to account for the emission behavior (see Figure 6). In this scheme the rate of interconversion between the two ^{3}MLCT excited states is more rapid than the rates of radiative or nonradiative deactivation from the individual ^{3}MLCT levels. The observed temperature dependence of the emission spectra of $(OC)_5W(pyz)W(CO)_5$ shown in Figure 3 has been fitted to the modified Boltzmann expression (eq 1).[7d,h,15] Here, I_u and I_l are the emission

$$\frac{I_u}{I_l} = \frac{g_u k_u}{g_l k_l} \exp\left(\frac{-\Delta E}{k_B T}\right) \quad (1)$$

intensities of the upper (u) and lower (l) MLCT levels measured at 16.80 × 10^3 and 13.75 × 10^3 cm^{-1}, respectively, k_u and k_l denote the radiative rate constants from these excited states, g is a degeneracy factor, ΔE represents the energy gap between the emitting levels, k_B is the Boltzmann constant, and T is temperature.[16] A least-squares analysis of the data in Figure 3 yields ΔE = 370 (±85) cm^{-1} and $g_u k_u / g_l k_l$ = 6.2. Although these results are the first of their kind obtained from a metal carbonyl system, they are in good agreement with those for other classical coordination complexes that are thermally equilibrated in fluid solution.[7a,d,h] Importantly, the ΔE value, being within a recognized equilibrium limit of ~1000 cm^{-1},[15a] is sufficiently small to rationalize the rapid thermal back-population.

When the solution temperature is further cooled to 80 K the observed emission spectrum takes on a very different distribution (see Figure 3). Two factors apparently give rise to this spectral change. The first one is that the MLCT transitions on cooling through the glass transition point display significant "luminescence rigidochromism", as alluded to above, and these bands both blue shift substantially. The second effect is that at 80 K the upper energy MLCT(y) emission gains considerable intensity from the now radiating ^{3}LF state, and the latter feature consequently dominates the high-energy side of the spectrum. Emission lifetimes and excitation spectra obtained from the complexes at 80 K also support this MLCT/LF interpretation (vide infra).

Not surprisingly, the dynamics of excited-state interconversion are much altered at 80 K. It appears that the thermal equilibrium between the ^{3}MLCT(y) and ^{3}MLCT(z) states is now lost and, indeed, all three MLCT/LF levels are nonequilibrated. This conclusion is supported by the lifetimes obtained at 80 K, which are different for each ^{3}MLCT emission band and further indicate the participation of the ^{3}LF levels (see Table II). The striking excitation wavelength dependence on the emission spectral distribution (see Figure 4) also confirms the lack of a thermal equilibrium in the frozen solutions. Excitation spectra obtained from complexes at 80 K (see Table III) indicate maxima corresponding to the MLCT and LF absorptions and are consistent with the nonequilibrated model of excited-state decay. This is illustrated by the excitation spectra of $(OC)_5W(pyz)W(CO)_5$, which are strongly dependent on the choice of the monitoring emission wavelength (see Figure 5). When the emission is recorded at 670 nm two excitation features are observed; the 494-nm band is attributed to the ^{3}MLCT manifold, and the 397-nm band indicates that the ^{3}LF state effectively nonradiatively populates the ^{3}MLCT emitting levels. When the emission is observed at 560 nm, the ^{3}LF state clearly dominates the excitation spectrum as it undergoes direct radiative decay to the ground state.

Conclusions

The temperature dependence and excitation wavelength dependence of the emission from $(OC)_5W-L-W(CO)_5$ (L = pyz, bpy, bpe) complexes in fluid solution may be understood in terms of two thermally equilibrated ^{3}MLCT excited states separated by approximately 370 cm^{-1}. When the solution is cooled through the glass transition point the MLCT levels become non-equilibrated and their absorption and emission bands undergo substantial energy shifts. A third ^{3}LF emission component is also observable from the glass solutions at low temperature.

