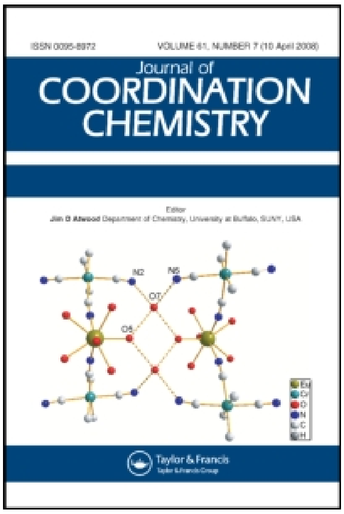

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ELECTRON SPIN RESONANCE OR Pd(I). III: The Nature of the Metal-ligand Bonds in Square Planar Complexes of Palladium(I)

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Electron Spin Resonance of Pd(I). III*
The Nature of the Metal-ligand Bonds in Square Planar Complexes of Palladium(I)

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ESR spectra for a variety of palladium(I) complexes produced in the powders and the frozen solutions of palladium(II) complexes by γ-ray irradiation have been interpreted in terms of the nature of the metal-ligand bonds. It has been found that the covalency for the palladium-ligand σ-bond increases in the order of Pd—O, Pd—Cl < Pd—N < Pd—S, Pd—C, and that the nature of the metal-ligand bond in palladium(I) complexes is very similar to that in copper(II) complexes. The ratio of the magnitude of the ligand field splitting for palladium(I) complex to that for the copper(II) complex with the same ligand has been estimated from the comparison of their g values.

INTRODUCTION

Although palladium(II) ion is known to form square planar complexes with a variety of ligands, the nature of palladium-ligand bonds has hardly been investigated except for some of the complexes with halogen ions for which nuclear quadrupole resonance spectra have been measured.[1, 2, 3] Although electron spin resonance (ESR) is one of the most useful techniques to investigate the covalent bonding in a variety of complexes, the complexes of palladium(II), which are diamagnetic with a $4d^8$ electronic configuration, cannot be the subject of ESR. In the preceding articles,[4, 5] it has been shown by means of ESR that upon irradiation by γ-rays palladium(II) ions in bis(acetylacetonato) palladium(II) (Pd(acac)$_2$) and chloropalladates are reduced to form the complexes of palladium(I) without any change in the symmetry of the ligand field. Shida and Hamill[6] have shown that γ-irradiation of organic rigid matrices at 77° K is a clean, effective method to obtain molecular ions of organic solutes. After their systematic investigations it has become possible to obtain either cations or anions of organic solutes by selecting suitable matrices. For example, alcohols, amines, and ethers are known to provide suitable matrices for obtaining solute anions. This method seems to be applicable to reduce inorganic solutes. In the present paper, the ESR spectra for a variety of palladium(I) complexes produced in the powders and the frozen solutions of palladium(II) complexes by γ-ray irradiation are reported, and the ESR parameters are interpreted in terms of the nature of the palladium-ligand bonds.

EXPERIMENTAL SECTION

Carboxylates of palladium(II) were prepared and recrystallized according to the method described in the literature.[7, 8] Other complexes of palladium(II) were prepared and recrystallized by standard methods. Ethanol (99.5%) and a mixture of ethyleneglycol(EG) and water (2 : 1 in volume) were used as glassy matrices. Powders of palladium(II) complexes or degassed solutions of palladium(II) complexes and an excess of ligand compounds were given at 77° K a γ-ray dosage of 1×10^6 R from a Co-60 source with the dose rate of 5×10^4 R/hr. The ESR spectra were recorded at 77° K on a JEOL 3BS X-band spectrometer by using 100 kHz modulation.

RESULTS

Some of typical ESR spectra for γ-irradiated powders and frozen solutions of palladium(II) complexes are shown in Figures 1–5. In all cases the spectra characteristic of the complexes with $S = 1/2$ with tetragonal symmetry of ligand field are observed at lower field than that corresponding

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* I and II; cf. Ref. 4 and 5, respectively.

