of 3.1%. Mechanisms consistent with these results will be discussed below.

Attempts to study the kinetics of the Ti^{III}–$Co(NH_3)_5NCS^{2+}$ reaction were unsuccessful due to the slowness of this reaction. Interference from aquation of Co(III) or photochemically induced oxidation of Ti(III) by water[15] at long times limited studies to initial rates. Two studies at 25°, 0.500 *M* ionic strength, 4.04×10^{-3} *M* Ti(III), 3×10^{-4} *M* Co(III), 0.126 *M* H^+, and 0.489 *M* Cl^-, in which the absorbance at 305 nm was measured either intermittently or continuously, showed less than 1% reaction in 2 hr, setting a limit of $k_{ox} \leq 3 \times 10^{-4}$ M^{-1} sec^{-1}. Studies at longer times or at higher temperatures exhibited an absorbance increase rather than a decrease, as might be expected from oxidation of Ti(III) without concomitant reduction of Co(III).[15] An initial rate study at 25°, 1.01×10^{-2} *M* Ti(III), 4.76×10^{-3} *M* Co(III), 0.314 *M* H^+, 0.455 *M* Cl^-, and 495 nm established a value of $k_{ox} \simeq 2.3 \times 10^{-5}$ M^{-1} sec^{-1} for the redox rate constant, consistent with the earlier estimate.

Discussion

If we consider the rate constant ratios for azide and isothiocyanate as potential bridging ligands, we obtain values for $k_{ox,N_3^-}/k_{ox,NCS^-}$ of $>3.6 \times 10^4$ at 0.13 *M* H^+ and $\sim 2.7 \times 10^5$ at 0.3 *M* H^+. This discrimination in favor of the azide complex is greater than that observed for any other reducing agent examined,[9,10] including those such as Cr^{2+} which are known to be inner-sphere, so it appears to be safe to conclude that at least the reaction of Ti(III) with $Co(NH_3)_5N_3^{2+}$ is of the inner-sphere type and that Ti(III) is capable of acting as an inner-sphere reducing agent toward Co(III) complexes.

Further evidence for the operation of an inner-sphere mechanism in the Ti^{III}–$Co(NH_3)_5N_3^{2+}$ reaction is provided by the form of the rate equation. The mechanism cannot involve a simple one-step reaction between $Co(NH_3)_5N_3^{2+}$ and Ti^{3+} or $TiOH^{2+}$ because of incompatibilities between the measured kinetic parameters and known thermodynamic parameters, as discussed earlier. Two mechanisms (Mechanisms I and II) can be proposed which are consistent with the form of the rate equation given by eq 4 and which are kinetically indistinguishable, differing only in the order of formation of the activated complexes.[22] Each mechanism involves the equilibrium shown in eq 3 and the formation of a binuclear complex which is a precursor to the electron-transfer step and which is present only in steady-state concentrations.

Mechanism I

$$Ti^{3+} + Co(NH_3)_5N_3^{2+} \underset{k_2}{\overset{k_1}{\rightleftarrows}} Co(NH_3)_5N_3TiOH^{4+} + H^+ \tag{5}$$

$$Co(NH_3)_5N_3TiOH^{4+} \xrightarrow{k_3} Co^{2+} + 5NH_3 + HN_3 + TiO^{2+} \tag{6}$$

$$-d \ln [Co(NH_3)_5N_3^{2+}]/dt = k_1k_3k_2^{-1} [Ti(III)][H^+]/(k_3k_2^{-1} + [H^+])(K_a + [H^+]) \tag{7}$$

$k_3k_2^{-1} = 0.045_5$ *M* and $k_1 = 47$ M^{-1} sec^{-1} if $K_a = 0.0136$ *M* (or 0.048_4 *M* and 44 M^{-1} sec^{-1} if $K_a = 0.0118$ *M*)

