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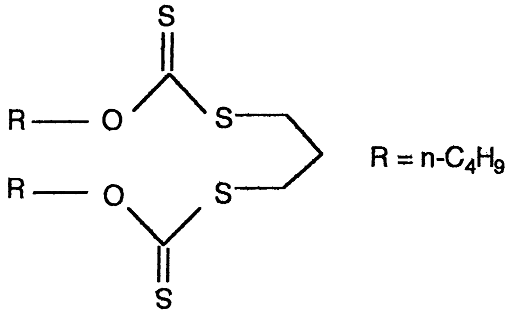
New Xanthic Acid Derivative as Selective Reagent for the Solvent Extraction of Palladium

Didarul Alam CHOWDHURY and Satsuo KAMATA*
Department of Applied Chemistry and Chemical Engineering, Faculty of Engineering,
Kagoshima University, 1-21-40 Korimoto, Kagoshima 890

Trimethylene-bis(n-butyl)xanthate (TrMBnBX) has been synthesized as a new sulfur-containing reagent for the extraction of precious metal ions. This compound exhibited high selectivity for extraction of Pd(II) and Ag(I) ions in dichloroethane, over Pt(IV), Au(III) and most of the base metal ions. A mixed aqueous system containing H_2SO_4 in presence of small amount of chloride ions provides the maximum extraction of Pd(II), where it forms a 1:1 complex with TrMBnBX.

It is well known that sulfur-containing ligands have a high affinity and high selectivity towards complexation with palladium and other precious metal ions, especially in their lower oxidation states. A wide variety of organic reagents incorporating sulfur as the binding sites have been studied in connection with the extraction of palladium, the important ones being dialkylsulfides,1),2) substituted thiourea,3) thiocarboxylic acids,4) 3,3-diethylthietane5) and alkylphosphine sulfides.6) Most of the above mentioned reagents are reported to provide quantitative extraction of palladium from acidic chloride solutions, but are usually interfered by the co-extraction of other platinum group metal ions. Slow kinetics of extraction also appears as one of the drawbacks of the currently employed extractants.1) 2) Moreover, the aqueous feed solution for these sulfur reagents are confined to acidic chloride medium only. So, it is important to develop new extractants having higher selectivity and a wider flexibility in the selection of the extraction medium. Here, we report the extraction of palladium(II) with TrMBnBX in terms of its selectivity, extraction and back-extraction properties and the probable mechanism of extraction.

Potassium n-butyl xanthate reacts in 2 - 3 h with dibromopropane in a 2:1 ratio in acetone at 40 °C to yield an oily liquid, which on purification by column chromatography (silica-gel, 9:1 benzene-ether eluent), produced the pure TrMBnBX. Composition and structural characterization of the new synthetic compound was done by NMR, IR and elemental analyisis data as presented in the following. TrMBnBX, $C_{13}H_{24}O_2S_4$ (M.W.,



Trimethylene-bis(n-butyl)xanthate (TrMBnBX)

340.60): Yield, 89%; Elemental analysis(%), Found(Calcd): C, 45.97(45.85); H, 7.08(7.10), NMR , δ(ppm) = 0.97(t, J=7.2 Hz, 6H, $-CH_3$); 1.55(dd, J=6.2 and 6.8 Hz, 8H, Me-CH_2-CH_2-); 2.17(m, J=7.6 Hz, 2H, -S-C-CH_2-C-S-); 3.25(t, J=8.2 Hz, 4H, -S-CH_2-C-); 4.60(t, J=7.8 Hz, 4H, -O-CH_2-), IR , νC=S, 1060 cm^{-1}; νC-O, 1219 cm^{-1}. In the pure form, TrMBnBX is a light-green liquid having boiling point above 200 °C and is denser than water. It is a neutral compound and is soluble in common polar and non-polar organic solvents. The partition coefficient of TrMBnBX between dichloroethane and water has been evaluated to be 9.94×10^2, indicating that a negligible fraction of the ligand is partitioned to aqueous phase at equilibrium. Unlike simple xanthates, the bis compound is highly stable in air and in presence of acids. Solutions of TrMBnBX (1.0×10^{-4} M) in dichloroethane has been found to remain unchanged after 12 h equilibration with aqueous HCl, H_2SO_4, HNO_3 and $HClO_4$ solutions of 3 M strength.

Solvent extraction experiments were carried out at room temperatures (25 ± 1 °C) in 50 ml vials having ground-glass stoppers and shaken with HIRASAWA Model SH-H1 Time Shakers. The organic phase (10 ml) containing TrMBnBX in dichloroethane was shaken with an equal volume of the aqueous phase containing the metal ion in $NaClO_4$ solution or in mixed acid media. After 1 or 12 h of shaking, the two phases were allowed to separate. Metal distribution data were then obtained from the measurement of its concentration either in the aqueous phase directly or in the organic phase through matrix destruction by wet-ashing, using Atomic Absorption Spectrometry.

