ESR study of the reaction of decacarbonyldimanganese with thallium(I) 3,6-di-*tert*-butyl-*o*-benzosemiquinolate in solutions

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The reaction of decacarbonyldimanganese $Mn_2(CO)_{10}$ (**1**) with thallium(I) 3,6-di-*tert*-butyl-*o*-benzosemiquinolate (**2**) in solution was studied by ESR spectroscopy. Irradiation of solutions containing **1** and **2** in organic solvents with visible light at 220—280 K leads to trinuclear MnTlMn complex (**3**). An analysis of hyperfine structure parameters indicates that **3** is a semiquinone complex of thallium. A possible mechanism of the formation of complex **3** and its molecular structure was discussed.

Key words: ESR spectra; thallium(I) 3,6-di-*tert*-butyl-*o*-benzosemiquinolate, decacarbonyldimanganese, interaction; paramagnetic trinuclear metal complexes.

The ability of *o*-quinones to act as acceptors of metal-centered radicals is well known.[1—3] These reactions yield *o*-semiquinone (SQ) complexes of the corresponding metals as the primary products. By now the interaction of pentacarbonylmanganese[1,3—10] formed on photolysis of decacarbonyldimanganese $Mn_2(CO)_{10}$ (**1**) with *o*-quinones has been studied in detail. No data concerning the activity of metal *o*-semiquinolates, including thallium *o*-semiquinolate, with respect to metal-centered radicals have been published.

In the present work we have studied by ESR spectroscopy the interaction of $Mn_2(CO)_{10}$ with thallium(I) 3,6-di-*tert*-butyl-*o*-benzosemiquinolate (**2**) in organic solvents (hexane, toluene, THF) under irradiation with visible light.

Solutions of a mixture of compounds **1** and **2** in THF, toluene, or hexane kept in the dark undergo no visible changes over a period of 8 h. The intensity of the ESR signal of semiquinolate **2** also does not change during this period. Irradiation of these solutions with nonfiltered visible light at 220—280 K leads to a decrease in the intensity of the ESR signal of compound **2** and to the appearance of a new signal in the ESR spectrum (Fig. 1). In hexane and toluene solutions, along with the spectrum of a new complex, the ESR spectrum of the $(3,6\text{-DBSQ})Mn(CO)_4$ complex (DBSQ is di-*tert*-butylbenzosemiquinolate) is also recorded. The latter compound is formed in the reaction of $Mn(CO)_5$ with *o*-quinone, arising in solutions of compound **2** in these solvents, according to the equilibrium[11]

$$\mathbf{2} \rightleftharpoons 1/2\ 3{,}6\text{-DBQ} + 1/2\ 3{,}6\text{-DBCatTl}_2\ , \qquad (1)$$

where DBQ is di-*tert*-butylbenzoquinone and DBCat is di-*tert*-butylcatecholate.

An analysis of the parameters of hyperfine structure (HFS) of the ESR spectrum of the new paramagnetic complex **3** indicates that it contains one Tl atom, two Mn atoms, and one radical anion of 3,6-di-*tert*-butyl-*o*-benzosemiquinone (Fig. 2, Table 1). Judging from the $a_i(H_{SQ})$ values lying in the range of 0.333—0.340 mT, compound **3** is a typical metal SQ complex in which the unpaired electron is localized on the ligand.[12]

The hyperfine coupling (HFC) constant with ^{55}Mn magnetic isotopes (100 %, $I = 5/2$, $\mu_N = 3.4611$),[13] $a_i(^{55}Mn)$, is 0.080—0.085 mT and is practically independent of the solvent and the temperature. This value is much lower than the minimum values $a_i(^{55}Mn) \approx 0.3$ mT observed for both chelate[3—10] and nonchelate SQ complexes of manganese(I).[6]

The constant of HFC with the ^{203}Tl (29.52 %, $I = 1/2$, $\mu_N = 1.5960$) and ^{205}Tl (70.48 %, $I = 1/2$, $\mu_N =$

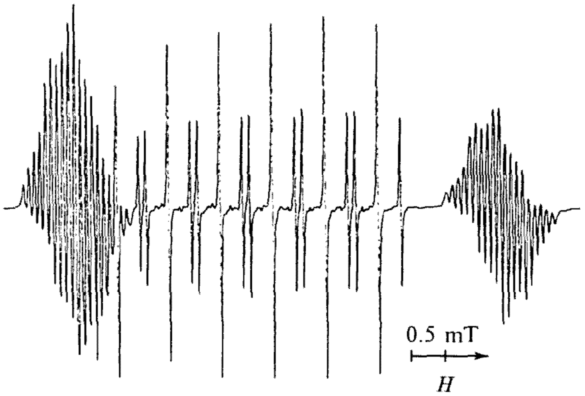

Fig. 1. ESR spectrum of complex **3** observed during photolysis of a solution of a mixture of compounds **1** and **2** in hexane (270 K); the sextet (1 : 1 : 1 : 1 : 1 : 1) of triplets (1 : 2 : 1) in the middle corresponds to the complex $(SQ)Mn(CO)_4$.