Mechanism II

$$TiOH^{2+} + Co(NH_3)_5N_3^{2+} \underset{k_5}{\overset{k_4}{\rightleftarrows}} Co(NH_3)_5N_3TiOH^{4+} \tag{8}$$

$$Co(NH_3)_5N_3TiOH^{4+} + H^+ \xrightarrow{k_6} Co^{2+} + 5NH_3 + HN_3 + TiO^{2+} + H^+ \tag{9}$$

$$-d \ln[Co(NH_3)_5N_3^{2+}]/dt = k_4K_a[Ti(III)][H^+]/(k_5k_6^{-1} + [H^+])(K_a + [H^+]) \tag{10}$$

$k_5k_6^{-1} = 0.045_5$ *M* or (0.048_4 *M*) and $k_4 = 157$ M^{-1} sec^{-1} (or 182 M^{-1} sec^{-1})

Exchange of solvent water[23] with water bound to Ti^{3+} occurs with a rate constant of ca. 10^5 sec^{-1} (presumably equal to ca. $2 \times 10^3[H_2O]$) and the rate constant for complex formation between Ti^{3+} and NCS^- is ca. 4×10^3 M^{-1} sec^{-1}.[24] Since both studies indicate a rate of substitution on Ti^{3+} of ca. $(2-4) \times 10^3$ M^{-1} sec^{-1}, the values assigned to the rate constants k_1 and k_4 above are sufficiently small to be consistent with a process involving substitution on Ti(III). Thus these results provide evidence for the occurrence of an inner-sphere reduction of $Co(NH_3)_5N_3^{2+}$ by Ti(III).

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Registry No. Ti(III), 22541-75-9; $Co(NH_3)_5N_3^{2+}$, 14403-83-9; $Co(NH_3)_5NCS^{2+}$, 14970-18-4.

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Resonance Raman Spectrum of Matrix-Isolated Re_3Cl_9

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Recent laser Raman studies of the orange matrix isolated $M^+Cl_2^-$ and $M^+O_3^-$ species have demonstrated that solid argon at 15°K is an effective medium for the study of resonance Raman spectra of unstable inorganic molecules.[1,2] In a study of polynuclear transition metal complexes, the Raman spectrum of solid Re_3Cl_9 has been reported.[3] Owing to a strong rhenium trichloride absorption band in the green visible region,[4] resonance Raman spectra can be observed with the argon ion laser lines. Since the equilibrium vapor over solid rhenium trichloride is known to contain Re_3Cl_9 molecular units,[5] it was decided to trap these molecules in argon matrices for spectroscopic observation. It is of particular interest to compare the spectra of the isolated molecular and aggregated or solid species to examine the effects of intermolecular bonding.

Experimental Section

The experimental techniques, vacuum vessel, Knudsen cells, and cryogenic apparatus have been described in previous publications from this laboratory.[2,6,7] Rhenium trichloride (Alfa Inorganics, Inc.) was loaded into a stainless steel Knudsen cell with a 2-mm orifice, the cell was placed in the heater, the vacuum vessel was evacuated to better than 10^{-5} Torr, and the Re_3Cl_9 was outgassed at 250° for 1 hr. The substrates were cooled to 12–15°K with closed-cycle helium refrigerators (Cryogenic Technology, Inc.), argon (Air Products 99.995%) deposition was started at 1–2 mmol/hr, and the Knudsen cell was warmed to 290–315°, which corresponds to a Re_3Cl_9 vapor pressure of about 1 μ.[5]

Sample concentration was monitored visually; excessive Re_3Cl_9 led to laser "burning" in the Raman studies; condensation periods were about 3 hr. Laser excitation was provided by the 4880- and 5145-Å lines of an argon ion laser (Coherent Radiation, Model 52 G). Dielectric filters (Corion Instrument Corp.) were used to eliminate unwanted laser plasma emission lines from recorded scans; the Raman band positions were calibrated by removing the dielectric filter and superimposing the emission lines on the spectrum. Frequency accuracy is ±1 cm^{-1}.

