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Redox Reactions Involving the Indium(III) Catecholate Complexes

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Abstract—Indium catecholate complexes 3,6-CatInR (3,6-Cat is the 3,6-di-*tert*-butyl-*o*-benzoquinone dianion (3,6-Q), R = Me (**I**) and Et (**II**)) are synthesized by the exchange reaction between $RInI_2$ and thallium catecholate 3,6-$CatTl_2$. Compounds **I** and **II** are trimeric in both the solution and crystalline state. The oxidation of compound **I** and earlier described complex $[3,6\text{-CatInI(THF)}]_2$ (THF is tetrahydrofuran) by various substrates (iodine, 3,6-Q, and tetramethylthiuram disulfide) is studied. Different indium(III) *o*-semiquinone complexes are the reaction products, depending on the reaction conditions.

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The chemistry of indium(III) complexes containing sterically hindered *o*-benzoquinone ligands has started to develop rather long ago. The first works were devoted to the study of *o*-semiquinolate derivatives $SQInX_2$ (SQ is the radical anion form of *o*-benzoquinone Q, X = Hal or Alk), which were generated in solutions under the EPR experimental conditions upon the oxidation of the corresponding InX_3 by various substituted *o*-benzoquinones [1–5]. The redox reactions of metallic indium and its subvalent halides with *o*-benzoquinones affording various *o*-semiquinolate and catecholate metal complexes were studied later [6–13]. However, the conclusions of these works concerning the compositions and structures of the synthesized compounds and actually based on the data of elemental analysis and IR spectroscopy seem rather doubtful in several cases. For example, the recent studies [14] showed that the indium(I) *o*-semiquinolate derivatives cannot be obtained in the systems studied [6–13]. Thus, several completely characterized (in the individual state) paramagnetic indium(III) complexes based on different *o*-quinone ligands are known to the present time [9, 11, 14]. The most part of these compounds were synthesized by the direct oxidation of metallic indium or its low-valence derivatives by quinones. Another promising method for the synthesis of paramagnetic metal *o*-semiquinolate complexes is the oxidation of the corresponding catecholate derivatives [15, 16]. This work is devoted to the study of the redox transformations of the indium(III) catecholate complexes in the reactions with different oxidative agents and to the examination of the compositions and structures of the formed paramagnetic compounds.

EXPERIMENTAL

All procedures on the preparation of the indium *o*-benzoquinone complexes and the reactions with them were carried out under reduced pressure without air oxygen and moisture.

IR spectra were recorded on an FSM-1201 FTIR spectrometer in Nujol in KBr pellets. EPR spectra were measured on a Bruker EMX spectrometer. Diphenylpicrylhydrazyl (g = 2.0037) was used as a standard for the determination of the g factor. NMR spectra were detected in a $CDCl_3$ solution on Bruker DPX-200 (200 MHz) and Bruker Avance III (400 MHz) instruments using tetramethylsilane as an internal standard.

The solvents used were purified and dehydrated according to standard procedures [17]. The following commercial reagents were used: Tl (high-purity grade), In (Aldrich), I_2 (special purity grade), tetramethylethylenediamine (TMED) (Aldrich), and tetramethylthiuram disulfide (TMTUDS) (high-purity grade). 3,6-Di-*tert*-butyl-*o*-benzoquinone (3,6-Q) [18], $EtInI_2$ [19], $MeInI_2$ [19], 3,6-$CatTl_2$ [20], and $[3,6\text{-CatInI(THF)}]_2$ [14] were synthesized according to described procedures.

Syntheses of $[3,6\text{-CatInMe}]_3$ (I) and $[3,6\text{-CatInEt}]_3$ (II). A solution of $RInI_2$ (0.303 g (R = Me), 0.314 g (R = Et), 0.79 mmol) in THF (10 mL) was poured to a suspension of 3,6-$CatTl_2$ (0.5 g, 0.79 mmol) in THF (30 mL). A resulted pale yellow solution was filtered on the Schott filter no. 4 to separate from a TlI precipitate. The solvent was removed under reduced pressure. White crystals of complexes **I** and **II** were obtained by cooling their solutions in diethyl ether. The yield of compound **I** was 0.56 g (68%), and that of compound **II** was 0.64 g (74%).

For $C_{45}H_{69}In_3O_6$ (**I**)

calculated (%):	C, 51.45;	H, 6.62;	In, 32.79.
Found (%):	C, 51.50;	H, 6.69;	In, 32.67.

IR for **I**, ν, cm^{-1}: 1402 s, 1396 s, 1354 s, 1282 m, 1255 s, 1246 s, 1220 s, 1207 m, 1141 m, 1011 w, 968 s, 939 m, 919 m, 801 m, 795 m, 659 s, 558 m. ^{1}H NMR for **I** (400 MHz, $CDCl_3$, 20°C), δ, ppm: 6.83 (s, 4H, $4CH_{arom}$), 6.54 (s, 2H, $2CH_{arom}$), 1.40 (s, 36H, $4Bu^t$), 0.94 (s, 18H, $2Bu^t$), 0.15 (s, 3H, Me), –0.19 (s, 6H, 2Me).

For $C_{48}H_{75}In_3O_6$ (**II**)

calculated (%):	C, 52.77;	H, 6.92;	In, 31.53.
Found (%):	C, 52.85;	H, 6.97;	In, 31.48.

IR for **II**, ν, cm^{-1}: 1400 s, 1394 s, 1352 s, 1282 m, 1253 s, 1238 s, 1221 s, 1204 m, 1147 m, 1011 w, 965 s, 938 m, 919 m, 807 m, 794 m, 659 s, 558 m. ^{1}H NMR for **II** (400 MHz, $CDCl_3$, 20°C), δ, ppm: 6.82 (s, 4H, $4CH_{arom}$); 6.50 (s, 2H, $2CH_{arom}$); 1.44 (s, 36H, $4Bu^t$); 1.06 (m, 2H, CH_2(Et)); 1.00 (s, 18H, $2Bu^t$); 0.90 (q, 4H, $2CH_2$(Et)); 0.87 (t, 3H, CH_3(Et)); 0.58 (t, 6H, CH_3(Et)).

