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Extraction of gold, palladium, and platinum from acidic media with cyclic sulfoxide derivative

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Abstract: The extraction of gold (III), palladium (II), and platinum (IV) from the acidic media with the cyclic sulfoxide derivative of α-dodecyl-tetrahydrothiophene 1-oxide (dtmso) was investigated. Gold (III), palladium (II), and platinum (IV) could be separated from the acidic media with suitable sulfoxide concentration and acidity. The extraction reaction of gold (III), palladium (II) or platinum (IV) is exothermic when dtmso is used as an extracting reagent. The coordination number was studied by the slope method. The results indicate that, in high acidity, the dtmso coordination number for extracting gold (III) or palladium (II) is 3, and that for platinum (IV) is 2. UV and FT-IR spectra were used to analyze the structure of the complex. Gold (III) is coordinated with the oxygen atom in S=O group in dtmso, and palladium (II) or platinum (IV) is coordinated with the sulfur atom in S=O group in dtmso.

Key words: cyclic sulfoxide; gold; palladium; platinum; solvent extraction; tetrahydrothiophene-1-oxide

1. Introduction

Extraction reagents containing sulfur have been attracting much attention for their excellent extraction ability to precious metals [1-2]. Symmetrical 2-ethylpentyl sulfoxides (RSO) (where R=alkyl) were proposed for use in the separation of rare earth metals by Yuan, *et al.* [3]. The mechanism of extracting palladium (II) with dialkyl sulfoxide from hydrochloric acid was discussed by Zhang [4]. The far-infrared spectrum, visible, and violet spectrum of the KSO-Pd (II) complex show that the extractive exists as the structure of chloride-bridged binuclear *trans*-$(PdLCl_2)_2$. Both the sulfur and oxygen atoms in KSO can coordinate with palladium (II). Chen investigated the extraction of gold (III), palladium (II), and platinum (IV) with petroleum sulfoxides (PSO) [5]. The extraction of Pd (II), Pt (IV), and Rh (III) from aqueous HCl solutions by di-*n*-heptyl sulphoxide (DHSO) in 1,1,2-trichloroethane (TCE), their extraction systems, and the chemical bonding in such species were discussed by Lewis [6]. The synthesis of the cyclic sulfoxide derivative of α-dodecyl-tetrahydrothiophene 1-oxide (dtmso) as a novel reagent to investigate its extraction behavior for palladium from hydrochloric acid media was reported [7-9]. The reagents are expected to have a much higher selectivity and reactivity for precious metal ions, classified as soft acid, than the conventionally used dialkyl sulfoxides because of their asymmetric structure.

In the present study, the extraction of gold (III), palladium (II), and platinum (IV) from acidic solutions with cyclic sulfoxide derivative-dtmso is studied. The extraction mechanism and complex structures are discussed.

2. Experimental

2.1. Reagents

The synthesis of cyclic sulfoxide derivative is described in Ref. [7]. Determined by element analysis, the purity of sulfoxides is more than 98%. Its chemical structure is shown in Fig. 1. An organic solution is prepared by diluting each extractant into sulfonated kerosene to a desired concentration. An aqueous solution is prepared by dissolving chloroauric acid, palladium chloride or chloroplatinic acid into aqueous hydrochloric acid, to a desired concentration. The other reagents are of analytical reagent grade.

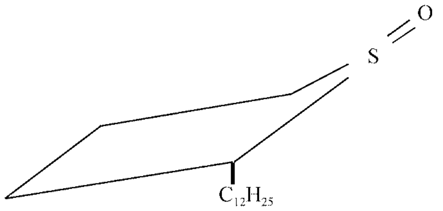

Fig.1. Configuration of sulfoxide.

2.2. Procedure

Equal volumes (3 mL) of both phases were mixed and vigorously shaken for 30 min, which was sufficient enough to attain equilibrium in a preliminary experi-

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ment. After phase separation, the aqueous concentration of gold (III), palladium (II), and platinum (IV) in the aqueous phase was determined by WFX-IB atom absorption spectrophotometer. These results were further used to estimate the extraction efficiency of precious metals. The amount of extracted metal ions was calculated from the differences in the metal concentrations in the aqueous phase between, before, and after the extraction. The loaded organic phases were determined with a V-7(HS) ultraviolet (UV) spectrophotometer and VEVTOR33 FT-IR spectrophotometer.

