the spectra resemble that of $CrCl_6^{3-}$, indicating little interaction between the metal centers. Trogler[12] has described the spectra for Mo and W with $n = 3$ in valence-bond terms, suggesting that the energy-level order given in Figure 3 is inappropriate for these singlet ground states. It is appropriate for the doublet states for $n = 2$ arising from the M(III)–M(IV) complex with five d electrons. This state possesses an orbitally degenerate $(a')^2(e')^3$ electron configuration, however, and is subject to Jahn–Teller distortion. In D_{3h} symmetry three electronic transitions are allowed ($a_1' \rightarrow e'$ (x,y), $a_1' \rightarrow a_2''$ (z), and $e' \rightarrow e''$ (z)). Three are observed for $Mo_2Cl_9^{2-}$ and $W_2Cl_9^{2-}$, but additional bands are present in the visible spectrum of $W_2Br_9^{2-}$. Trogler has made some tentative assignments, but the interpretation is complicated by the Jahn–Teller distortion and possible effects of spin–orbit coupling. Definitive work in all of these systems will require single-crystal structures and spectra.

Conclusions

In two-center ruthenium(II,III) mixed-valence complexes such as the Creutz–Taube ion, the bridging ligand is usually an aromatic or a linear conjugated molecule. In this case (D_{2h} symmetry), there is only one important pathway for electron transfer between centers—i.e., Ru ($4d\pi$)–ligand ($2p\pi$) interaction. The effective (ligand-mediated) Ru···Ru electronic interaction can be interpreted in terms of a single electronic splitting energy J (0.4 eV for the Creutz–Taube ion), and only one intervalence absorption transition, at energy $2J$ for a delocalized complex, is found. In the trihalo complexes considered here, however, the lower Ru d-orbital triplet is split both by $d\sigma$–$d\sigma$ and $d\delta$–$d\delta$ interactions mediated by the three X bridges. Thus, two electronic coupling terms, J_σ and J_δ are required to characterize the metal–metal interaction. These quantities cannot be derived unambiguously from the spectral data so far obtained, as the electronic origins are not yet established. However, if we assume that the e'/e'' and a'_1/a''_2 splittings are symmetrical and approximate electronic origins by band maxima, the data of Table I would lead to $J_\sigma = 1.1$ eV and $J_\delta = 0.17$ eV for the Cl complex and $J_\sigma = 1.0$ eV and $J_\delta = 0.12$ eV for the Br complex. As the energies of the band maxima (particularly for the $e' \rightarrow e''$ $\sigma \rightarrow \sigma^*$ excitation) will in fact be significantly greater than those of the 0–0 band origins, these values give an approximate upper limit for J_σ and a lower limit for J_δ (assuming symmetrical level splitting). The relative values of these approximate coupling terms are consistent with qualitative chemical concepts of σ and δ bond strengths.

Registry No. $\{[Ru(NH_3)_3]_2Cl_3\}Cl_2$, 38731-16-7; $\{[Ru(NH_3)_3]_2Br_3\}Br_2$, 58320-17-5.

Contribution from the Strategic Metals Recovery Research Facility and Department of Chemistry,
University of Arizona, Tucson, Arizona 85721

Reactivity of Palladium Dithizonate with Lewis Acids and Bases

ENXIN MA† and HENRY FREISER*

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Palladium cannot be removed from palladium dithizonate ($Pd(Dz)_2$) by thiocyanate, cyanide (pH 8), or ethylenediaminetetraacetate (pH 3–8) or by copper perchlorate, silver perchlorate, mercury(II) chloride, or mercury(II) perchlorate in acidic solutions. Palladium dithizonate does react with mercury perchlorate in perchloric acid as well as silver perchlorate at pH 2–4. The products of the reaction with mercury perchlorate studied in four organic solvent systems were examined. The equilibrium constants ($-\log K$) of the postulated reaction $2Pd(Dz)_2(o) + Hg^{2+} + 2ClO_4^- \rightleftarrows 2Pd(ClO_4)Dz(o) + Hg(Dz)_2(o)$ were estimated as 2.79 + 0.19 ($CHCl_3$), 1.35 ± 0.07 (CCl_4), 2.56 ± 0.20 (C_6H_6), and 1.92 ± 0.10 (C_6H_5Cl). From these, a comparison of the stability of the two palladium dithizonates was made and the cause of the reaction was discussed. The reaction with silver is not a metal exchange but is different from that with mercury, and a mixed-metal secondary dithizonate may be involved.

