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Platinum-containing Paramagnetic Species in the Reactions of Pt(II) Complexes

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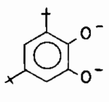
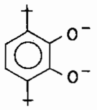
To continue the investigation of transition metal complexes with *o*-quinonic ligands [1–4] we have studied the reactions of Pt(II) and Pt(0) compounds with *o*-quinones and their one-electron reductive products. Tetrakis(triphenylphosphine)platinum, bis-(triphenylphosphine)platinum dichloride, allylplatinum(bis-triphenylphosphine)chloride, 3,5- and 3,6-di-tert-butylbenzoquinones-1,2,perchloroxantrenquinone-2,3 were used as starting reagents.

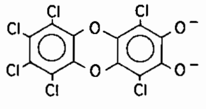
All above mentioned quinones react quantitatively with tetrakis(triphenylphosphine)platinum by oxidative addition [5, 6] at room temperature to form complexes of overall formula $(PPh_3)_2PtCat$ (I–III), where Cat is the fully reductive form of corresponding quinone:



I



II



III

Bis(triphenylphosphine)platinum catehols are orange-red crystalline compounds, the composition of which has been confirmed by element analysis.

Earlier it was shown [1, 2], that due to specific features of quinonic ligands the complexes with such substituents easily take part in redox reactions. The catecholate platinum derivatives possess analogous reactivity. These compounds are readily oxidized by such oxidants as silver trifluoroacetate, $CuCl_2$ or $FeCl_3$.

The oxidation reactions were carried out in vacuum ampouls with the molar ratio of starting reagents $(PPh_3)_2PtCat$/oxidant being 1:1 or 1:2. The process was monitored by electron paramagnetic resonance, which allowed us to register intermediate paramagnetic semiquinolate platinum complexes

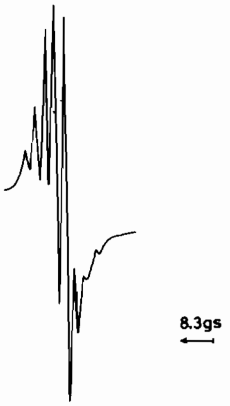


Figure 1. ESR spectrum of IVa in THF solution at room temperature.

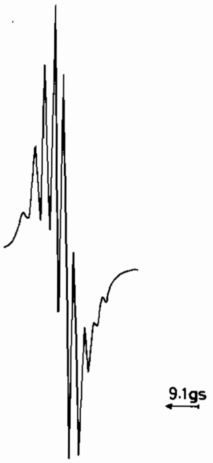
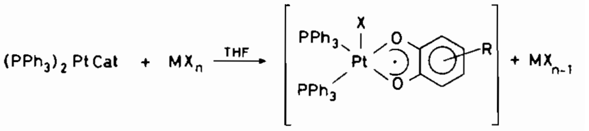
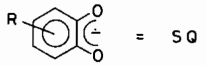


Figure 2. ESR spectrum of IVb in THF solution at room temperature.



IV (a-c)

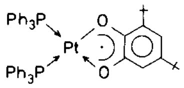
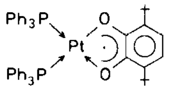
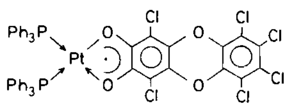


SQ is the corresponding semiquinone.

The hyperfine structure (HFS) of IV(a–c) complexes (see Fig. 1–3) confirms the unpaired electron interaction with the equal ^{31}P nuclei, one or two protons and also ^{195}Pt magnetic isotopes (I = ½, natural abundance 35%). The hyperfine coupling constants a_P and $a_{H(SQ)}$ are equal, $a_{Pt} = 4a_P$ (Table).

The comparison of isotropic g_i and hyperfine coupling of ESR spectra registered with analogous parameters of ESR spectra for corresponding 'free' *o*-semiquinolate-anions [7] indicates that the unpaired electron in IV(a–c) complexes is localized essentially on the paramagnetic *o*-semiquinolate

TABLE. ESR Spectral Parameters of $(PPh_3)_2Pt(SQ)X$.

Complex	g_i	a_{Pt}, gs	a_P, gs	a_H, gs
	1.9990 ± 0.0005	13.0	3.3	3.3
	1.9991 ± 0.0005	12.8	3.2	3.2
	2.0004 ± 0.0005	12.5	2.6	–

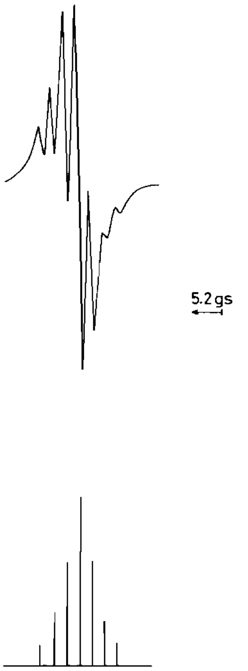


Figure 3. ESR spectrum of IVc in CH_2Cl_2 solution at room temperature.