Results

The laser Raman experiments with Re_3Cl_9 were marked by two different spectra, depending upon Re_3Cl_9 concentration, which are contrasted in Figure 1. At lower concentrations, Re_3Cl_9 was deposited from a 300 ± 3° effusion cell for 3 hr which gave an orange sample. The 4880-Å excitation produced a series of sharp bands at 277, 552, 827, 1102, and 1375 cm^{-1}. These bands, labeled ν_c, $2\nu_c$, $3\nu_c$, $4\nu_c$, and $5\nu_c$ in Figure 1(a) and in Table I, exhibited a regularly decreasing intensity pattern with a first overtone:fundamental intensity ratio of 0.53. No spectrum was observed with any of the other five strong argon ion laser lines from 4579 to 5145 Å. The 4880-Å excited progression was accompanied by subprogressions which consisted of sets of three broader signals shifted 72, 142, and 211 ± 2 cm^{-1} from the primary series. These bands were observed only with 4880-Å excitation. Another experiment was run under the same conditions and the spectrum was reproduced.

Higher concentration of Re_3Cl_9 and the resulting red sample were produced by effusion from a 315 ± 3° cell for 3 hr. The 5145-Å excitation of this sample gave a steadily diminishing series at 256, 505, 755, and 1009 cm^{-1} and a lone band at 216 cm^{-1} which is illustrated in Figure 1(b). These signals were observed only with 5145-Å excitation, although the 256-cm^{-1} fundamental was found weakly with 4880- and 4765-Å illumination. The first overtone:fundamental intensity ratio was 0.18.

Discussion

The Raman spectra of matrix-isolated rhenium trichloride parallel studies on matrix-isolated iodine from this laboratory.[8] At low concentrations, matrix-isolated I_2 molecules gave a resonance Raman vibrational progression originating at 212 cm^{-1}, near the gas-phase value, while higher concentrations produced I_2 aggregates which yielded a vibrational series starting at 180 cm^{-1}, the solid value. Rhenium trichloride vapor exists predominantly as the trimeric species Re_3Cl_9.[5] However, the crystal shows extensive intermolecular bonding which is accomplished through chlorine bridges using the out-of-plane chlorines.[4] Thus, the matrix spectra of Re_3Cl_9 are expected to vary according to concentration.

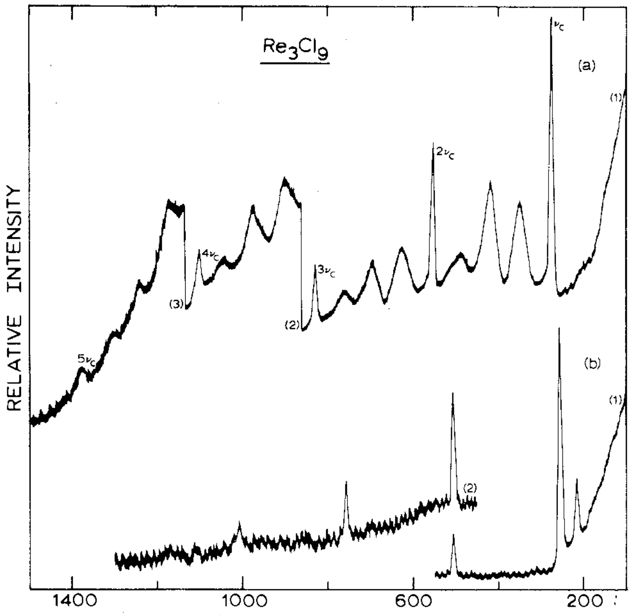

Figure 1. Resonance Raman spectra of matrix-isolated Re_3Cl_9. Spectrum (a) recorded after vapor deposition from 300 ± 3° Knudsen cell; 150 mW of 4880-Å power used at sample; scans (1), (2), and (3) employed 1, 0.3, and 0.1 × 10^{-9} A ranges, respectively. Spectrum (b) recorded after vapor effusion from 315 ± 3° cell for 3 hr in a separate experiment; 125 mW of 5145-Å power used at sample; scans (1) and (2) employed 0.3 and 0.1 × 10^{-9} A ranges, respectively. All spectra used 5-Å dielectric filter, 50-cm^{-1}/min scan speed, and 3-sec rise time.