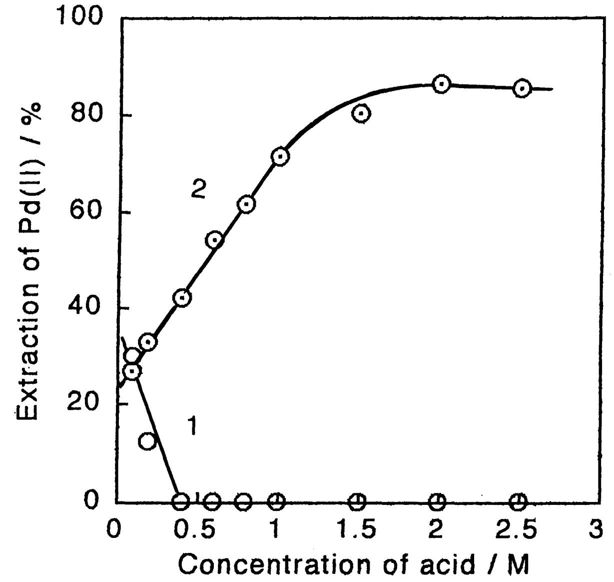
In order to assess the use of the new sulfur compound in solvent extraction, we measured its relative extractability towards various metal ions in dichloroethane, using 1 h shaking time at constant ionic strength of 0.1 M $NaClO_4$ (1M = 1 mol dm^{-1}) in the aqueous phase. The results as shown in Table 1, clearly indicate that the present reagent is highly selective for Pd(II) and Ag(I) ions, over most of the base metals as well as Pt(IV) and Au(III) ions. The observed selectivity pattern suggests that the reagent can be utilized in the selective extraction of palladium from chloride solutions where Ag(I) is removed by prior precipitation as AgCl.

Table 1. Extractability of TrMBnBX toward various metal ions

Metal ion	Pd(II)	Ag(I)	Pt(IV)	Au(III)	Cu(II)	Fe(III)	Ni(II)	Zn(II)	Pb(II)	Co(II)	Cd(II)
Extraction / %	57.3	96.6	0.0	1.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0

[TrMBnBX] = 2.5×10^{-3} M in dichloroethane; [M^{n+}] = 1.0×10^{-4} M in 0.1 M $NaClO_4$;
Shaking Time = 1 h; Shaking Speed = 300 oscillations per min.

As a part of the ultimate solvent extraction procedure, the effects of common mineral acids on the extraction of palladium with TrMBnBX have been studied in the range of 0.1 to 2.5 M concentration of acids. Considerable extraction of Pd(II) is possible only at very low concentrations of hydrochloric acid, the extractability amounting to about 30% at 0.1 M of the acid, under the present experimental conditions. With further increase in the concentration of HCl, the extraction falls off sharply reaching almost zero extraction at around 0.3 M and, no extraction is possible in the higher acid range. This indicates that at considerably higher concentrations of chloride ions, the predominent palladium complex7) 8) in the aqueous phase viz. $PdCl_4^{2-}$ is more stable than the corresponding Pd(II)-TrMBnBX complex. In the presence of pure H_2SO_4, the extraction process results in the spontaneous precipitation of the corresponding palladium salt9) in the aqueous phase, in the whole range of concentration studied. However, the addition of small amount of chloride (0.1 M HCl or 0.1 M NaCl) to the pure sulfuric acid system enabled reversible extraction of palladium in dichloroethane. The extraction behavior of Pd(II) in pure HCl and that in H_2SO_4-NaCl mixed system are compared in Fig. 1. The H_2SO_4 - NaCl system was found to give the optimum extraction of about 98%, reaching equilibrium in 2 h and is characterized with excellent phase separation properties.



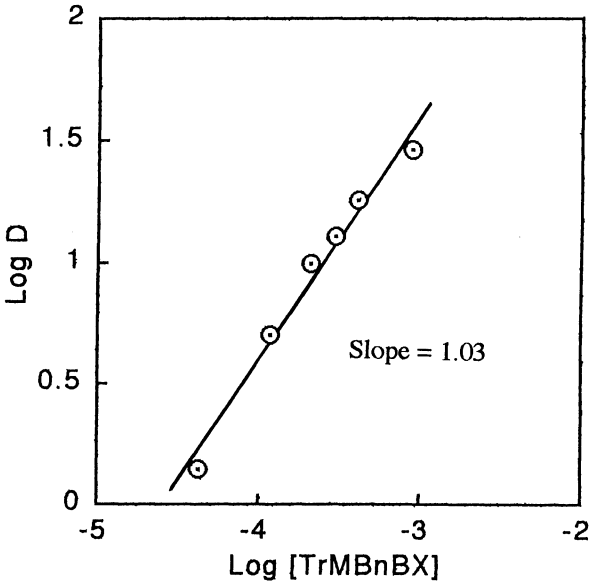


Fig.1. Effect of increasing acid concentration on the extraction of Pd(II) with TrMBnBX. [TrMBnBX] = 2.5×10^{-3} M; [Pd(II)] = 1.0×10^{-4} M; Shaking Time = 1 h.
Curve 1: HCl-only; Curve 2:H_2SO_4-NaCl(0.1 M)

Fig.2. Log D vs Log[TrMBnBX] plot for the extraction of Pd(II) with TrMBnBX from H_2SO_4(1.0 M)-NaCl(0.1 M) system. Shaking Time = 12 h.

