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A Brief Study on Organomercury Compounds

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ABSTRACT: The effects of five organomercury compounds (methylmercuric chloride, phenylmercuric acetate, phenylmercuric borate, phenylmercuric citrate, and diphenylmercury) on photosynthetic electron transport (PET) in spinach chloroplasts were studied. The structures of organomercury compounds have been studied in terms of the secondary bonds formed by mercury atoms with the surrounding atoms. These connections, albeit labile, have a significant influence on the crystal structure, as seen by a unique coordination around the mercury atom. This influence must be investigated thoroughly because the mercury coordination polyhedra in the crystal structure of organomercury compounds are far from regular. The review has been limited to structures in which the secondary bonds of mercury are shorter than the sum of the van der Waals. The upper limit of distances within the coordination polyhedron cannot be clearly demonstrated, however distances greater than the total of the van der Waals radii may also have an impact on the structure. Long-range interactions may have a significant impact on both the overall molecular structure and the stability of secondary bonds. The long-range interactions mimic the solvation effect in chemical reactions in solutions. From this perspective, X-ray diffraction data are valuable for studying the chemical reaction mechanism in the organic chemistry of mercury.

KEYWORDS: EPR spectroscopy, organomercurials, photosynthetic electron transport

I. INTRODUCTION

Mercury is one of the nitrogen/sulphur-seeking metals classified as class B, which are distinguished by their high affinity for the N- and S-donor ligands found in many biomacromolecules [1]. As a result, Hg^{2+} ions have a higher affinity for sulfur-containing amino acids than for other amino acids. They attack -SH bonds, and Hg^{2+}'s predilection for sulfhydryl and thioether groups at catalytically active sites in enzymes provides the biochemical basis for much mercury toxicity. The formation constant for Hg^{2+} and the anionic form of a sulfhydryl group R-S- is $\geq 10^{10}$-fold larger than that determined for carboxyl or amino groups [2]. Mercury exhibits many adverse effects on plants, eg it inhibits seed germination and seedling growth of higher plants [3, 4] and toxic effects of mercury are reflected also by decrease of the total protein content [5], reduction of water content, chlorophyll concentration and nutrient translocation in plants [6-8] as well as by reduced photosynthesis and transpiration [9]. In Euglena gracilis, $HgCl_2$ inhibited synthesis of chlorophyll [10]. Atsublethal concentrations mercury displaced the Mg^{2+} ion of the tetrapyrrol ring, causing imbalances in protochlorophyll formation as well as affecting both chlorophyll synthesis and degradation [11]. Mercury ions can form more or less stable complexes with many biomolecules, what is reflected also in their effectiveness related to the inhibition of photosynthetic processes in algae and plant chloroplasts. Hg^{2+} ions are able to interact with some components of the photosynthetic electron transport (PET) chain, eg with plastocyanin on the donor side of photosystem (PS) 1 [12, 13], with ferredoxin [14] or with FB-iron-sulphur cluster [15] which are localized on the acceptor side of PS 1. Further possible sites of Hg^{2+} ions action are situated in the oxygen evolving complex [14, 16, 17], in the core of PS 2 [18] and between QA and QB on the acceptor side of PS 2 [19]. On the other hand, there is less data in the literature concerning the effects of organomercury compounds on photosynthesis. Phenylmercuric acetate inhibited Hill activity, ferredoxin-NADP oxidoreductase and photophosphorylation [20, 21]. Godbold and Huttermann [22] found that photosynthesis was inhibited to a lower extent in spruce plants exposed to $HgCl_2$ than in those exposed to methylmercuric chloride. Singh and Singh [23] observed a synergetic effect at the application of CH_3HgCl in combination with $HgCl_2$. Phenylmercuric acetate is known to be a pesticide and is used as an ingredient in Agrosan preparation [24]. Phenylmercuric borate is known as a local external antiseptic agent. The toxic effect of methylmercury cation ($MeHg^+$) on the photosynthetic activity of Chlorella vulgaris was shown to increase under high illumination and unfavourable low temperature. Increased toxic action of $MeHg^+$ resulted from the decreased capacity of PS 2 for reparation [25]. Kukarskikh et al [26] determined chlorophyll fluorescence parameters in green microalgae

Chlamydomonas reinhardtii and found that after MeHg+ treatment algal cells indicated damage on the donor side of PS 2 and impairment of the electron transfer from QA to QB occurred. A disturbance of the electron transfer between photosystems was also confirmed by an increase in the steady-state level of P700 photooxidation. The above results demonstrated that MeHg+ treatment damaged the PET at several sites, although the inhibitory effect of MeHg+ on photosynthetic processes of algae was much stronger than the effect of HgCl2. Antal et al [27] investigated the effect of HgCl2 and MeHg+ on photosynthetic activity of diatom Thalassosiraweissflogii and found that MeHg+ applied in the concentration range 10–6-10–7 mol dm–3 decreased the photochemical activity of the PS 2 reaction centres in cells of this microalgae after a prolonged lag phase, whereas HgCl2 decreased the activity of PS 2 only at higher concentrations. Similar results were obtained by Graevskaya et al [28]. However, these authors observed that PS 2 inactivation by MeHg+ was not complete and about 10% of the cells kept high level of PS 2 activity, suggesting the adaptation of algae to the MeHg+ treatment. Methylmercury chloride and HgCl2 decreased the rate of PS 2 reparation and increased a heat pathway of excitation dissipation in PS 2 antennae complex. Different toxic effects of mercuric chloride and methylmercuric chloride on the freshwater alga Poterioochromonasmalhamensis were reported by Röder [29]. The goal of this work is to determine the site and mode of action of organomercury compounds (methylmercuric chloride, phenylmercuric borate, phenylmercuric acetate, phenylmercuric citrate and diphenylmercury) in photosynthetic apparatus of spinach chloroplasts.