Introduction

The most common strategy for recovering metal ions from organic solvent extracts of metal chelates is to increase the acidity of the aqueous phase

$$M^{n+} + nHL(o) \underset{\text{back-extn}}{\overset{\text{extn}}{\rightleftarrows}} ML_n(o) + nH^+$$

where (o) refers to species in the organic phase. Occasionally, it is more expeditious to use other Lewis acids (metal ions) and bases (masking agents) to accomplish this purpose. Thus, Ag(I) and Hg(II), but not Cu(II), ions were found to be much more effective in the back-extraction of Ni(II) from a $CHCl_3$ solution of its dithizonate than was H^+.[1] Similarly, the Lewis bases cyanide and EDTA were found superior to H^+ for the same reaction. Hence, in the course of our systematic study of the extraction behavior of palladium, which forms chelates of such stability with dithizone (diphenylthiocarbazone) that even concentrated acids are not effective in its back-extraction, we decided to explore the possible use of a number of metal ions that form strong dithizonates, as well as the use of some masking agents for this purpose. Although a reaction occurred, the results were not the expected simple metal displacement reaction.

Experimental Section

Materials. Diphenylthiocarbazone (dithizone), HDz (Matheson Coleman and Bell), was purified by extracting a $CHCl_3$ solution with several portions of aqueous NH_3 (1.0 M), discarding the $CHCl_3$ phase, carefully neutralizing the aqueous phase with 6 M H_2SO_4, and back-extracting the purified dithizone into pure $CHCl_3$. Its purity was verified by determining the ratio of the absorbance values at 605 and 445 nm. All of the other chemicals used were of AR grade.

Apparatus. Absorption spectra were obtained with a Varian Cary 219 spectrophotometer using a 2.0 nm/s scan rate. Atomic absorption measurements of aqueous Pd solutions were made with a Varian AA-6 spectrometer having a spectral band-pass of 0.2 nm and equipped with a Westinghouse Pd hollow-cathode lamp at 245.2 nm with an air–C_2H_2 flame. An Eberbach box type shaker (280 oscillations/min) was used for phase equilibration.

Analyses. The concentration of aqueous palladium stock solution was determined by an indirect EDTA titration using zinc nitrate as

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† On study leave from Shanghai Institute of Organic Chemistry, Academia Sinica, Shanghai, China.

(1) K. Ohashi and H. Freiser, *Anal. Chem.*, **52**, 2214 (1980).

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Table I. Maximum Absorption of Palladium Dithizonate, $Pd(Dz)_2$, and Mercury Dithizonate, $Hg(Dz)_2$

	$Pd(Dz)_2$				$Hg(Dz)_2$	
solvent	$\lambda_{max}(1)$, nm	10ϵ	$\lambda_{max}(2)$, nm	10ϵ	λ_{max}, nm	10ϵ
$CHCl_3$	637	34.2 ± 0.3	450	37.9 ± 0.3	490	69.2 ± 0.5
CCl_4	637	30.9 ± 0.4	450	37.2 ± 0.4	490	67.7 ± 0.8
C_6H_6	642	26.7 ± 0.2	452	38.1 ± 0.2	489	62.6 ± 0.5
C_6H_5Cl	642	32.5 ± 0.2	452	37.3 ± 0.1	490	65.9 ± 0.4

Table II. Equilibrium Constants ($-\log K$) of the Reaction $2Pd(Dz)_2(o) + Hg^{2+} + 2ClO_4^- \rightleftarrows 2Pd(ClO_4)Dz(o) + Hg(Dz)_2(o)$ in Different Solvents and 2 M $HClO_4$

