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Electronic Spectra of Tris(μ-halo)bis(triammineruthenium)(2+) Ions: Evidence for Delocalized Mixed-Valence D_{3h} Ru(II,III) Ground States

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The electronic absorption spectra of tris(μ-chloro)bis(triammineruthenium)(2+) chloride hydrate and tris(μ-bromo)bis(triammineruthenium)(2+) bromide hydrate have been measured in a number of solvents at room temperature and in glycerol solution and glasses down to 10 K. Both complexes have a comparatively narrow absorption band in the near-infrared region ($\nu_{max} = 7.15 \times 10^3$, 6.87×10^3 cm^{-1}; $\Delta\nu_{1/2} = 1.87 \times 10^3$, 1.90×10^3 cm^{-1}; $\epsilon_{max} = 1.60 \times 10^3$, 1.58×10^3 M^{-1} cm^{-1}, respectively, for the trichloro and tribromo complexes in D_2O at 300 K). This is absent in the corresponding mononuclear single-valence Ru(II) and Ru(III) complexes. The band maxima are insensitive to solvent dielectric characteristics, and the transitions are attributed to intervalence-type excitations in delocalized binuclear ions. Intense broader, visible bands are also found ($\nu_{max} = 17.0 \times 10^3$, 15.7×10^3 cm^{-1}; $\Delta\nu_{1/2} = 4.55 \times 10^3$, 4.60×10^3 cm^{-1}; $\epsilon_{max} = 3.97 \times 10^3$, 3.24×10^3 M^{-1} cm^{-1}, respectively, in H_2O at 300 K). The visible band is assumed to be dominated by coupling to symmetric vibrational modes, and an average effective frequency of 200 ± 30 cm^{-1} is calculated for the trihalo complexes from the temperature dependence of the second moment of the band envelope. This is consistent with results of a concurrent resonance Raman study,[16] in which the frequencies of the totally symmetric modes coupled to the visible electronic excitations are found to be 145 and 310 cm^{-1} (trichloro) and 106 and 247 cm^{-1} (tribromo), respectively. These results are consistent with a delocalized mixed-valence electronic ground state for both ions. Assuming a cofacial bioctahedral structure, the infrared and visible absorption bands are attributed to $\delta^* \rightarrow \sigma^*$ (short-axis polarized) and $\sigma \rightarrow \sigma^*$ (long-axis polarized) transitions, respectively. The nature of the metal–metal bonding in the complexes is discussed with reference to that in halogen-bridged complexes of transition metals other than ruthenium.

Introduction

Ruthenium "blue" solutions formed from "$RuCl_3$" and concentrated HCl have a long and controversial history. As Bino and Cotton[1] observed recently, 178 years after their first description no definitive structures of the blue species have been established. Proposals have included monomers, dimers, and polymers. There is accumulating evidence, however, that the compounds are mixed-valence species and hence at least binuclear. Similar intensely colored species are formed from ruthenium ammine complexes and concentrated halide acids.[2-5] Again, suitable crystals have not been available for a structure determination. There is reasonable indirect evidence, however, that at least one species formed in these solutions has the cofacial bioctahedral geometry with three bridging halide ligands.[6] This evidence includes the observation that the chloride complex decomposes to the facial isomer of $Ru(NH_3)_3Cl_3$,[5,7] the identification of the charge on the cation as 2+ by ion exchange,[5] the isolation of salts of compositions $[Ru_2Cl_3(NH_3)_6]I_2 \cdot H_2O$, $[(Ru_2Cl_3(NH_3)_6]ZnCl_4$,[7] and $[Ru_2Cl_3(NH_3)_6]ZnBr_4$,[8] and the analysis of the vibrational spectra.[8] Consequently, we have assumed that the species are correctly identified as binuclear, tris(μ-chloro)bis(triammineruthenium)(2+) chloride and tris(μ-bromo)bis(triammineruthenium)(2+) bromide compounds.