It is known that o-semiquinone radical ligands can serve as spin labels in the coordination sphere of a metal atom.[30] Any changes in the coordination environment of the metal center are reflected in the EPR spectra, thus allowing one to rapidly obtain reliable information on structural features of complexes in solution, e.g., investigate the dissociation or exchange of neutral ligands, the solvation, and the expansion or dynamics of the coordination sphere.[31-37] The stability of compounds containing o-semiquinonetype ligands, including their resistance to changes in the external conditions (temperature, solvent, and so on), is of importance. Many known maingroup metal mono-o-semiquinone complexes are unstable, which hinders their isolation and investigation. In particular, most of the studied mercury(II) o-semiquinolate compounds decompose in solution already at –20 °C (the most stable ones remain unchanged overnight), and they were characterized mainly by EPR.[38-41] An interesting feature of these complexes is that the hyperfine coupling constants of magnetic mercury isotopes (199,201Hg) depend on the steric properties of alkyl substituents bound to the metal atom.[42] However, the structures of these paramagnetic derivatives have not been studied in more detail because of their low stability, and the nature of this dependence remains unclear.There are a few stable mercury(II) radical complexes containing nitronylnitroxide and nitroxide radicals, in which the paramagnetic ligand is linked to the metal atom by either a covalent [43-46] or a donoracceptor bond.[46]Recently, it has been shown that the replacement of the o-benzoquinone ligand by its nitrogensubstituted analog, viz., 4,6-di-tert-butyl-N-(2,6-diisopropylphenyl)o-iminobenzoquinone (imQ), made it possible to synthesize the stable paramagnetic phenylmercury(II) complex (1), which was isolated in the individual state and characterized by EPR spectroscopy and X-ray diffraction.
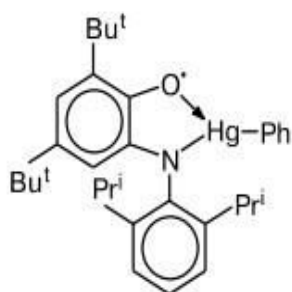
Compound. 1

It was found that compound **1** has a spin density distribution uncommon for this type of complexes, is characterized by the unusual geometry of the ligand environment of the metal center, and exhibits a dependence of the hyperfine coupling constants ai (199,201Hg) on the solvent. The present study is a continuation of the research on the structural

features of new stable mercury(II) o-imino-benzosemiquinolate complexes containing different alkyl and aryl substituents at the metal atom.

Chloroplast preparation:

Chloroplasts were prepared from spinach (Spinacia oleracea L.) purchased locally by the procedure of Walker [47] partly modified by Sersen et al [48] using a TRIS buffer (20 mmol dm–3; pH = 7.0) containing 0.4 mmol dm–3 saccharose and 20 mmol dm–3 MgCl2. The chlorophyll content was determined according to Wellburn [49].

Measurements of PET: The photosynthetic electron transport through PS 2 and PS 1 in the suspension of spinach chloroplast (30 mg Chldm–3) was measured in a phosphate buffer (pH = 7.2) containing 5 mmol dm–3 MgCl2, 15 mmol dm–3 NaCl and 0.4 mmol dm–3 saccharose according to the work of Xiao et al [33]. By monitoring the rates of photoreduction of artificial electron acceptor DCPIP (40 µmol dm–3) the electron transport through PS 2 was determined. On the other hand, the PET through PS 1 was monitored by photooxidation of DCPIPH2 in the same buffer as in previous experiment. In the control sample the supply of electrons from PS 2 to PS 1 was stopped by DCMU (20 µmol dm–3) and sodium ascorbate (40 µmol dm–3) as an artificial electron donor of PS 1 and methylviologen (0.1 mmol dm–3) as a final electron acceptor of PS 1 was used in this experiment. The investigated photoprocesses were recorded spectrophotometrically as changes in the absorbance of DCPIP at 595 nm, ie as its decrease (in the case of PET through PS 2), or its increase (in the case of PET through PS 1). The incubation time after adding of studied compounds to chloroplast suspension was approximately 1 min in both experiments. The irradiation of the chloroplast suspension was carried out by a 250 W halogen lamp through a 5 cm water filter. The intensity of irradiation was 900 µE m–2 s –1 PAR (photosynthetically active radiation). Due to low aqueous solubility of studied organomercury compounds, these were dissolved in DMSO. The DMSO content up to 4% did not affect the photochemical activity in spinach chloroplasts.

EPR measurements:

The first derivative EPR spectra were recorded at following instrument parameters: microwave power 5 mW; modulation amplitude 0.5 mT; sweep of magnetic field 20 mT; registration time 6 min; recorder time constant 0.5 s. The chloroplast suspensions placed in a flat cell were irradiated directly in the resonator from 0.5 m distance using a 250 W halogen lamp (280 µE s–1 m –2 PAR) through a 10 cm water filter to exclude warming of the samples. The content of Chl in the samples was 4 g dm–3, the molar ratio Chl : inhibitor was ~ 0.1. The studied organomercury compounds were added into the chloroplast suspension in the form of DMSO solution and the incubation time after adding of studied compounds was approximately 5 min. The DMSO content in the samples (10%) had no observable effect on the EPR spectra of chloroplasts.All the above mentioned experiments were carried out at a room temperature of 25ºC.

