June, 1977] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (6), 1437—1440 (1977)

ESR of Hot Ions: Low Spin Pt(III) Complex Ions Produced by γ-Irradiation

Chikara AMANO* and Shizuo FUJIWARA
Department of Chemistry, Faculty of Science, The University of Tokyo,
Hongo, Bunkyo-ku, Tokyo 113

(Received December 9, 1976)

Tervalent platinum complex ions have been observed by the electron spin resonance method upon γ-irradiation of both bivalent and quadrivalent complexes. From their g-values, the tervalent complex ions can be classified into two types, one axially symmetric and the other rhombic, the former having typical g-values of 2 ($g_{//}$) and 2.4($g_\perp$), and the latter a g_1-value slightly lower than the free electron value of 2.0023. It has been shown by means of ligand field theory that both types have $5d^7$ low spin electron configuration. The hyperfine interaction due to ^{195}Pt is one order of magnitude larger than that in cobalt complexes with $3d^7$ low spin configuration, indicating that the configuration interaction involving 6s-orbital is more important than that for 3d transition metal complexes involving 4s-orbital, and that 5d electrons penetrate deeply into inner shells, resulting in core polarizarion.

γ-Irradiation produces metal complex ions with unusual valence states, Co^{2+}, Ni^+, Pd^+, Zn^+, Cd^+ *etc.*[1-4] All these hot ions are produced through reduction of original complexes having the usual valence. Thus univalent platinum complexes which seem to have $5d^9$ electron configuration are expected to be produced by γ-irradiation of bivalent complexes. The electronic states of transition metal ions belonging to the 5d group remain unclarified. Neither visible nor ultraviolet absorption spectra have been assigned to any transitions between multiplet states, and the order of one-electron energy levels has not been established. Almost all the complexes with d^9 electron configuration studied thus far show the same type of g-value: $g_{//}>g_\perp>2$. It has not been clarified whether univalent platinum complexes show this type of g-value.

In the present work eleven bivalent platinum complexes and three quadrivalent ones were γ-irradiated at 77 K and their ESR spectra were recorded. The present paper reports on a new valence state of tervalent platinum complex ions along with a discussion on their electronic state.

Experimental

Both platinum metal and hydrogen hexachloroplatinate(VI) ($H_2PtCl_6 \cdot 6H_2O$) were used to synthesize bivalent and quadrivalent platinum complexes. Copper(II) ions contained in commercial $H_2PtCl_6 \cdot 6H_2O$ were removed in synthetic processes; they were not found in potassium tetrachloroplatinate(II). The complexes subjected to γ-irradiation are summarized in Table 1. Each complex of polycrystalline state was put into a radiation-protected sample tube for ESR measurement, in 50—100 mg amount. The sample tubes were immersed in liquid nitrogen and subjected to γ-irradiation at 77 K. They were inverted on γ-irradiation, the upper half of the tubes shielded with lead blocks to prevent production of paramagnetic centers. The tubes were again inverted before ESR measurement. The total dose was 10^6 R with a 5×10^4 R/h dose rate at 77 K, and 10^7 R with a 5×10^5 R/h dose rate at room temperature. ESR spectra were recorded with a JEOL 3BSX spectrometer.

Results and Discussion

[Pt(py)₄]Cl₂·3H₂O. The ESR absorption shown in Fig. 1 was obtained on γ-irradiation of a polycrystalline sample. The strong absorption at about 2800 G shows a large g-shift ($\Delta g=g-2.0023$), which suggests that the paramagnetic center is due to a platinum complex; the large g-shift is caused mainly by the strong spin-orbit interaction. Platinum has a large spin-orbit coupling constant, *e.g.* 3368 cm^{-1} for Pt^+ ion.[5] The strong singlet line is accompanied by weak doublet satellite lines at 2300 and 3100 G. The doublet

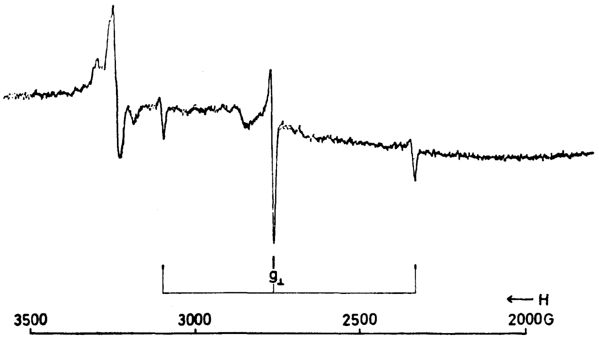

Fig. 1. The ESR spectrum of $[Pt(py)_4]^{3+}$ produced by γ-irradiation.