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Registry No. $(OC)_5W(pyz)W(CO)_5$, 70738-71-5; $(OC)_5W(bpy)W(CO)_5$, 81178-10-1; $(OC)_5W(bpe)W(CO)_5$, 81178-12-3; $(OC)_5W(bpa)W(CO)_5$, 81178-11-2; $(OC)_5W(pyz)$, 65761-19-5; $(OC)_5W(bpy)$, 81178-09-8; $(OC)_5W(bpe)$, 113110-66-0; $(OC)_5W(bpa)$, 113110-67-1.

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Knudsen Effusion Mass Spectrometric Investigation of Palladium–Germanium Clusters

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The equilibria involving the gaseous species Pd, PdGe, $PdGe_2$, and $PdGe_3$ above the condensed system Pd–Ge have been investigated by means of the Knudsen effusion mass spectrometric technique at temperatures between 1694 and 1946 K. The equilibrium constants, K_p, for the various reactions were evaluated, and the respective reaction enthalpies were determined. By combination of these reaction enthalpies with the appropriate ancillary data, the atomization energies ($\Delta H_a{}^\circ{}_0$) and standard heats of formation ($\Delta H_f{}^\circ{}_{298}$), in kJ mol^{-1}, were obtained for $PdGe_2$(g) and $PdGe_3$(g), respectively, and are as follows: 600 ± 25, 516 ± 25; 989 ± 40, 503 ± 40.

Introduction

Investigations into the physical and chemical properties of small atomic and molecular aggregates, particularly metal clusters, are of considerable current interest.[1-3] Most experimental bond energies of diatomic metals and small metal clusters have been measured by Knudsen effusion mass spectrometry and have been summarized in several reviews.[4-6]

The present investigation has been performed as part of our research program aimed at the determination of thermodynamic

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Table I. Measured Total Ion Intensities for the Pertinent Ions of the Pd/Ge System

	ion intensities,[a] A			
temp, K	Pd^+	$PdGe^+$	$PdGe_2^+$	$PdGe_3^+$
1778	6.769(−10)	2.064(−11)	5.909(−12)	
1810	1.079(−9)	3.294(−12)	8.145(−12)	
1748	4.621(−10)	1.040(−11)	3.869(−12)	
1783	8.573(−10)	2.663(−11)	6.855(−12)	1.449(−12)
1841	1.986(−9)	5.358(−11)	1.090(−11)	2.023(−12)
1826	1.672(−9)	3.944(−11)	6.317(−12)	1.348(−12)
1796	1.061(−9)	2.216(−11)	4.738(−12)	
1694	2.005(−10)	4.001(−12)	8.773(−13)	
1783	8.452(−10)	1.312(−11)	4.387(−12)	2.028(−12)
1822	1.500(−9)	3.338(−11)	6.141(−12)	2.246(−12)
1855	2.887(−9)	5.699(−11)	9.124(−12)	2.896(−12)
1903	6.147(−9)	1.720(−10)	2.018(−11)	4.045(−12)
1946	1.266(−8)	1.905(−10)	2.770(−11)	4.315(−12)

[a] Numbers in parentheses represent powers of 10; thus, for the first entry, 6.769(−10) = 6.769×10^{-10}.

properties and the nature of bonding of small transition-metal-containing aggregates.[5-7] Palladium is an important element for petroleum reforming catalysts, and the knowledge of the interaction between a Pd atom and another atom has basic importance. The previous all-electron ab initio calculations of palladium-containing molecules by Shim and collaborators have shown an intriguing bonding behavior of this metal.[8-10] The bond in the palladium dimer is formed by interaction of the palladium atoms in their $(4d)^9(5s)$ configuration and is almost entirely due to the $5s\sigma_g$ molecular orbital.[8] The 4d orbitals are essentially localized, but exchange caused by the various occupations of the holes in the d shell gives rise to a narrow "band" of 30 low-lying electronic states. In PdC the bond results from a C atom interacting with a Pd atom in the $(4d)^{10}$ configuration. As the two atoms approach, charge flows into the empty $2p\sigma$ orbital of C, and a small fraction is back-donated from the $2p\pi$ and the 2s orbitals into the empty 5s and 5p orbitals of the palladium atom, leading to a polar σ-bonded molecule with a sizable dipole moment.[9,10] To further expand and deepen our understanding of the bonding behavior of palladium with group IV elements, we have studied the molecules observed in the equilibrium vapor above the palladium–germanium condensed system. The thermodynamic data and the results of the all-electron ab initio calculations for the molecule PdGe have previously been published.[11] The thermodynamic results for the molecules $PdGe_2$ and $PdGe_3$ are reported in this paper and are discussed together with the results for other similar molecules.