II. LITERATURE REVIEW

Compounds 1—10 were synthesized by the metathesis reaction of the monosodium salt of o-iminobenzoquinone (imSQNa) with the organomercury reagent RHgX in tetrahydrofuran in the absence of atmospheric oxygen and moisture (Scheme 1). The reaction is completed in a few minutes and is accompanied by a change in the color from blue, which is typical of imSQNa, to emeraldgreen (in the case of compound 10, to violet). Mercury(II) complexes (imSQHgR) 1—10 were isolated as intensely colored crystalline compounds.
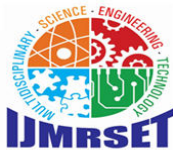
Scheme 1
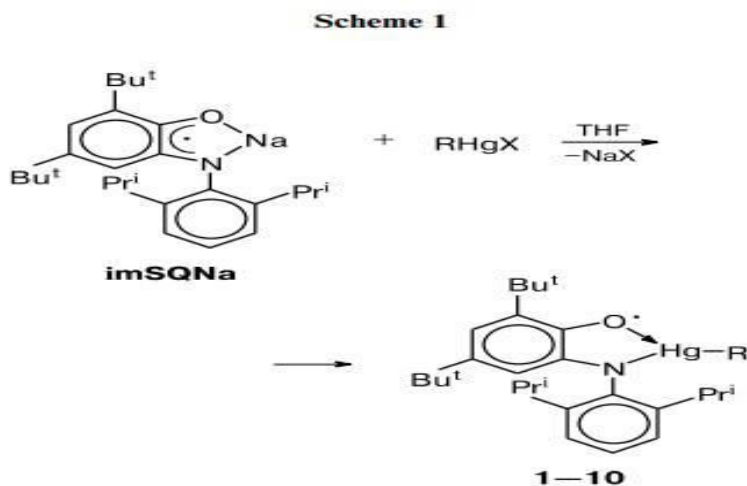
X = Cl, OAc; R = Ph (1), Et (2), Prn (3), Bun (4), Pri (5), Hexc (6), CH2SiMe3 (7), pFPh (8), Fc (9), pMe2NPh (10)

Like compound 1, [31] all the newly synthesized complexes yield wellresolved EPR signals (Fig. 1) as a triplet (1 : 1 : 1) of doublets (1 : 1) attributed to the coupling of an unpaired electron with the nitrogen atom 14N (99.63%, I = 1, μN = 0.4037)[50] and the proton 1H (99.98%, I = 1/2, μN = 2.7928)20 at position 5 of the o-iminoquinone ring. The EPR spectra of all complexes also show a satellite splitting on the magnetic mercury isotopes 199Hg (17.0%, I = 1/2, μN = 0.5059) and 201Hg (13.2%, I = 3/2, μN = –0.5602).[50] The parameters of the EPR spectra of compounds 1—10 are given in Table 1. It should be noted that the distinguishing feature of the EPR signals for the whole series of the synthesized mercury o-iminosemiquinone complexes is a small value of the hyperfine coupling constant ai (1H). This constant is, on average, 0.25 mT, whereas main group metal o-iminobenzosemiquinone complexes are characterized by larger constants (~0.35 mT).[51] The value of ai (1H) in the range of 0.18—0.20 mT is typical of metaprotons in phenoxyl radicals.[52] This indicates thatan excess spin density in complexes 1—10 is concentrated at the oxygen atom, i.e., the o-iminobenzosemiquinone ligand shows the coordination mode similar to that of the amidophenoxy ligand.
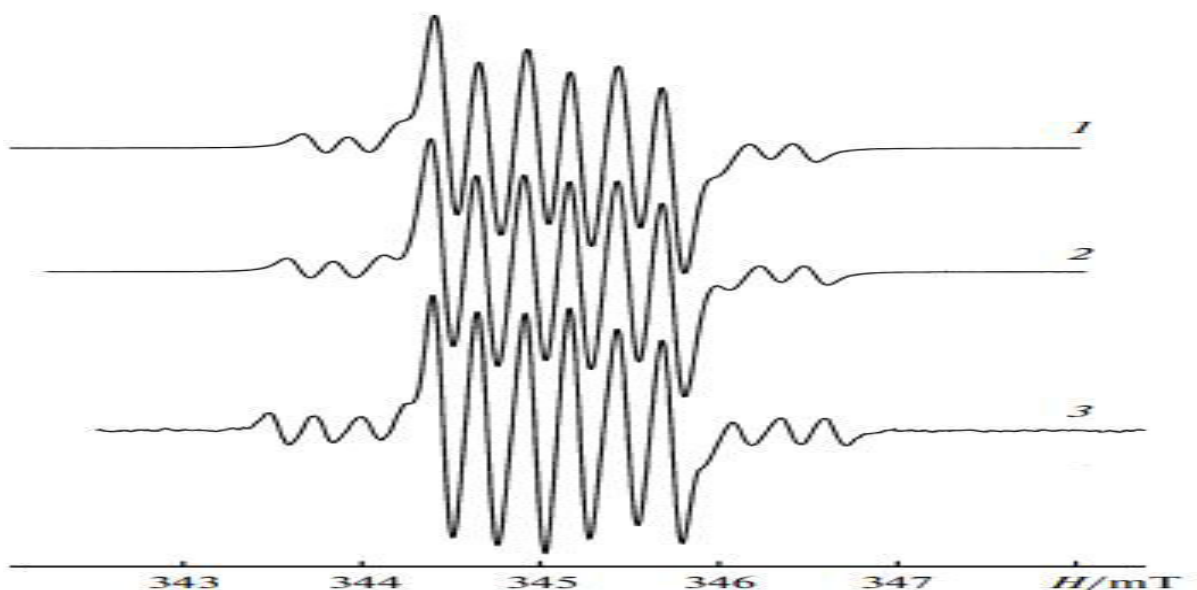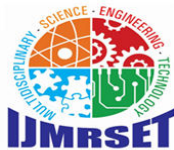