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TABLE I

ESR parameters for palladium(I) complexes

Complex[a]	Host lattice	Solute (mM/1)	$g_{//}$[b]	$g_{\perp}$[b]	$\lvert A_{//}(Pd)\rvert$[c] ($\times 10^{-3}$ cm^{-1})	$\lvert A_{\perp}(Pd)\rvert$[c] ($\times 10^{-3}$ cm^{-1})
$[Pd(CN)_4]^{3-}$	$K_2[Pd(CN)_4]3H_2O$		2.177	2.042		
$[Pd(SCN)_4]^{3-}$	$K_2[Pd(SCN)_4]$		2.176	2.042		
	EtOH	$K_2[Pd(SCN)_4](5) + KSCN(50)$	2.190	2.053		2.4
	EG–H_2O	$K_2[Pd(SCN)_4](50) + KSCN(500)$	2.202	2.050	3.9	2.4
$[Pd(tu)_4]^{+}$	$[Pd(tu)_4]Cl_2$		2.232	2.043		2.4
	EG–H_2O	$[Pd(tu)_4]Cl_2(50) + tu(500)$	2.209	2.042	4.3	2.6
$[Pd(NO_2)_4]^{3-}$	EG–H_2O	$K_2[Pd(NO_2)_4](50) + KNO_2(500)$	2.314	2.079		[d]
$[Pd(en)_2]^{+}$	EG–H_2O	$K_2PdCl_4(50) + en(100)$	2.301	2.060		
$[Pd(NH_3)_4]^{+}$	$[Pd(NH_3)_4][PdCl_4]$		2.306			
	EG–H_2O	$K_2PdCl_4(50) + NH_3(500)$	2.344	2.065		[e]
$[Pd(EtNH_2)_4]^{+}$	EtOH	$Li_2PdCl_4(50) + EtNH_2(500)$	2.351	2.068		[e]
$[Pd(n\text{-}BuNH_2)_4]^{+}$	EtOH	$Li_2PdCl_4(50) + n - BuNH_2(500)$	2.345	2.067		[e]
	EG–H_2O	$K_2PdCl_4(50) + n - BuNH_2(500)$	2.337	2.065		[e]
$[PdCl_2(PhCN)_2]^{-}$	$PdCl_2(PhCN)_2$		2.405	2.065		
$[Pd(oxine)_2]^{-}$	$Pd(oxine)_2$		2.416	2.082		
$[Pd(2\text{-}Me\text{-}oxine)_2]^{-}$	$Pd(2\text{-}Me\text{-}oxine)_2$		2.560	2.074		
			2.733[f]	2.072[f]		
$[Pd(acac)_2]^{-}$	$Pd(acac)_2$[g]		2.519	2.094	4.6	3.8
	EtOH	$Pd(acac)_2(2)$	2.488	2.093		3.6
$[Pd(bzac)_2]^{-}$	EtOH	$Pd(bzac)_2(2)$	2.497	2.093		3.6
$[Pd(C_2O_4)_2]^{3-}$	$K_2[Pd(C_2O_4)_2]3H_2O$		2.540	2.107	4.8	3.6
	EG–H_2O	$K_2[Pd(C_2O_4)_2](5) + K_2C_2O_4(50)$	2.550	2.107		3.6
Pd(I) acetate	$[Pd(OAc)_2]_3H_2O$		2.580	2.099		3.3
	$CaPd(OAc)_4$, 4HOAc		2.555	2.098	5.0	3.6
	$CdPd(OAc)_4$, H_2O, HOAc		2.514	2.086	4.9	3.8
	$PbPd(OAc)_4$, 2HOAc		2.457	2.093		4.0
Pd(I) propionate	$[Pd(OCOC_2H_5)_2]_n$		2.576	2.100		3.3
Pd(I) benzoate	$[Pd(OCOC_6H_5)_2]_n$		2.584	2.106		3.4
$[PdCl_4]^{3-}$	K_2PdCl_4[h]		2.515	2.083		[i]
	$(NH_4)_2PdCl_4$[h]		2.527	2.086		[i]
	$[Pd(NH_3)_4][PdCl_4]$		2.565	2.091[j]		
	EG–H_2O	$K_2PdCl_4(50) + KCl(1000)$	2.541	2.073		[i]

[a] Abbreviations: tu, thiourea; en, ethylenediamine; oxine, 8-hydroxyquinolinate; 2-Me-oxine, 2-methyl-8-hydroxyquinolinate; acac, acetylacetonate; bzac, benzoylacetonate; OAc, acetate.

[b] Accurate to ± 0.005.

[c] Accurate to $\pm 0.1 \times 10^{-3}$ cm^{-1}.

[d] $|A_{\perp}(N)| = 2.0 \pm 0.1 \times 10^{-3}$ cm^{-1}.

[e] $|A_{\perp}(N)| = 1.2 \pm 0.1 \times 10^{-3}$ cm^{-1}.

[f] Measured at 77° K after heating to room temperature.

[g] Ref. 4.

[h] Ref. 5.