	$-\log K$ at various concns of Hg(II)							
solvent	2×10^{-5} M	3×10^{-5} M	5×10^{-5} M	1×10^{-4} M	2×10^{-4} M	5×10^{-4} M	1×10^{-3} M	av K
$CHCl_3$	3.07		2.98	2.88	2.65	2.58	2.56	2.79 ± 0.19
CCl_4	1.48	1.34	1.24	1.33				1.35 ± 0.07
C_6H_6			2.74	2.89	2.50	2.34	2.35	2.56 ± 0.20
C_6H_5Cl	2.04	2.01	1.73	1.87	1.95			1.92 ± 0.10

titrant with Eriochrome Black T as indicator.[2] The concentration of mercury stock solution was determined by EDTA titration with xylenol orange as indicator.[3] The concentration of dithizone was based on absorbance measurements at 605 nm ($\epsilon = 40600$).[4]

The concentration of palladium in aqueous media containing mercury was determined by an atomic absorption spectrometer (AAS). Preliminary experiments demonstrated that neither 2 M $HClO_4$ nor Hg^{2+} up to 10^{-2} M interfered with the Pd determination even at Pd levels as low as 10^{-6} M.

Procedures. Solutions of $Pd(Dz)_2$ and $Hg(Dz)_2$ were prepared by equilibration for 1 h, 15 mL of 9.5×10^{-5} M dithizone in one of the four organic solvents ($CHCl_3$, CCl_4, C_6H_6, C_6H_5Cl) with 10 mL of an aqueous solution containing enough Pd^{2+} or Hg^{2+} to consume about 20% of the dithizone. The excess dithizone was removed by washing the organic phase with dilute aqueous NH_3 several times. The spectra of the dithizone-free extracts were found to correspond to those of the primary Pd and Hg dithizonates. After these extracts were washed with water or diluted acid, the spectra did not change.

Distribution equilibrium experiments between organic solutions of $Pd(Dz)_2$ and various aqueous phases were conducted at 25 °C in 40-mL screw-cap glass vials with fitted polyethylene stoppers containing 10 mL of each phase for a 24-h shaking period. The phases were then separated and centrifuged. An aliquot of the aqueous phase was used for the determination of Pd via AAS, and the absorption spectrum of the organic phase was measured in the range 350–750 nm.

Results and Discussion

According to Irving's interesting monograph[5] on dithizone the extraction constant for the Pd chelate is by far the highest ($\log K_{ex} = 42.5$) and, therefore, is not at all likely to be dissociated by other metal ions. On examining the original reference,[6] however, we found that, when correctly calculated from the data cited there, a value of $\log K_{ex}$ of 25.0 is obtained, two orders of magnitude lower than that for Hg(II) ($\log K_{ex} = 27.0$[7]). Hence, it is quite reasonable to expect metal displacement reactions with $Pd(Dz)_2$ using mercury(II) and, perhaps, silver(I).

Aqueous solutions of various reagents including $Cu(ClO_4)$, $AgClO_4$, $Hg(ClO_4)_2$, and $HgCl_2$ in acidic media as well as NH_4CNS, NaCN (at pH 8), and Na_2EDTA (pH 3 and 8) were shaken vigorously with organic solutions of primary palladium dithizonate ($Pd(Dz)_2$) for 6 h, and following phase separation the aqueous and organic layers were examined. In all cases but that of $Hg(ClO_4)_2$ and $AgClO_4$, the visible spectra of the organic solutions were unchanged. In no case did any of the aqueous phase contain any palladium. Although some reaction occurred with both mercury and silver, clearly it was not the simple neutral exchange reaction.

