

tween the values of the activation entropy may be regarded to stem from the different composition of the media employed. It is evident that primary loss of ammonia, followed by the predicted spontaneous redox reaction²³ of the nitroaquo-tetraammine complex, can also explain Banerjea's results.

Banerjea also studied the reaction in nitric acid media. In this solution he found a much larger acid-independent rate. We do not agree with Banerjea, who called this reaction an aquation, as this would imply that the same reaction could have two widely differing rates. It is not contradictory to describe this reaction as part of an acid-catalyzed reaction in a saturation region. In this connection it is important to note that also Jolly and co-workers³ found a constant rate in acid solutions, up to 55 wt % H₂SO₄, this rate being an order of magnitude larger than the rate in neutral solutions.

The final conclusion is then that our detailed analysis of the medium dependence in which all assumptions have been tested and the comparison with previously reported results together give a firm support to the postulated mechanism.

In order to get more detailed information on this mechanism, we are now extending our study to other nitroammine-cobalt(III) complexes.

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Registry No. [Co(NH₃)₅(NO₂)](ClO₄)₂, 15040-54-7; *trans*-[Co(NH₃)₄(NO₂)(H₂O)](ClO₄)₂, 58408-30-3; *trans*-[Co(NH₃)₄(NO₂)(OH)]⁺, 57665-42-6.

Supplementary Material Available: Tables containing the observed and calculated reaction constants for the *trans*-hydroxynitrotetraamminecobalt(III) and the nitropentaamminecobalt(III) ions, as a function of the medium and the four temperatures (6 pages). Ordering information is given on any current masthead page.

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Resonance Raman Spectra of the Mixed-Valence Compounds

Pd₂(NH₃)₄Cl₆ and PdPt(NH₃)₄Cl₆

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Resonance Raman spectra have been observed for the two mixed-valence compounds PdPt(NH₃)₄Cl₆ and Pd₂(NH₃)₄Cl₆, using a variety of exciting lines. For the former compound resonance progressions involving the three Raman-active metal-chlorine stretching vibrations are observed, compatible with the assignment of the resonant electronic transition to a metal-metal mixed-valence transition. For the latter, the spectra are found to depend markedly on the exciting line used and they indicate the presence of two allowed transitions in the visible region. The spectra differ from those of PdPt(NH₃)₄Cl₆; they exhibit overtones and combination tones involving several stretching and bending fundamentals of the Pd(IV) constituent complex. For Pd₂(NH₃)₄Cl₆, the resonance effects are attributed to excitation within ligand → Pd(IV) charge-transfer bands. The analogous mixed-valence transition is inferred to lie in the infrared region, contrary to a previous report. Far-infrared spectra of the compounds are also reported.

Introduction

Compounds containing atoms of the same metallic element in more than one oxidation state have been broadly classified by Robin and Day.¹ They proposed essentially three categories of mixed-valence compounds, depending on the degree of electronic interaction between the valence sites. In class I compounds the valences are firmly "trapped" at markedly different coordination sites, with no significant electronic interaction between them. At the other extreme, in class III compounds, valence delocalization is essentially complete and no distinction can be made between valence sites. Class II compounds comprise those materials with intermediate properties. Valences remain quite firmly trapped and the sites distinguishable, but there is sufficient overlap between orbitals on adjacent metal atoms to permit electron transfer between

the two sites. Such materials typically exhibit intense, broad absorption in the visible region due to intervalence charge-transfer transitions.

The resonance Raman (RR) spectra of many simple compounds² and biological materials³ possessing electronic transitions in the visible region have been extensively studied. Mixed-valence compounds so far have not, despite the fact that in several respects those of class II are potentially extremely interesting candidates for investigation by this technique. Our earlier report⁴ indicated that such compounds (specifically mixed-valence antimony compounds) may display striking RR effects.

While the theoretical study of the RR effect is currently in a state of active development, most treatments agree that, at least qualitatively, the resonance enhancement of modes in

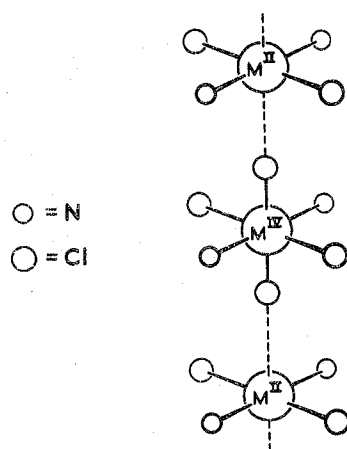


Figure 1. Chain structure established for the mixed-valence compounds $\text{Pd}^{\text{II}}\text{Pd}^{\text{IV}}(\text{NH}_3)_4\text{Cl}_6$ and $\text{Pd}^{\text{II}}\text{Pt}^{\text{IV}}(\text{NH}_3)_4\text{Cl}_6$.

a Raman spectrum may occur by two kinds of mechanism. First, there is a single-state contribution, by which vibrational modes (usually totally symmetric ones) whose potential surfaces are displaced in the electronic transition show enhancement of intensity and may exhibit overtone and combination tone progressions (cf. the treatments of Albrecht⁵ and Jacon et al.⁶). Second, a two-state contribution may lead to the enhancement of modes active in vibronic coupling between two allowed excited states. The relationship between RR and electronic spectra may, however, be complicated by interference effects.⁷ The relative importance of these contributions in the special circumstances of resonance with a mixed-valence transition, remains to be discovered. However we anticipate that "single-state" effects will be large, since in the excited state an electron has effectively been transferred from one species to another; large changes in the dimensions of the scattering molecule may accompany such a transition.