3. Results and discussion

3.1. Influential factors of extracting metals with cyclic sulfoxide derivative

Fig. 2 shows the effects of the sulfoxide concentration on the percentage extraction of gold (III), palladium (II), and platinum (IV). In 4 mol·L^{-1} hydrochloric acid media, when the sulfoxide concentration was below 0.2 mol·L^{-1}, the efficiency (*E*) of the extracting gold (III) or palladium (II) by sulfoxide first increased with increasing sulfoxide concentration, then it was stable, more than 99%, as the sulfoxide concentration increased. From Fig. 2, the extracting efficiency of gold (III) and palladium (II) was 80% and 10%, respectively, when the sulfoxide concentration was 0.05 mol·L^{-1}, where gold (III) can initially be separated from the solution containing palladium (II) and platinum (IV). Platinum (IV) was extracted to the extent of only about 5wt% when the sulfoxide concentration was 0.2 mol·L^{-1}, whereas, it was up to 90% at the dtmso concentration of 0.8 mol·L^{-1}.

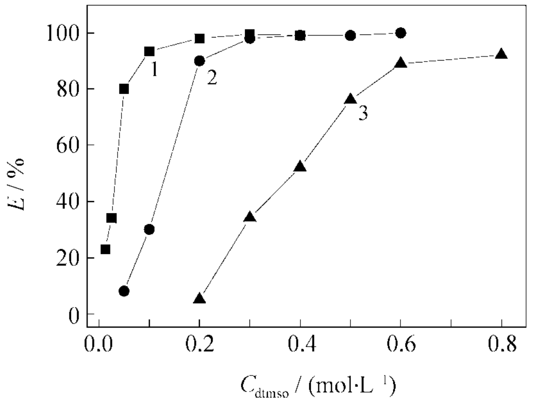

Fig. 2. Dependence of extracting efficiency on the concentration of sulfoxide: 1—gold (III); 2—palladium (II); 3—platinum (IV).

The effects of acidity on the percentage extraction of gold (III), palladium (II), and platinum (IV) are shown in Fig. 3. Here, in the region of hydrochloric acid with a concentration below 6 mol·L^{-1}, the extraction of gold (III), palladium (II), and platinum (IV) from hydrochloric acid solutions with dtmso in sulfonated kerosene has been compared. For extracting gold (III) with 0.1 mol·L^{-1} dtmso and palladium (II) with 0.2 mol·L^{-1} dtmso, the plots of the percentage extraction for metals appear to lie on a convex curve having a maximum percentage of extraction at 1-2 mol·L^{-1} hydrochloric acid. From Fig. 3, the extraction efficiency for palladium (II) with 0.2 mol·L^{-1} dtmso is 93% in 1 mol·L^{-1} hydrochloric acid media, and that for platinum (IV) in the same conditions is 2.3%. As a result, palladium (II) can be separated from platinum (IV). The percentage extraction of platinum (IV) increases with an increase in acidity, from 1 to 4 mol·L^{-1}, however, that decreases when the hydrochloric acid concentration is more than 5 mol·L^{-1}, because of the competing extraction of HCl_2^- [9]. After separating gold (III) and palladium (II), platinum (IV) can be extracted by 0.8 mol·L^{-1} dtmso from 4 mol·L^{-1} hydrochloric acid media.

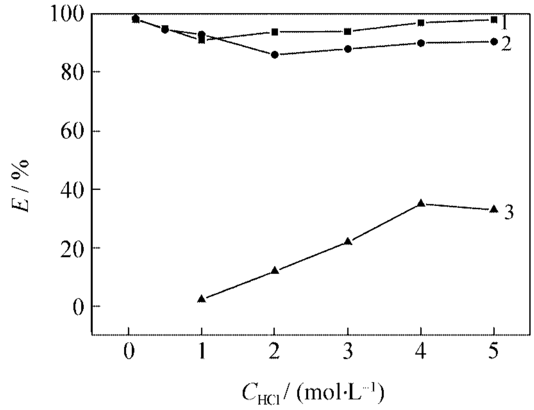

Fig. 3. Dependence of extracting efficiency on the acidity: 1—gold (III) (0.1 mol·L^{-1}dtmso); 2—palladium (II) (0.2 mol·L^{-1}dtmso); 3—platinum (IV)(0.2 mol·L^{-1}dtmso).

