Generation of platinum(III) species by mechanical treatment of solid K_2PtX_6 (X = Cl, Br) salts

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A mechanical treatment of the solid salts K_2PtX_6 containing a small admixture of K_2PtX_4 (X = Cl, Br) in the atmosphere of air or argon leads to the formations of paramagnetic platinum d^7-complexes.

The most stable platinum complexes are diamagnetic and contain platinum in the +2 and +4 oxidation states. Paramagnetic compounds in the intermediate +3 oxidation state are much rarer[1] than species containing platinum ions in the even-electron configurations. Probably, owing to this reason the information on Pt^{III} compounds with simple inorganic ligands is limited. A number of compounds and complexes which were originally thought to involve the trivalent metal are now known to contain two platinum atoms, one in the +2 oxidation state and the other in the tetravalent state (see, for example, ref. 2). Therefore, the existence of paramagnetism with the magnetic moment close to the spin only value and hyperfine structure in the EPR spectra due to ^{195}Pt nuclei (nucleus spin $I = 1/2$; natural abundance, 33.7%) may be considered as evidence[†] for Pt^{III} compound formation.

One of the first unequivocal evidence for the formation of platinum(III) complexes has been obtained[4] in the case of *cis*-$Pt(NH_3)_2(SCN)_2$ oxidation by iodine into $Pt(NH_3)_2(SCN)_2I$. The EPR spectrum of the latter is a broad intense signal with $g_{ef} = 2.18$ and the line width $\Delta H = 56$ mT at 20 °C. The formation of platinum(III) complexes has also been observed[5] under $H_2PtCl_6 \cdot 6H_2O$ thermolysis. The EPR spectrum of the species obtained corresponds to the spin-Hamiltonian of the axial symmetry with the parameters $g_{\|} = 1.98$, $g_{\perp} = 2.18$, $A_{\|} = 14$ mT, and $A_{\perp} = 6$ mT, where $A_{\|}$ and $A_{\perp}$ are the hyperfine splitting constants on ^{195}Pt nuclei in the parallel and perpendicular orientations, respectively.

The interaction of $H_2PtCl_6 \cdot 6H_2O$ with concentrated sulfuric acid leads[6] to the formation of the platinum(III) sulfate complex $[PtO(SO_4)]^-$. The platinum(III) dithiolate complexes $[Pt(S_2C_2R_2)_2]^-$ (R = CN,[7,8] Ph[9]) have also been studied. For these compounds, the hyperfine structures have been resolved, and the EPR spectra may be fitted to the spin-Hamiltonian of the rhombic symmetry.

The paramagnetic resonance of Pt^{3+} ions in Al_2O_3,[10] $BaTiO_3$,[11] and YAl garnets[12] has been investigated. The EPR spectra correspond to the spin-Hamiltonian of the axial symmetry for the first two cases, and the spin-Hamiltonian is of the rhombic symmetry in the third case. In the latter two cases, the hyperfine structure due to ^{195}Pt nuclei has been observed. To our best knowledge this is the only information on the paramagnetic platinum(III) complexes with simple inorganic ligands.

It is well known that mechanical treatment in mills (where destruction is accompanied by the friction of particles with each other) of covalent crystals such as diamond, graphite, silica, *etc*., generates free radicals predominantly located at the surface[13] of particles. The mechanical treatment of magnesium oxide ionic crystals under frictional conditions also leads to electron transfer from an anionic lattice point to a cationic one with the formation of reactive radical-ion pairs[13] $\{Mg^{2+}O^{2-}\} \rightarrow \{Mg^{\cdot+}O^{\cdot-}\}$.

By analogy with the above data, we may expect that cooperative lattice vibrations can induce oscillations of separate atoms that constitute the complex anion $[PtCl_6]^{2-}$. If the intensity of the vibrations is sufficiently large, it results in the Pt–Cl bond cleavage with the loss of a chlorine atom and the formation of the trivalent platinum ion $[PtCl_5]^{2-}$ at an anionic lattice point:

$$K_2PtCl_6 \xrightleftharpoons{\text{mechanical treatment}} K_2PtCl_5 + Cl\cdot \qquad (1)$$

The aim of this study was to prove this hypothesis. Platinum(II) can serve as a trap for chlorine and shift equilibrium (1) to the right. Thereby, the formation of platinum(III) in appreciable amounts should be expected in the presence of platinum(II) salt admixtures to the treated K_2PtCl_6.