The Pd(II)-TrMBnBX stoichiometry for the extractable complex has been determined by slope ratio method for the aqueous system containing 1.0 M H_2SO_4 and 0.1 M NaCl, employing a 12 h shaking time to ensure complete equilibration. Figure 2 shows the plot of log D vs log[TrMBnBX], which produces straight line of slope equal to 1.03, demonstrating that a 1:1 metal-reagent stoichiometry is the most probable configuration of the extracted complex in the organic phase. Here D stands for the distribution ratio for Pd(II), defined as, $D = [Pd(II)]_{org} / [Pd(II)]_{aq}$. From the results in the previous section, it is understood that Pd(II) is not extracted with the present reagent if it exists as $PdCl_4^{2-}$ or as $PdSO_4$ in the aqueous phase, before extraction. So, a mixed chloro species of palladium7) 8) must be responsible in the actual extraction reaction. On the other hand, at constant concentration of H_2SO_4 (1.0 M), a plot of log D against log[Cl^-] yields a straight line of slope equal to -1.97, signifying that two chloride ions are released on complexation and consequent extraction. Similarly, plot of logD vs log[SO_4^{2-}] at equilibrium, under constant ligand (1.0×10^{-3} M) and chloride ion (0.1 M) concentrations, approximately described a straight line of slope equal to 1.01. This indicates that Pd(II) formed a sulfato complex with the ligand on extraction. It was observed that at constant H_2SO_4 concentration, replacement of 0.1 M NaCl by 0.1 M HCl had no effect on the distribution ratio of palladium. This would mean that the concentration of hydrogen ion may have little or no effect on the equilibrium extraction mechanism as was observed in the extraction of palladium with α-butylthiolauric acid from ammonium chloride medium.[4] On the basis of these results, a possible extraction mechanism may be formulated as:

$$PdCl_2SO_4^{2-} + L_{(org)} \rightleftharpoons PdLSO_{4(org)} + 2Cl^- \quad \text{........(1)}$$

$$K_{ex} = [PdLSO_4]_{(org)}[Cl^-]^2 / [PdCl_2SO_4^{2-}][L]_{(org)} \quad \text{........(2)}$$

$$\log D = \log K_{ex} - 2\log[Cl^-] + \log[L] \quad \text{........(3)}$$

where, L represents the TrMBnBX molecule, K_{ex} is the extraction co-efficient, D is the distribution ratio for the metal ion, the subscript (org) refers to the species in the organic phase and the other species refer to exist in the aqueous phase.

Quantitative stripping of palladium from the loaded organic phase (Pd-TrMBnBX-SO_4) has been possible with 0.5 M thiourea (dissolved in 0.1 M HCl) solution. The back-extraction kinetics was found to be much faster than the original extraction process, reaching equilibrium in 3 min, the percent stripping being 60 in a single step. Following a cross-current multiple-contact procedure,[10] only three contacts were needed for 100% recovery of palladium from the organic phase, employing 3 min contact time.

In conclusion, it can be suggested that TrMBnBX, as synthesized from commercially available chemicals is highly promising reagent for the selective extraction of palladium. In the mixed sulfate-chloride medium, the reagent forms a 1:1 extractable complex with Pd(II) and the extraction phenomena can be explained by simple equilibrium expressions. Further studies are in progress to explore TrMBnBX and other bis xanthates for their use in the solvent extraction of precious metal ions.

References

1) R.I. Edwards, The Canadian Institute of Mining and Metallurgy, **21**, 24 (1979).
2) K. Inoue and Y. Baba, Proc. Internl. Solvent Extr. Confec., ISEC, 86, DECHEMA, **2**, 263 (1986).
3) E.E. Rokovskii, N.N. Shvedova, and A.N. Shkil, *Zr. Anal. Khim.*, **39**, 1463 (1984).
4) Y. Baba, A. Goto, and K. Inoue, *Solvent Extr. Ion Exch.*, **4**, 255 (1986).
5) M. Koba, K. Yoshizuka, and K. Inoue, Proc. Symp. Solvent Extr., (1991), p.133.
6) Y. Baba and K. Inoue, *Ind. Eng. Chem. Res.*, **27**, 1613 (1988).
7) R.I. Edwards and W.A.M. teRieli, " Handbook of Solvent Extraction", ed. by T.C. Lo, M.H.I. Baird, and C. Hanson, John Wiley, New York, (1983), p.725.
8) J.V. Rund, *Inorg. Chem.*, **13**, 738 (1974).
9) G.A. Yagodin and O.A. Sinegribova, as in Ref. 7) p. 809.
10) G. Pouskouleli, S. Kelebek, and G. Demopoulos, Proc. of the 6th International Confec. on Hydrometallurgy, (1986), p.174.

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