The effects of extraction temperature on the distribution ratio are shown in Fig. 4. The extraction of the metals was carried out at different temperatures with different amounts of extractants at the same acidity (4 mol·L^{-1}).

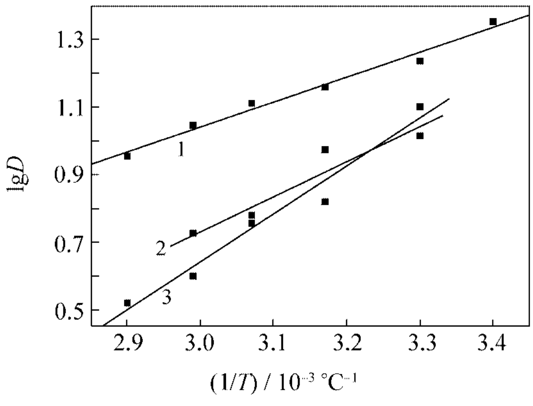

Fig. 4. Influence of temperature on the distribution ratio: 1—gold (III); 2—palladium (II); 3—platinum (IV).

In accordance with the following thermodynamic equilibrium equation (1):

$$\frac{K_{\text{ex}}}{T} = \frac{-\Delta H}{RT^2} \qquad (1)$$

where K_{ex} is the equilibrium constant, H the reaction heat, T the temperature, R the constant.

When the concentration of the extractants and aqueous acidity is fixed, K_{ex} can be replaced by D. The relation of distribution ratio (D) with temperature (T) can be shown as

$$\ln D = \frac{-\Delta H}{RT} \qquad (2)$$

The log-log plots of the distribution ratio versus temperature have excellent linearity. For gold (III), palladium (II), and platinum (IV), the distribution ratio decreases as the temperature increases. On the basis of the reaction isotherm, the reaction heat can be calculated as follows.

$\Delta H^{\ominus}_{\text{gold}} = -\ 15.3\ \text{kJ·mol}^{-1}$,

$\Delta H^{\ominus}_{\text{palladium}} = -\ 20.7\ \text{kJ·mol}^{-1}$,

$\Delta H^{\ominus}_{\text{platinum}} = -\ 27.2\ \text{kJ·mol}^{-1}$.

It shows that extraction reaction of gold (III), palladium (II) or platinum (IV) is exothermal when dtmso is used as the extracting reagent.

In the experiment, after being scrubbed thrice by 0.1 mol·L^{-1} HCl, 10%-20% metals were transferred from the loaded organic phase to scrubbing aqueous liquor, the loaded organic phase of gold (III), palladium (II), and platinum (IV) was once stripped by Na_2SO_3 solution.

The stripping percentage of the loaded organic phase of metals increases, as shown in Fig. 5, up to 76%-92%, depending on the different kinds of metals, and with an increase in stripping agent concentration. It indicates that the extracted metal complex exists in a bonded complex, which can only be reduced by a reducing agent, for example Na_2SO_3, because of the metal-sulfoxide bonding.

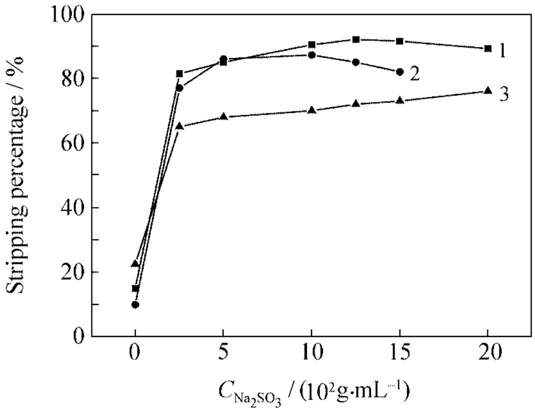

Fig. 5. Dependence of stripping percentage on stripping agent concentration: 1—gold (III); 2—palladium (II); 3—platinum (IV).

3.2. Mechanism of extracting gold (III), palladium (II), and platinum (IV)

(1) Determination of coordination number.