Table I. Wave Number Shifts and Assignments in Resonance Raman Spectra of Re_3Cl_9

	Argon matrix	
Solid[a,b]	Figure 1(b)[b,c]	Figure 1(a)[d]
250 (ν_c)	256 (ν_c)	277 (ν_c)
		349 ($\nu_c + \nu_b$)
		419 ($\nu_c + 2\nu_b$)
		488 ($\nu_c + 3\nu_b$)
495 ($2\nu_c$)	505 ($2\nu_c$)	555 ($2\nu_c$)
		628 ($2\nu_c + \nu_b$)
		696 ($2\nu_c + 2\nu_b$)
		765 ($2\nu_c + 3\nu_b$)
745 ($3\nu_c$)	755 ($3\nu_c$)	827 ($3\nu_c$)
		898 ($3\nu_c + \nu_b$)
		970 ($3\nu_c + 2\nu_b$)
		1039 ($3\nu_c + 3\nu_b$)
998 ($4\nu_c$)	1009 ($4\nu_c$)	1102 ($4\nu_c$)
		1172 ($4\nu_c + \nu_b$)
		1242 ($4\nu_c + 2\nu_b$)
		1312 ($4\nu_c + 3\nu_b$)
		1375 ($5\nu_c$)

[a] Reference 3. [b] 5145-Å laser excitation. [c] Signal at 216 cm^{-1} assigned to out-of-phase ν_c type mode of Re_3Cl_9 units. [d] 4880-Å laser excitation.

The 256, 505, 755, and 1009 cm^{-1} band progression in the higher concentration spectrum of Figure 1(b) is in reasonable agreement with the solid spectrum[3] which exhibited a progression of bands at 250, 495, 745, and 998 cm^{-1}. Even the sharp single feature at 216 cm^{-1} in the matrix aggregate spectrum has a counterpart near 205 cm^{-1} in the solid spectrum. The regularly decreasing intensity pattern in the vibrational overtone series is characteristic of the resonance Raman effect.[1,2,9]

The 5145-Å (19,435 cm^{-1}) exciting line, which yielded resonance Raman spectra with the higher concentration sample and the solid,[3] falls within the absorption band of Re_3Cl_9 solutions, which exhibit a maximum near 19,400 cm^{-1}.[4]

In agreement with the literature on metal–metal bonding,[3] the 256, 505, 755, and 1009 cm^{-1} series is assigned to the fundamental Re–Re totally symmetric cluster breathing mode (A_1' in idealized D_{3h} point group) and its first three overtones. The 216-cm^{-1} band is not appropriate for the E' cluster mode, which is expected at the A_1' wave numbers divided by ($2^{1/2}$).[10] This extra band is characteristic of the spectra of solid[11] and aggregated iodine[8] where a weak (189 ± 1)-cm^{-1} satellite band was observed beside the 180-cm^{-1} fundamental. This feature is due to out-of-phase stretching of I_2 molecules in the unit cell. Notice that the 216-cm^{-1} band is absent in the isolated spectrum of Figure 1(a). We believe the 216-cm^{-1} band is best explained as out-of-phase Re–Re cluster breathing modes of Re_3Cl_9 units in the aggregate formed in the matrix. This band shows some resonance intensity enhancement but is weaker than the signal from the totally symmetric cluster fundamental.

The intense fundamental at 277 cm^{-1} labeled ν_c in Figure 1(a) and its overtone series are assigned to the symmetric Re–Re cluster breathing mode (A_1') in the isolated Re_3Cl_9 molecular unit. The shift to lower wave number is characteristic of aggregation and intermolecular bonding which gives a 256-cm^{-1} fundamental for the matrix aggregate and a 250-cm^{-1} fundamental in the solid where intermolecular bonding is complete.

The broader subseries of bands which appear 72, 142, and 211 cm^{-1} shifted below the fundamental and first two overtones clearly originate with the resonance-enhanced Re–Re cluster mode. These subbands are attributed to combination bands involving, most probably, some other totally symmetric mode and ν_c. Three other totally symmetric modes that should strongly couple with ν_c are symmetric stretching modes of the out-of-plane chlorines and the bridged chlorines, and a symmetric Cl–Re–Cl valence angle bending mode involving the out-of-plane chlorines on each Re atom. The best present assignment for the 72-cm^{-1} combination band series is to the symmetric valence angle bending mode of the out-of-plane chlorines, ν_b. Thus, the bands in the isolated monomeric Re_3Cl_9 resonance Raman spectrum, reading right to left, are ν_c, $\nu_c + \nu_b$, $\nu_c + 2\nu_b$, $\nu_c + 3\nu_b$, $2\nu_c$, $2\nu_c + \nu_b$, $2\nu_c + 2\nu_b$, $2\nu_c + 3\nu_b$, $3\nu_c$, ... These assignments are listed in Table I.