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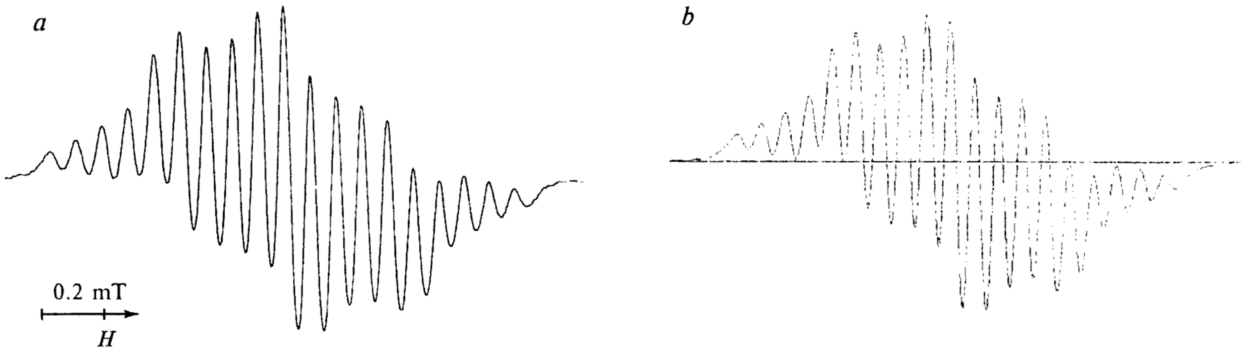
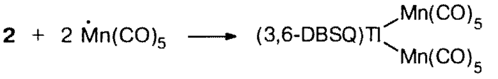


Fig. 2. High-field component of the experimental (toluene, 230 K) (*a*) and theoretical (ΔH = 0.03 mT) (*b*) ESR spectra of complex **3**.

1.6115)[13] magnetic isotopes, a_i(Tl), in the ESR spectra of complex **3** varies depending on the solvent and the temperature from 5.775 to 6.888 mT. These a_i(Tl) values are typical of thallium SQ complexes.[14–16] This makes it possible to conclude that the chelate ring of complex **3** incorporates a Tl atom.

The question of the formal oxidation state of thallium and also the state and arrangement of carbonylmanganese fragments in complex **3** has not been entirely solved. Judging from the existing experimental and published data, structure **3a**, which supposes the addition of two pentacarbonylmanganese radicals to semiquinolate **2** giving a complex of formally three-valence thallium with Tl—Mn σ-bonds, seems to be the most probable structure for complex **3**.

$$\mathbf{1} \xrightarrow{h\nu} 2\,\dot{\mathrm{M}}\mathrm{n(CO)_5} \qquad (2)$$



$$\mathbf{2} + 2\,\dot{\mathrm{M}}\mathrm{n(CO)_5} \longrightarrow \mathrm{(3,6\text{-}DBSQ)Tl}\begin{matrix}\diagup \mathrm{Mn(CO)_5} \\ \diagdown \mathrm{Mn(CO)_5}\end{matrix} \qquad (3)$$

3a

Although the a_i(Tl) parameters observed in the ESR spectra of complex **3** are approximately twice as high as the maximum values for the known thallium(III) SQ complexes,[14,15] the very strong positive dependence of a_i(Tl) on the solvating capacity of the solvent,[16] typical of thallium(I) SQ complexes, is weakly pronounced in the case of complex **3** (see Table 1). This corresponds to the assumed structure **3a** in which the coordination sphere of thallium is filled and no vacant sites are left for coordination of solvent molecules, unlike the situation existing in the structures of thallium(I) SQ complexes. The observed tendency to an increase in g_i with an increase in the solvating capacity of the solvent (see Table 1) is also more likely characteristic of thallium(III) SQ complexes.[14,15]

The a_i(Tl) values in complex **3a**, which are unusually high for thallium(III) SQ complexes, may be due to the character of its σ-substituents. The a_i(Tl) constants in the known SQ complexes of thallium(III), $\mathrm{SQTlR_2}$ (where R is alkyl[14] or aryl[15]), depend on the nature of substituents R: they increase with an increase in their σ-donor ability and their bulk. Manganese pentacarbonyl is a strong σ-donor substituent, and, hence, in complex **3a**, the effective positive charge on the Tl atom affecting the a_i(Tl) value should be lowered. Therefore, although complex **3a** is formally a complex of thallium(III), its a_i(Tl) value may be higher than those of other derivatives.