Oxidation of [3,6-CatInI(THF)]$_2$ (III) with iodine. A solution of I_2 (0.094 g, 0.37 mmol) in THF (10 mL) was poured to a solution of [3,6-CatInI(THF)]$_2$ (0.4 g, 0.37 mmol) in THF (30 mL). The color of the reaction mixture changed from pale yellow to intensely green. The formed complex 3,6-SQInI$_2$(THF)$_x$ (**IV**) was characterized by EPR spectroscopy in solution.

Tetrahydrofuran was removed under reduced pressure, and a dry residue was dissolved in diethyl ether (25 mL). Complex (3,6-SQ)$_2$InI (**V**) was isolated by the slow evaporation of the solution in Et_2O as a finely crystalline substance colored in saturated green. The yield of complex **V** was 0.13 g (52%).

For $C_{28}H_{40}InIO_4$ (**V**)

calculated (%):	C, 49.2;	H, 5.91;	In, 16.83;	I, 18.60.
Found (%):	C, 49.35;	H, 5.96;	In, 16.75;	I, 18.53.

IR for **V**, ν, cm^{-1}: 1496 s, 1484 s, 1477 s, 1466 s, 1453 s, 1445 s, 1430 s, 1390 s, 1358 s, 1346 s, 1342 s, 1339 s, 1289 w, 1277 m, 1236 w, 1205 m, 1202 m, 1181 m, 1152 w, 1037 w, 1025 s, 998 w, 961 s, 953 s, 929 w, 918 w, 867 s, 839 m, 830 s, 804 m, 777 w, 704 w, 679 s, 654 s, 553 m, 494 s.

Tetrahydrofuran was removed under reduced pressure from the reaction mixture containing compound **IV**, and a dry residue was dissolved in hexane (25 mL) and filtered on the Schott filter no. 4. The solution was evaporated and kept at ambient temperature. The yield of complex (3,6-SQ)$_3$In was 0.09 g (47.4%).

Reaction of (3,6-SQ)$_3$In with TMED. Tetramethylethylenediamine (1 mL) was added to a solution of (3,6-SQ)$_3$In (0.31 g, 0.4 mmol) in hexane (30 mL). The color of the reaction mixture changed from blue-green to pale green, and a pale green finely crystalline precipitate of (3,6-SQ)In(TMED)(3,6-Cat) (**VI**) was formed. A precipitate of compound **VI** was separated from a solution of 3,6-Q on the Schott filter no. 3 and washed with hexane three to four times. The yield of compound **VI** was 0.21 g (85%).

For $C_{34}H_{56}InN_2O_4$ (**VI**)

calculated (%):	C, 60.80;	H, 8.40;	In, 17.10;	N, 4.17.
Found (%):	C, 60.87;	H, 8.45;	In, 17.03;	N, 4.12.

IR for **VI**, ν, cm^{-1}: 1492 s, 1481 s, 1471 s, 1450 s, 1434 s, 1405 s, 1398 s, 1392 s, 1354 s, 1346 s, 1292 m, 1288 s, 1279 s, 1252 s, 1246 s, 1200 s, 1181 w, 1168 w, 1146 m, 1125 w, 1104 w, 1074 w, 1059 w, 1049 w, 1024 s, 1014 m, 1005 w, 972 s, 963 m, 951 s, 938 s, 922 m, 835 m, 804 w, 797 s, 787 s, 777 m, 765 w, 704 w, 692 s, 677 m, 656 s, 584 w, 547 w, 495 m, 490 m, 486 w.

Oxidation of complex III by 3,6-di-*tert*-butyl-*o*-benzoquinone. A solution of 3,6-Q (0.163 g, 0.74 mmol) in diethyl ether (15 mL) was poured to a solution of compound **III** (0.4 g, 0.37 mmol) in diethyl ether (25 mL). The reaction occurred with a rate of mixing reactants and was accompanied by a change in the color of the solution from pale yellow to intensely green. Complex **V** was isolated as a finely crystalline substance colored in saturated green by the slow evaporation of the solution. The yield of compound **V** was 0.38 g (75%).

Oxidation of complex III by iodine in the presence of TMED. Tetramethylethylenediamine (1 mL) and a solution of I_2 (0.094 g, 0.37 mmol) in THF (10 mL) were added to a solution of complex **III** (0.4 g, 0.37 mmol) in THF (30 mL). The reaction occurred with a rate of mixing reactants, and the color of the solution changed from pale yellow to violet. Tetrahydrofuran was removed under reduced pressure, and the dry residue was dissolved in hexane (25 mL). After the solution was cooled, complex 3,6-SQInI$_2$(TMED) (**VII**) was obtained as a crystalline substance colored in saturated violet. The yield of **VII** was 0.11 g (85%).

For $C_{20}H_{36}InI_2N_2O_2$ (**VII**)

calculated (%):	C, 34.07;	H, 5.15;	In, 16.28;	I, 35.99.
Found (%):	C, 34.13;	H, 5.23;	In, 16.21;	I, 35.94.

IR for **VII**, ν, cm^{-1}: 1483 s, 1469 s, 1453 s, 1440 s, 1426 s, 1408 s, 1387 s, 1363 s, 1354 s, 1345 s, 1293 m, 1285 s, 1274 m, 1243 w, 1201 m, 1181 w, 1121 m, 1105 w, 1098 w, 1060 m, 1048 m, 1041 m, 1021 s, 1017 s, 1006 m, 999 m, 963 s, 951 s, 926 w, 835 s, 804 w, 795 s, 766 w, 700 w, 677 s, 654 s, 584 w, 543 w, 521 w, 494 s, 467 w.