It is also interesting to note the much more rapid decrease in overtone intensity for the aggregate, as compared to isolated Re_3Cl_9, in Figure 1. The same effect was found for matrix-isolated iodine.[8]

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Experimental Complications in Studies of the Reaction of Copper(II) with Penicillamine and Related Thiols

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We have observed unusual experimental complications during our examination of some intensely colored mixed-valence copper complexes[1] formed by partial reduction of copper(II) by certain thiols. Mixed-valence complexes are of interest because they are present in some multi-copper proteins.[2,3] In the single-copper proteins stellacyanin[4] and plastocyanin[5] a copper to sulfur bond has been proposed, yet the redox chemistry associated with the interaction of copper with thiols is unclear. Drugs such as penicillamine which react with copper(II) to cause partial reduction and give intensely colored complexes have been used successfully in the treatment of chronic copper toxicity (Wilson's disease),[6,7] yet the reaction between penicillamine and copper(II) has not been well characterized. Recently, research has been directed toward an understanding of the reactions between copper(I) and copper(II) and ligands containing the disulfide group.[8,9]

Our examination of the reaction of copper(II) with penicillamine in aqueous solution reveals that certain important factors which greatly influence the course of the reaction and which relate to the composition of the colored species both in solution and in the solid state have not been reported before.[10-14] These factors must be considered in future discussions of the reactivity of copper in the presence of both thiol and disulfide groups. To circumvent some of the problems encountered with penicillamine, the reaction of a more simple ligand, α-mercaptoisobutyric acid, MIBA, was examined in detail.

Experimental Section

Cupric chloride (Matheson Coleman and Bell) was refluxed with thionyl chloride and dried under vacuum. Cuprous chloride was prepared by reduction of cupric chloride with sodium sulfite. D(−)- and DL-penicillamine and D(−)-penicillamine disulfide (Aldrich) were used without purification. α-Mercaptoisobutyric acid (MIBA) was prepared using the procedure of Biilmann.[15] MIBA disulfide, MIBA(SS), was prepared by oxidizing MIBA with copper chloride, mp 197–200°. Anal. Calcd for $C_8H_{14}S_2O_4$: C, 40.34; H, 5.88. Found: C, 40.30; H, 6.01.

The electronic absorption spectra were measured with a Cary 14 spectrophotometer. Magnetic susceptibilities were determined by the Gouy method using $Hg[Co(SCN)_4]$ as the standard. ESR spectra were obtained using a Varian E-4 spectrometer. Infrared spectra were obtained using a Perkin-Elmer 237B spectrometer. Analytical and molecular weight data were obtained by Galbraith Laboratories Inc., Knoxville, Tenn. Copper analyses were done by electrogravimetry.

Preparation of Complexes. Complexes were prepared by mixing an aqueous $CuCl_2$ solution ($\sim 10^{-3}$ *M*) with a freshly prepared aqueous thiol solution ($\sim 10^{-3}$ *M*) usually in 0.1 *M* acetate. Both solutions were purged before mixing with purified nitrogen. The solutions were normally mixed in a flask after introduction via metal-tipped syringes. In some of the penicillamine reactions, however, a syringe pump was used to ensure reproducible mixing. In these reactions the solutions were passed through a small mixing chamber (approximately 0.2 ml in volume) before entering the flask.

The complexes were also prepared in solution by combining solid CuCl with the disulfide in aqueous solution in the presence of 0.1 *M* acetate. Penicillamine disulfide was quite soluble, whereas MIBA(SS) was initially present as a slightly soluble solid. In these reactions all solutions and flasks were purged with nitrogen. The formation of the products and the dissolution of the insoluble solids occurred over a period of hours.

The penicillamine and MIBA complexes slowly precipitate from