The electronic structures of these compounds have not been examined in any detail. Magnetic moment measurements[4,5] indicate that the compounds possess one unpaired electron per dimer, as expected for a mixed-valence ruthenium(II,III) complex. An analysis of the infrared spectrum was undertaken, assuming D_{3h} symmetry.[8] A single Ru–Cl stretching frequency was assigned. This implies a delocalized electronic structure, with equivalent ruthenium atoms, but since the analysis was incomplete in the absence of Raman spectra, this inference cannot be regarded as conclusive. In the present work the electronic spectra and, in particular, the temperature dependence of the intense visible absorption band are examined. Assignments are made of the intervalence absorption bands, and evidence for a delocalized electronic structure is obtained.

Table I. Room-Temperature Spectral Data for $[(NH_3)_3RuX_3Ru(NH_3)_3]X_2$[a]

solvent	Cl^-		Br^-	
H_2O		17.0 (3.97 (2)) [4.6]		15.7 (2.24 (3)) [4.4]
D_2O	7.15 (0.187) [1.6]	17.0	6.87 (0.190) [1.58]	15.79
glycerol		17.0		15.70
Me_2SO	6.99	17.1	6.66	15.79
DMF	dec	dec	6.73	15.79

[a] Tabulated as band maxima (10^3 cm^{-1}); molar extinction coefficient in parentheses (10^3 M^{-1} cm^{-1}) and half-bandwidth in square brackets (10^3 cm^{-1}).

Experimental Section

Materials. All procedures were carried out under an atmosphere of argon with deoxygenated solvents.

Tris(μ-chloro)bis(triammineruthenium)(2+) chloride was prepared from hexaammineruthenium(II) chloride and concentrated HCl by using the method of Bottomley and Tong.[4] The crude product was purified by dissolving it in degassed water, reprecipitating by addition of degassed acetone, and allowing the resulting suspension to stand overnight at 5 °C before collecting the product by filtration.

Tris(μ-bromo)bis(triammineruthenium)(2+) bromide was prepared in a similar manner[4] from hexaammineruthenium(II) bromide and constant-boiling HBr that had been freshly distilled over red phosphorus.

Methods. Spectra were recorded on a Cary 17I spectrophotometer. Low-temperature spectra were obtained on glasses formed from solutions in deoxygenated glycerol. These were contained in thick-walled Pyrex ampules and were subjected to several freeze–evacuate–thaw cycles using liquid nitrogen. The ampule was then suspended in a silica cryogenic flow tube and cooled by a stream of He obtained by boil off from liquid He in a Dewar located directly under the spec-

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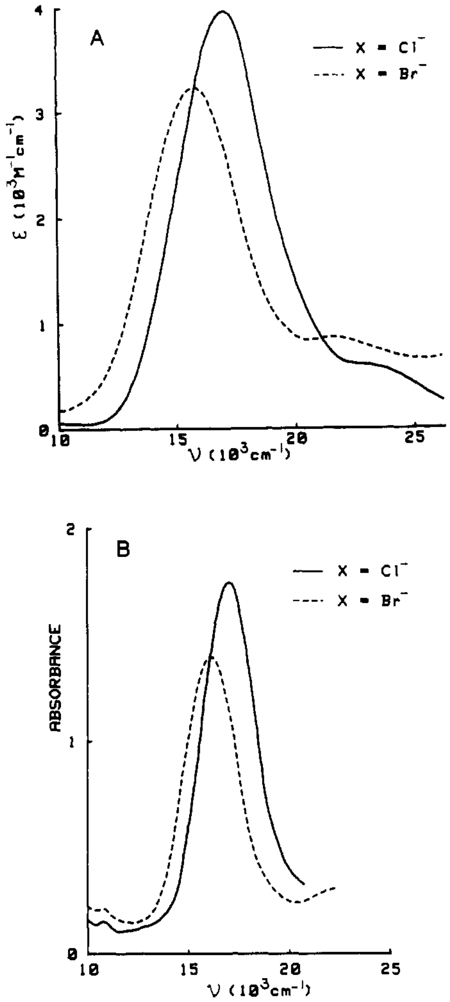

Figure 1. Electronic spectra of $[Ru(NH_3)_3]_2X_3^{2+}$ complexes (X = Cl, Br) in range (10–25) × 10^3 cm^{-1} (A) H_2O solution at ambient temperature; (B) glycerol glass at 10 K.