The mechanism of extracting precious metals, such as, gold (III), palladium (II) or platinum (IV), is discussed as follows. In higher acidity, sulfoxide extracts precious metals, for example platinum, in the form of ion association extraction (Eq. (3)).

$$\begin{aligned}&Pt^{4+} + mH^+ + q\text{dtmso}_{(o)} + nCl^- \rightleftharpoons \\ &\quad [(H^+)_m(PtCl_n^{4-n})(\text{dtmso})_q]_{(o)}\end{aligned} \qquad (3)$$

The corresponding equilibrium constant K_{ex} of Eq. (3) is defined by Eq. (4).

$$K_{\text{ex}} = \frac{[(H^+)_m(PtCl_n^{4-n})(\text{dtmso})_q]_{(o)}}{[Pt^{4+}][H^+]^m\,[\text{dtmso}_{(o)}]^q[Cl^-]^n} \qquad (4)$$

The distribution ratio of platinum is defined as

$$D = \frac{C_{\text{pt}_{(o)}}}{C_{\text{pt}}} \qquad (5)$$

The concentration of platinum in the aqueous phase can be shown as

$$C_{\text{pt}} = [\text{pt}^{4+}][1 + \sum \beta_n(Cl^-)^n] \qquad (6)$$

In accordance with Eqs. (4)-(6), Eq. (7) can be obtained.

$$\begin{aligned}&\lg D = \lg K_{\text{ex}} + q\lg[\text{dtmso}] + m\lg[H^+] + \\ &\quad \lg\frac{[Cl^{-1}]}{[1 + \sum \beta_n(Cl^-)^n]}\end{aligned} \qquad (7)$$

The metal-distribution data for the concentration of the extractant is plotted in the form of lg$D$ against lg[L], then Eq. (8) can be obtained.

$$\lg D = \lg K_{\text{ex}} + q\lg[\text{dtmso}] + m\lg[H^+] + C \qquad (8)$$

where C is a constant.

Eq. (8) can be applied equally to the extraction of gold (III) or palladium (II). The representative plots of this type are shown in Fig. 6. With regard to the extraction of gold (III), palladium (II), and platinum (IV) in 4 mol·L^{-1} hydrochloric acid solutions, by dtmso, the slopes of these plots are obtained as follows: q_{gold}= 2.8, q_{pd}=3.2, and q_{pt}=2.2, respectively. The results show that the coordination numbers for gold (III) and palladium (II) are 3, and that for platinum (IV) is 2, when dtmso is used as an extractant.

Fixing the chlorine ion concentrations at 4 mol·L^{-1}, and applying the sulfoxide concentration of 0.1, 0.2, and 0.6 mol·L^{-1} for extracting gold, palladium, and platinum, respectively, one can see that the influence of hydrion concentration on lg$D$ is obvious, as seen in Fig. 7. It is evident that the slopes of the plots for gold (III) and palladium (II) are 1, that is, $m_{\text{gold}}=1$, and $m_{\text{pd}}=1$, however, platinum (IV) has two slopes for the plots, that is, $m_{\text{pt}}=2$. As a result, Eq. (3) can be shown in Eq. (9):

$$2H^{+}+2\text{dtmso}\rightleftharpoons[H(\text{dtmso})]_2^{2+},$$

$$[H(\text{dtmso})]_2^{2+}+[PtCl_6^{2-}]\rightleftharpoons[H^{+}(\text{dtmso})]_2[PtCl_6)^{2-}] \tag{9}$$

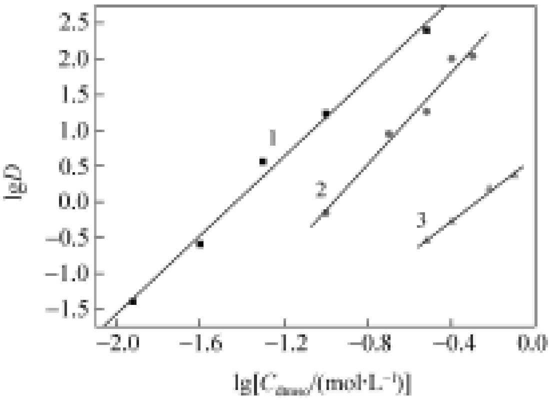

Fig. 6. Influence of distribution ratio on sulfoxide concentration: 1—gold (III); 2—palladium (II); 3—platinum (IV).