The samples were activated in a dry air atmosphere[‡] for 1 h at room temperature in a closed glass vibroreactor containing

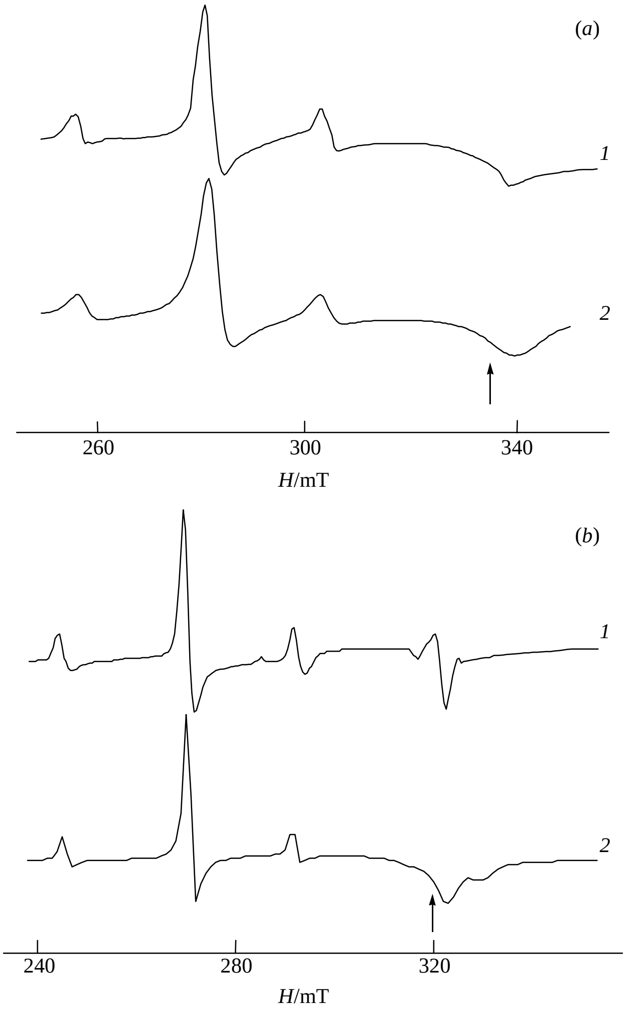

Figure 1 EPR spectra, measured at (*a*) room temperature and (*b*) 77 K, of Pt^{3+} complexes generated by mechanical treatment of a K_2PtCl_6–K_2PtCl_4 mixture. (*1*) The experimental spectrum and (*2*) the simulated spectrum. The arrow indicates the EPR signal with $g = 2.0036$.

[†] The platinum(III) complexes can also form dimeric complexes with a Pt–Pt bond, which are diamagnetic due to this bonding.[3]

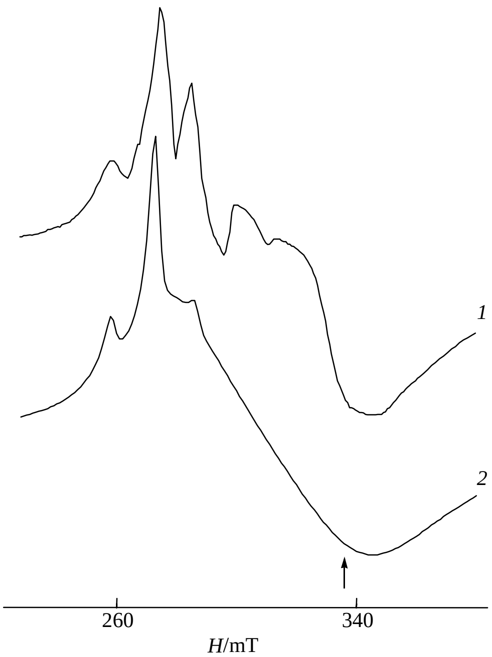

Figure 2 The EPR spectra of Pt^{3+} complexes generated by mechanical treatment of a K_2PtBr_6–K_2PtBr_4 mixture. (*1*) The experimental spectrum and (*2*) the simulated spectrum. The arrow indicates the EPR signal with $g = 2.0036$.