Characteristically, class II mixed-valence transitions give rise to extremely broad absorption bands. Usually no vibrational structure is resolvable, even at low temperatures, indicating that several vibrational modes contribute to this breadth. RR spectroscopy may enable us to identify these vibrations, and in the most favorable cases may assist the assignment of mixed-valence electronic spectra. It must however be stated that very broad electronic transitions are not desirable from the point of view of RR spectroscopy; mixed-valence bands are sometimes broader than the range of exciting wavenumbers currently available, and in such cases complete excitation profiles cannot as yet be determined.

Platinum and palladium form many class II mixed-valence compounds containing atoms of valency 2+ and 4+.¹ We report here detailed Raman spectral studies on two such compounds: $\text{Pd}_2(\text{NH}_3)_4\text{Cl}_6$ and $\text{Pd}^{\text{II}}\text{Pt}^{\text{IV}}(\text{NH}_3)_4\text{Cl}_6$. Their formulas can be more fully written in the form $\text{trans}[\text{M}^{\text{II}}(\text{NH}_3)_2\text{Cl}_2]\text{-trans}[\text{M}^{\text{IV}}(\text{NH}_3)_2\text{Cl}_4]$.

The two compounds are hereafter referred to as [Pd-Pd] and [Pd-Pt], respectively. Both crystallize with chain structures of the form shown in Figure 1; interatomic distances⁸ are given in Table I. This is a typical class II structure, with the valences on similar but not identical sites. Many analogous compounds exist containing other halogen or ammine ligands. Each of these materials shows intense absorption in the visible region, the absorption having been attributed^{1,9} to a metal \rightarrow metal, $d_{z^2} \rightarrow d_{z^2}$, transition. The compounds exist only as solids; there is no interaction between the constituent M(II) and M(IV) complexes in solution. The electrical conductivity of some of the crystals has been shown to be highly anisotropic,¹⁰ with much greater conductivity parallel to the chain axis than perpendicular to it.

Table I. Interatomic Distances (Å) in the Compounds $\text{Pd}^{\text{II}}\text{Pd}^{\text{IV}}(\text{NH}_3)_4\text{Cl}_6$, [Pd-Pd], and $\text{Pd}^{\text{II}}\text{Pt}^{\text{IV}}(\text{NH}_3)_4\text{Cl}_6$, [Pd-Pt]^a

Bond	[Pd-Pd]	[Pd-Pt]
$\text{Pd}^{\text{II}}\text{-Cl}$ off-axis	2.29	2.28
$\text{Pd}^{\text{II}}\text{-N}$	1.90	1.95
$\text{Pd}^{\text{II}}\text{-Cl}$ axial	3.22	3.30
$\text{M}^{\text{IV}}\text{-Cl}$ axial	1.99	2.03
$\text{M}^{\text{IV}}\text{-Cl}$ off-axis	2.29	2.28
$\text{M}^{\text{IV}}\text{-N}$	1.99	1.95

^a Reference 8.

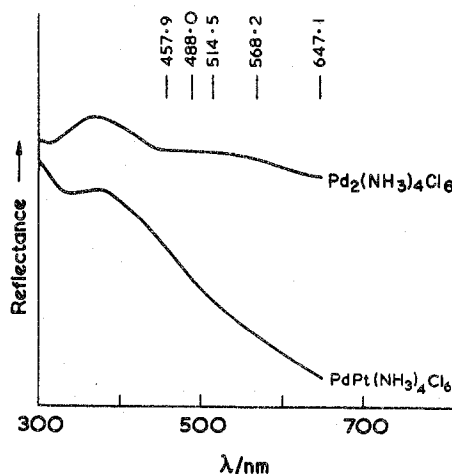


Figure 2. Diffuse reflectance spectra of the mixed-valence compounds $\text{Pd}^{\text{II}}\text{Pd}^{\text{IV}}(\text{NH}_3)_4\text{Cl}_6$ and $\text{Pd}^{\text{II}}\text{Pt}^{\text{IV}}(\text{NH}_3)_4\text{Cl}_6$ at room temperature.