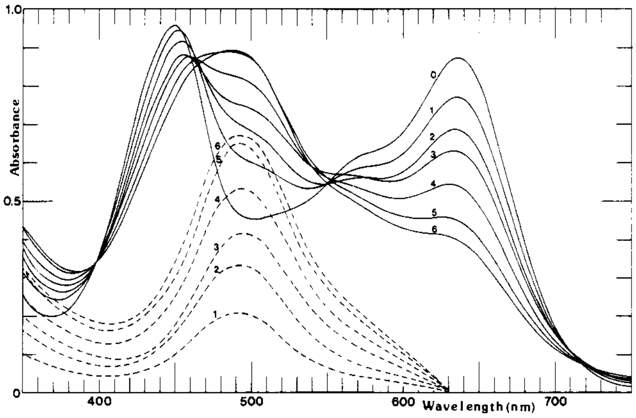

Figure 1. Spectra of chloroform phase after reaction of $Pd(Dz)_2$ (original concentration 2×10^{-5} M) with various concentrations of mercury ion (M) in 2 M $HClO_4$ (solid line) and the products of the postulated reaction (dashed line): (0); (1) 2×10^{-5}; (2) 5×10^{-5}; (3) 1×10^{-4}; (4) 2×10^{-4}; (5) 5×10^{-4}; (6) 1×10^{-3}.

Palladium, like a few metal ions that react with dithizone such as Hg(II), Cu(I,II) and Ag(I), is known to form two distinct dithizone complexes. Primary palladium dithizonate, having a 1:2 stoichiometry, forms over a wide range of pH and has long provided the basis for a sensitive spectrophotometric determination of Pd.[8-10] Under conditions of relatively low ligand to metal ratios, the secondary palladium dithizonate, having a 1:1 stoichiometry, can be formed, even in acidic media.[5]

The reaction between $Pd(Dz)_2$ and Hg(II) can be followed spectrophotometrically. The absorbance values at $\lambda_{max}(1)$ for $Pd(Dz)_2$ around 640 nm (Table I) in the organic phase decreased following equilibration with aqueous $Hg(ClO_4)_2$ accompanied by absorbance increases at 490 nm, the λ_{max} for the primary mercury dithizonate, $Hg(Dz)_2$ (see Figure 1). In addition, when the spectra of $Pd(Dz)_2$ and $Hg(Dz)_2$ were appropriately taken into account, an additional spectrum appeared which, since the secondary mercury dithizonate is

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known to be unstable in contact with acidic aqueous media, was assumed to be that of a secondary palladium dithizonate, probably $Pd(ClO_4)Dz$. In view of the failure of Pd to appear in the aqueous phase following the reaction, this seemed to be a reasonable assumption. A tentative description of the reaction then is

$$2Pd(Dz)_2(o) + Hg^{2+} + 2ClO_4^- \xrightleftharpoons{K} 2Pd(ClO_4)Dz(o) + Hg(Dz)_2(o) \quad (1)$$

From the absorbance measurements at various wavelengths, which permitted the construction of a difference spectrum corresponding to $Pd(ClO_4)Dz$ and the stoichiometric relationships inherent in eq 1, concentrations of each of the reactants and products were calculated and used to evaluate the equilibrium constant K (eq 2). The results shown in Table II provide strong evidence in the relatively invariant K values under different experimental conditions in one solvent system as well as a rational progression of K values in different solvent systems that generally reflects their "polarity".

$$K = \frac{[Pd(ClO_4)Dz]_o^2[Hg(Dz)_2]_o}{[Pd(Dz)_2]_o^2[Hg^{2+}][ClO_4^-]^2} \quad (2)$$

The absence of a reaction when $HgCl_2$ was used in place of $Hg(ClO_4)_2$ can be understood in terms of the adverse effect of strong chloride complexation (log $\beta_4 = 15.2$[11]) on the Hg activity and, therefore, on the extent of the reaction in eq 1.