grinding bodies of glass. The working frequency used in an MMVE 0.005 vibratory micromill was 50 Hz. The amplitude was 5.5 mm. The specific energy intensity was 15 W kg^{-1}. The K_2PtX_6 and K_2PtX_4 (X = Cl, Br) salts were prepared according to the standard procedure[14] and carefully dried. The EPR measurements were performed using an SE/X-2544 spectrometer with the working frequency 9.4 GHz. An Mn^{II} sample in an MgO matrix was used as a standard for quantitative measurements. The spectra were taken in the solid polycrystalline samples at room temperature and 77 K.

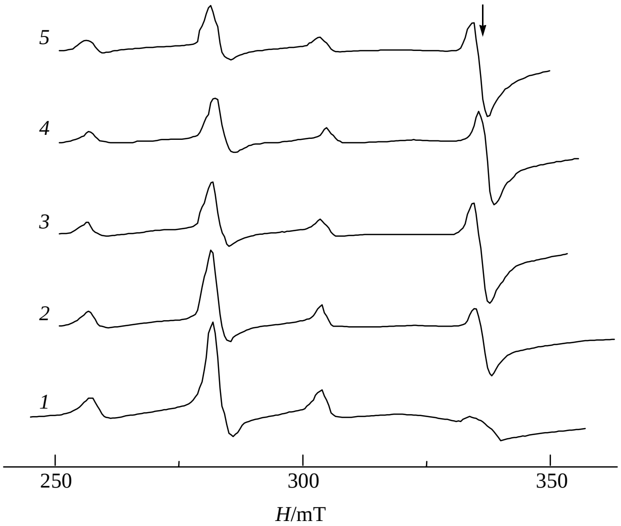

Figure 3 EPR spectra of the mechanically treated K_2PtCl_6 solid salt with the additives of K_2PtCl_4 (5 mol%). The spectra were measured (*1*) 1, (*2*) 14, (*3*) 134, (*4*) 157 and (*5*) 189 h after the completion of mechanical treatment at room temperature. The arrow indicates the EPR signal with $g = 2.0036$.

Table 1 The EPR spectra parameters for platinum(III) complexes with the axially symmetric spin-Hamiltonian.

Compound	$g_\perp$	$g_\|$	$A_\perp$/ 10^{-4} cm^{-1}	$A_\|$/ 10^{-4} cm^{-1}	Reference
Pt^{3+} in $PtCl_4$	2.18	1.98	6^a	14^a	5
Pt^{3+} in Al_2O_3	2.328	2.011	—	—	10
Pt^{3+} in $BaTiO_3$	2.459	1.950	135	0	11
Pt^{3+} in K_2PtCl_6	2.371^b	1.983^b	500^b	<65^b	This work
	2.385^c	2.000^c	511^c	0±35^c	This work
Pt^{3+} in K_2PtBr_6	2.45	1.95	317	<420	This work

^{a}Hyperfine splitting constant/mT. ^{b}At room temperature. ^{c}At 77 K.

We have found that mechanical treatment of the K_2PtCl_6 salt results in the appearance of a relatively weak EPR signal with the resolved hyperfine structure due to ^{195}Pt nuclei. As we expected, more intense signals were observed in the samples obtained by mechanical treatment of a K_2PtCl_6 powder which contained a small K_2PtCl_4 additive (5–15 mol%). The mechanical activation of K_2PtCl_6 in an atmosphere of Cl_2 does not lead to the appearance of the characteristic EPR signal. Analogous effects occurred when K_2PtBr_6 with an admixture of K_2PtBr_4 was treated. The observed spectra can be fitted to the spin-Hamiltonian of the axial symmetry:

$$H = g_\| \beta H_z S_z + g_\perp \beta (H_x S_x + H_y S_y) + A_\| S_z I_z + A_\perp (S_x I_x + S_y I_y), \qquad (2)$$

where $S = 1/2$ and $I = 1/2$ are electron and nucleus spins, respectively; β is the Bohr magneton; the other parameters are given in Table 1. The EPR spectra parameters for other known platinum(III) compounds, which are characterised by the spin-Hamiltonian of the axial symmetry, are also presented in Table 1.