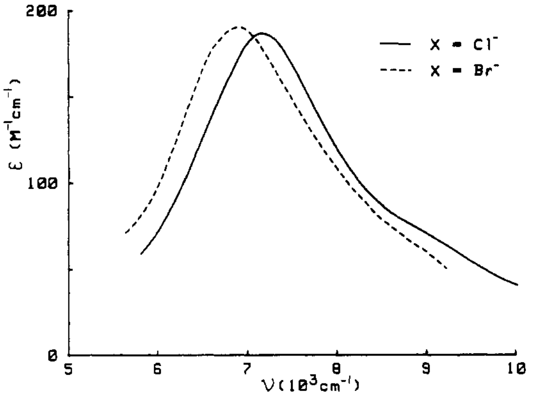

Figure 2. Near-infrared absorption spectra of $[Ru(NH_3)_3]_2X_3^{2+}$ (X = Cl, Br) ions in D_2O at ambient temperatures (background not subtracted).

trophotometer. The temperature was controlled by adjusting both the boil-off heater voltage and the flow rate using a flow bypass clamp. The temperatures were measured with a previously calibrated cryogenic linear temperature sensor attached to the ampule by reading its resistance on a digital voltmeter.

Results

Solution electronic absorption spectra were recorded in several solvents at room temperature. Typical spectra are presented in Figures 1 and 2, and the results for each solvent are given in Table I. The aqueous solution visible absorption spectra at room temperature are in agreement with those previously reported by Bottomley and Tong[4] and by Mercer and Gray,[5] although the latter report a 10% higher extinction coefficient for the chloride complex in 0.5 M H_2SO_4.

Table II. Temperature Dependence of the Visible Absorption Band in Glycerol Solutions and Glasses of $\{[Ru(NH_3)_3]_2X_3\}X_2\cdot H_2O$

$\{[Ru(NH_3)_3]_2Cl_3\}Cl_2\cdot H_2O$		$\{[Ru(NH_3)_3]_2Br_3\}Br_2\cdot H_2O$	
T, K	$10^{-3}\Delta\nu_{1/2}$, cm^{-1}	*T*, K	$10^{-3}\Delta\nu_{1/2}$, cm^{-1}
10	3.10	4	3.10
20	3.12	10	3.10
60	3.40	20	3.05
100	3.55	60	3.05
118	3.75	85	3.20
140	3.82	110	3.30
150	3.95	150	3.50
200	4.15	200	3.75
250	4.39	250	4.00
300	4.60	296	4.40

The temperature dependence of the visible absorption band in glycerol solutions and glasses was measured between 4 and 300 K. The data are presented in Table II. The band maxima showed small bathochromic shifts over this temperature range; thus ν_{max} for the bromide complex decreased from 16.1 × 10^3 cm^{-1} at 4 K to 15.7 × 10^3 cm^{-1} at 296 K. The integrated areas of the visible absorption bands in glycerol were constant to within approximately 3% from 300 down to 200 K. At temperatures below 200 K, there is a reasonably reproducibile transition to a regime at 150 K in which the apparent oscillator strength increases linearly with decreasing temperature. This is attributed to volume contraction of the glass. Provided that the oscillator strength is independent of temperature, the observed apparent intensity increase at low temperature is consistent with a coefficient of thermal expansion of ≈7 × 10^{-3} K^{-1} from 0 K to the melting point of glycerol.

Discussion

The observation of relatively intense low-energy electronic absorption bands in the near-infrared and red end of the visible spectrum indicates that the transitions are likely to be intervalence bands. There are no such low-energy bands in the related mononuclear ruthenium(II) or ruthenium(III) complexes. The further observation that the energies of the transitions are insensitive to changes in the polarity of the solvent indicates that the electronic structure is delocalized, with the two ruthenium atoms in the binuclear complex equivalent on the electronic and vibrational time scales.