[i] $|A_{\perp}(Cl)| = 1.5 \pm 0.1 \times 10^{-3}$ cm^{-1}.

[j] Superposition of the two signals for $[Pd(NH_3)_4]^{+}$ and $[PdCl_4]^{3-}$.

to $g = 2.00$. As mentioned below, the paramagnetic complexes produced in the powders of palladium(II) complexes are identical with those produced in alcoholic glassy matrices in which it has been established that solutes are reduced by γ-ray irradiation.[6] Therefore it is most probable that these signals are attributed to the palladium(I) complexes which are formed by the reduction of the original palladium(II) complexes without any change of the symmetry of the ligand field, as in the case of $Pd(acac)_2$ and chloropalladate.[4, 5] The ESR parameters for a variety of palladium(I) complexes are summarized in Table I.

The spectra for $[Pd(thiourea)_4]^{+}$ produced in the powder of $[Pd(thiourea)_4]Cl_2$ and in the EG–H_2O matrix are shown in Figures 1a and 1b, in both of which a part of six-line hyperfine signals due to ^{105}Pd, a 22.6% abundant isotope having a nuclear spin of 5/2, can be observed surrounding a strong line of the $g_\perp$ component. The hyperfine lines of the parallel component can also be observed in Figure 1b under higher gain. Although both the spectra are similar in shape, suggesting the formation of an identical paramagnetic complex in both cases, the ESR parameters differ from each other considerably. This indicates that the influence of the host lattice upon the ESR parameters is not negligible.

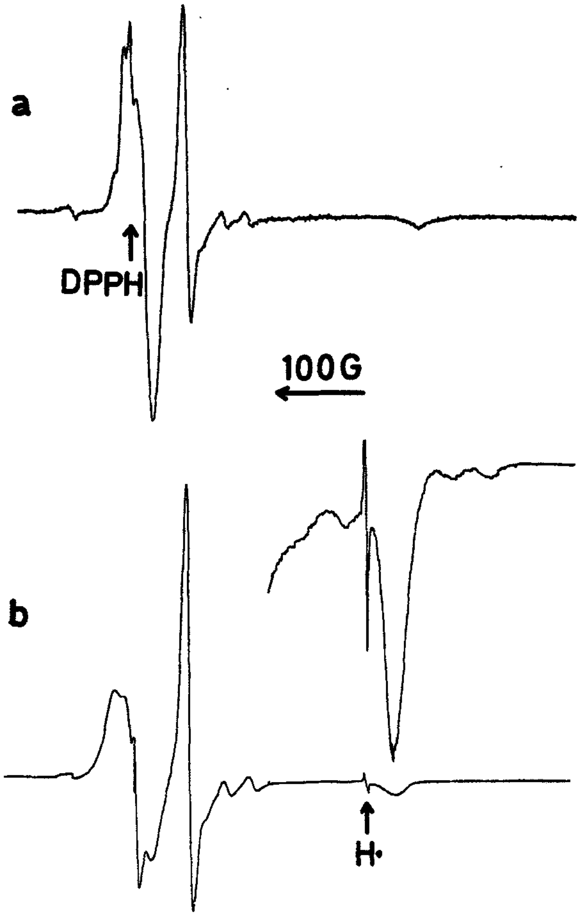

FIGURE 1 The ESR spectra for γ-irradiated (a) powder of $[Pd(thiourea)_4]Cl_2$ and (b) EG-H_2O matrix containing $[Pd(thiourea)_4]Cl_2$(50mM/l) and thiourea(500mM/l). Inset is recorded under higher gain. H· denotes one of the hyperfine signals of hydrogen atoms produced in quartz tube.