Experimental Section

[Pd-Pd] was prepared by the second method described by Cohen and Davidson.¹¹ Chlorine was passed for several minutes through an aqueous suspension of $\text{trans}[\text{Pd}(\text{NH}_3)_2\text{Cl}_2]$. On standing of the solution in a vacuum desiccator for several days, black needles of [Pd-Pd] slowly formed. Anal. Calcd: Cl, 43.09; N, 11.35; H, 2.45. Found (microanalytically): Cl, 43.05; N, 11.9; H, 2.4.

The reaction with chlorine yields (initially) $\text{trans}[\text{Pd}^{\text{IV}}(\text{NH}_3)_2\text{Cl}_4]$; this is only stable in the presence of chlorine. Raman spectra of this complex were obtained from a dilute aqueous solution containing chlorine.

[Pd-Pt] was prepared¹¹ from $\text{trans}[\text{Pd}(\text{NH}_3)_2\text{Cl}_2]$ and $\text{trans}[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$. Anal. Calcd: Cl, 36.53; N, 9.62; H, 2.08. Found (microanalytically): Cl, 36.4; N, 9.6; H, 2.1.

Raman spectra were recorded by the rotating-sample technique,^{12,13} using a Spex 1401 spectrometer, in conjunction with Coherent Radiation Ar⁺, Kr⁺, and Model 490 dye lasers. Further details of the instrumental system are available elsewhere.¹⁴

Far-infrared spectra were obtained using a Beckman-RIIC FS-720 interferometer, by the Physico-Chemical Measurements Unit, Harwell, England.

Electronic spectra, by diffuse reflectance, were obtained by use of a Cary 14 spectrometer.

Results

Electronic Spectra. Room-temperature diffuse reflectance spectra of [Pd-Pd] and [Pd-Pt] are shown in Figure 2. The spectrum of the red-brown [Pd-Pt] shows the reflectance steadily rising across the visible region to a broad maximum at ca. 29000 cm^{-1} . Cohen and Davidson¹¹ reported that, for both compounds, the absorption of visible light is much greater with light polarized parallel than with that polarized perpendicular to the chain axis. Hush¹⁵ quoted a value of 18870 cm^{-1} for the $d_{z^2} \rightarrow d_{z^2}$ transition in [Pd-Pt].

The black [Pd-Pd] absorbs strongly throughout the visible region. Polarized single-crystal transmission spectra were measured by Yamada and Tsuchida.¹⁶ Spectra recorded with light polarized parallel to the chain axis exhibit an intense, broad maximum at ca. 13000 cm^{-1} . Spectra recorded with either parallel or perpendicular polarization show strong, broad

Table II. Correlation of the Representations of the Internal Fundamentals of *trans*-[M^{IV}N₂Cl₄] Species from *D*_{4h} to *D*_{2h} Symmetry^a

Activity	<i>D</i> _{4h}	<i>D</i> _{2h}	Activity
Raman	2 a _{1g}	3 a _g	Raman
	b _{1g}		
	b _{2g}		
Ir	e _g	b _{1g}	Ir
	2 a _{2u}	b _{2g} + b _{3g}	
Inactive Ir	b _{2u}	3 b _{2u}	Ir
	3 e _u		

^a In correlating, the *y* and *z* axes are interchanged so that, in *D*_{2h}, the *z* axis coincides with the chain axis of the mixed-valence crystal.

absorption toward the blue end of the visible region, at ca. 24000 cm⁻¹. Hush¹⁵ quoted a value of 16150 cm⁻¹ for the d_{z²} → d_{z²} transition of this compound.

The lowest energy allowed (charge-transfer) transitions in the constituent complexes *trans*-[Pd^{II}(NH₃)₂Cl₂]¹⁷ and *trans*-[Pt^{IV}(NH₃)₂Cl₄]¹⁸ occur at 250 and 270 nm, respectively. The Pd(IV) constituent is unstable but is red, suggesting a lower energy for the lowest charge-transfer band of this complex than for the yellow Pt(IV) complex.

Vibrational Spectra Selection Rules. The compounds crystallize with space group symmetry *D*_{2h},⁸ this is the same as the symmetry of the sites occupied by the metal atoms and of the line group of the chain, taking no account of hydrogen atoms. Vibrational spectra of class II mixed-valence compounds are characteristically approximate superpositions of the spectra of the constituent single-valence species.¹ The internal fundamentals for the constituent divalent complex (*D*_{2h} symmetry neglecting protons) belong to the irreducible representations 2 a_g + b_{1g} + 2 b_{1u} + 2 b_{2u} + 2 b_{3u}, of which all g modes are Raman active and all u modes ir active. Four of these fundamentals may be described as stretching vibrations, a_g + b_{2u} (Pd-Cl) and a_g + b_{3u} (Pd-N), and the remainder as bending vibrations.

For the tetravalent complex, the internal modes under *D*_{4h} and the correlation to *D*_{2h} are given in Table II. Stretching modes (under *D*_{2h}) belong to the irreducible representations 2 a_g + b_{1u} + b_{3u} (M-Cl) and a_g + b_{2u} (M-N).