The molecular orbital scheme for the interaction of the metal d orbitals in a cofacial bioctahedron of D_{3h} symmetry has been described in several recent papers[9–12] and is illustrated in Figure 3. With the 3-fold metal–metal axis chosen as the *z* direction, the vacant σ^* orbitals (e_g^* in octahedral complexes) are the *xz* and *yz* orbitals. The occupied d orbitals derived from the t_{2g} set in octahedral complexes are the z^2, xy, and $x^2 - y^2$. The two z^2 orbitals interact to form σ and σ^* molecular orbitals with a'_1 and a''_2 symmetries, respectively. The paired xy and $x^2 - y^2$ orbitals interact, presumably weakly, to give δ and δ^* molecular orbitals of e′ and e″ symmetries. With eleven 4d electrons obtained from the $d^6 + d^5$ configurations of ruthenium(II) and ruthenium(III), a single vacancy occurs in the a''_2 σ^* orbital (Figure 3). Two electronic transitions are allowed to this vacant orbital: from the $e''\delta^*$ orbital (*x*,*y* polarized) and from the a'_1 σ orbital (*z* polarized).

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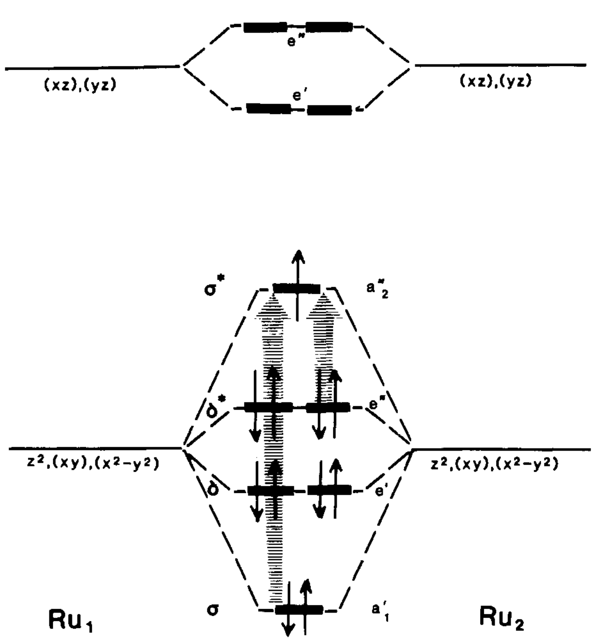

Figure 3. Proposed qualitative Ru 4d-level ordering in delocalized D_{3h} complexes. The long and short arrows indicate respectively $\sigma \rightarrow \sigma^*$, $a'_1 \rightarrow a''_2$ and $\delta^* \rightarrow \sigma^*$, $e'' \rightarrow a''_2$, excitations. The visible and near-infrared electronic transitions of $[Ru(NH_3)_3]_2X_3^{2+}$ ions are assigned to these respective excitations in mixed-valence Ru(II,III) delocalized complexes.

The transition from the e''δ orbital is symmetry forbidden. Consequently, we assign the near-infrared absorption band to the $\delta^* \rightarrow \sigma^*$ transition and the visible absorption band to the $\sigma \rightarrow \sigma^*$ transition.

The intensity of the near-infrared band is expected to be less than that of the visible band, the former being expected to be x,y polarized along the short axis of the complex and the latter z polarized along the long metal–metal axis. This expectation is met, with the extinction coefficient of the visible bands approximately 20 times larger than that of the near-infrared band, for both the chloro and bromo complexes. The difference in oscillator strengths is even greater, for the width of the near-infrared band is only about one-third that of the visible band. A quantitative analysis of the near-infrared band has not been attempted, however, for the transition depends on both σ and δ interactions, doubling the number of parameters that must be extracted from the data.