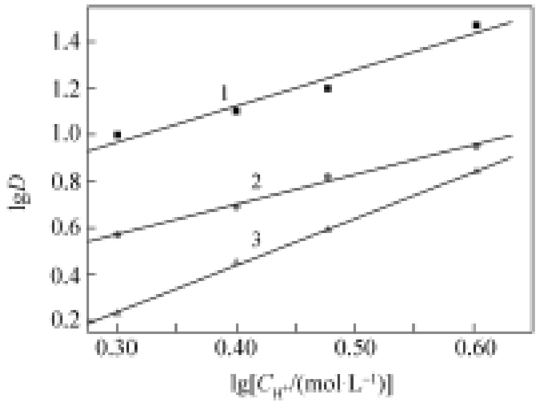

Fig. 7. Dependence of distribution ratio on hydrion concentration: 1—gold (III); 2—palladium (II); 3—platinum (IV).

On the basis of the same mechanism, the extraction of gold (III) can be shown in the following:

$$H^{+}+3\text{dtmso}\rightleftharpoons[H(\text{dtmso})_3]^{+},$$

$$[H(\text{dtmso})_3]^{+}+[AuCl_4^{-}]\rightleftharpoons[H(\text{dtmso})_3(AuCl_4)] \tag{10}$$

The extraction of palladium (II) can be shown in the following:

$$H^{+}+3\text{dtmso}\rightleftharpoons[H(\text{dtmso})_3]^{+},$$

$$[H(\text{dtmso})_3]^{+}+PdCl_3^{-}\rightleftharpoons[H(\text{dtmso})_3(PdCl_3)] \tag{11}$$

(2) UV spectra of the organic solvent.

Gold (III), palladium (II) or platinum (IV) was extracted from 4 mol·L^{-1} hydrochloric acid media by dtmso dissolved in cyclohexane. The solution containing the organic phase was separated, and the loaded organic phase of metal was examined with a UV spectrophotometer as shown in Fig. 8. The characteristic absorption peaks of the aqueous phase containing gold (III), palladium (II), and platinum (IV) are at λ 310, 278, and 260 nm, as given in curve 2.1, 3.1, and 4.1, respectively. However, they shift to 350, 310, and 278 nm, as shown in curves 2.2, 3.2, and 4.2, in the loaded organic phase, obtained from 4.0 mol·L^{-1} HCl media. The shift of absorption peak to higher wavenumber shows that the complexing reaction happens between the ligand and metal.

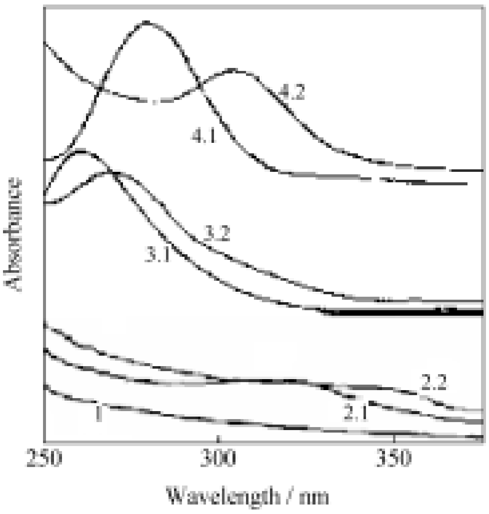

Fig. 8. UV spectra of organic solvent: 1—unloaded organic phase; 2—loaded organic solvent phase of gold (III); 3—loaded organic solvent of platinum (II); 4—loaded organic solvent of palladium (IV).

(3) FT-IR spectra of the organic solvent.

The structures of extracted complexes were discussed by FT-IR spectra as shown in Fig. 9. It is reported that the S–O stretching frequencies were used to distinguish O- from S-bonding. In fact, compared to free dimethyl sulfoxide, γ(SO) increases in the S-bonded species (1080-1154 cm^{-1}) and decreases in the O-bonded species (862-997 cm^{-1}) [10].