Far-Infrared Spectra. Results and assignments are given in Table III together with published data for constituent Pd(II)¹⁹ and Pt(IV)²⁰ complexes. The spectra can be quite simply assigned by comparison with those of the single-valence

species. There is no measurable splitting of the bands assigned to the degenerate e_u fundamentals of the tetravalent complex, although one of them (250 cm⁻¹ in the free Pt(IV) complex) appears broad in the mixed-valence case. All internal modes expected to occur in this region of the spectrum are accounted for, with two exceptions. No counterpart of the band attributed to the bending fundamental at 173 cm⁻¹ for the Pt(IV) complex was identified; it may be coincident with another band in this region. Also one bending fundamental of the M(IV) species (b_{2u} in *D*_{4h}) attains ir activity in the *D*_{2h} symmetry point group. This mode is expected to be weak and there is no feature in the mixed-valence spectrum with which it could be identified.

The ir spectra are important for the interpretation of the Raman spectra, in that they show no apparent deviation from the rule of thumb that vibrational spectra of mixed-valence compounds are approximate superpositions of the single-valence spectra. In general the fundamentals assigned to the tetravalent constituents show greater shifts between [Pd-Pd] and [Pd-Pt] than the modes of the Pd(II) component. We note also that the metal-chlorine stretching fundamentals are raised in wavenumber in the mixed-valence compounds.

Raman Spectra of [Pd-Pt]. Raman spectra recorded with several different exciting lines are shown in Figure 3; data and assignments are listed in Table IV, together with published results for the constituent Pd(II)²¹ and Pt(IV)²⁰ complexes.

Raman spectra excited with any of the exciting lines used exhibit progressions of bands containing overtones of three closely spaced bands in the 300–340-cm⁻¹ region. The three fundamentals are assigned to the three metal-chlorine stretching vibrations (all of a_g symmetry), by comparison with the spectra of the constituents and of [Pd-Pd] (Table V). The lowest frequency fundamental, the shoulder at ca. 309 cm⁻¹, is assigned to the Pd-Cl stretch (cf. [Pd-Pd]). The higher members of the overtone progressions overlap, with the result that, except in the case of the first overtones, a broad envelope with no resolved structure is observed. Combination tones may also be present. The RR effect, measured by the *I*(2ν₁)/*I*(ν₁) value or by the length of the overtone progression (corrected for spectral response), appears to be at a maximum in the yellow-green region of the visible spectrum; five overtones are observed with 568.2 nm (17595 cm⁻¹) or 514.5 nm (19430 cm⁻¹) excitation. Thus the maximum in the excitation profile coincides approximately with the published value of 18870 cm⁻¹ for the d_{z²} → d_{z²} transition, but it is clear from an inspection of the Raman spectra that the excitation profiles for the three metal-chlorine stretching fundamentals do not all

Table III. Far-Infrared Data (cm⁻¹) for the Compounds Pd^{II}Pd^{IV}(NH₃)₄Cl₆, [Pd-Pd], and Pd^{II}Pt^{IV}(NH₃)₄Cl₆, [Pd-Pt], and Constituent Single-Valence Complexes, as Mulls

[Pd-Pd]		[Pd-Pt]		<i>trans</i> -Pd-(NH ₃) ₂ Cl ₂ ^b	<i>trans</i> -Pt-(NH ₃) ₂ Cl ₄ ^c	Assignment ^d
LN ^a	RT ^a	LN	RT	RT	RT	
60 m	60 m					} Lattice modes
90 w, sh	} 91 s					
98 s						
147 w	146 w	140 w	137 w	137		Pd ^{II} ; bend
161 m	160 w	164 m	162 m	162		Pd ^{II} ; bend
					173 m	M ^{IV} ; bend (a _{2u})
186 s	185 s	177 s	174 s			
					183 s	M ^{IV} ; bend (e _u)
230 s, sh	224 s	222 s	216 m	222		Pd ^{II} ; bend
250 vs, br	248 vs, br	250 sh	245 sh	245		Pd ^{II} ; bend
		256 vs, br	256 vs, br		250 vs	M ^{IV} ; bend (e _u)
345 vs, br	341 vs, br	347 vs	344 vs	333		ν(Pd ^{II} -Cl)
370 s	366 s	357 vs	354 vs		349 vs	ν(M ^{IV} -Cl) (e _u)
				496		ν(Pd ^{II} -N)
					516 ms	ν(Pd ^{IV} -N) (a _{2u})

^a LN = 77 K; RT = ambient temperature. ^b From ref 19. ^c From ref 20. ^d Symmetry labels relate to *D*_{4h} symmetry of the Pt^{IV} complex.