TABLE 1. BIVALENT AND QUADRIVALENT PLATINUM COMPLEXES

Pt(II):	$K_2[Pt(NO_2)_4]\cdot 2H_2O$, $K_2[Pt(CN)_4]\cdot 3H_2O$, $K_2[Pt(C_2O_4)_2]$, $[Pt(NH_3)_4]Cl_2$, $[Pt(py)_4]Cl_2\cdot 3H_2O$, $[Pt(acac)_2]$, *cis*-$[Pt(py)_2Cl_2]$,$[Pt(gly)_2]$, $[Pt(dmgH)_2]$, $[Pt(xant)_2]$, *trans*-$[Pt(Py)_2Cl_2]$
Pt(IV):	$K_2[PtCl_6]$, $K_2[PtI_6]$, $K_2[Pt(SCN)_6]$

C_2O_4: oxalate, py: pyridine, acac: acetylacetonate,
gly: glycinate, dmgH: dimethylglyoximate, xant: ethylxanthate

---

* Present address: Department of Engineering Physics, The University of Electro-Communications, Chofugaoka, Chofu, Tokyo 182.

TABLE 2. PREDICTED g-VALUES FOR FOUR CASES

Case	Configuration	Multiplet	$g_{//}$	$g_{\perp}$	Order
A	d^9	$^2B_{1g}$	$2+8\zeta/E(^2B_{2g})$[a]	$2+2\zeta/E(^2E_g)$	$g_{//}>g_{\perp}>2$
B	d^9	$^2A_{1g}$	2	$2+6\zeta/E(^2E_g)$	$g_{\perp}>g_{//}=2$
C	d^7	$^2A_{1g}$	2	$2+(3+6a_1b_1)\zeta/E(^2E_g{}^a)$ $+(3+6a_2b_2)\zeta/E(^2E_g{}^b)$	$g_{\perp}>g_{//}=2$
D	d^7	$^2B_{1g}$	$2+(4+8a_1b_1)\zeta/E(^2B_{2g})$[a] $+(4+8a_2b_2)\zeta/E(^2B_{2g}{}^b)$[b]	$2+(1+2a_1b_1)\zeta/E(^2E_g{}^a)$ $+(1+2a_2b_2)\zeta/E(^2E_g{}^b)$	$g_{//}>g_{\perp}>2$

a) Energy value of multiplet when that of the ground multiplet is set to zero. b) $a_1=-10B/\{(4B+C+A)^2+100B^2\}^{1/2}$, $b_1=(4B+C+A)/\{(4B+C+A)^2+100B^2\}^{1/2}$, $a_2=-10B/\{(4B+C-A)^2+100B^2\}^{1/2}$, $b_2=(4B+C-A)/\{(4B+C-A)^2+100B^2\}^{1/2}$, $A=(116B^2+8BC+C^2)^{1/2}$. A, B, and C are Racah's parameters.

has a large splitting of *ca.* 800 G, presumably due to the hyperfine interaction with ^{195}Pt, only one stable isotope with nonzero nuclear spin 1/2. Since the natural abundance of ^{195}Pt is 33.8%, the relative absorption strength of one of the doublets to the main singlet should be 1/4 (Fig. 1). The shift of the singlet from the center of the doublet toward upper field is due to the large hyperfine interaction with ^{195}Pt nucleus.[6] The spectral feature shows that the paramagnetic platinum complex ion produced takes axial symmetry and the absorption at 2800 G is a perpendicular component. The parallel component should be much weaker than the perpendicular one. It would be observed near 3300 G, where the strong absorption of unidentified radicals obscures the observation of the parallel component. Careful investigation shows that no parallel component was found at any other magnetic field strength.

The value of $g_{\perp}$ was found to be 2.377 ± 0.002, which can be directly calculated from the main singlet line, that of $g_{//}$ being probably 2. The principal value of the hyperfine splitting tensor due to ^{195}Pt, $A_{\perp}$, also obtained by use of the usual second order perturbation formula, is 877×10^{-4} cm^{-1}.[6]

As regards the valence state of paramagnetic platinum complexes, two possibilities should be considered, univalent complexes with 5d^9 electron configuration and tervalent complexes with 5d^7 electron configuration. The g-values for possible ground states for these two valences have been calculated by means of ligand field theory (Table 2).[2] The experimental g-values are consistent in cases B and C. However, B corresponds to the structure of uniaxially compressed D_{4h}, found to be very rare for d^9 configuration, while C corresponds to the uniaxially elongated structure, which seems reasonable in consideration of the tetragonaly four-coordinated structure of the original complex. The complexes having d^7 low spin configuration have been shown to take this multiplet in several cases.[7,8] Thus, the paramagnetic center observed can be assigned to a tervalent platinum complex ion which takes $^2A_{1g}$ as the ground multiplet, having one unpaired electron in 5d$_{z^2}$ orbital.