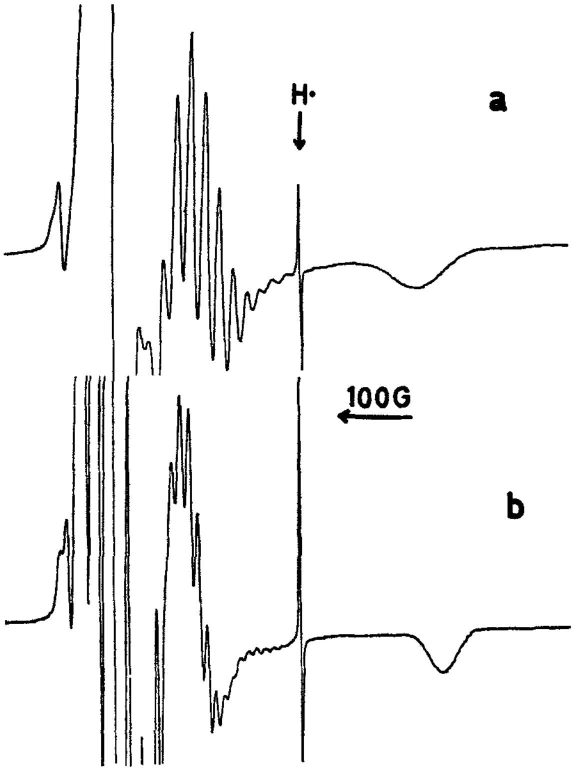

FIGURE 2 The ESR spectra for γ-irradiated matrices. (a) $K_2[Pd(NO_2)_4]$(50mM/l) and KNO_2(500mM/l) in EG-H_2O. (b) Li_2PdCl_4(50mM/l) and n-$BuNH_2$(500mM/l) in EtOH.

As is seen in Figure 2, the $g_\perp$ components for $[Pd(NO_2)_4]3-$ produced in the EG–H_2O glass and for $[Pd(n\text{-}BuNH_2)_4]^+$ in the ethanol glass are split into nine lines, a part of which is hidden in the strong signals due to radicals formed in the matrices. The nine lines can be attributed to the hyperfine interaction between the electron and the four ^{14}N nuclei of ligands. In addition, several weak lines probably due to an interaction with both of ^{105}Pd and ^{14}N can be observed surrounding the nine lines. The $g_\perp$ component for $[Pd(oxine)_2]^-$ (Figure 3a) is split into several lines which can probably be attributed to an interaction with two ^{14}N nuclei of ligands. In marked contrast to $[Pd(oxine)_2]^-$, $[Pd(2\text{-}Me\text{-}oxine)_2]^-$ gives an abnormally large $g_{//}$ as shown in Figure 3b. Surprisingly, a new spectrum with far larger $g_{//}$ appears in place of this spectrum when this sample is once heated up to room temperature (Figure 3c).

The spectrum for $[Pd(C_2O_4)_2]^{3-}$ produced in the powder of $K_2[Pd(C_2O_4)_2]\cdot 3H_2O$ is shown in Figure 4a, in which the parallel component of ^{105}Pd hyperfine signals as well as the perpendicular component can be observed. Whereas the same complex produced in the EG–H_2O matrix gives rather broad spectrum which is shown in Figure 4b. These spectra are similar in shape to those for

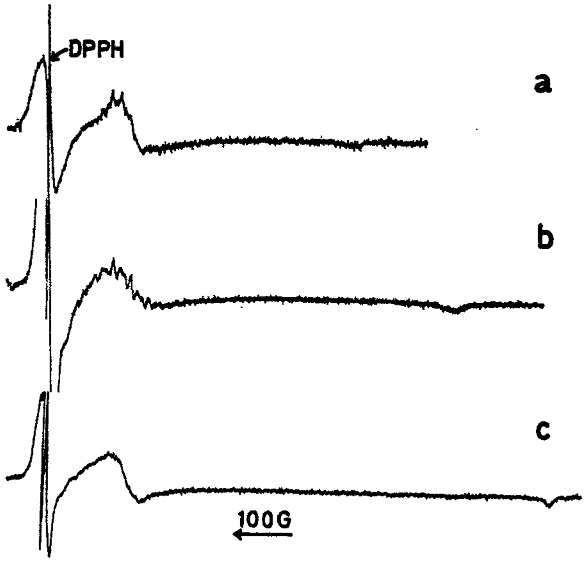

FIGURE 3 The ESR spectra for γ-irradiated powder of (a) $Pd(oxine)_2$ and (b) $Pd(2\text{-}Me\text{-}oxine)_2$. (c) is the spectrum observed at 77° K after heating the sample (b) to room temperature.