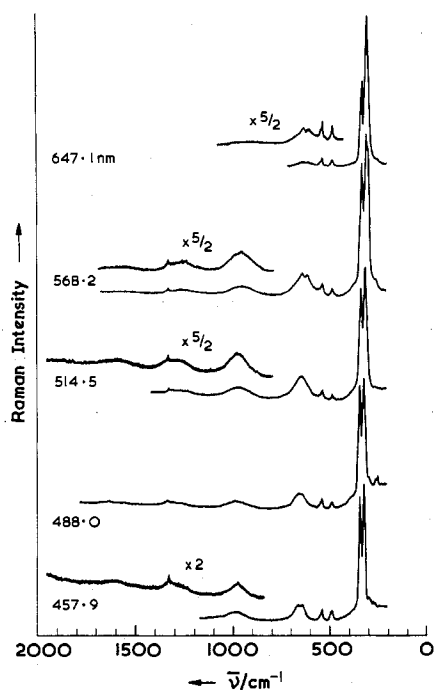


Figure 3. Raman spectra of the mixed-valence compound $\text{Pd}^{\text{II}}\text{Pt}^{\text{IV}}(\text{NH}_3)_4\text{Cl}_6$ obtained with different exciting wavelengths; spectral resolution ca. 2 cm^{-1} .

Table IV. Raman Spectral Data (cm^{-1}) for the Compound $\text{Pd}^{\text{II}}\text{Pt}^{\text{IV}}(\text{NH}_3)_4\text{Cl}_6$, [Pd-Pt], and Constituent Single-Valence Complexes

[Pd-Pt] ^a		<i>trans</i> - [Pd ^{II} - (NH ₃) ₂ - Cl ₂] ^b	<i>trans</i> - [Pt ^{IV} - (NH ₃) ₂ - Cl ₄] ^d	Assignment
ν	$\Delta\nu_{1/2}$			
174 m			174	$\delta(\text{ClPtCl})$
220 w		224		$\delta(\text{Pd}^{\text{II}})$
261 vw			229 vw	$\delta(\text{Pt}^{\text{IV}})$
309 sh		295		$\nu(\text{Pd-Cl})$
323 vs			327 vs	$\nu(\text{Pt-Cl})$
344 vs			343 vs	$\nu(\text{Pt-Cl})$
490 w		494		$\nu(\text{Pd-N})$
541 m			522 m ^b	$\nu(\text{Pt-N})$
552 vw ^b			542 m	
649 m	{ (614) (648)	73		$2\nu(\text{M-Cl})$
981 w (953)	104			$3\nu(\text{M-Cl})$
1283 vw (1307)	134			$4\nu(\text{M-Cl})$
1623 vw (1629)	156			$5\nu(\text{M-Cl})$
≈ 1965 vw (-)	≈ 200			$6\nu(\text{M-Cl})$

^a Values in parentheses refer to 568.2-nm excitation; others, to 488.0-nm excitation. ^b Residuals of ir-active fundamentals. ^c From ref 21. ^d From ref 20.

peak at the same exciting wavenumber. In particular the lowest wavenumber fundamental, tentatively assigned to $\nu(\text{Pd}^{\text{II}}\text{-Cl})$, is most clearly resolved, and its overtones are most prominent, with 568.2-nm excitation. With shorter wavelength excitation, the other two fundamentals and their overtones dominate the spectrum. The wavenumber shifts of the overtone envelope maxima shift to slightly higher values with shorter exciting wavelengths (see Table IV). A precise study of the excitation profiles is clearly desirable, but the deconvolution problems presented by the many closely overlapping bands preclude this at present; excitation profiles are particular objects of attention in other compounds of this type at present under study. Some, such as Wolfram's red salt (see below) give rise to much simpler Raman spectra.

Raman Spectra of [Pd-Pd]. Raman spectra are shown in Figure 4 and data and assignments are listed in Table V. The

Table V. Raman Spectral Data (cm^{-1}) for $\text{Pd}^{\text{II}}\text{Pd}^{\text{IV}}(\text{NH}_3)_4\text{Cl}_6$, [Pd-Pd], and Constituent Single-Valence Complexes

ν	[Pd-Pd]		<i>trans</i> - [Pd ^{II} - (NH ₃) ₂ - Cl ₂] ^b	<i>trans</i> - [Pd ^{IV} - (NH ₃) ₂ - Cl ₄] ^c	Assignment
	Red ^a	Blue ^a			
241	s	ms			$\delta(\text{NPd}^{\text{IV}}\text{Cl})$
256	w,	s			
295	w,	w, sh		295	$\nu(\text{Pd}^{\text{IV}}\text{-Cl})$
≈ 303	sh	w,	295		$\nu(\text{Pd}^{\text{II}}\text{-Cl})$
		sh(?)			
316	s	s		317	$\nu(\text{Pd}^{\text{IV}}\text{-Cl})$
≈ 482	w,				2×241
	br				
495	w,	w, sh	494		$\nu(\text{Pd}^{\text{II}}\text{-N})$
	sh				
509	m	s			$\nu(\text{Pd}^{\text{IV}}\text{-N})$
556	m,				$241 + 316$
	br				
625	w,				2×316
	br				
760	vw,	w			$509 + 256$
	br				
816	vw	vw			$\rho_{\text{T}}(\text{NH}_3)$
≈ 875	vw,				$241 + 2 \times$
	br				316
1016	m				2×509
1271	vw				$2 \times 509 +$
					256
1518	w				3×509
≈ 1761	vw				$3 \times 509 +$
					256
≈ 2010	vw				4×509

^a "Red" and "blue" refer to the 647.1- and 488.0-nm exciting lines, and the descriptions s, m, w, vw, br, and sh refer to strong, medium, weak, very weak, broad, and shoulder, respectively. ^b Reference 21. ^c Refers to a dilute solution of the complex in water containing an excess of chlorine.