The characteristic absorption peak of free dtmso occurs at 1041 cm^{-1}. After pre-reaction with 4 mol·L^{-1} hydrochloric acid, the change of situation and strength of the characteristic absorption peak is not clear. After extraction, the loaded organic phase of gold (III) evidently appears as a new peak, at 935 cm^{-1}, which is contributed by the complex, with oxygen-gold bonding. The loaded organic phase of palladium (II) appears as a new peak at 1118 cm^{-1}, which is contributed by the complex, with sulfur-palladium bonding. The FT-IR spectrum of the loaded dtmso of platinum (IV) is similar to that of free dtmso, except for a decreased strength of peak at 1040 cm^{-1}, which is contributed by protonated sulfoxide. The X-ray structure of an octahedral Pt (IV) complex, $[Et_4N][PtCl_5(\text{dtmso})]$, has been reported, showing the S-bonding of dtmso. Panina [11], reported that in $[Pt(IV)Cl_5(dmso\text{-}S)]^-$ and $[Pt(II)Cl_3(dmso\text{-}S)]^-$, γ(SO) increases to 1220 and 1241 cm^{-1}, respectively, with respect to free dtmso. It is deduced that the peak at 1150-1240 cm^{-1} contributed by Pt (IV) (dtmso-S) complex [14] is covered by an intense peak at 1256 cm^{-1} from dtmso, hence it cannot be found.

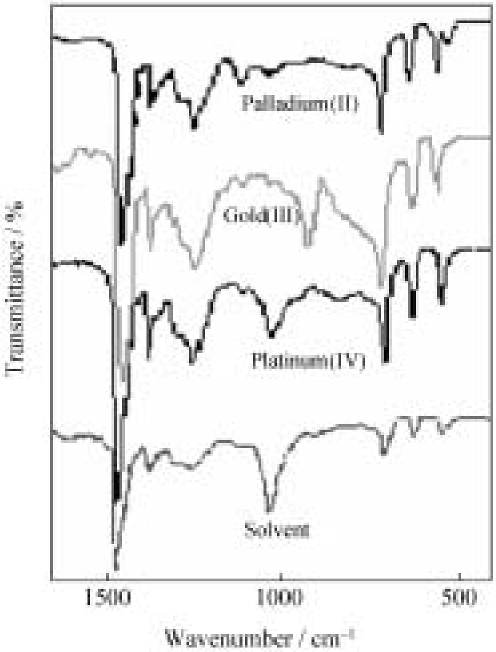

Fig. 9. FT-IR spectra of organic phase from 4 mol·L^{-1} hydrochloric acid.

In the higher acidity region, dtmso extracts precious metals in the form of acid association extraction [6], therefore the extraction of gold (III), palladium (II), and platinum (IV) in this case appears in an ion-pair formation, between solvated hydronium cations and the chlorometallate anion. Metal ion competes with hydrion in the extracted complex, and then intercoordination transfer occurs because of the stronger binding energy of the metal-sulfoxide. As a result, $[H(dtmso)_3(AuCl_4)]$ may be changed to $[H(dtmso)][(Au(III)(dtmso\text{-}O)_2Cl_4)]$, $[H(dtmso)_3(PdCl_3)]$ to $[H(dtmso)Cl][Pd(II)(dtmso\text{-}S)_2\,Cl_2)]$, and $[H^+(dtmso)]_2[(PtCl_6)^{2-}]$ to $[HCl]_2[(Pt(IV)\,(dtmso\text{-}S)_2Cl_4]$, respectively.

It is reported that the *cis*-, *trans*-configuration of complex, can be estimated on the basis of the symmetry of the characteristic absorption peak of sulfoxides. The peak of 935 has excellent symmetry, and it seems to show that the *trans*-$[AuCl_4(dtmso\text{-}O)_2]^-$ exists in the extracted gold (III) complex. The symmetrical peak of 1118 cm^{-1} shows that *trans*-$PdCl_2(dtmso\text{-}S)_2$ exists in the extracted Pd (II) complex.

4. Conclusions

(1) Gold (III), palladium (II), and platinum (IV) could be separated from the acidic media in a suitable sulfoxide concentration and acidity.

(2) The extraction of gold (III), palladium (II) or platinum (IV) is based on the same mechanism, that is, ion association extraction in higher acidity media when dtmso is used as an extractant.

(3) In a complex, inter-ligand transfer occurs. The complex with oxygen-gold bonding exists in gold sulfoxide complex, and the complex with sulfur-palladium (or platinum) bonding exists in palladium (or platinum) sulfoxide complex.

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