Reaction of complex I with iodine. A solution of I_2 (0.145 g, 0.57 mmol) in THF (10 mL) was added to a solution of complex **I** (0.4 g, 0.38 mmol) in THF (30 mL). It was accompanied by a change in the color of the reaction mixture from pale yellow to intensely green. The formed complex 3,6-SQInI(Me) (**VIII**) was characterized by EPR spectroscopy. For 15 min the color of the solution changed to blue-green, indicating the subsequent symmetrization of compound **VIII**. The presence of $(3,6\text{-SQ})_3In$ in the system was proved by its reaction with TMED under the EPR experimental conditions.

Reaction of complex III with TMTUDS. A solution of TMTUDS (0.089 g, 0.37 mmol) in THF (10 mL) was poured to a solution of complex **III** (0.4 g, 0.37 mmol) in THF (30 mL). The reaction mixture was heated at 60°C for 3 h, and the color of the solution changed from pale yellow to brown. The formed complex 3,6-SQInI(SS) (**IX**) (SS is the dimethyldithiocarbamate anion) was characterized by EPR spectroscopy in solution.

Tetrahydrofuran was removed under reduced pressure, and the dry residue was dissolved in hexane. The color of the solution changed to blue-green and a white precipitate formed. The formation of complex **VI** after the addition of TMED to the reaction mixture under the EPR experimental conditions indicated that the system contained $(3,6\text{-SQ})_3In$ as a symmetrization product of complex **IX**.

Reaction of complex I with TMTUDS. A solution of TMTUDS (0.137 g, 0.57 mmol) in THF (10 mL) was added to a solution of complex **I** (0.4 g, 0.38 mmol) in THF (30 mL). The reaction mixture was heated at 60°C for 30 min, and the change in the color of the solution from pale yellow to green was observed. The obtained complex 3,6-SQInMe(SS) (**X**) was characterized by EPR spectroscopy in solution.

Tetrahydrofuran was removed under reduced pressure, and the dry residue was dissolved in hexane. The resulting blue-green solution was separated from a white precipitate formed on the Schott filter no. 4. The presence of $(3,6\text{-SQ})_3In$ in the solution was proved by its reaction with TMED under the EPR experimental conditions. A white precipitate of $MeInSS_2$ [21] was washed with hexane and characterized by NMR, IR spectroscopy, and elemental analysis. The yield of $MeInSS_2$ was 0.14 g (66%).

For $C_7H_{15}InN_2S_4$				
calculated (%):	C, 22.71;	H, 4.08,	In, 31.01,	S, 34.64.
Found (%):	C, 22.78;	H, 4.14;	In, 30.97;	S, 34.67.

IR, ν, cm^{-1}: 1519 s, 1406 m, 1395 s, 1250 s, 1157 m, 1053 w, 1020 w, 978 s, 694 w, 571 w, 505 m. ^1H NMR (200 MHz, $CDCl_3$, 20°C), δ, ppm: 3.44 (s, 12H, CH_3(TMTUDS)); 0.49 (s, 3H, CH_3).

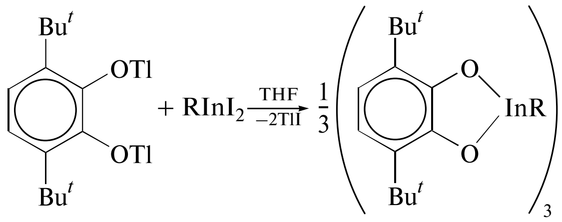
Oxidation of complex I by 3,6-di-*tert*-butyl-*o*-benzoquinone. A solution of 3,6-Q (0.251 g, 1.14 mmol) in Et_2O (15 mL) was poured to a solution of complex **I** (0.4 g, 0.38 mmol) in Et_2O (20 mL). The reaction occurred with a rate of mixing reactants and was accompanied by a change in the color of the solution from pale yellow to green. The formed complex $(3,6\text{-SQ})_2InMe$ (**XI**) was characterized by EPR spectroscopy in a frozen matrix of Et_2O at 150 K.

X-ray diffraction analyses of complexes **I** and **VII** were carried out on a Smart Apex diffractometer (MoK_α, graphite monochromator). Structures **I** and **VII** were solved by a direct method followed by refinement using the full-matrix least-squares method for F^2 (SHELXTL) [22]. An absorption correction was applied using the SADABS program [23]. All non-hydrogen atoms were refined in the anisotropic approximation. Hydrogen atoms were placed in the geometrically calculated positions and refined in the riding model. Selected bond lengths and angles in molecules **I** and **VII** are given in Table 1. The crystallographic data and the main refinement parameters are listed in Table 2.

The crystallographic data for complexes **I** and **VII** were deposited with the Cambridge Crystallographic Data Centre (nos. 888763 (**I**) and 888764 (**VII**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

Catecholate complexes **I** and **II** are formed due to the exchange reaction between dithallium salt 3,6-$CatTl_2$ and the corresponding alkylindium diiodide $RInI_2$ (Scheme 1). Compounds **I** and **II** were isolated in the individual state by direct crystallization from their solution in diethyl ether.



3,6-$CatTl_2$

R = Me (**I**)
R = Et (**II**)

Scheme 1.

The IR spectra of the synthesized complexes exhibit the absorption bands corresponding to vibrations of the C–O bonds (1200–1300 cm^{-1}) characteristic of the metal catecholates [15].