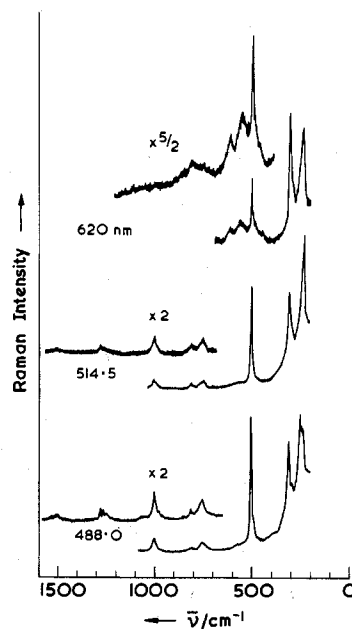


Figure 4. Raman spectrum of the mixed-valence compound $\text{Pd}^{\text{II}}\text{Pd}^{\text{IV}}(\text{NH}_3)_4\text{Cl}_6$ obtained with different exciting wavelengths; spectral resolution ca. 2 cm^{-1} . Two of the wavelengths (488.0 and 514.5 nm) are Ar⁺ ion lines, whereas the third (620.0 nm) is a dye laser line whose frequency corresponds to that quoted by Hush¹⁵ for the $d_{z^2} \rightarrow d_{z^2}$ transition of this compound.

$\text{Pd}^{\text{II}}\text{-Cl}$ stretching fundamental is assigned to the weak shoulder at ca. 305 cm^{-1} by comparison with the [Pd-Pt] spectrum. The band at 295 cm^{-1} , although close in wave-

number to that observed for the free Pd(II) complex, has no close counterpart in the spectrum of [Pd-Pt]; it is, however, at the same wavenumber as that of a band in the spectrum of a dilute solution of the Pd(IV) complex and is therefore thought to arise from the Pd(IV) species. The bands at 241 and 256 cm^{-1} most probably arise from bending fundamentals. Since they exhibit combination tones with stretches associated with Pd(IV), they are assigned to the two components derived from the e_g bending fundamental of the tetravalent species. This bending mode occurs at 229 cm^{-1} in the Pt(IV) complex, but we were unfortunately unable to detect it in the spectrum of the Pd(IV) complex. The components have symmetry $b_{2g} + b_{3g}$; we have no means at present of distinguishing them.

The nature of the Raman spectrum obtained depends markedly on the exciting line used. With a red line (e.g., 647.1 nm, 15450 cm^{-1}), several weak overtone and combination tones involving two fundamentals, at 316 and 241 cm^{-1} , are observed. These are assigned to a Pd^{IV}-Cl stretch and a ClPdN bend, respectively. Surprisingly, the strongest second-order band is the combination of the two, at 556 cm^{-1} , rather than an overtone. This is remarkable in that, while the overtones are clearly totally symmetric, the combination tone cannot be so since the bending mode belongs to either the b_{2g} or the b_{3g} irreducible representation. Nontotally symmetric combination tones have been observed in RR spectra of salts of the square-planar AuBr₄⁻ anion.²²

With shorter wavelength excitation these higher order features disappear and a different RR spectrum develops. (With the yellow 568.2-nm line both types of spectrum can be faintly observed.) The (Pd^{IV}-N) stretching fundamental at 509 cm^{-1} and another bending one at 256 cm^{-1} increase in intensity relative to the other fundamentals, and new higher order features (involving the Pd^{IV}-N stretching fundamental) are seen. These comprise an overtone progression out to 4ν and combination tones based on the 256- cm^{-1} bending mode. Again, the combination tones involving the bend cannot be totally symmetric. The 816- cm^{-1} band occurs for all exciting lines and is tentatively assigned to a rocking mode of ammonia (cf. ref 20).