The equivalence of the Mn atoms in the ESR spectrum of compound **3** indicates that they are arranged symmetrically with respect to the plane of the complex. This is in agreement with the assumed structure **3a**. The small $a_i(^{55}\mathrm{Mn})$ value attesting to low electron spin density on the manganese atoms is also consistent with structure **3a**, in which the Mn atoms are removed from the Tl atom by no less than 2.8 Å (the sum of the covalent radii of Tl and Mn).[17]

The fact that complexes of the $\mathrm{XTl[Mn(CO)_5]_2}$ type are known in the chemistry of thallium[18–22] is also evidence in support of structure **3a**. Furthermore,

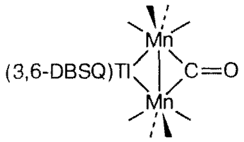
Table 1. Parameters of isotropic ESR spectra of complexes **2** and **3** in various solvents at 230 K ($\Delta g_i = \pm 0.0002$, $\Delta a_i = \pm 0.005$ mT)

Solvent	Complex 2			Complex 3			
	g_i	a_i(Tl) /mT	$a_i(\mathrm{H_{SQ}})$ /mT	g_i	a_i(Tl) /mT	$a_i(^{55}\mathrm{Mn})$ /mT	$a_i(\mathrm{H_{SQ}})$ /mT
Hexane	1.9956	2.619	0.327	2.0002	6.050	0.082	0.330
Toluene	1.9979	4.295	0.337	2.0001	6.144	0.085	0.340
THF	1.9990	6.058	0.334	2.0000	6.888	0.084	0.336

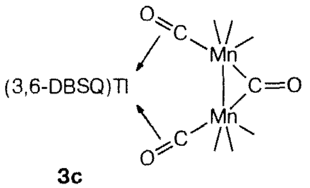
the previously made[19] assumption that the complex $\mathrm{Tl[Mn(CO)_5]_3}$ is formed *via* oxidative addition of compound **1** to $\mathrm{Tl[Mn(CO)_5]}$ (Eq. (4)), occurring on irradiation of a solution of the reactants with visible light, has been confirmed by IR spectroscopy.[22] A structural analog of **3a**, namely, the indium(III) complex $\mathrm{(acac)In[Mn(CO)_5]_2}$, has also been described.[23]

$$\mathbf{1} + \mathrm{Tl[Mn(CO)_5]} \xrightleftharpoons{h\nu} \mathrm{Tl[Mn(CO)_5]_3} \qquad (4)$$

The two other possible structures (**3b** and **3c**), which imply that $\mathrm{Mn_2(CO)_9}$, formed on decarbonylation of the initial compound **1**, has added as a neutral ligand to semiquinolate **2**,[24] are less probable.



3b



3c

Preliminary data indicate that stability of complex **3** depends on the solvent. It is stable up to 290 K in hexane solutions, while in THF it rapidly decomposes even at 250 K. The steady-state concentration of complex **3** observed depends on the intensity of the irradiation, the temperature, and the initial relative concentrations of compounds **1** and **2** as well. At higher temperatures, the rates of the variation of the intensities of the ESR signals of compounds **2** and **3** are still proportional to each other, but the relative rate of the accumulation of complex **3** decreases. This indicates that with an increase in the temperature, the rate of decomposition of this complex increases. Complex **3** may be sensitive to light, like the previously described[22] complex $\mathrm{Tl[Mn(CO)_5]_3}$, which accumulates on irradiation of a THF solution of an equimolar mixture of reactants with visible light only at −78 °C.

Due to the so high lability of complex **3**, we were not able to isolate it in the individual state. An experiment with $\mathrm{Mn_2(^{13}CO)_{10}}$ may help to obtain some additional information concerning its structure.

Experimental

Decacarbonyldimanganese (Aldrich) was purified prior to use by vacuum sublimation. Thallium(I) 3,6-di-*tert*-butyl-*o*-benzosemiquinolate was obtained by a reported procedure.[25] Organic solvents were purified by standard procedures. Photolysis was carried out directly in the resonator of a radiospectrometer. An incandescent lamp (KGM 24-150) equipped with a focusing device was used as the radiation source. The ESR spectra were recorded on a Bruker ER 200D SRC spectrometer with a standard (ER 4102 ST) or double (ER 4105 DR) resonator (operating at 9.35 MHz). The temperature of the samples was controlled using an ER 4111 VT temperature-control unit. The *g*-factor was determined using diphenylpicrylhydrazyl as the reference compound.

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