According to the X-ray diffraction data, complex **I** is trimeric (Fig. 1). All indium atoms in trimer **I** have a distorted tetragonal pyramidal environment. The oxygen atoms of the catecholate ligands form a base of a tetragonal pyramid, whereas the carbon atoms of the methyl groups occupy apical positions. The catecho-

Table 1. Selected bond lengths (Å) and angles (deg) in complexes **I** and **VII**

Bond	*d*, Å	Bond	*d*, Å
	I		
In(1)–O(1)	2.2512(13)	O(6)–C(30)	1.383(3)
In(1)–O(2)	2.2787(15)	C(1)–C(2)	1.407(3)
In(1)–O(3)	2.1885(14)	C(2)–C(3)	1.403(3)
In(1)–O(6)	2.1769(14)	C(3)–C(4)	1.401(3)
In(2)–O(1)	2.2362(14)	C(4)–C(5)	1.393(3)
In(2)–O(2)	2.2442(13)	C(5)–C(6)	1.398(3)
In(2)–O(4)	2.2191(14)	C(6)–C(1)	1.392(3)
In(2)–O(5)	2.1982(14)	C(15)–C(16)	1.405(3)
In(3)–O(3)	2.1763(14)	C(16)–C(17)	1.406(3)
In(3)–O(4)	2.1918(13)	C(17)–C(18)	1.396(3)
In(3)–O(5)	2.2066(14)	C(18)–C(19)	1.387(3)
In(3)–O(6)	2.1833(13)	C(19)–C(20)	1.398(3)
In(1)–C(43)	2.124(2)	C(20)–C(15)	1.401(3)
In(2)–C(44)	2.123(2)	C(29)–C(30)	1.403(3)
In(3)–C(45)	2.122(2)	C(30)–C(31)	1.405(3)
O(1)–C(1)	1.380(2)	C(31)–C(32)	1.391(3)
O(2)–C(2)	1.383(3)	C(32)–C(33)	1.379(3)
O(3)–C(15)	1.387(2)	C(33)–C(34)	1.397(3)
O(4)–C(16)	1.395(2)	C(34)–C(29)	1.413(3)
O(5)–C(29)	1.393(2)		
	VII		
In(1)–O(1)	2.2033(16)	O(2)–C(2)	1.291(3)
In(1)–O(2)	2.1960(16)	C(1)–C(2)	1.464(3)
In(1)–N(1)	2.385(2)	C(2)–C(3)	1.436(3)
In(1)–N(2)	2.341(2)	C(3)–C(4)	1.366(3)
In(1)–I(1)	2.7719(3)	C(4)–C(5)	1.430(4)
In(1)–I(2)	2.8125(3)	C(5)–C(6)	1.362(4)
O(1)–C(1)	1.290(3)	C(1)–C(6)	1.436(3)
Angle	ω, deg	Angle	ω, deg
	I		
C(43)In(1)O(6)	124.12(7)	O(4)In(2)O(1)	84.58(5)
C(43)In(1)O(3)	127.33(8)	C(44)In(2)O(2)	112.95(7)
O(6)In(1)O(3)	72.89(5)	O(5)In(2)O(2)	84.30(5)
C(43)In(1)O(1)	111.00(7)	O(4)In(2)O(2)	126.42(5)
O(6)In(1)O(1)	123.90(5)	O(1)In(2)O(2)	67.95(5)
O(3)In(1)O(1)	82.66(5)	C(45)In(3)O(3)	119.56(7)
C(43)In(1)O(2)	108.09(8)	C(45)In(3)O(6)	112.87(7)
O(6)In(1)O(2)	85.75(5)	O(3)In(3)O(6)	73.00(5)
O(3)In(1)O(2)	123.57(5)	C(45)In(3)O(4)	130.38(7)
O(1)In(1)O(2)	67.10(5)	O(3)In(3)O(4)	73.43(5)
C(44)In(2)O(5)	122.23(8)	O(6)In(3)O(4)	116.63(5)
C(44)In(2)O(4)	120.11(7)	C(45)In(3)O(5)	124.72(8)
O(5)In(2)O(4)	74.30(5)	O(3)In(3)O(5)	114.63(5)
C(44)In(2)O(1)	113.17(7)	O(6)In(3)O(5)	72.99(5)
O(5)In(2)O(1)	124.18(5)	O(4)In(3)O(5)	74.68(5)
	VII		
O(1)In(1)O(2)	73.94(6)	N(2)In(1)I(1)	98.51(6)
O(2)In(1)N(2)	156.14(7)	N(1)In(1)I(1)	93.66(5)
O(1)In(1)N(2)	86.45(7)	O(2)In(1)I(2)	93.85(4)
O(2)In(1)N(1)	87.09(6)	O(1)In(1)I(2)	85.11(4)
O(1)In(1)N(1)	85.72(6)	N(2)In(1)-(2)	170.13(5)
N(2)In(1)N(1)	77.83(7)	I(1)In(1)I(2)	95.806(7)
O(2)In(1)I(1)	100.84(4)	C(1)O(1)In(1)	113.64(14)
O(1)In(1)I(1)	174.76(4)	C(2)O(2)In(1)	113.91(14)

late fragments are nonequivalent: two diolate ligands including the O(5), O(6) and O(3), O(4) atoms are coordinated by three indium atoms. The third ligand containing the O(1) and O(2) atoms is bound to two metal atoms In(1) and In(2) only and is nearly orthogonal to the former two catecholate fragments. The corresponding dihedral angles between the planes of the ligands are 90.4° and 94.5°. The C–O bonds (1.380(2)–1.395(2) Å) in complex **I** are longer than the corresponding distances characteristic of the metal catecholate complexes [24, 25], which is due to the bridging nature of all oxygen atoms in complex **I**. At the same time, the considered bonds significantly exceed the corresponding C–O distance in the *o*-semiquinone derivatives [24, 25]. The nature of the six-membered carbon rings of the quinone ligands C(1–6), C(15–20), and C(29–34) is aromatic, and all C–C bonds are equalized and range from 1.379(3) to 1.413(3) Å. These data confirm the dianionic nature of the O,O ligands in complex **I**. The In–O bond lengths (2.1763(14)–2.2787(15) Å) significantly exceed the sum of covalent radii of the corresponding elements (2.08 Å [26]), which is also explained by the bridging nature of the oxygen atoms in complex **I**. The trimeric structure of complex **I** is similar to the earlier published tin(II) catecholate complex [27].