Experimental Section

The mass spectrometer used in the present investigation is a single-focusing instrument coupled with a Knudsen effusion cell. The technique and the experimental procedure have been described elsewhere.[5]

The Knudsen cell was constructed from a $^1/_2$-in. solid tantalum rod with a 0.040-in.-diameter orifice. The sample charge of 190 mg of palladium powder, 200 mg of germanium powder and 17 mg of silver wire (for calibration purposes), was placed in a graphite crucible. The sample and crucible were then placed within the tantalum cell. The molecular beam effusing from the Knudsen cell into the ionizing region was ionized with 20-V electrons. The electron emission current was maintained at 0.4 mA, throughout the experiments.

The ionic species observed were identified by their mass-to-charge ratio (m/e), shutter effect, isotopic intensity distribution, and ionization efficiency curves (where possible). At all temperatures, the ion currents of $PdGe_2^+$ and $PdGe_3^+$ were too small for the reliable appearance of potential measurements of these species. The measured total multiplier anode currents for the pertinent species are listed in Table I.

The Gibbs energy functions and heat content functions needed in the evaluation of the reaction enthalpies were taken from the literature for Pd(g)[12] and PdGe(g).[11]

For the molecule $PdGe_2$, for which spectroscopic data are not available, we have considered different structures and assumptions in calculating the vibrational frequencies. The symmetric structure Ge–Pd–Ge as well as the asymmetric structure Pd–Ge–Ge were considered, each with a bent geometry. A bond angle of 110° was assumed for both configurations. In our previous investigation of the gold-germanium triatomic molecules,[13] more numerous data had been available and a comparison of the corresponding second-law and third-law reaction enthalpies indicated the bent structures to be the preferred ones. The Ge–Ge bond distance was assumed to be the same as that calculated for the germanium dimer, $r_e = 2.42$ Å ($k = 1.75$ mdyn/Å).[14] The Pd–Ge bond distance was estimated as $r_e = 2.50$ Å ($k = 2.03$ mdyn/Å), in analogy to the experimental value for AuGe.[15] The bending force constant was taken as one-tenth of the average of the stretching force constants involved, $k/l_1l_2 = 0.189$ mdyn/Å. A stretching–stretching interaction of 0.065 mdyn/Å was employed for both structures, based on the following considerations: C_3 has normal stretching frequencies of 1230 and 2040 cm^{-1} for the Σ_g^+ and Σ_u^+ species, respectively.[16,17] The values correspond to a stretching force constant of 10.25 mdyn/Å and an interaction constant of 0.45 mdyn/Å. Assuming that the stretching force constants are relatively insensitive to the electronic configuration, with a 1.48 mdyn/Å stretching assumed for Ge–Ge bonds in Ge_3, this gives us an stretch–stretch interaction constant of 0.065 mdyn/Å within Ge_3. This same assumed stretch–stretch interaction was used for the polyatomic palladium–germanium molecules.

Two structures were assumed in evaluating the atomization energy for the gaseous molecule $PdGe_3$. These are the linear configurations Pd–Ge–Ge–Ge and Ge–Pd–Ge–Ge. All bond distances and force constants were taken as the same as for $PdGe_2$ above. We refrained to consider additional possible geometries such as bent chains or trigonal pyramids, because the limited number of experimental data available for the $PdGe_3$ molecule did not permit a second- and third-law comparison of the reaction enthalpies that could have given an indication as to which of the possible geometries would be the preferred one.