Fig. 1. Isotropic EPR spectrum of complex 10 in hexane (1), THF (2), and pyridine (3) at T = 298 K.

The abovedescribed structural features of the complexes were confirmed by X-ray diffraction data for compounds 3, 7, and 9. The molecular structures of the complexes are shown in Fig. 2. Selected bond lengths and bond angles in the complexes are given in Table 2. According to the X-ray diffraction data, the coordination units in complexes 1, 19 3, 7, and 9 have similar structures. The mercury atom in compounds 3, 7, and 9 is in a trigonal T-shaped environment and is located close to the plane formed by the O(1), N(1), and C(27) atoms (the deviations from the plane are 0.018, 0.011, and 0.012 Å for 3, 7, and 9, respectively; the corresponding value for 1 is 0.071 Å19). The N(1)—Hg(1)—C(27) angle is close to 180° and is in the range of 167.2(3)—174.05(15)°. The O(1)—C(2) bond lengths in compounds 1, 3, 7, and 9 are in the range of 1.261(4)—1.2681(19) Å and are slightly smaller than the corresponding lengths in most of the structurally characterized metal complexes containing the monoreduced form of the o-iminobenzoquinone ligand. On the contrary, the N(1)—C(1) bond length (1.337(9)—1.344(2) Å) is typical of metal o-iminosemiquinolate complexes.[53] The Hg—N and Hg—O bond lengths are unusual for the radical aniontype coordination of imQ. As a rule, the metal—oxygen and metal—nitrogen bond lengths in metal complexes with o-iminosemiquinone radical anions are slightly larger than the sums of the covalent radii of the corresponding elements.[51,52,53] In the mercury radical complexes under consideration, the Hg(1)—N(1) bond (2.080(6)—2.1067(14) Å) is slightly shorter, whereas the Hg(1)—O(1) bond (2.485(2)—2.500(5) Å) is substantially longer than the corresponding sum of the covalent radii of the elements (Hg—N, 2.11 Å; Hg—O, 2.10 Å).[54] This indicates that the former bond is strong covalent, whereas the latter bond is weak donoracceptor. These characteristics provide evidence that the coordination of the radical ligand in the synthesized paramagnetic mercury(II) complexes is much more similar to the amidophenoxytype mode than to the typical o-iminosemiquinone mode. The sixmembered ring C(1)—C(6) displays an orthoquinoidtype distortion characteristic of o-iminosemiquinones[51,53,54] and it is manifested in the alternation of the C—C bond lengths. Thus, the C(1)—C(2), C(1)—C(6), C(2)—C(3), and C(4)—C(5) distances are in the range of 1.417(11)—1.475(10) Å and they are much longer than the C(3)—C(4) and C(5)—C(6) bonds (1.348(5)—1.375(2) Å).

Table 1. EPR parameters of complexes 1—10 (hexane, 298 K)

Complex	$a_i(^1H)$	$a_i(^{14}N)$	$a_i(^{199}Hg, ^{201}Hg)$	g
			mT	
imSQHgPh (1)	0.23	0.51	1.30; 0.48	1.9964
imSQHgEt (2)	0.25	0.52	0.68; 0.25	1.9969
imSQHgPr^n (3)	0.25	0.52	0.67; 0.25	1.9970
imSQHgBu (4)	0.25	0.53	0.68; 0.25	1.9970
imSQHgPr^i (5)	0.25	0.53	0.32; 0.12	1.9968
imSQHgHex^c (6)	0.26	0.54	0.32; 0.12	1.9968
imSQHgCH$_2$SiMe$_3$ (7)	0.25	0.53	1.18; 0.44	1.9974
imSQHg(p-FPh) (8)	0.25	0.51	1.42; 0.52	1.9964
imSQHgFc (9)	0.24	0.51	1.72; 0.63	1.9971
imSQHg-(p-Me$_2$NPh) (10)	0.24	0.52	1.42; 0.52	1.9970