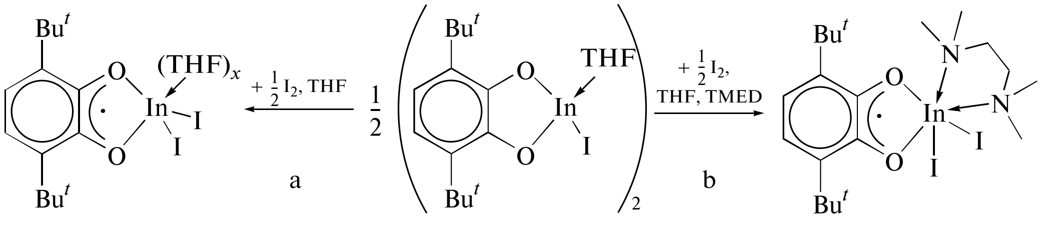
The structures of complexes **I** and **II** are retained in solution, which is indicated by the data of ^{1}H NMR spectroscopy. The NMR spectra exhibit nonequivalence of both the alkyl substituents at the indium atom and the catecholate ligands. The integral intensities of the protons assigned to two different alkyl groups and to two nonequivalent catecholate fragments are in a ratio of 1 : 2.

It has previously been shown that catecholates of nontransition metals react with one-electron oxidants and O-, N-, S-, and C-centered radical species [15, 28, 29] to form *o*-semiquinolate complexes of the corresponding metals identified by EPR spectroscopy. As part of this work we studied the reactivity of the synthesized alkylindium catecholate complexes using compound **I** and earlier described complex **III** [14] as examples with respect to different oxidants.

The oxidation of complex **III** by iodine in THF is accompanied by a change in the color of the solution from yellow to intensely green and by the appearance of an EPR signal corresponding to monoradical indium *o*-semiquinolate derivative **IV** (Scheme 2a). The spectrum is a decet of triplets, and its hyperfine structure is caused by the interaction of an unpaired electron with two protons of the *o*-semiquinone ring ^{1}H (99.98%, $I = 1/2$, $\mu_N = 2.7928$) [30] and nuclei of magnetic isotopes ^{115}In (95.7%, $I = 9/2$, $\mu_N = 5.534$) and ^{113}In (4.3%, $I = 9/2$, $\mu_N = 5.229$) [30]. The EPR spectrum of compound **IV** is characterized by the following parameters: $a_i(2^1\text{H}) = 3.6$, $a_i(^{115}\text{In}) = 5.0$, $a_i(^{113}\text{In}) = 4.7$ Oe, and $g_i = 2.0038$.

Table 2. Crystaloographic data and the parameters of X-ray diffraction experiments and refinement for complexes **I** and **VII**

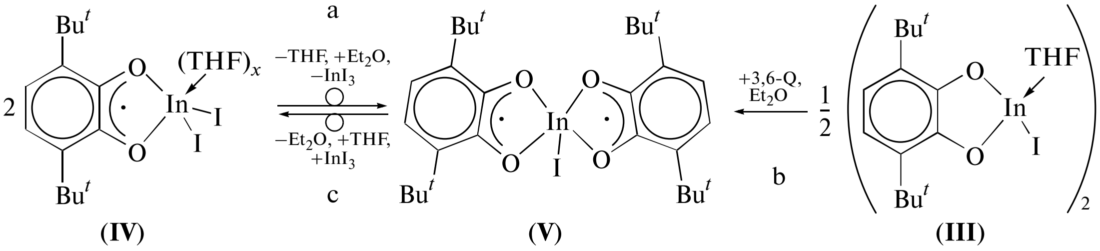
Parameter	Value	
	I	**VII**
FW	1050.46	705.13
Temperature, K	100(2)	100(2)
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$
a, Å	10.7657(4)	27.8203(14)
b, Å	13.2169(5)	13.3020(7)
c, Å	18.1888(7)	28.1178(14)
α, deg	108.4890(10)	90
β, deg	98.2570(10)	92.8580(10)
γ, deg	105.1970(10)	90
V, Å^3	2294.81(15)	10392.5(9)
Z	2	16
F(000)	1068	5456
ρ_{calcd}, g/cm^{-3}	1.520	1.803
μ, mm^{-1}	1.538	3.302
Crystal size, mm	0.23 × 0.17 × 0.14	0.18 × 0.15 × 0.15
θ Range, deg	2.02–26.00	1.86–26.00
Ranges of reflection indices	$-13 \le h \le 13$, $-16 \le k \le 15$, $-22 \le l \le 21$	$-34 \le h \le 34$, $-16 \le k \le 16$, $-34 \le l \le 34$
Number of reflections	14003	44320
Number of independent reflections	8982	10193
R_{int}	0.0146	0.0321
Goodness-of-fit on (F^2)	1.049	99.8
R_1/wR_2 ($I > 2\sigma(I)$)	0.0267/0.0654	0.0263/0.0566
R_1/wR_2 (for all parameters)	0.0307/0.0675	0.0361/0.0594
Residual electron density (max/min), e Å^{-3}	1.246/–0.493	0.896/–0.886



(IV) **(III)** **(VII)**

Scheme 2.