Discussion

The first question concerns the number of allowed electronic transitions in the visible region. The spectra of [Pd-Pd] clearly imply the presence of two allowed transitions, in the red region at ca. 15000–16000 cm^{-1} and in the blue at ca. 20000 cm^{-1} , resonances which give rise to markedly different RR spectra. With [Pd-Pt], the changes in the RR spectra are more subtle and take place over a smaller range of exciting wavenumbers. We consider that the different excitation profiles exhibited by the metal-chlorine stretching modes in [Pd-Pt] are indicative of interference effects.⁷ It has been demonstrated^{22,23} that forbidden states lying close to the resonant electronic state can cause excitation profiles not to correspond precisely with the electronic spectrum. In the case of [Pd-Pt], such interference is probably with underlying ligand-field states of the constituent complexes. For instance, the Pt(IV) complex has $d \rightarrow d$ transitions at 340 and 435 nm,¹⁸ and the Pd(II) complex, at 350 and 380 nm.¹⁷ With this proviso, the results obtained for [Pd-Pt] are entirely compatible with the presence of a broad, mixed-valence transition (at, or close to, the published value of 18870 cm^{-1}), in that vibrational modes of both constituent ions show overtone progressions. The transfer of an electron between the d_z^2 orbitals of the two metal atoms would be expected to have the greatest effect upon the axial metal(IV)-chlorine bonds. The results for [Pd-Pt] can be contrasted with those for the related mixed-valence compound Wolfram's red salt,²⁴ [Pt^{II}(EtNH₂)₄]-*trans*-[Pt^{IV}(EtNH₂)₄Cl₂]Cl₄·4H₂O, which contains similar chlorine-bridged chains.¹ Irradiation within the mixed-valence $d_z^2 \rightarrow$

d_z^2 transition of this complex yields a RR progression out to 6ν , where ν refers to the Pt^{IV}-Cl axial stretching fundamental at 316 cm^{-1} . The rest of the Raman spectrum is completely swamped by this intense progression. However in [Pd-Pt] all three a_g metal-chlorine stretching fundamentals show striking RR enhancements as well as the appearance of overtones. Assuming a dominant single-state mechanism for RR enhancement in the case of a mixed-valence transition, the involvement of all three fundamentals may indicate that none of them is predominantly "axial" in character and that vibrations of the axial and off-axis metal-chlorine bonds remain strongly coupled in the mixed-valence structure. This coupling appears to extend to the M^{II}-Cl stretching fundamentals to some degree; all three have a_g symmetry and similar frequencies. An alternative explanation for the involvement of all three fundamentals in the RR effect is the possible mixing of d_z^2 and $d_{x^2-y^2}$ orbitals, since they belong to the same representation (a_g) in the D_{2h} symmetry point group. However in this case we might expect the metal-nitrogen stretching fundamentals to show resonance effects as well. Since no higher order bands involving the metal-nitrogen modes appear in the spectrum of [Pd-Pt], we feel that such mixing is probably small.

A further question concerns the nature of the electronic transitions in the visible spectrum of [Pd-Pd]. One would expect that irradiation within analogous electronic transitions should give rise to analogous RR effects for two compounds of the same structure. From the very marked differences between the RR spectra of [Pd-Pd] and [Pd-Pt] we conclude that neither of the two transitions in the visible spectrum of [Pd-Pt] corresponds to the transition at ca. 18870 cm^{-1} in the spectrum of [Pd-Pd]. The results therefore cast serious doubt on the assignment¹⁵ of the 16150- cm^{-1} band in [Pd-Pd] to the mixed-valence $d_z^2 \rightarrow d_z^2$ transition. The RR effects associated with both of the [Pd-Pd] transitions are more consistent with an assignment to ligand (chlorine)-Pd(IV) charge-transfer transitions, in that the vibrations of the divalent component show no resonance effects, and are, indeed, very weak in the Raman spectrum. The $d_z^2 \rightarrow d_z^2$ transition is presumably at lower wavenumbers than 16150 cm^{-1} ; it is probably in the 12000–13000- cm^{-1} region, where Yamada and Tsuchida reported strong absorption polarized parallel to the z axis. In the visible region, especially near 20000 cm^{-1} , the spectra show strong absorptions perpendicular to this axis; mixed-valence transitions (unless they are between different chains, which seems unlikely in view of the much longer metal-metal distances between chains²⁵ and the anisotropic conductivity data¹⁰), should show parallel polarization. We note that the constituent Pd(IV) complex is red.

The possibility of other metal-metal d-d transitions must be considered. Mixed-valence transitions can only occur if there is a finite overlap between the orbitals of the two metal atoms.¹ While a second d-d transfer is formally possible,²⁶ we anticipate that the much the strongest overlap will occur between orbitals with the largest electron density along the z axis, namely the d_z^2 orbitals.

A striking feature of the RR spectra of [Pd-Pd] is the involvement of non totally symmetric bending modes. This may indicate (see, e.g., ref 28 and 29) enhancement by a vibronic coupling process, and the RR results could shed light on the interpretation of the electronic spectrum of the tetravalent complex. Unfortunately the symmetry species to which the bending fundamentals belong are not known precisely, and the electronic spectra of the mixed-valence compounds require more detailed reexamination, preferably at low temperature.

