluble in most non-polar organic solvents including kerosene, hexane, and chloroform whereas insoluble in polar organic solvents such as methanol and acetone.

In Figure 1, the dithiocarbamate derivative of lipophilic cellulose was compared with its amine counterpart for extraction of Pd(II) at various concentrations of HCl that revealed the enhanced extractability of **6** compared to **5**, and also suggested the different mechanism involved viz. cation and anion exchange mechanism, respectively. Particularly, at higher acidic concentration, the Pd^{II} extraction with **5** was evidently declined as represented by the following scheme:

$$2R\text{-}NH_3{}^+Cl^- + PdCl_4{}^{2-} \rightleftharpoons (R\text{-}NH_3{}^+)_2PdCl_4{}^{2-} + 2\ Cl^-. \qquad (1)$$

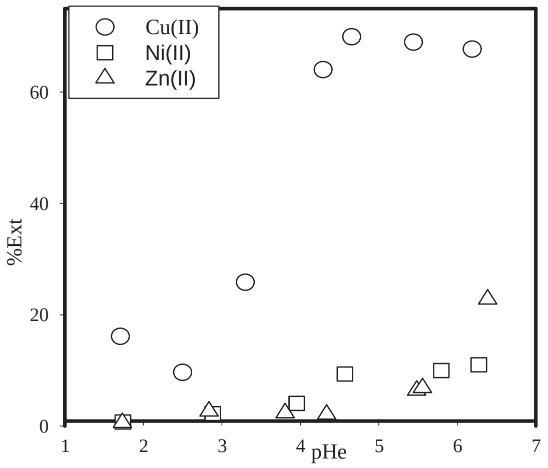


Figure 2. Extraction behavior of **6** for different base metal ions as chloroform a diluent as a function of pH. Reagent concentration = 2.00 kg m^{-3}. Diluent = chloroform. Initial metal ion concentration = 1 mM. Aqueous/organic phase ratio = 1:1. Shaking time = 24 h. Temperature = 303 K.

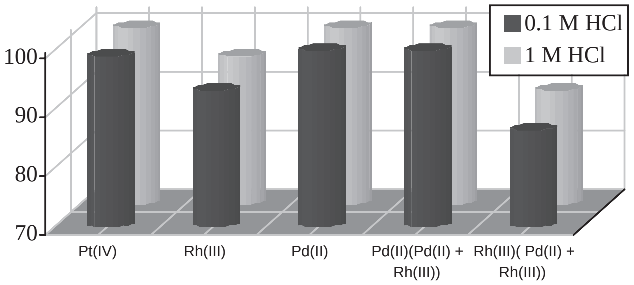


Figure 3. Extraction profile of PGM ions with **6** using chloroform as diluents at different HCl concentration. Reagent concentration = 2.00 kg m^{-3}. Diluent = chloroform. Initial metal ion concentration = 1 mM. Aqueous/organic phase ratio = 1:1. Shaking time = 24 h. Temperature = 303 K.

The extraction tests of some base metal ions such as Cu^{II}, Ni^{II}, and Zn^{II} were also carried out at different pH values as shown in Figure 2. It clearly suggested that Cu^{II} was selectively extracted at equilibrium pH (the pH at equilibrium for complexation) > 4 over Ni^{II} and Zn^{II} that inferred the preferences of the dithiocarbamate moieties to planar complexation. It also inspired us to tests the extraction behavior of some other PGM ions such as Pt^{IV}, Rh^{III}, and Pd^{II} in either single or mixture of metal ions solutions such as Rh^{III} and Pd^{II} from their mixture solutions. It has revealed that all PGM metal ions were effectively extracted at both acidic concentration studied in this case as depicted in Figure 3, whereby there is feebly increased preferences for Pt^{IV} and Pd^{II} over Rh^{III} attributing to the slightly increased selectivity of **6** for soft base metal ions such as Pd^{II} and Pt^{IV} rather than Rh^{III}, a border-line metal ions categorized by HSAB principle. Moreover, Rh^{III} extraction was further suppressed in the presence of Pd^{II} where there was no effect for the extraction of Pd^{II} as depicted in Figure 3. Moreover, on changing the HCl concentration, slight increment has occurred for PGM ions extraction on using 0.1 M and 1 M HCl, as expected.

References

1 K. Inoue, K. Yoshizuka, K. Ohto, H. Nakagawa, *Chem. Lett.* **2001**, 698.
2 W. M. Hearon, G. D. Hiatt, C. R. Fordyce, *J. Am. Chem. Soc.* **1943**, *65*, 2449.
3 K. Ward, C. Tu, M. Lakstigala, *J. Am. Chem. Soc.* **1954**, *76*, 6102.
4 G. Wenz, S. Choi, H. Kern, 216th ACS National meeting, Boston, Aug 23–27, **1998**, Abstr. No., poly-007.
5 T. Heinze, T. Liebert, *Prog. Polym. Sci.* **2001**, *26*, 1689.
6 L. Petrus, D. G. Gray, J. N. Bemiller, *Carbohydr. Res.* **1995**, *268*, 319.
7 G. B. Jones, G. Hynd, J. M. Wright, A. Sharma, *J. Org. Chem.* **2000**, *65*, 263.
8 J. B. Lee, T. J. Nolan, *Tetrahedron* **1967**, *23*, 2789.