This patterns differs from the alternation of the bond lengths in phenoxyl radicals, where the short bonds are separated by two long bonds[55] (the socalled paraquinoidtype distortion). Therefore, a weak coordination of the oxygen center to the mercury atom in amidophenoxyl leads to a change in the typeof distortion of the radical ligand from paraquinoid to orthoquinoid. A method was proposed [52] for the analysis of the C—C, C—O, and C—N bond length distribution in metal o-iminoquinone complexes to estimate the formal oxidation state of the redoxactive ligand. The formal oxidation states of the o-iminosemiquinone ligands in complexes 1, 3, 7, and 9 calculated according to this method are –0.61, –0.58, –0.69, and –0.44, respectively. It was noted that such considerable deviations from an integer value are characteristic of complexes with a substantial degree of π-donation from the ligand to the metal. This intramolecular donoracceptor interaction can account for the T-shaped coordination environment of the mercury atom. The fact that the N(1)—Hg(1)—C[56] angle is close to 180° attests to the nearly sp hybridization of the metal orbitals. Due to two sphybridized orbitals, the mercury atom forms two covalent bonds with the nitrogen atom of the redoxactive ligand and the carbon atom of the alkyl (aryl) substituent. This hybridization state can be stabilized by an additional interaction

between the free unhybridized p orbital of the metal atom and the π-system of the o-iminoquinone ligand. Another orthogonal unhybridized p orbital is involved in the coordination bonding of the phenoxyl oxygen atom. As can be seen from Table 1, the hyperfine coupling constant of the magnetic mercury isotopes in the EPR spectra is very sensitive to the nature of the hydrocarbon substituent at the metal atom. Its value increases by almost a factor of three in going from the isopropyl substituent to the ferrocenyl substituent (from 0.67 (R = Pr^i) to 1.72 mT (R = Fc) in hexane). The proton and nitrogen hyperfine coupling constants remain unchanged within experimental error. An analysis of the structural parameters for complexes 1, 3, 7, and 9 shows that the increase incients are in the range of 0.77—0.97 (the constants ai (199Hg) in pyridine are not included in the correlation). The hyperfine coupling constant of the magnetic mercury isotopes increases with increasing polarity of the solvent.
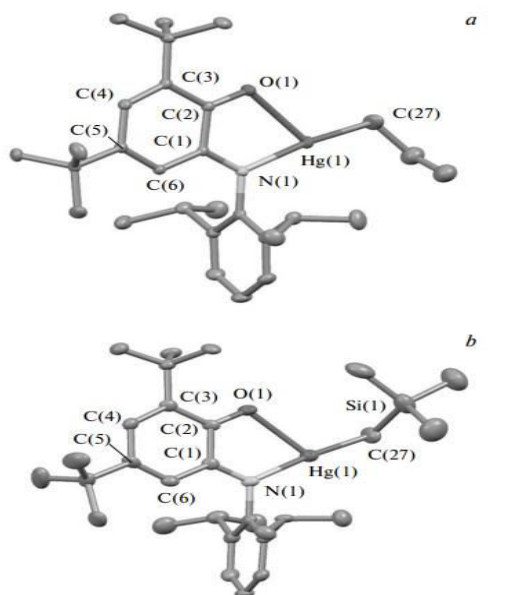

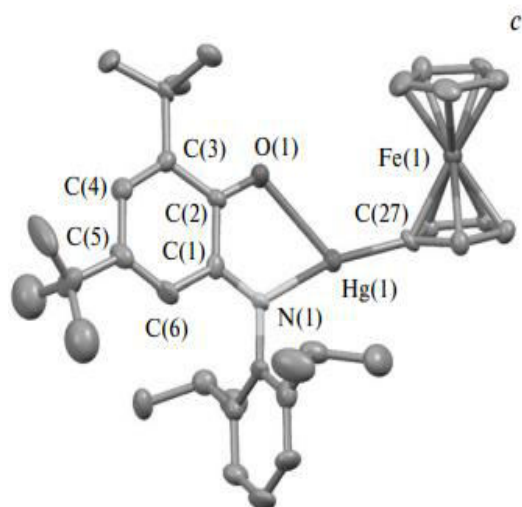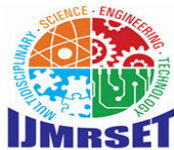**Fig. 2. Molecular structures of complexes**

Fig. 3; The thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted.

It is noteworthy that the hyperfine coupling constants found in pyridine do not fit the nearly linear a_i (^{199}Hg) — ET plots. This indicates that the polarity of the solvent is not the only parameter that has an effect on the spectroscopic characteristics of the resulting radical complexes. Taking into account that pyridine is a strongly coordinating solvent capable of forming strong donoracceptor bonds with metal cations, the solvation mechanism of the solvent effect on the constant a_i (^{199}Hg), which has been described earlier for o-semiquinone and o-iminosemiquinone derivatives of thallium(I)6,28 and lead(II),8 cannot be ruled out as well. The solvation mechanism is additionally confirmed by the temperature dependence of the EPR spectra of complexes 1—10. As the temperature decreases, the equilibrium shifts to the right (Scheme 2), resulting in an increase in the hyperfine coupling constant of the magnetic metal isotopes.[6,8,28] An increase in the donor number of the solvent should lead to an increase in the heat of solvation, which determines the sensitivity of the equilibrium reaction (see Scheme 2) to changes in the temperature. Actually, the change in the donor properties of the solvent affects the slope of the linear dependence a_i (^{199}Hg). The latter is more than two times larger in pyridine than in hexane. In the series of compounds 1—10, complex 9 containing two redoxactive centers, viz., the o-iminosemiquinolate ligand and the ferrocenyl substituent, is of particular interest. Hence, the redox properties of complex 9 were studied by cyclic voltammetry (CV). According to the CV data, compound 9 undergoes three reversible oneelectron redox steps in the potential range under study.
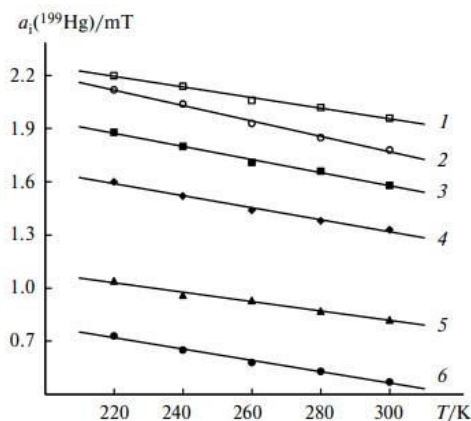