Equation 2 can be considered to be a composite of the formation of $Hg(Dz)_2$ ($K_{ex}(Hg(Dz)_2)$) and that of $Pd(ClO_4)Dz$ (K_{ex}(Pd ClO_4)Dz)), from which the formation of $Pd(Dz)_2$ ($K_{ex}(Pd(Dz)_2)$) is subtracted, or

$$K_3 = [K_{ex}(Pd(ClO_4)Dz)^2][K_{ex}(Hg(Dz)_2)]/K_{ex}(Pd(Dz)_2)^2 \quad (3)$$

With use of the K_3 value obtained here of $K = 10^{-2.79}$, $K_{ex}(Hg(Dz)_2) = 10^{27.0}$,[7] and the corrected value from ref 6 of $K_{ex}(Pd(Dz)_2) = 10^{25.1}$, the secondary chelate $Pd(ClO_4)Dz$ formation constant can be calculated as $10^{10.2}$. This is far larger than might be expected on the basis of the reasonable assumption that the coordination of the second dithizonate ligand to Pd is not too much weaker than the first. Frequently the formation constants of successive chelating ligands are within a factor of 10–100 of each other. Even if one were to assume that the formation constant of Pd–ClO_4 is as high as 10^3, there would have to be a minimum factor of 10^{12} between the stepwise formation constants of $Pd(Dz)_2$. Certainly, this interesting chelate system merits further study.

The reaction of $Pd(Dz)_2$ in organic solvents with $AgClO_4$ resembles that with $Hg(ClO_4)_2$ in that a color change (from green to violet) was observed in the organic layer while no Pd was detected in the aqueous phase. It differs in that no primary dithizonate complex is formed (no increase in absorbance at 460 nm, characteristic of the primary silver dithizonate). The secondary silver dithizonate is described as violet colored but also as very insoluble in most organic solvents. Although our results did not allow us to fully explain this reaction now, we considered it of sufficient interest to report here.

From a practical point of view, these reactions suggest that back-extractions of Pd from extracted chelates such as the dithizonates are more difficult than anticipated earlier. In order to utilize ligands that form highly stable Pd chelates, further study of chelate reactivity is required.

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Registry No. $Pd(Dz)_2$, 12213-17-1; $Hg(Dz)_2$, 14783-59-6; $Hg(ClO_4)_2$, 7616-83-3; $AgClO_4$, 7783-93-9.

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Contribution from the Strategic Metals Recovery Research Facility and Department of Chemistry,
University of Arizona, Tucson, Arizona 85721

Solvent Extraction Equilibria and Kinetics in the Palladium(II)-Hydrochloric Acid-7-(1-Vinyl-3,3,5,5-tetramethylhexyl)-8-quinolinol System

ENXIN MA† and HENRY FREISER*

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Investigation of the extraction equilibria of palladium by chloroform solutions of 7-(1-vinyl-3,3,5,5-tetramethylhexyl)-8-quinolinol (Kelex 100, HL) from aqueous chloride solutions demonstrated that the extracted species is the simple chelate PdL_2, which, according to the kinetic study, is formed through stepwise replacement of pairs of coordinated chloride ions by the protonated ligand. Measurement of distribution ratios of Kelex 100 between chloroform and aqueous hydrochloric acid yielded values of the distribution constant of the neutral ligand, which is the predominant organic-phase species even up to 2.0 M HCl, as well as that of the ion pair H_2L^+,Cl^-. The metal chelate extraction constant and the rate of the aqueous-phase reaction $PdCl_2L^- + H_2L^+ \rightleftharpoons PdL_2 + 2H^+ + 2Cl^-$ were determined.

In spite of the widespread use of organic chelating agents for the analysis of the platinum-group metals, very little fundamental information of the reactions, i.e. the kinetic and thermodynamic parameters, has been reported. Palladium extraction by chelating agents can usually be accomplished even from acidic media, under conditions where most metals cannot be extracted. This provides high selectivity in the recovery and purification of palladium. Usually the time required for the achievement of equilibrium is so long, however, as to constitute a practical disadvantage. In this laboratory we are undertaking systematic mechanistic studies of chelation extractions of palladium[1] in order to learn more of the intrinsic nature of such reactions and how to develop systems of optimal characteristics.

Palladium extraction by 8-quinolinol (oxine), an amphoteric chelating agent widely used in analytical chemistry, has been shown to occur in the range pH 0–10.[2] The study of the extraction of Pd by 7-(1-vinyl-3,3,5,5-tetramethylhexyl)-8-

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