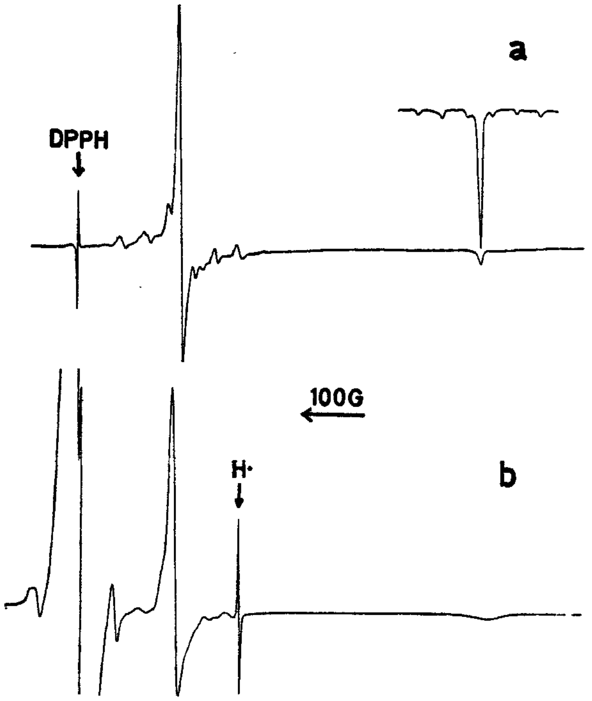

FIGURE 4 The ESR spectra for γ-irradiated (a) powder of $K_2[Pd(C_2O_4)_2]3H_2O$ and (b) $EG\text{-}H_2O$ matrix containing $K_2[Pd(C_2O_4)_2](5mM/l)$ and $K_2C_2O_4(50mM/l)$. Inset is recorded under higher gain.

$[Pd(acac)_2]^-$.[4] Similar spectra are also obtained for γ-irradiated powders of dicarboxylatopalladium(II). Figure 5a shows the spectrum for $[PdCl_4]^{3-}$ produced in the $EG\text{-}H_2O$ matrix. The $g_\perp$ component is split into incompletely resolved thirteen lines, a part of which are hidden in the signals of radicals. The thirteen lines are attributed to an interaction between the electron and the four ^{35}Cl nuclei. γ-Irradiated Vauquelin's salt, $[Pd(NH_3)_4][PdCl_4]$ gives two signals of $g_{//}$ component as shown in Figure 5b. In this case, the signal of the smaller $g_{//}$ can be attributed to $[Pd(NH_3)_4]^+$ and that of the larger to $[PdCl_4]^{3-}$, since PdN_4-type complex has smaller $g_{//}$ than $PdCl_4$-type usually. The $g_\perp$ components for the above two complexes are superposed.

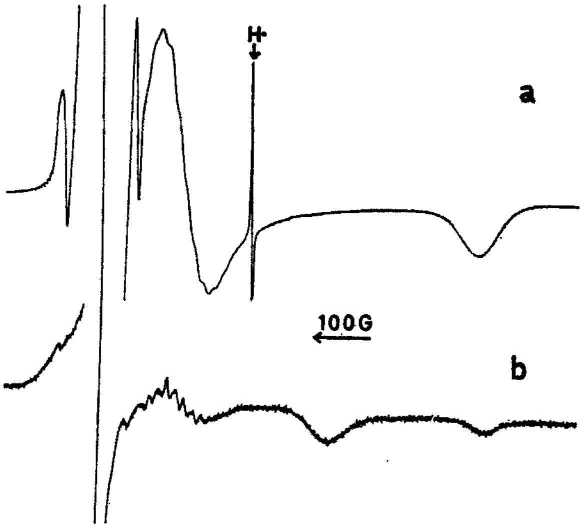

FIGURE 5 The ESR spectra for γ-irradiated (a) $EG\text{-}H_2O$ matrix containing $K_2PdCl_4(50mM/l)$ and $KCl(1000mM/l)$ and (b) powder of $[Pd(NH_3)_4][PdCl_4]$.

In the complexes examined, $[Pd(CN)_4]^{3-}$, $[PdCl_2(PhCN)_2]^-$, $[Pd(oxine)_2]^-$, $[Pd(acac)_2]^-$, and $[Pd(C_2O_4)_2]^{3-}$ are stable at room temperature in solid phase at least for a few weeks. However their spectra are too broad to be observed at room temperature except for $[Pd(C_2O_4)_2]^{3-}$ produced in $K_2[Pd(C_2O_4)_2]\cdot 3H_2O$. The other complexes of palladium(I) die at room temperature within a few minutes, being stable at 77° K. γ-Irradiated powders of palladium chloride, potassium tetrabromopalladate, and bis(dimethylglyoximato) palladium(II) gave only the signals of radicals.