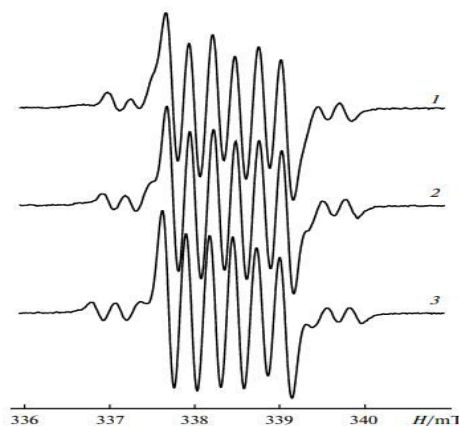**Fig. 4. Isotropic EPR spectrum of complex 7 in THF at 300 (1), 260 (2), and 220 K (3)**

Fig. 5. Effect of the temperature on the hyperfine coupling constant a_i (^{199}Hg) for complexes 1 (3), 3 (5), 6 (6), 8 (2), 7 (4), and 10 (1) in THF.
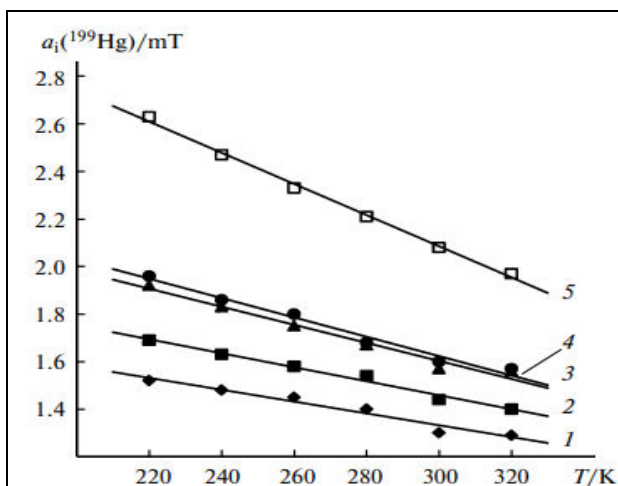
Fig. 6. Effect of the temperature on the hyperfine coupling constant ai (199Hg) for complex 1 in hexane (1), toluene (2), ethyl acetate (3), THF (4), and pyridine (5).
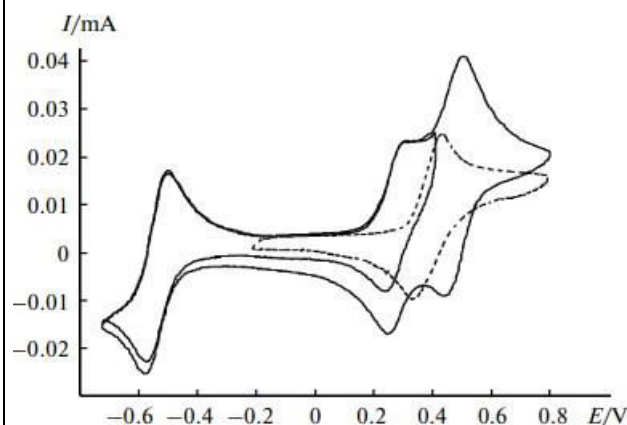

Fig. 7. Cyclic voltammetry for complex 9: the solid line indicates the starting complex; the dashed line indicates the electrolysis product at +0.39 V (CH2Cl2—CH3CN, 1 : 1); V = 0.2 V s–1, Ag/AgCl/KCl, C = 2•10–3 mol L–1, glassy carbon electrode, Ar, 0.1 M Bu4NClO4.