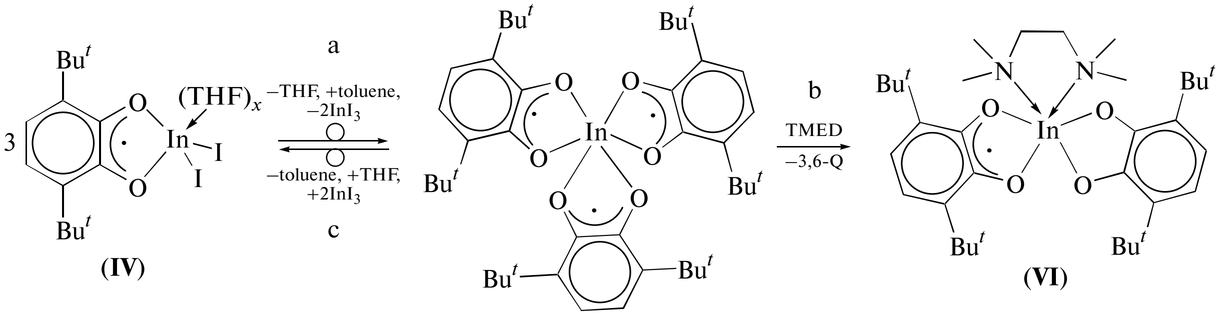
The removal of THF from a solution of compound **IV** followed by the dissolution of the residue in diethyl ether results in the disappearance of the isotropic EPR spectrum and the appearance of a signal in the frozen matrix of the solvent at 150 K characteristic of biradical species ($D = 255$ Oe, $E = 20$ Oe, and $r = 4.80$ Å, where r is the distance between the radical centers calculated according to [31]). This indicates that in diethyl ether compound **IV** undergoes the fast and nearly quantitative symmetrization to form compounds **V** and InI_3 (Scheme 3a).



Scheme 3.

Compound **V** was isolated in the individual state from Et_2O as a finely crystalline substance colored in saturated green and was characterized by EPR, IR spectroscopy, and elemental analysis. Complex **V** is also formed by the oxidation of the starting catecholate derivative **III** with *o*-benzoquinone in diethyl ether (Scheme 3b). Complex **IV** is formed when solvent Et_2O is replaced by THF for compound **V** and if the system contains indium triiodide (Scheme 3c).

If the dry residue formed after THF removal from the reaction mixture containing complex **IV** is dissolved in hydrocarbon solvents (toluene or hexane), the symmetrization of compound **IV** occurs; however, other products are formed under these conditions (Scheme 4a).



Scheme 4.

A solution of compound **IV** in toluene is characterized by the blue-green color, the absence of a resolved isotropic EPR spectrum, and the presence of a signal in the frozen solvent matrix typical for systems with $S > 1/2$. This signal has previously been observed for the triradical derivative $(3,6\text{-SQ})_3In$ [14]. Indeed, earlier known [14] tris(3,6-di-*tert*-butyl-*o*-benzosemiquinolato)indium was isolated from the reaction mixture. Moreover, the addition of TMED to the solution results in the ligand exchange accompanied by the formation of free *o*-benzoquinone and formation of mixed-ligand complex **VI** (Scheme 4b). A similar reaction of $(3,6\text{-SQ})_3In$ with α,α'-bipyridine (Bipy) has been studied earlier [14]. The formation of compound **VI** is accompanied by a change in the color of the solution from blue-green to grassy green typical for 3,6-Q (a solution of compound **VI** is weakly green) and the appearance of the well resolved isotropic EPR spectrum (Fig. 2). The signal is a decet of quintets, and its hyperfine structure is caused by the interaction of an unpaired electron with four protons of two *o*-benzoquinone ligands and nuclei of magnetic metal isotopes. The spectrum is characterized by the following parameters: $a_i(4^1H) = 1.9$ Oe, $a_i(^{115}In) = 7.4$ Oe, $a_i(^{113}In) = 7.0$ Oe, and $g_i = 2.0035$. The value of hyperfine coupling constant $a_i(^1H)$ for compound **VI** is nearly two times lower than the corresponding parameter for compound **IV** and for the most part of the known mono-*o*-benzosemiquinone metal complexes [1–5]. The described parameters of the EPR spectrum are similar to those characterizing the known complex (3,6-SQ)In(Bipy)(3,6-Cat) [14]. This fact indicates that in complex **VI** an unpaired electron rapidly (in the EPR time scale) migrates over two *o*-benzoquinone ligands in different redox states (radical anion and dianion) as in compound (3,6-SQ)In(Bipy)(3,6-Cat). Complex **VI** was isolated in the individual state as a finely crystalline pale green substance and character-

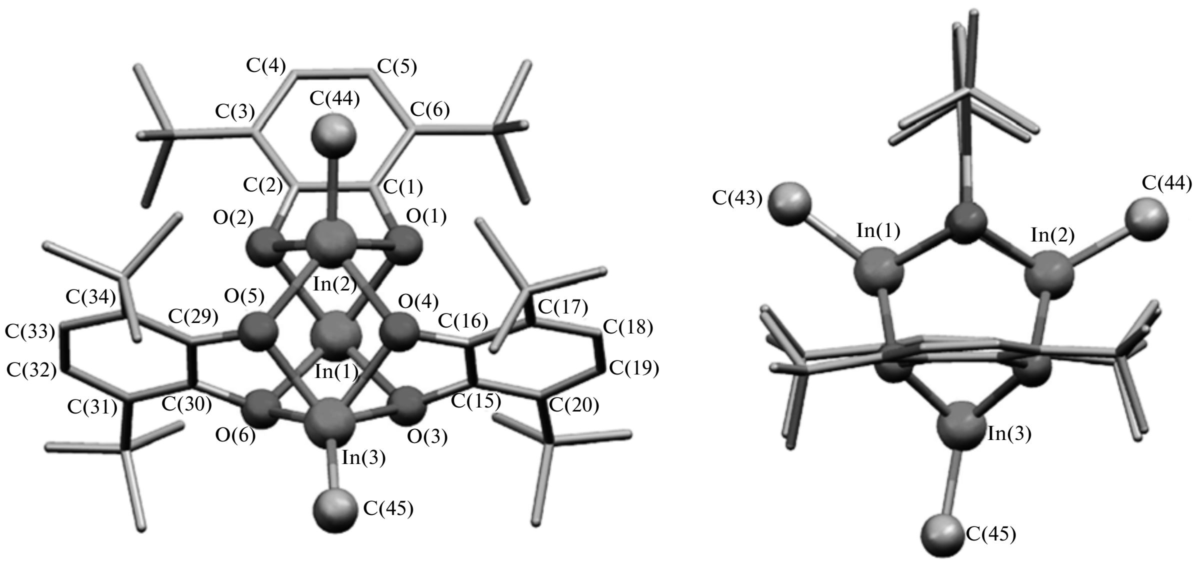


Fig. 1. Views of the molecular structure of complex **I**. Hydrogen atoms are omitted.

ized by EPR, IR spectroscopy, and elemental analysis. The reaction of $(3,6\text{-SQ})_3In$ with TMED affording compound **VI**, which is unambiguously identified by EPR, can be used as a qualitative reaction to the presence of $(3,6\text{-SQ})_3In$ in the system.