The EPR spectra for the case of the axial symmetry of the spin-Hamiltonian have been simulated. The values of g-factors and hyperfine interaction constants were obtained by using the perturbation theory of the second order (Figures 1 and 2). The good agreement between experimental and simulated spectra confirms the correctness of the spectra interpretation. The occurrence of hyperfine structures in the perpendicular orientation due to ^{195}Pt isotope proves that the spectra correspond to Pt^{III} compounds. We have observed an appreciable temperature dependence of the line width [Figure 1(*b*)]. This can be attributed to the temperature-dependent spin–lattice relaxation time. No hyperfine splitting can be detected for the parallel orientation of the magnetic field even at 77 K. Hence, the hyperfine parameter $A_\|$ must be smaller than the line width. This gives a value of $(0\pm35)\times10^{-4}$ cm^{-1} at 77 K or $<65\times10^{-4}$ cm^{-1} at room temperature.

Let us compare the spectra parameters for different Pt^{III} compounds with the axially symmetric spin-Hamiltonian (Table 1). For these complexes, the $g_\|$ values are close to 2, and the values of $g_\perp$ are higher than 2. The axial character of the spectra and the g-values point[10] to the localisation of an unpaired electron at the $5d_{z^2}$ orbital, and hence to a square-pyramidal structure of the complex. Unusually high values found for the hyperfine constants of Pt^{III} compounds formed in the K_2PtCl_6 matrix probably arise from the appreciable admixture of the 6*s* orbital to the $5d_{z^2}$ orbital.[10]

The initial amount of Pt^{3+} was estimated[§] at 1×10^{18} spin g^{-1} from the EPR spectra. The intensity of the EPR signals corresponding to the Pt^{3+} ions decreased with time. The decrease of the Pt^{3+} signal intensity was accompanied by the appearance and intensity growth of the singlet with $g = 2.000$ and $\Delta H = 3$ mT (Figure 3). The decrease in the amount of paramagnetic platinum(III) ions and the simultaneous accumulation of paramagnetic centres with the g-factors close to the inherent values for free electrons apparently means that the decay of Pt^{3+} proceeds through electron transfer from platinum(III) to regenerate diamagnetic platinum(IV) and to form structural defects in the K_2PtCl_6 ion crystal matrix of the *F*-centre type. Taking into account the absence of 'free' chloride ions in the system and the diffusively retarded mobility in solids, the stoichiometric consequence of the reaction should be the formation of a coordinatively unsaturated platinum(IV) anion. As a result, the creation of the single-charged anion as a point defect in an anionic point of the lattice should be expected:

$$[PtCl_5]^{2-} \longrightarrow [PtCl_5]^{-} + e^- \ (F\text{-centre}). \qquad (3)$$

[‡] The reaction also takes place in an argon atmosphere.

[§] The concentration of Pt^{3+} was measured immediately after the mechanical treatment (for 1 h) of K_2PtCl_6 with a K_2PtCl_4 additive (15 mol%). The yield of platinum(III) formed under the same conditions but in the absence of K_2PtCl_4 was approximately equal to 2×10^{17} spin g^{-1}.

The electron transfer in reaction (3) to the point of localisation of a structural defect that is able to accept it, probably, proceeds as a relay-race charge-transfer process through the neighbouring platinum(IV) complex anions with intermediate platinum(III) formation.

The time dependence of the concentration of paramagnetic centres with $g = 2.000$ exhibits a maximum. In this case, the platinum(III) can probably serve as a sink for defects of the *F*-centre type: reduction of platinum(III) by free electrons should give platinum(II). In other words, despite the low mobility and a relatively low concentration of Pt^{3+} ions, the effective reaction of diffusively forbidden platinum(III) disproportionation into Pt^{II} and Pt^{IV} reaction should be expected in the K_2PtCl_6 solid matrix.

Thus, mechanical treatment of the solid salts K_2PtX_6 (X = = Cl, Br) leads to the formation of metastable and hence potentially reactive species: platinum(III) complexes and, possibly, coordinatively unsaturated platinum(IV) complexes. The reactivity of these compounds towards organic substrates of different nature is under study in our laboratories.

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