The vibrational frequencies for the molecules $PdGe_2(g)$ and $PdGe_3(g)$ were calculated by using a modified Schachtschneider program,[18] employing the Wilson FG matrix method.[19] These calculated values were as follows:

	vibrational frequencies, cm^{-1}				
Pd–Ge–Ge, bent	321	50	244		
Ge–Pd–Ge, bent	310	52	253		
$Pd-Ge_3$, linear	355	271	137	79 (2)	340
$Ge-Pd-Ge_2$, linear	368	284	161	80 (2)	370

In the calculation of the thermal functions for $PdGe_2$ and $PdGe_3$, the electronic contribution was taken to be the same as the experimental values of AuGe(g).[15] The computed Gibbs energy functions and heat content functions for the molecules $PdGe_2$ and $PdGe_3$ are listed in Table II, together with those of PdGe.[11]

The measured ion intensities (Table I) were related to the corresponding partial pressures P_i according to the relation $P_i = k_i I_i T$. The calibration constants k_i have been determined by using the known $Ag_2(g) = 2Ag(g)$ equilibrium.[20] The values, in atm A^{-1} K^{-1}, are as follows: Ag, $1.55 \times 10^{-2} \pm 0.15$; Pd, 1.36×10^{-2}; PdGe, 0.86×10^{-2}; $PdGe_2$, 0.58×10^{-2}; $PdGe_3$, 0.43×10^{-2}. Here we wish to draw attention to the inadvertant omission of the factor 10^{-2} of the corresponding k_i values of our previous publication.[11]

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Table II. Gibbs Energy Functions (GEF = $-(G^\circ_T - H^\circ_0)/T$) in J K^{-1} mol^{-1} and Heat Content Functions (HCF = $H^\circ_T - H^\circ_0$) in kJ mol^{-1} for the Molecules PdGe, $PdGe_2$, and $PdGe_3$

		T = 298	T = 1400	T = 1600	T = 1800	T = 2000	T = 2200
PdGe	GEF	237.8	293.1	298.2	302.6	306.7	310.3
	HCF	10.11	52.58	60.56	68.57	76.58	84.60
$PdGe_2$, bent	GEF	290.6	373.7	381.4	388.3	394.5	400.1
	HCF	14.45	81.10	93.28	105.4	117.4	129.4
GePdGe, bent	GEF	284.2	367.3	375.1	381.9	388.1	393.7
	HCF	14.44	81.10	93.27	105.4	117.4	129.4
$PdGe_3$, linear	GEF	312.9	435.6	447.0	457.2	466.3	474.6
	HCF	21.21	119.7	137.6	155.6	173.4	191.2
$GePdGe_2$, linear	GEF	309.1	431.1	442.5	452.6	461.7	470.0
	HCF	20.97	119.4	137.3	155.2	173.1	190.9

Table III. Summary of the Effect of $PdGe_2$ Structure on the Reaction Enthalpies and Entropies of the Gaseous Reaction $PdGe_2$ + Pd = 2PdGe

	ΔH°_0, kJ mol^{-1}		ΔS°_{298}, J K^{-1} mol^{-1}	
structure	2nd law	3rd law	2nd law	3rd law
Pd–Ge–Ge, bent	99.9 ± 43.4	94.5 ± 5.5	40.4 ± 24.0	37.5
Ge–Pd–Ge, bent	99.9 ± 43.4	106.1 ± 5.7	40.5 ± 24.0	43.9

Table IV. Third-Law Enthalpy for the Gaseous Reaction $PdGe_2$ + Pd = 2PdGe, Assuming a Bent Pd–Ge–Ge Structure for $PdGe_2$

T, K	log K_p	$-\Delta[(G^\circ_T - H^\circ_0)/T]$, J K^{-1} mol^{-1}	ΔH°_0, kJ mol^{-1}.
1778	−1.001	32.36	91.6
1810	−0.936	33.12	92.4
1748	−1.246	31.61	97.0
1783	−0.946	32.48	90.2
1841	−0.905	33.81	94.2
1826	−0.860	33.49	91.2
1796	−1.038	32.80	94.6
1694	−1.069	30.22	85.7
1783	−1.361	32.48	104.4
1822	−0.945	33.40	93.8
1855	−0.937	34.10	96.5
1903	−0.650	34.99	90.3
1946	−1.013	35.60	107.0
			av 94.5 ± 5.5