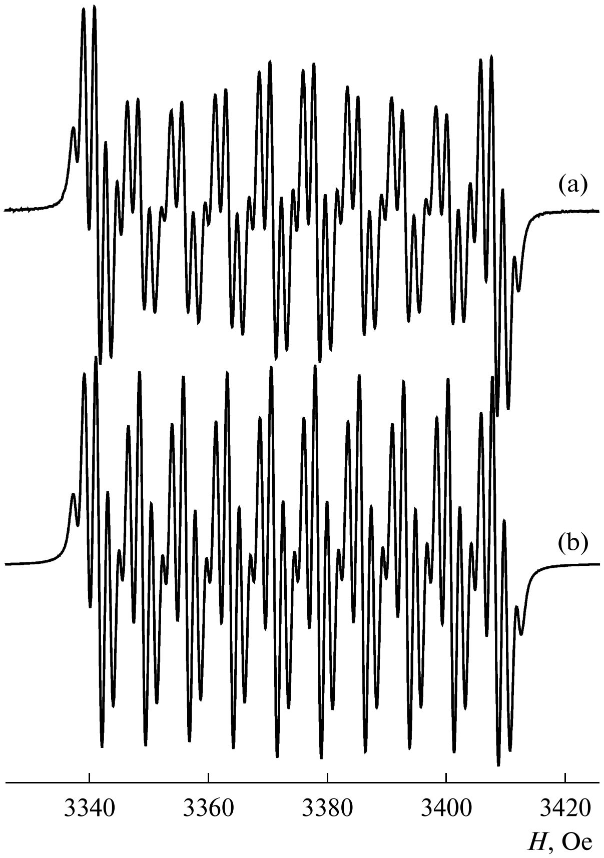


Fig. 2. (a) Experimental and (b) calculated EPR spectra of complex **VI** (toluene, 290 K).

As in the case of compound **V** (Scheme 3c), the reciprocal replacement of solvent toluene (hexane) by THF, if the system contains InI_3, results in the disappearance of $(3,6\text{-SQ})_3In$ and formation of compound **IV** (Scheme 4c).

Thus, the existence of this or another indium *o*-benzosemiquinone complex in the system considered depends rigidly on the solvent. In THF the most stable is $3,6\text{-SQInI}_2(THF)_x$, $(3,6\text{-SQ})_2InI$ is most stable in diethyl ether, and only $(3,6\text{-SQ})_3In$ is present in toluene (hexane).

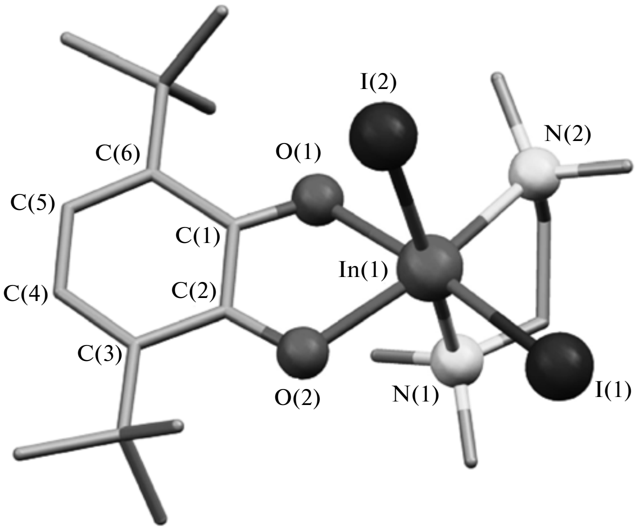


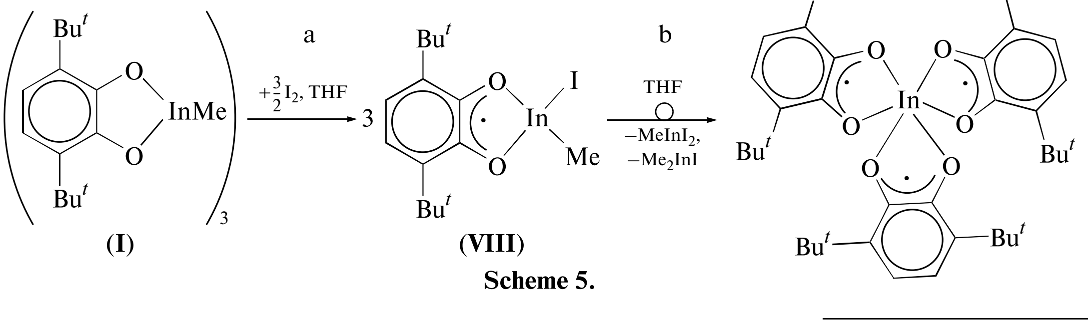
Fig. 3. Molecular structure of complex **VII**. Hydrogen atoms are omitted.

Unfortunately, it is impossible to isolate complex **IV** from a THF solution. However, the oxidation of complex **III** by iodine in the presence of TMED is accompanied by a change in the color of the solution from pale yellow to violet and affords indium *o*-benzosemiquinone complex **VII** (Scheme 2b). Unlike compound **IV**, complex **VII** is stable in all solvents and is isolated in good yield from hexane as a crystalline violet substance. It is most likely that the coordination bond of indium with TMED is rather strong and retained upon solvent replacement. At the same time, the indium–oxygen(THF) bonds are destroyed upon solvent removal, resulting in the formation of a coordinatively unsaturated molecule of 3,6-$SQInI_2$, which undergoes further symmetrization.