The reversible reduction of the o-iminobenzosemi quinone ligand is observed during a cathodic potential scan at ERed 1/2 = –0.55 V. The oxidation of complex 9 involves two consecutive oneelectron steps (EOx1 1/2 = = 0.27 V; EOx2 1/2 = 0.48 V). In the potential range under consideration, both the ferrocenyl and o-iminobenzosemiquinone moieties can be equally involved in electrochemical transformations. To reveal the sequence of redox transformations, we performed the electrolysis of complex 9 for three hours at a controlled potential of 0.39 V. In the range from 650 to 900 nm, the absorption spectrum of the starting compound 9 shows a broad band corresponding to the charge transfer in the imSQ moiety. Similar lowintensity absorption bands have been observed earlier and are characteristic of metal o-iminosemiquinolate complexes.[57] The electrolysis is accompanied by the disappearance of the absorption band in the longwavelength region of the spectrum and the appearance of a new band with a maximum at 393 nm characteristic of free o-iminobenzoquinone.[58] The changes in the electronic absorption spectrum are consistent with the results of the electrochemical experiment. Thus, the first redox transition is absent in the cyclic voltammetry curve, and the potential of the second anodic step shifts to 0.39 V. The cathodic branch shows the reduction peak of the o-iminobenzoquinone ligand at –0.78 V.31 These data suggest the mechanism of redox transformations of complex 9 presented in Scheme 3. The monocationic complex generated during the electrolysis at a controlled potential is unstable and undergoes decomposition accompanied by the release of free o-iminobenzoquinone from the coordination sphere. The formation of the latter is evidenced by the electrochemical and spectroscopic data. Consequently, of the two potential redox centers in complex 9, the o-iminosemiquinone ligand is involved in the first electrochemical step followed by the oxidation of the ferrocenyl moiety. To summarize, we synthesized for the first time a series of stable organomercury compounds based on the o-iminosemiquinone ligand. In these derivatives, the amido phenoxytype coordination mode of the radical ligand prevails. It was shown that the hyperfine coupling constant of the magnetic mercury isotopes in the paramagnetic complexes depends not only on the nature of the hydrocarbn substituent at the metal atom but also on the properties of the solvent, in which the EPR spectrum is recorded. Not only the increase in the polarity of the medium but also the ability of the solvent molecules to be involved in specific solvation cause an increase in the constant ai (199,201Hg).
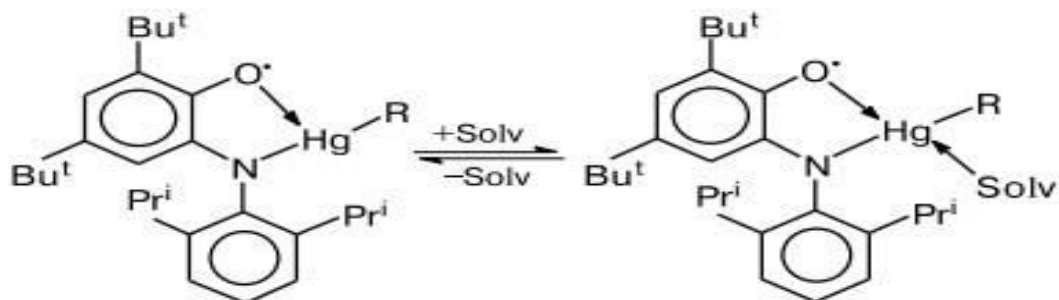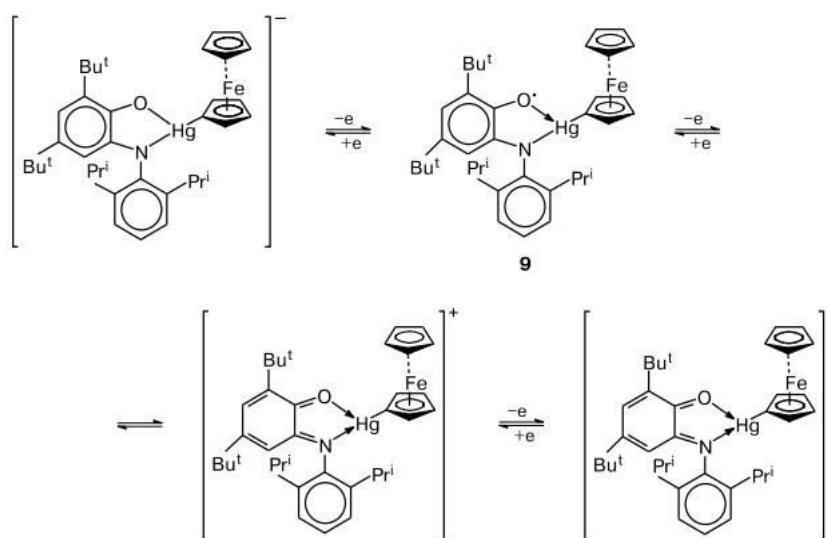
Scheme 2

Scheme 3

III. EXPERIMENTAL

Experiments on the synthesis and investigations of mercury (II) o-iminobenzosemiquinolate complexes were carried out under reduced pressure in the absence of traces of oxygen and water. The IR spectra were recorded on a FSM-1201 Fourier trans form infrared spectrometer in Nujol in KBr cells. The electronic absorption spectra were measured on a PerkinElmer Lambda 25 spectrometer. The EPR spectra were recorded on a Bruker EMX spectrometer using 2,2-diphenyl-1-picrylhydrazyl (g = 2.0037) as the reference for the determination of the g factor. The precise parameters were determined by simulating the EPR spectra with the use of the Bruker WinEPRSimFonia software. The oxidation potentials were measured under an argon atmosphere by cyclic voltammetry in a threeelectrode electrochemical cell using an IPC-pro potentiostat. A stationary glassy carbon electrode (d = 2 mm) was used as the working electrode, a platinum plate (S = 18 mm2) served as the auxiliary electrode, and a silver chloride electrode (Ag/AgCl/KCl) with a waterimpermeable membrane was used as the reference electrode. The potential scan rate was 0.2 V s–1; 0.1 M Bu4NClO4 (99%, accros), which was twice recrystallized from aqueous EtOH and dried in vacuo at 50 °C for 48 h, served as the supporting electrolyte. The microelectrolysis of complex 9 was performed using a PI-50-1.1 potentiostat and stationary platinum electrodes (S = 30 mm2) in an undivided threeelectrode cell (V = 2 mL) at a potential of 0.39