Table V. Third-Law Enthalpy for the Gaseous Reaction $PdGe_3$ + 2Pd = 3PdGe, Assuming a Linear Structure for Pd–Ge–Ge–Ge

T, K	log K_p	$-\Delta[(G^\circ_T - H^\circ_0)/T]$, J K^{-1} mol^{-1}	ΔH°_0, kJ mol^{-1}
1783	−1.848	81.79	209
1841	−1.812	84.22	219
1826	−1.885	83.63	219
1783	−2.904	81.79	245
1822	−2.230	83.46	230
1855	−2.212	84.75	236
1903	−1.575	86.35	222
1946	−2.097	87.42	248
			av 228 ± 13

Results

A. $PdGe_2$. The enthalpy of the reaction

$$PdGe_2(g) + Pd(g) = 2PdGe(g) \qquad (1)$$

was evaluated by both the second- and the third-law methods using the standard relationships $\ln K_p = -\Delta H^\circ_T/RT + \Delta S_T/R$ and $\Delta H^\circ_0 = -T\{R \ln K_p + \Delta[(G^\circ_T - H^\circ_0)/T]\}$, respectively.

The second-law enthalpy change, ΔH°_T, was determined as 90.2 ± 43.2 (T = 1811 K) from 13 data sets in the temperature range 1694–1946 K. The corresponding enthalpy values, referenced to 0 K, are summarized in Table III for the two assumed geometries. Also listed are the ΔS_{298} values calculated from the intercept of the second-law plot.

The large error in the second-law enthalpy value is attributed to the limited number of data sets, to the errors in the measured ion intensities of $PdGe_2$, which were about 20% due to the low signals, and to the errors in the estimated molecular constants used for calculating the thermal functions. The individual third-law reaction enthalpies, assuming the bent Pd–Ge–Ge structure, are shown in Table IV.

A selected reaction enthalpy was calculated, giving twice the statistical weight to the more reliable third-law evaluation. The resulting reaction enthalpy change is $\Delta H^\circ_0 = 96.3 \pm 16$ (ΔH°_{298} = 95.9) kJ mol^{-1}. This enthalpy change, when combined with the dissociation energy of PdGe(g), $D^\circ_0 = 252.0 \pm 10.5$ kJ mol^{-1},[11] yields an atomization energy $\Delta H_a{}^\circ{}_0$ ($PdGe_2$) = 600 ± 25 ($\Delta H_a{}^\circ{}_{298}$ = 610) kJ mol^{-1}, assuming an asymmetric bent $PdGe_2$ structure.

B. $PdGe_3$. The third-law enthalpy change, ΔH°_0, for the reaction

$$PdGe_3(g) + 2Pd(g) = 3PdGe(g) \qquad (2)$$

has been evaluated for the two assumed structures of $PdGe_3$(g). The resulting values in kJ mol^{-1} are as follows:

	ΔH°_0	ΔH°_{298}
$PdGe_3$, linear	228 ± 13	225 ± 13
$GePdGe_2$, linear	237 ± 13	234 ± 13

No second-law values could be obtained because of the very limited number of data and because of the quite large uncertainties in the measured low ion currents of $PdGe_3{}^+$. The species $PdGe_3$(g) was measured very close to the detection limits of the instrument. The major peaks were observed at m/e = 324–326. The relative abundance of these three peaks agreed within the experimental errors of those calculated for $PdGe_3$(g). The third-law evaluation of reaction 2 for the assumed geometry, Pd–Ge–Ge–Ge, is shown in Table V as an illustration of the measured uncertainties. The atomization energy for this molecule, $\Delta H_a{}^\circ{}_0$, was obtained as 989 ± 40 ($\Delta H_a{}^\circ{}_{298}$ = 1003) kJ mol^{-1} by using the enthalpy of reaction 2 and the dissociation energy of PdGe(g).[11] Here we have used $\Delta H^\circ_0 = 233 \pm 40$ kJ mol^{-1}, the average value for the two assumed geometries, as the selected enthalpy of reaction 2.