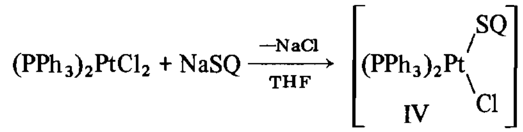
ligand. ESR spectroscopy also shows that phosphine ligands occupy the equivalent position in the relation to SQ-ligand in platinum coordinative sphere, both being near to the nodal plane of molecular orbital occupied by the unpaired electron. The last circumstance explains the low value of a_P constant. It is emphasized for comparison that A_{31_P} is 10.2–11 gs [4] in bis(triphenylphosphine)*o*-semiquinolate copper(I) derivatives. These copper(I) complexes have a distorted tetrahedral geometry which is more favourable for effective interaction of phosphine ligand orbitals with the unpaired electron molecular orbital. Thus, on the basis of these facts the compounds IV(a–c) can be inferred to be pentacoordinate complexes with tetrahedral pyramid geometry with the ligand X being at the apex.

The lifetime of *o*-semiquinolate platinum derivatives is not large during experimental conditions and is calculated, at 25 °C, to be 5 minutes for IVa and IVb complexes and 15 minutes for IVc compound. Their death is likely to be due to rapid reaction with initial oxidant by the following equation:

$$(PPh_3P)_2Pt(SQ)Cl + MX_n \xrightarrow{THF} (PPh_3)_2PtX_2 + MX_{n-1}$$

The resulting products of cateholate complexes interaction with oxidant excess, *viz.* $(PPh_3)_2PtCl_2$, CuCl or metallic silver and corresponding *o*-quinone confirm the above proposal.

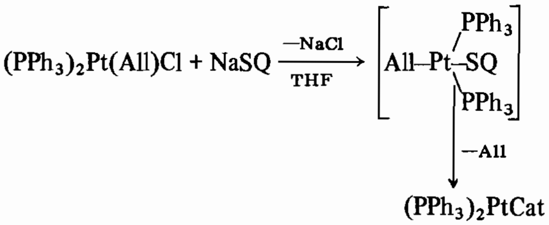
It is known that platinum(II) complexes of type L_2PtX_2 do not react with *o*-quinones [8]. However they easily interact with one-electron reductive derivatives of *o*-quinones – alkali metal *o*-semiquinolates at room temperature. The reaction of $(PPh_3)_2PtCl_2$ with sodium 3,5-di-tert-butyl-benzosemiquinolate-1,2 was carried out under vacuum at a molar ratio of starting reagents 1:1 and 1:2. With any reagent ratio the reaction products turned out to be the above described bis(triphenylphosphine)platinum cateholate, 3,5-di-tert-butyl-benzoquinone-1,2 and NaCl, but with the difference that unreacted initial platinum complex remains at a ratio 1:1. Pentacoordinate *o*-semiquinolate platinum complex of type IV can be inferred to form in this case:



$$(PPh_3)_2PtCl_2 + NaSQ \xrightarrow[THF]{-NaCl} \left[(PPh_3)_2Pt\begin{matrix}^{SQ}\\_{Cl}\end{matrix} \right]_{IV}$$

Unfortunately, we could not monitor formation of IV in the system by ESR probably due to the rapid reaction of IV with sodium *o*-semiquinolate, the latter being in excess as a result of the initial poor solubility of bis(triphenylphosphine)platinum dichloride. This leads to the reduction of semiquinolate platinum compounds at the expense of electron transfer from free *o*-semiquinone anion–radical.

It is of interest that the reaction of sodium *o*-semiquinolate with $(\mathrm{All})\mathrm{ClPt}(\mathrm{PPh_3})_2$ leads to $(\mathrm{PPh_3})_2\mathrm{PtCat}$ formation and allyl radical liberation:



$$(\mathrm{PPh_3})_2\mathrm{Pt(All)Cl} + \mathrm{NaSQ} \xrightarrow[\mathrm{THF}]{-\mathrm{NaCl}} \left[\mathrm{All{-}Pt(SQ)(PPh_3)_2}\right] \xrightarrow{-\mathrm{All}} (\mathrm{PPh_3})_2\mathrm{PtCat}$$

It should be noted that in this case the reduction of *o*-semiquinolate ligand to cateholate occurs as a result of the rapid intramolecular electron transfer from All–Pt bond to SQ-ligand simultaneously with allyl radical elimination. The formed allyl radical was detected as spin-adduct with tert-butyl-nitroso compound (allyl-tert-butyl-nitroxid radical) by ESR. Such process of intramolecular electron transfer from All–Pd bond to SQ-ligand was observed in the AllPd-SQ reaction with donor molecules [3].

Thus, experimental data suggest that the reactions of both cateholate platinum complexes with various oxidants and Pt(II) complexes of the type $(\mathrm{PPh_3})_2\mathrm{PtX^IX^{II}}$, where $\mathrm{X^I} = \mathrm{X^{II}} = \mathrm{Cl}$ or $\mathrm{X^I} = \mathrm{Cl}$, $\mathrm{X^{II}} = \mathrm{All}$, with sodium *o*-semiquinolate proceed through intermediate formation of pentacoordinate *o*-semiquinolate platinum derivatives. The latter high reactivity depends upon the ease of *o*-semiquinolate ligand redox transformation.

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