V. The electrolysis time was 3 h. The conversion of complex 9 was 98 %. An (Ag/AgCl/KCl) electrode with an electroconductive waterimpermeable membrane was used as the reference electrode. The solvents were purified and dehydrated according to recommendations.[59] Organomercury compounds RHgCl (R = Et, Prn, Bun, Pri ,Hexc, CH2SiMe3, Ph, p-F-Ph, Fc),33 RHgOAc (p-Me2N-Ph),[60] and sodium o-iminobenzosemiquinolate imSQNa21 were synthesized according to known procedures. The compound imSQNa was used in the in-situ synthesis. The complex imSQHgPh (1) was synthesized according to a procedure described earlier.19 Synthesis of complexes 2—10 (general procedure). A solution of sodium o-iminobenzosemiquinolate (0.8 mmol) in THF (20 mL) was slowly added to a solution of the organomercury compound RHgCl (0.8 mmol) in the same solvent (10 mL), which was accompanied by a change in the color of the reaction mixture from brightblue to emeraldgreen (in the case of complex 10, to violet). Then the solution was kept at ~20 °C for 20 min, the solvent was removed under reduced pressure, the dry residue was treated with hexane (25 mL), and a precipitate of NaCl or NaOAc was filtered off on a Schott glass filter (porosity 4). Hexane was removed under reduced pressure, and the residue was dissolved in ethanol. The solution was kept at –18 °C overnight. Crystals of mercury o-iminobenzosemiquinolate complexes were separated from the mother liquor by decantation and dried under reduced pressure. Complex 10 was crystallized from hexane at –18 °C. In the case of compound 9, the dry residue obtained after the removal of hexane was dissolved in pentane. Then the solvent was kept at –18 °C to obtain a crystalline product. In the crystalline state, all mercury (II) o-iminobenzosemiquinolate complexes are stable to atmospheric moisture and oxygen. Solid samples decompose without melting upon heating above 130 °C. The compounds are readily soluble in most of organic solvents.

Table 2. Crystallographic characteristics and the Xray data collection and structure refinement statistics for complexes 3, 7, and 9

Parameter	3	7	9
Molecular formula	$C_{29}H_{44}HgNO$	$C_{30}H_{48}HgNOSi$	$C_{36}H_{46}FeHgNO$
Molecular weight	623.24	667.37	765.18
Temperature/K	100(2)	100(2)	150(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2(1)/n$	$C2/c$	$P2(1)/c$
a/Å	13.5652(3)	25.758(3)	20.023(3)
b/Å	12.7584(2)	14.8399(14)	14.710(3)
c/Å	17.5357(3)	20.801(2)	11.2383(19)
α/deg	90	90	90
β/deg	112.7028(19)	128.0320(10)	101.557(4)
γ/deg	90	90	90
V/Å	2799.77(9)	6262.9(10)	3243.0(10)
Z	4	8	4
ρ_{calc}/g cm^{-3}	1.479	1.416	1.567
μ/mm^{-1}	5.517	4.974	5.203
$F(000)$	1252	2696	1532
Crystal dimension/mm	0.20×0.10×0.10	0.20×0.08×0.05	0.14×0.13×0.05
θ-Scan range/deg	3.19—30.00	2.02—26.00	1.73—26.00
hkl ranges	$-19 \le h \le 19$	$-31 \le h \le 31$	$-24 \le h \le 22$
	$-17 \le k \le 17$	$-18 \le k \le 18$	$-18 \le k \le 17$
	$-24 \le l \le 24$	$-25 \le l \le 25$	$-8 \le l \le 13$
Number of reflections	54185	26530	18598
Number of unique reflections	8119	6158	6345
R_{int}	0.0375	0.0815	0.0872
GOOF (F^2)	1.046	0.990	1.042
R_1/wR_2 ($I > 2\sigma(I)$)	0.0213/0.0481	0.0417/0.0798	0.0603/0.1265
R_1/wR_2 (based on all reflections)	0.0287/0.0504	0.0753/0.0872	0.1092/0.1395
Residual electron density density ρ_{max}/ρ_{min}/e Å^{-3}	1.261/–1.068	1.760/–0.638	3.842/–1.766

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IV. CONCLUSION

The organomercury compounds phenylmercuric borate, phenylmercuric acetate, phenylmercuric citrate, and methylmercuric chloride all suppressed PET in spinach chloroplasts. Their IC50 values were nearly ten times greater than those found for HgCl2. The reduced inhibitory efficiency of organomercury compounds can be attributed to their interaction with amino acid residues in peptides, yet their stability constants are consistently lower than those of the comparable complexes generated with HgCl2. Based on the EPR results, we propose that the sites of action for the examined organomercury compounds are QA or QB quinones on the acceptor side of PS 2 and the terminal ferredoxin acceptor in PS1. Covalent mercuration of nucleic acids before the effective chemical synthesis of oligonucleotides. Organomercury nucleic acids were, hence, first employed in applications that do not rely on site-specific mercuration, such as density labelling for pycnographic analysis or affinity tagging. These applications largely fell out of favour before oligonucleotide synthesis became mainstream, leaving their full potential unattained. Recently, synthetic oligonucleotides site-specifically mercurated at predetermined natural or artificial hot spots have brought about a renaissance of organomercury nucleic acid chemistry. Potential new applications include the use of organomercury oligonucleotides as hybridization probes, notably in SNP genotyping. The scope of some established applications, such as radiolabelling through halodemercuration, could potentially be expanded to oligonucleotides. Finally, while coordinative Hg^{II}-mediated base pairing has already been harnessed in DNA nanotechnology, the use of organomercury oligonucleotides in this field remains an unexplored but interesting possibility.

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