The estimated uncertainty in the thermal functions and temperature measurements for this investigation have been included in the error terms given for all the selected enthalpies.

The heats of formation, $\Delta H_f{}^\circ{}_{298}$, for the gaseous molecules $PdGe_2$ and $PdGe_3$ were derived as 516 ± 25 and 503 ± 40 kJ mol^{-1}, respectively. The calculations were made by employing the heat of vaporization of Pd(g) as $\Delta H_v{}^\circ{}_{298}$ = 376.4 ± 2.1 kJ mol^{-1} and that of Ge(g) as $\Delta H_v{}^\circ{}_{298}$ = 374.5 ± 2.1 kJ mol^{-1}, from Hultgren et al.[12]

Discussion

In the present investigation the atomization energies, $\Delta H_a{}^\circ{}_0$ of the gaseous molecules $PdGe_2$ and $PdGe_3$ have been determined as 600 ± 25 and 989 ± 40 kJ mol^{-1}, respectively. The comparatively large errors are mainly due to two sources. The low signal levels measured for $PdGe_2{}^+$ and $PdGe_3{}^+$ cause errors of the magnitude reflected in the respective standard deviations of the third-law reaction enthalpies. These errors reflect the quality of the data. The other major contribution to the estimated overall error is due to uncertainties in the thermal functions that had to be calculated on the basis of assumed geometries and molecular constants. These errors will become smaller as spectroscopic measurements of the respective molecular parameters become available, permitting the calculation of more accurate thermal functions. For the molecule PdGe, a dissociation energy of $D^\circ_0 = 252.0 \pm 10.5$ kJ mol^{-1} has previously been measured by the authors.[11] This latter value compares to the dissociation energy of 256.6 ± 12 kJ mol^{-1} reported by Peeters et al.[21] Miedema and Gingerich[22] have calculated a dissociation energy for PdGe of 308 kJ mol^{-1}, using an empirical atomic cell model. This calculated value is higher than the experimental dissociation energy, but is in reasonable agreement.

The following bond dissociation energies, in kJ mol^{-1}, between the Pd atom and the various germanium clusters, have been obtained from the experimental atomization energies:

molecule	$\Delta H_{\mathrm{a}}{}^{\circ}{}_{0}(\mathrm{MGe}_n) - \Delta H_{\mathrm{a}}{}^{\circ}{}_{0}(\mathrm{Ge}_n)$
PdGe	252
$PdGe_2$	340
$PdGe_3$	366

In arriving at these values the ancillary $\Delta H_{\mathrm{a}}{}^{\circ}{}_{0}(\mathrm{Ge}_2) = 260$ kJ mol^{-1} [14] and $\Delta H_{\mathrm{a}}{}^{\circ}{}_{0}(\mathrm{Ge}_3) = 623$ kJ mol^{-1} [13] were used.

In a previous investigation of gold–germanium clusters[13] the corresponding bond dissociation energies Au–Ge, Au–Ge_2, and Au–Ge_3 (270, 260, and 274 kJ mol^{-1}, respectively) were found to be nearly the same, which may be attributed to single-bond formation between the gold atom and germanium. As can be seen above, in the case of the palladium atom, these bond dissociation energies increase, suggesting the presence of multiple bonds between palladium and germanium.