Registry No. Pd^{II}Pd^{IV}(NH₃)₄Cl₆, 51064-32-5; Pd^{II}Pt^{IV}(NH₃)₄Cl₆, 50600-81-2; *trans*-[Pd^{IV}(NH₃)₂Cl₄], 51064-31-4.

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- (25) The Pd-Pd distance along the chains is 5.21 Å and between the chains (nearest) is ca. 7.58 Å. Furthermore, metal atoms of different oxidation states can only be adjacent to one another, where there is disorder in the crystal due to chains slipping past each other. See ref 8.
- (26) The nature of the second d-d transition will depend to a first approximation on the relative order of the d orbitals of the tetravalent atom. It has been established²⁷ that the empty orbital on Pd(II) in complexes such as *trans*-[Pd^{II}(NH₃)₂Cl₂] is d_{x²-y²}. The pronounced z-axis compression suffered by the Pd(IV) complex under discussion should make d_{z²} the highest in energy. The other unfilled d orbital on this d⁶ atom may then be d_{yz} or d_{x²-y²} (where y is the Pd-N direction). In either case symmetry and overlap considerations predict one other mixed-valence transition: d_{yz} → d_{yz} or d_{z²} → d_{x²-y²}, respectively. The latter transition will only take place if there is significant d_{z²}-d_{x²-y²} mixing (both have a_g symmetry in the D_{2h} symmetry point group) and should be at lower energy than d_{z²} → d_{z²}.
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Structures of Simple Organometallic Ions Derived from Nuclear Magnetic Resonance Studies of the Oriented Species

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The ions CH₃Hg⁺, (CH₃)₃Sn⁺, and (CH₃)₃Pb⁺ have been oriented in lyotropic nematic media and their proton nuclear magnetic resonance (NMR) spectra in the homogeneously oriented state have been analyzed in terms of scalar and dipole-dipole nuclear couplings. These couplings include those between protons and the 16.8% abundant mercury-199, 7.67% tin-117, 8.68% tin-119, and 21.11% lead-207. The metal-carbon bond lengths have been calculated from experimental data assuming a tetrahedral carbon and using a reference distance r_{C-H} of 1.096 ± 0.005 Å. Such a procedure reveals a systematic trend of shorter metal-carbon distances determined by the NMR method compared to the best recent electron diffraction results (on the order 3-5%). Relative comparisons between the NMR results for the ions reported here and the dimethyltin ion published previously are much more reliable and the magnitude for the decrease in metal-carbon bond length with charge on the metal atom and its coordination number is obtained. Special care has been used to eliminate error arising from the uncertainty in the scalar coupling between metal atom and protons which may depend on the state of solvation of these organometallic ions.

Introduction

The orientation of complex ions in nematic lyomesophases was recently achieved by several chemical techniques.^{1,6} The nuclear magnetic resonance (NMR) spectra of these oriented ions are suitable for the study of their relative nuclear positions in fluid media by methods already established for small oriented molecules.^{7,8} The present study is a report on the structures of the organometallic ions trimethyltin, trimethyllead, and methylmercury. Previous reports from these laboratories have been made with respect to the structures of dimethyltin⁵ and dimethylthallium³ ions. This present work completes a series of simple organometallic ions in which metal-carbon distances can be compared with considerable precision. The scattering of x rays by small carbon and hydrogen atoms in close proximity to heavy-metal atoms is a notoriously difficult problem and leads to an absence of data for hydrogen positions and data of low precision for carbon positions.⁹ The diffraction of electrons in the gas phase is appropriate for the study of related molecular species but not ions. Nevertheless, comparison with related molecular species is an important aspect of this investigation. Unfortunately some of these related molecules were studied quite early in

the history of the electron diffraction technique before the advent of high-speed computers. The original experimental data did not have the quality that later scientific technology brought to almost all modern experimental methods. References to these related studies will be made during comparative discussion.

Experimental Section

Sodium decyl sulfate from Mann Research Laboratories, Inc., was recrystallized from ethyl alcohol several times and dried under vacuum.

Methylmercury nitrate was prepared from methylmercury chloride (Alfa Inorganics) and silver nitrate (M & B Ltd.). A suspension of 2.5 g of methylmercury chloride in water was added slowly, while stirring, to a well-agitated solution of silver nitrate (1.698 g) in deionized water. Light was excluded during the reaction as much as possible. After filtering from the silver chloride formed, the solution of methylmercury nitrate was further treated with 0.2 g of methylmercury chloride in suspension to ensure complete reaction of the silver nitrate. Final filtration was followed by evaporation to dryness in a vacuum evaporator. The crystals of methylmercury nitrate were recrystallized twice from carbon tetrachloride to give a final yield of 1.9 g (68.5%). The proton magnetic resonance spectrum at high gains showed no observable impurities in aqueous solution.

Trimethyltin Nitrate. The chloride salt (Alfa Inorganics) was made up to 2.0 g/30 ml of deionized water. Dowex-1 resin (15 ml wet) was prepared in a column in the basic form. The solution of tri-

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