In contrast to the transition metal complexes of the 3d group, no systematic studies have been made on the electronic state of the 5d group. Optical absorption spectra of some Pt(II) complexes were studied by Chatt, Gamlen, and Orgel.[9] The order of the one electron energy level for $[PtCl_4]^{2-}$ was determined: $5d_{x^2-y^2}>5d_{xy}>5d_{yz,zx}>5d_{z^2}$, though the position of 5d$_{z^2}$ was uncertain. However, it seems difficult to assign an absorption band to a certain transition between multiplets because of the presence of strong spin-orbit coupling. Krigas and Rogers studied γ-irradiation of $K_2[PtCl_4]$ by the ESR method and found the formation of $[PtCl_5]^{2-}$ with 5d^7 electron configuration.[10] Since the original $[PtCl_4]^{2-}$ takes a tetragonally four-coordinated structure, one chlorine ion appears to be attached to the axial position in the course of oxidation. It is concluded that one electron energy level of $[PtCl_5]^{2-}$ has the order: $5d_{x^2-y^2}>5d_{z^2}>5d_{xy}>5d_{yz,zx}$. The unusually high energy of 5d$_{z^2}$ was explained to be caused by the presence of the axial chloride ion. The present g-values of $[Pt(py)_4]^{3+}$ are also in line with this order. However, there can be no chloride ion at the axial position, since the absorption of the perpendicular part (Fig. 1) has a very narrow width of about 20 G, showing neither hyperfine splitting by chlorine nucleus nor line broadening due to unresolved structure by chlorine.

Let us compare the hyperfine splitting of $[Pt(py)_4]^{3+}$ with that of bivalent cobalt complexes having 3d^7 low spin configuration. A comparison between tervalent nickel and tervalent palladium and tervalent platinum complexes would have been preferable, but we could not obtain the A-values of either tervalent nickel or tervalent palladium of low spin type. We chose β-cobaltphthalocyanine as an example, since this is one of the few bivalent cobalt complexes taking low spin configuration. A-values of β-cobaltphthalocyanine have been reported to be 160×10^{-4} cm^{-1} ($A_{//}$) and 280×10^{-4} cm^{-1} ($A_{\perp}$).[7] In order to see the effect of electron orbitals, we compared the values which can be obtained by dividing the experimental A-values by nuclear moment of each isotope. They are 60.3 for the cobalt complex and 1480 for the platinum complex on a ceartin scale, which shows that the latter is about twenty times greater than the former. In 5d transition metal complexes the valence electrons mainly in metal 5d orbitals could penetrate deeply near the metal nucleus because of the incomplete shielding of the nuclear potential by the other inner closed shell electrons, resulting in large core polarization.

$K_2[Pt(NO_2)_4]\cdot2H_2O$. There is a strong absorption at 2500 G with a weak satellite at 1900 G (Fig. 2). This should be due to platinum complexes because of the large g-shift and the large hyperfine splitting. From the line shape this can be ascribed to the perpendicular component, which splits slightly to form g_2 and g_3 component. A parallel component is also observed at

Table 3. ESR parameters of low spin Pt^{3+} complexes

A) Axial symmetry

Complexes	$g_{//}$	$g_{\perp}$	$A_{//}$	$A_{\perp}$ (10^{-4} cm^{-1})
$[Pt(py)_4]^{3+}$	($\approx$2)	2.377	—	877
$[Pt(NH_3)_4]^{3+}$	($\approx$2)	2.395	—	940
cis-$[Pt(py)_2Cl_2]^+$	($\approx$2)	2.544	—	768
$[PtCl_6]^{3-}$	($\approx$2)	2.659	—	591

B) Rhombic symmetry

Complexes	g_1	g_2	g_3	A_1	A_2	A_3 (10^{-4} cm^{-1})
$[Pt(gly)_2]^+$	1.939	2.338	2.674	1025	—	1210
$[Pt(NO_2)_4]^-$	1.910	2.572	2.622	1690	—	—

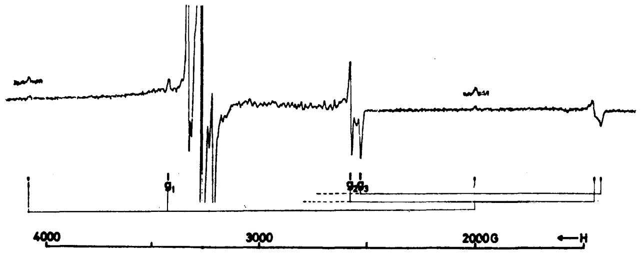

Fig. 2. The ESR spectrum of $[Pt(NO_2)_4]^-$ produced by γ-irradiation. The splitting of $g_{\perp}$ part shows the small distortion of ligand configuration.

slightly upper field than that of strong absorptions due to unidentified radicals with g-value of 2. Very weak satellites are observed at both 2000 and 1400 G. The ESR parameters obtained are given in Table 3.