The theoretical results for PdGe[10,11] are used to support this conclusion. The bond in PdGe is formed by interaction between a Pd atom in its $^1S(4d)^{10}$ ground term and a Ge atom in the $(4s)^2(4p\sigma)^1(4p\pi)^1$ configuration. As the atoms approach each other charge is donated from the $4d\pi$ and $4d\sigma$ orbitals of palladium into the $p\sigma$ and $p\pi$ orbitals of germanium. Back-donation leads to population in particular of the Pd 5s orbital. This behavior is similar to that calculated for PdC,[9,10] but unlike the case of PdC, the respective net charge transfer in PdGe from Pd to Ge is very small. While there are no theoretical calculations available for the $PdGe_2$ and $PdGe_3$ molecules and for germanium–gold molecules, the complex bonding behavior for PdGe shows significant d-electron participation in the formation of the bond. For gold–germanium molecules one can expect that the 5s electron of the gold atom contributes predominantly to the bond formation, while the d electrons remain localized. The observed significant increase in the bond energy per bond in $PdGe_2$ and $PdGe_3$ above that in PdGe may therefore be attributed to an increasing participation of the 4d electrons in these polyatomic molecules.

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Infrared, Raman, Resonance Raman, and Excitation Profile Studies of $Rh_2(O_2CCH_3)_4L_2$ ($L = AsPh_3, SbPh_3$)†

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The infrared, Raman, and resonance Raman spectra of the complexes $Rh_2(O_2CCH_3)_4L_2$ ($L = AsPh_3, SbPh_3$) have been studied and compared in detail with those of the analogous complex with $L = PPh_3$. The resonance Raman spectra are particularly rich, many overtone progressions being detected in each case at resonance with the axially polarized $\sigma \rightarrow \sigma^*$ transition at ca. 360 nm. The principal progression-forming mode is invariably ν_1, ν(Rh–Rh), implying a substantial geometric change along this coordinate on excitation to the σ^* state. The excitation profiles of the enhanced bands of all three complexes reach a maximum within the contour of the $\sigma \rightarrow \sigma^*$ band, which implies that there are also minor geometric changes to other coordinates on excitation to the σ^* state.

Introduction

In a previous publication on the series of complexes $Rh_2(O_2CR)_4(PPh_3)_2$, where R = H, CH_3, C_2H_5, or C_3H_7, it was shown that changes in the carboxylate alkyl group cause only a small, ca. ±7 cm^{-1}, variation in ν_1, ν(Rh–Rh), whereas the totally symmetric ν(Rh–O) vibration, ν_2, is strongly dependent on the mass of the R group.[1] Consequently, the important distinction between bands arising from the key skeletal fundamentals, ν(M–M) and ν(M–O), of dimeric tetracarboxylates can be made on the basis of sensitivity of ν(M–O) to the carboxylate alkyl group. In the present study of the complexes $Rh_2(O_2CCH_3)_4L_2$ ($L = AsPh_3, SbPh_3$),[2] the axial ligands only are substituted for PPh_3, in consequence of which ν_1 would be expected to change but not, to a first approximation (via the G matrix), ν_2. Thus a complementary method for distinguishing between ν_1 and ν_2 is developed. The reason for assuming that it might be possible to make the distinction between these two fundamentals on this basis is the realization that there is considerable sensitivity of ν(Mo–Mo) to the masses and nature of the axial ligands in the dimolybdenum series $Mo_2(O_2CCF_3)_4$ (398–395 cm^{-1})[3,4] and $Mo_2(O_2CCF_3)_4L_2$, where $L = CH_3OH$ (386 cm^{-1}),[3] pyridine (368–367 cm^{-1}),[4,5] PPh_3 (377[3] or 367[6] cm^{-1}), $AsPh_3$ (375 cm^{-1}),[7] and $AsEt_3$ (368 cm^{-1}).[7] Earlier X-ray studies of the three dirhodium tetraacetate complexes[2] and Raman studies of $Rh_2(O_2CCH_3)_4(PPh_3)_2$[8] are now amplified by detailed studies of the Raman, resonance Raman, and infrared spectroscopy of the $AsPh_3$ and $SbPh_3$ complexes and,

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† Tetrakis(μ-acetato)bis[(triphenylarsine)rhodium(II)](*Rh–Rh*); tetrakis(μ-acetato)bis[(triphenylstibine)rhodium(II)](*Rh–Rh*).

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