DISCUSSION

In palladium(I) complexes, palladium(I) has a $4d^9$ electronic configuration which is analogous to copper(II) with a $3d^9$ configuration. In addition, the ESR spectra for palladium(I) complexes show tetragonal symmetry of ligand field within experimental error. Therefore it is reasonable to interpret their ESR parameters in terms of a molecular orbital theory which has been applied to square planar complexes of copper(II).[9, 10, 11] In this case the pertinent antibonding molecular orbitals for the positive hole have the form

$$\sigma = \alpha d_{x^2-y^2} - \alpha' \Phi_l(x^2 - y^2) \tag{1a}$$

$$\pi = \beta d_{xy} - \beta' \Phi_l(xy) \tag{1b}$$

$$\pi_1 = \begin{cases} \beta_1 d_{xz} - \beta_1' \Phi_l(xz) \\ \beta_1 d_{yz} - \beta_1' \Phi_l(yz) \end{cases} \tag{1c}$$

where $\Phi_l(j)$ denotes the linear combination of the ligand orbitals belonging to the same irreducible representation as d_j orbitals of palladium. The four ligands are placed on the $\pm x$ and $\pm y$ axes. For palladium(I) complexes the σ-antibonding orbital is the ground-state orbital and π and π_1 are excited states connected to the σ orbital through the spin-orbit interaction. The principal g values and the ^{105}Pd hyperfine coupling constants have been shown to be represented by the following equations:

$$\Delta g_{/\!/} = g_{/\!/} - 2.0023 = -8k_{/\!/}^2 \lambda_0 / \Delta_{/\!/} \tag{2a}$$

$$\Delta g_{\perp} = g_{\perp} - 2.0023 = -2k_{\perp}^2 \lambda_0 / \Delta_{\perp} \tag{2b}$$

$$A_{/\!/} = P(-\kappa - \tfrac{4}{7}\alpha^2 + \Delta g_{/\!/} + \tfrac{3}{7}\Delta g_{\perp}) \tag{3a}$$

$$A_{\perp} = P(-\kappa + \tfrac{2}{7}\alpha^2 + \tfrac{11}{14}\Delta g_{\perp}) \tag{3b}$$

where $k_{/\!/}$ and $k_{\perp}$ are the orbital reduction factors; λ_0 is the spin-orbit coupling constant for the free palladium(I) ion; $\Delta_{/\!/}$ and $\Delta_{\perp}$ are $E(\pi) - E(\sigma)$ and $E(\pi_1) - E(\sigma)$, respectively; κ is the Fermi-contact term; and $P = 2\gamma_N \beta \beta_N < d_{x^2-y^2} | r^{-3} | d_{x^2-y^2} >$ with N referring to the palladium nuclei. In Eqs. (3a) and (3b) small ligand terms are neglected.

If the values of $g_{/\!/}$, $g_{\perp}$, $A_{/\!/}$, and $A_{\perp}$ can be known, α^2 and κ can be estimated from the simultaneous solution of Eqs. (3a) and (3b). The values of α^2 and κ estimated for some of palladium(I) complexes are given in Table II. In this calculation $P = -5.2 \times 10^{-3}$ cm^{-1} is used,[4] and the sign of $A_{/\!/}$ and $A_{\perp}$ is assumed positive in every case so that the sign of α^2 and κ calculated from Eqs. (3a) and (3b) may be positive. The error in the values of α^2 and κ caused by the neglect of ligand terms is supposed to be less than 5%.[12] The bonding parameters in Table II indicate that the palladium-sulfur bond is highly covalent, whereas the palladium-oxygen bond is appreciably covalent in acetylacetonate and is almost ionic in oxalate and acetate. For bis(ethyldithiocarbamato)copper(II), bis(acetylacetonato)copper(II), and dioxalato-copper(II) α^2 has been estimated at 0.59, 0.75, and 0.84, respectively.[10, 13] These values are comparable in their magnitude to those obtained for the corresponding or similar complexes of palladium(I). In addition, the ^{14}N superhyperfine coupling constant for [Pd(amine)$_4$]$^+$ 1.2 × 10^{-3} cm^{-1} is nearly equal to that reported for the ammine complex of copper(II) 1.3 × 10^{-3} cm^{-1}.[13] These facts along with the previous results for chloro-complexes[5] suggest that the metal-ligand σ-bonds of palladium(I) and copper(II) complexes are very similar in their natue to each other.

TABLE II

Bonding parameters for palladium(I) complexes

Complex	Host lattice	α^2	κ
$[Pd(SCN)_4]^{3-}$	EG–H_2O	0.55	0.66
$[Pd(tu)_4]^+$	EG–H_2O	0.62	0.71
$[Pd(acac)_2]^-$ [a]	$Pd(acac)_2$	0.74	1.0
$[Pd(C_2O_4)_2]^{3-}$	$K_2[Pd(C_2O_4)_2]3H_2O$	0.84	1.0
Pd(I) acetate	$CaPd(OAc)_4$, 4HOAc	0.92	1.0
Pd(I) acetate	$CdPd(OAc)_4$, H_2O, HOAc	0.81	1.0

[a] Ref. 4.