Since original $[Pt(NO_2)_4]^{2-}$ has square-planar configuration of ligand ions, the tervalent platinum complex produced through oxidation should show a line with axial symmetry, if the original configuration is maintained. However, the line shape (Fig. 2) indicates that the tervalent platinum has a slightly deformed ligand configuration. Some of the complexes having d^7 low spin configuration have been shown to have smaller $g_{//}$- or g_1-value like this. As an example, β-cobalt-phthalocyanine has $g_{//}$ of 1.91.[7] Griffith tried to explain this by means of ligand field theory.[11] He assumed several ground multiplets which arise from different orders of one electron energy levels, and concluded that the ground state is $|d_{zx}\bar{d}_{zx}d_{yz}\bar{d}_{yz}d_{xy}\bar{d}_{xy}d_{z^2}|$ and that the smaller $g_{//}$ than 2 is due to the third order terms of spin-orbit interaction. It is uncertain, however, whether the sum of many spin-orbit terms can result in $g_{//}$ smaller than 2. On the other hand, we presume that g_1 smaller than 2 is caused by the lowering of symmetry from D_{4h}. In D_{2h} symmetry, $5d_{z^2}$ orbital mixes with $5d_{x^2-z^2}$ to form new one-electron eigenfunctions. It can be assumed from the small splitting of $g_{\perp}$ component observed that the distortion from D_{4h} to D_{2h} is small. We obtained one-electron eigenfuctions in D_{2h} ligand field $5d_{xy}$, $5d_{yz}$, $5d_{zx}$, $5d_{z^2}'=(1+a^2)^{-1/2}(5d_{z^2}+a5d_{x^2-y^2})$ and $5d_{x^2-y^2}'=(1+a^2)^{-1/2}(5d_{x^2-y^2}-a5d_{z^2})$, where a is a small mixing coefficient. Considering electron-electron repulsion, the ground multiplet becomes $|^2A_{1g}1/2\rangle=|5d_{yz}5\bar{d}_{yz}5d_{zx}5\bar{d}_{zx}5d_{xy}5\bar{d}_{xy}5d_{z^2}'|$. Applying the usual perturbation formula to calculate g-values, we have $g_1=2+8a^2(1+a^2)^{-1}/E(^2B_{1g}-{}^2A_{1g})$. This predicts that g_1 is slightly greater than 2, a disappointing result. The simple model presented here gives no reasonable explanation of the observed g-value.

cis-*[Pt(py)$_2$Cl$_2$]*. Although this complex does not have a fourfold axis, the electronic state can be explained approximately in terms of D_{4h}. The ligand field of *cis*-type complexes has D_{4h} symmetry contrary to their geometrical symmetry.[12] The ESR spectrum which can be assigned to $[Pt(py)_2Cl_2]^+$ from its large g-shift showed that the complex has D_{4h} or C_{4v} symmetry in spite of the lack of a fourfold axis in geometrical structure. This suggests that the tervalent platinum complex ion does not suffer from distortion through oxidation. $g_{//}$ is probably 2, though it was not observable in the superposition of the strong absorption of unidentified radicals. *trans*-$[Pt(py)_2Cl_2]$ was also examined, but it gave no ESR absorption other than that of radicals at 3300 G. This indicates that the tervalent complex of the *cis*-type is produced in a greater amount than the *trans*-type by a factor of at least 100.

trans-*[Pt(gly)$_2$]*. This complex has a asymmetry between the axis of N–Pt–N and that of O–Pt–O in the plane formed by ligand and a central platinum ion. Thus, the ESR spectrum of the tervalent platinum complex produced by oxidation should show asymmetric shape with three different principal values of g-tensor (Fig. 3). The g_1-value less than 2, 1.939 also obtained in this case, suggests that a g_1-value smaller than 2 may be due to the lack of a fourfold axis.