The temperature dependence of the visible absorption band was analyzed according to a model[13,14] in which the electron is considered coupled to a single vibrational mode of effective frequency ω_0 in both ground and excited states; the electronic coupling between the two sites is given by the parameter J, and the bandwidth is determined by distance dispersion arising from differences in geometry in the ground and excited electronic states and by frequency dispersion arising from differences in vibrational frequencies of ground and excited states. The second moment, μ_2, of the absorption exchange is then given by

$$\mu_2 = \mu(\Delta) + \mu_2(\gamma) + \mu_2(\mathrm{LW}) \quad (1)$$

where the three contributions arise from distance (Δ), frequency (γ), and line width (LW) dispersion, respectively. General formulas for these have been previously given.[15] A complete analysis is not possible from the present data alone. We shall assume provisionally that the second moment of the rather broad band is dominated by $\mu_2(\Delta)$. In harmonic approximation, assuming that excitation to the upper electronic state involves no rotation of normal coordinates, we thus have, for a Gaussian band shape

$$\Delta\nu_{1/2}(\Delta) \simeq (8 \ln 2)^{1/2}\sum_j h\omega_j\chi_j \coth (h\omega_j/2k_BT) \quad (2)$$

where

$$\chi_j = \tfrac{1}{2}\omega_j^2(Q^f_{0j} - Q^i_{0j})^2 \quad (3)$$

In eq 2 and 3, ω_j is the average of the frequencies of the jth mode in ground and excited states, and $|Q^f_{0j} - Q^i_{0j}|$ is the shift of the jth equilibrium normal coordinate accompanying excitation.

For the tribromide and (more approximately) for the trichloride, the temperature dependence of the visible bands is then calculated from the data of Table II to arise from coupling of the electronic excitation to symmetrical vibrational modes of mean frequency 200 ± 30 cm^{-1}. This value is consistent with a recently completed resonance Raman study[16] of these complexes in which resonance-enhanced totally symmetrical vibrational frequencies of 310 and 145 cm^{-1} for the chloro complex and 247 and 106 cm^{-1} for the bromo complex were observed. These represent Ru–X stretch and X–Ru–X bend A_1 frequencies, respectively. Since the calculated value is only an effective frequency, it is not expected to correspond to any single vibrational mode. The correspondence between the calculated effective and observed mean frequencies is consistent with the assignment of the electronic band to the $\sigma \rightarrow \sigma^*$ transition, which affects the ruthenium–halide bridge bonds.

The oscillator strength f of the electronic transition is expressed as

$$f = 4.6 \times 10^{-9}\epsilon_{\max}\Delta\nu_{1/2} \quad (4)$$

where $\epsilon_{\max}$ is the extinction coefficient of the band maximum in M^{-1} cm^{-1} and $\Delta\nu_{1/2}$ is in cm^{-1}. For a nondegenerate transition, this is related to the transition dipole length D as

$$f = 1.085 \times 10^{-5}\nu_{\max}|D|^2 \quad (5)$$

where D is in angstroms.

From the results in H_2O solution at 300 K (Table II), we find, for the visible bands, that $f = 0.069$, $|D| = 0.64$ Å for the tribromo ion and $f = 0.084$, $|D| = 0.67$ Å for the trichloro ion. The values of the transition dipole lengths for the visible transitions in the trihalo complexes are thus comparable with that of the intervalence band (6.37 × 10^3 cm^{-1}) of the strongly coupled Creutz–Taube ion,[16] $[Ru(NH_3)_5]_2(\mathrm{pyrazine})^{5+}$, i.e. 0.69 Å.

The electronic spectra of other tris(μ-halo) binuclear complexes have been incompletely explored. There are, of course, the analogous ruthenium "blue" species formed from "$RuCl_3$" and HCl. Mercer and Dumas[18] suggest that one of these has a structure analogous to that of the ammine complex, i.e. $(H_2O)_3RCl_3Ru(H_2O)_3^{2+}$. It too possesses a broad, intense visible absorption band, presumably arising from a similar $\sigma \rightarrow \sigma^*$ transition. The near-infrared spectra do not appear to have been reported.

The spectra of a number of $M_2X_9^{n-}$ species for M = Cr, Mo, or W with n = 3 or 2 have been described.[9,17,18] For $Cr_2Cl_9^{3-}$

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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 (4dπ)–ligand (2pπ) 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 dσ–dσ and dδ–dδ 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,
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Reactivity of Palladium Dithizonate with Lewis Acids and Bases

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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 $2Pd(Dz)_2(o) + Hg^{2+} + 2ClO_4^- \rightleftharpoons 2Pd(ClO_4)Dz(o) + Hg(Dz)_2(o)$ 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

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

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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