As the covalency for the palladium-ligand σ-bond increases, $k_{/\!/}^2$ and $k_{\perp}^2$ decrease from unity and $\Delta_{/\!/}$ and $\Delta_{\perp}$ increase, resulting in the decrease of $\Delta g_{/\!/}$ and $\Delta g_{\perp}$. Consequently the values of $\Delta g_{/\!/}$ and $\Delta g_{\perp}$ can be chosen as a gross indication of covalent character in metal-ligand σ-bond.[10] With this in mind, it can be concluded from Table I that the covalency for the palladium-ligand bond increases in the order of Pd—O, Pd—Cl < Pd—N < Pd—S, Pd—C. This trend is in the expected direction, being similar to that found for square planar complexes of copper(II).[10, 13]

It is interesting to compare more quantitatively the magnitude of g values for the palladium(I) and copper(II) complex with the same ligand. Since the values of α^2 for palladium(I) and copper(II) complexes with the same ligand are comparable in magnitude to each other, it is assumed that the

TABLE III

The values of $q_{//}$ and $q_{\perp}$ for some of complexes

Complex	Host lattice		Cu(II)			$q_{//}$	$q_{\perp}$
	Pd(I)	Cu(II)	$g_{//}$	$g_{\perp}$	Ref.		
ethylenediamine	EG–H_2O	$[Cu(en)_2]Cl_2 \cdot H_2O$	2.200	2.044	16	1.1	1.2
ammine	EG–H_2O	$[Cu(NH_3)_4]SO_4 \cdot H_2O$	2.223	2.051	17	1.1	1.3
oxinate	$Pd(oxine)_2$	oxine	2.246	2.059[a]	18	1.0	1.2
acetylacetonate	$Pd(acac)_2$	$Pd(acac)_2$	2.266	2.053	9	0.87	0.96
oxalate	EG–H_2O	H_2O	2.316	2.078	19	1.0	1.2
acetate	$[Pd(OAc)_2]_3H_2O$	$[Cu(OAc)_2]_2\ 2H_2O$	2.344	2.073[a]	20	1.0	1.2
chloride	K_2PdCl_4	$CdCl_2$	2.339	2.070	21	1.1	1.4

[a] $(g_x + g_y)/2$.

values of the orbital-reduction factors for both complexes are also nearly equal to each other. Then the following equation is obtained from Eqs. (2a) and (2b):

$$q_j = \frac{\lambda_0(\mathrm{Pd})/\Delta g_j(\mathrm{Pd})}{\lambda_0(\mathrm{Cu})/\Delta g_j(\mathrm{Cu})} \sim \frac{\Delta_j(\mathrm{Pd})}{\Delta_j(\mathrm{Cu})}\ (j = //, \perp) \qquad (4)$$

According to this equation, the ratio of the ligand field splittings for palladium(I) complexes to those for the corresponding copper(II) complexes can be estimated from the values of q_j, which can be calculated from their g values. As the values of λ_0, $-828\ \mathrm{cm}^{-1}$ and $-1412\ \mathrm{cm}^{-1}$ are taken for copper(II) and palladium(I) free ions respectively.[14] q_j calculated for some of complexes are shown in Table 3 along with the g values reported for copper(II) complexes. As is seen from Table III, $q_{//} = 0.9$–1.1 and $q_{\perp} = 1.0$–1.4 with $q_{\perp}/q_{//} = 1.1$–1.3 for a variety of ligands. This indicates that the $\Delta_{//}$ for palladium(I) complex is comparable in magnitude to that for the corresponding copper(II) complex, while the $\Delta_{\perp}$ for palladium(I) complex is appreciably larger than that for the copper(II) complex. It has been generally accepted that palladium(II) complexes have far larger ligand field splittings than copper(II) complexes.[15] Therefore it is concluded that the ligand field splittings for palladium(II) complexes are decreased by the reduction of the central metal ion, in accordance with the previous result.[5] In this case, the reduction, by which an electron is added into the antibonding σ-orbital, is supposed strongly effective in weakening the metal-ligand bond.