K_2[PtCl$_6$]. A tervalent platinum complex was produced on γ-irradiation at room temperature. This tervalent platinum has different ESR parameters from

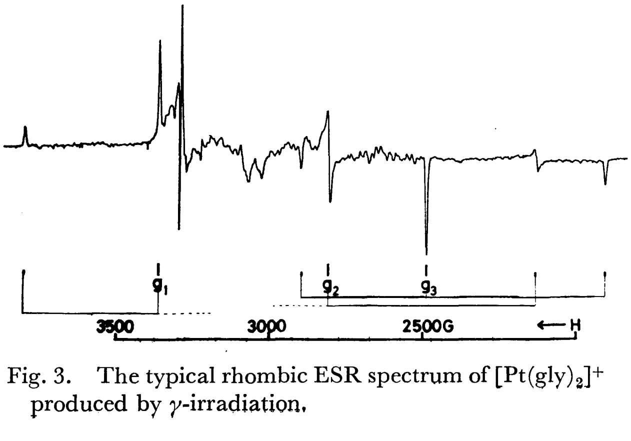

Fig. 3. The typical rhombic ESR spectrum of $[Pt(gly)_2]^+$ produced by γ-irradiation.

the paramagnetic chlorine-coordinated platinum complexes reported by Krigas and Rogers.[10] $g_{//}$ was not observable, but it is probably 2, considering that ESR absorption was not observed at any other position than near 3300 G where unidentified absorption of complex structure was observed. On the other hand, γ-irradiation at 77 K gave ESR absorption, which may come from platinum complexes by considering its large g-shift, $+0.379$. However, the hyperfine splitting due to ^{195}Pt was not clearly observed. The $g_{\perp}$-value is similar to that of the $[PtCl_5]^{2-}$ reported by the above authors.

In contrast to the formation of univalent complexes upon γ-irradiation of bivalent nickel and bivalent palladium complexes, γ-irradiation of bivalent platinum complexes gives tervalent complexes but not univalent ones. Since ionization probability is proportional to electronic density, it seems reasonable that the tervalent platinum complexes are produced in a greater amount than tervalent nickel or palladium complexes. The tervalent platinum complexes usually take 5d^7 low spin electron configuration and show typical g-values like those of 3d complexes: $g_{\perp}>g_{//}\approx 2$. The g_1-value smaller than 2 observed in rhombic complexes seems to come from the lack of a fourfold axis, but no simple explanation can be given. The A-values of the tervalent platinum complexes are usually one order greater than those of the cobalt complexes, suggesting that 5d electrons penetrate deeply into the closed shell and result in the large core polarization. The yield of the tervalent platinum complexes varies from complex to complex, as shown typical between *cis*- and *trans*-$[Pt(py)_2Cl_2]$. It is interesting to see whether univalent platinum complexes would show the typical g-values of 3d^9 and 4d^9 complexes: $g_{//}>g_{\perp}>2$.

We wish to thank Dr. Yoji Arata for reading this manuscript.

References

1) S. Fujiwara, T. Watanabe, and H. Tadano, *J. Coord. Chem.*, **1**, 196 (1971).

2) C. Amano and S. Fujiwara, *Bull. Chem. Soc. Jpn.*, **46**, 1379 (1973).

3) M. Nakamura and S. Fujiwara, *J. Coord. Chem.*, **1**, 221 (1971).

4) J. Isoya and S. Fujiwara, *Bull. Chem. Soc. Jpn.*, **45**, 2182 (1972).

5) J. S. Griffith, "The Theory of Transition-Metal Ions," Cambridge University Press (1961), p. 438.

6) B. Bleaney, *Philos. Mag.*, **42**, 441 (1951); By using the second order perturbation formula, the resonant field is shown to be

$$H_{du} = [h\nu + A_{\perp}/2 + \{(h\nu + A_{\perp}/2)^2 - (A_{//}^2 + A_{\perp}^2)/2\}^{1/2}]/2g_{\perp}\beta$$

for the upper component of the hf doublet,

$$H_{dl} = [h\nu - A_{\perp}/2 + \{(h\nu - A_{\perp}/2)^2 - (A_{//}^2 + A_{\perp}^2)/2\}^{1/2}]/2g_{\perp}\beta$$

for the lower component and $H_s = h\nu/g_{\perp}\beta$ for that of the singlet.

7) J. M. Assour and W. K. Kahn, *J. Am. Chem. Soc.*, **87**, 207 (1965).

8) S. Geschwind and J. P. Rameika, *J. Appl. Phys.*, **33**, 721 (1961).

9) J. Chatt, G. A. Gamlen, and L. E. Orgel, *J. Chem. Soc.*, **1958**, 486.

10) T. Krigas and M. T. Rogers, *J. Chem. Phys.*, **55**, 3035 (1971).

11) J. S. Griffith, *Nature*, **182**, 81 (1959).

12) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Company Inc. (1962).