The molecular structure of diacetatopalladium(II) has been determined to consist of a nearly equilateral triangle of palladium atoms which are joined together by double acetate bridges such that the coordination at the metal atom is approximately square planar.[22] Dipropionato- and dibenzoatopalladium(II) have also been supposed to have polymeric structure.[7] However γ-irradiated these complexes show only six-line hyperfine interaction with a ^{105}Pd nucleus. This indicates that an unpaired electron is not delocalized over the whole polymeric molecule but is localized on a PdO_4-unit. A similar result has recently been reported for γ-irradiated diacetatocopper(II) monohydrate.[23] In $MPd(OCOCH_3)_4$, $x CH_3COOH$, $y H_2O$, where M are divalent metal ions, two metal ions have been supposed to be linked by acetate bridges.[8] These complexes, with $M = Ca^{2+}$, Cd^{2+}, and Pb^{2+}, give the ESR spectra similar to that for γ-irradiated dicarboxylato-palladium(II). However their ESR parameters and bonding parameters change depending on M, as shown in Tables I and II. This seems to show that the two metal ions interact with each other probably through acetate bridges, as suggested by Brandon and Claridge.[8]

As mentioned above, $[Pd(2\text{-}Me\text{-}oxine)_2]^-$ shows an abnormally large $g_{//}$ in contrast to $[Pd(oxine)_2]^-$. If we assume that $Pd(2\text{-}Me\text{-}oxine)_2$ has the same molecular structure as $Pd(oxine)_2$[24] except that the former has two methyl groups, the distance between the methyl carbon atom on a ligand and the oxygen atom on another ligand becomes only 2.4 Å as calculated assuming a C—C bond length of 1.4 Å. Since this is much less than the sum of the Van der Waal's radii of Methyl group (2.0 Å) and oxygen atom (1.40 Å), there must be a steric repulsion between the methyl groups and the oxygen atoms, causing an elongation of the metal-ligand bond in this complex. We propose that this elongation is a cause for the abnormally large $g_{//}$ of this complex. This steric repulsion could also have something to do with the change in the spectrum by heating.

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REFERENCES

1. D. Nakamura, Y. Kurita, K. Ito, and M. Kubo, *J. Am. Chem. Soc.* **82,** 5783 (1960).
2. K. Ito, D. Nakamura, Y. Kurita, K. Ito, and M. Kubo, *J. Am. Chem. Soc.* **83,** 4526 (1961).
3. C. W. Fryer and J. A. S. Smith, *J. Chem. Soc.* **1970,** 1029.
4. S. Fujiwara and M. Nakamura, *J. Chem. Phys.* **52,** 6299 (1970).
5. S. Fujiwara and M. Nakamura, *J. Chem. Phys.* **54,** 3378 (1971).
6. T. Shida and W. Hamill, *J. Am. Chem. Soc.* **88,** 5371 (1966).
7. T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer, and G. Wilkinson, *J. Chem. Soc.* **1965,** 3632.
8. R. W. Brandon and D. V. Claridge, *Chem. Comm.* **1968,** 677.
9. A. H. Maki and B. R. McGarvey, *J. Chem. Phys.* **29,** 31 (1958).
10. D. Kivelson and R. Neiman, *J. Chem. Phys.* **35,** 149 (1961).
11. D. W. Smith, *J. Chem. Soc.* **1970,** 3108.
12. B. R. McGarvey, *J. Phys. Chem.* **71,** 51 (1967).
13. H. R. Gersmann and J. D. Swalen, *J. Chem. Phys.* **36,** 3221 (1962).
14. J. S. Griffith, *The Theory of Transition-Metal Ions* (Cambridge University Press, 1962), p. 437.
15. N. S. Hush and J. M. Hobbs, *Prog. Inorg. Chem.* **10,** 259 (1968).
16. I. M. Procter, B. J. Hathaway, and P. Nicholls, *J. Chem. Soc. 1968,* 1678.
17. E. H. Karlson and R. D. Spence, *J. Chem. Phys.* **24,** 471 (1956).
18. G. Rist, J. Ammeter, and Hs. H. Gunthard, *J. Chem. Phys.* **49,** 2210 (1968).
19. B. G. Malmstom and T. Vanngard, *J. Mol. Biol.* **2,** 118 (1960).
20. B. Bleany and K. D. Bowers, *Proc. Roy. Soc.* (*London*) **A214,** 451 (1952).
21. J. H. M. Thornley, B. W. Mangum, J. H. E. Griffiths, and J. Owen, *Proc. Phys. Soc.* (*London*) **78,** 1263 (1961).
22. A. C. Skapski and M. L. Smart, *Chem. Comm.* **1970,** 658.
23. U. Sakaguchi, Y. Arata and S. Fujiwara, *J. Chem. Phys.* **53,** 464 (1970).
24. C. K. Pront and A. G. Wheeler, *J. Chem. Soc.* **1966,** 1286.