Complex **VII** was characterized by EPR, IR spectroscopy, elemental analysis, and X-ray diffraction analysis. Crystals of complex **VII** suitable for X-ray diffraction analysis were obtained from a hexane–methylene chloride mixture. The crystallographic cell includes two crystallographically independent molecules 3,6-$SQInI_2$(TMED) with similar bond lengths and angles and, hence, further we will consider only one of them (Fig. 3). The indium atom has a distorted octahedral environment. The O(1), O(2), N(2), and I(1) atoms form a base of an octahedron, and the N(1) and I(2) atoms occupy the apical position. The In–O distances (2.1960(16)–2.2033(16) Å) are considerably longer and the C–O bonds (1.290(3)–1.291(3) Å), considerably shorter than the corresponding distance in the known indium(III) catecholate complexes [14], and lie in the range characteristic of the *o*-benzosemiquinolate metal derivatives [24, 25]. The quinoid type of distortion typical of the radical anion form Q of the ligand is observed for the six-membered carbon ring C(1)–C(6). This is manifested as an alternation of the C–C bond lengths when two short bonds are separated by two long bonds. The C(1)–C(2), C(2)–C(3), C(4)–C(5), and C(1)–C(6) distances (1.430(4)–1.464(3) Å) are significantly longer than the C(3)–C(4) and C(5)–C(6) bonds (1.362(4)–1.366(3) Å). All facts presented confirm the radical anion nature of ligand 3,6-Q in complex **VII**. The In(1)–N(1) (2.385(2) Å) and In(1)–N(2) (2.341(2) Å) bond lengths significantly exceed the sum of covalent radii of the corresponding elements (2.17 Å [26]), but they are smaller than the sum of their van der Waals radii (4.2 Å [26]) and have the donor–acceptor nature. The *tert*-butyl groups in compounds **I** and **VII** exist in the screened conformation, and two methyl groups are directed to the catecholate oxygen atoms. The O···H(Me) distances in compounds **I** and **VII** (2.36(2)–2.75(2) Å) are close to the sum of van der Waals radii of these atoms (2.7 Å [26]). This suggests that complexes **I** and **VII** include intramolecular O···H interactions.

The EPR spectrum of compound **VII** is a broad poorly resolved signal of an overall extension of 67 Oe and with $g_i = 2.0060$. The poor resolution of the signal can be explained by the fact that its hyperfine structure is caused by the interaction of an unpaired electron with two protons and nuclei of the magnetic indium isotopes and also with the nuclei of the I(2) and N(1) atoms, which occupy the apical position and are almost orthogonal to the 3,6-SQ fragment. This spectrum should contain more than 500 lines, and a well resolved signal cannot be detected at a considerable linewidth (more than 1.5 Oe). A similar situation has previously been observed for another paramagnetic complex based on 4,6-di-*tert*-butyl-N-(2,6-diisopropylphenyl)-*o*-iminobenzoquinone (imQ), imSQInI_2(TMED), where imSQ is the radical anion of imQ [32].

The reaction of $[3,6\text{-CatInMe}]_3$ with iodine in THF (Scheme 5a), as in the case of compound **III**, is accompanied by a change in the color of the solution from pale yellow to intensely green and the appearance of an isotropic EPR signal belonging to formed complex **VIII**. The spectrum is a decet of triplets, and its hyperfine structure is caused by the interaction of an unpaired electron with magnetic nuclei of the atoms of the *o*-semiquinone ligand and metal and is similar to the hyperfine structure of the spectrum of complex **IV**. The EPR signal is characterized by the following parameters: $a_i(2\,^1H) = 3.7$ Oe, $a_i(^{115}In) = 13.5$ Oe, $a_i(^{113}In) = 12.8$ Oe, and $g_i = 2.0038$.

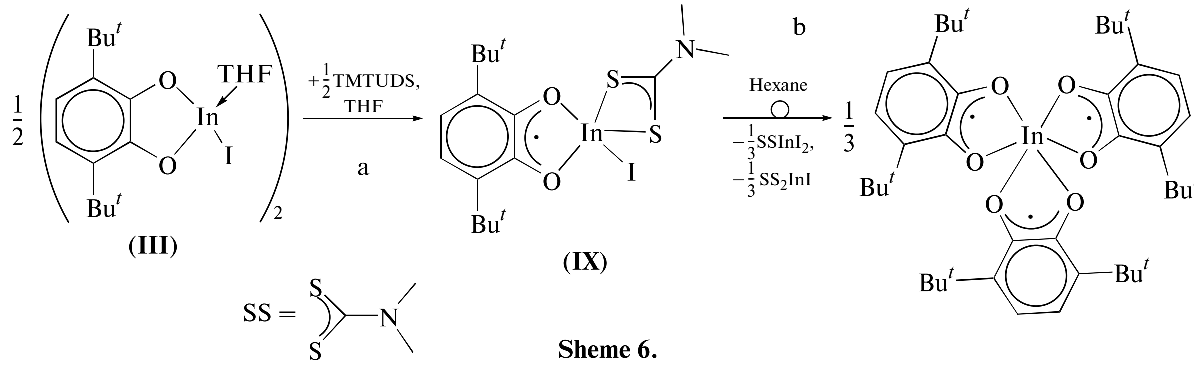


Scheme 5.

However, the observed isotropic EPR spectrum disappears within ~15 min, which is accompanied by a change in the color of the solution from green to blue-green. The addition of TMED to the formed solution changes the color of the reaction mixture and results in the appearance of the EPR spectrum belonging to complex **VI**, which unambiguously indicates the presence of (3,6-SQ)$_3$In in the system. Thus, complex **VIII** is unstable even in a THF solution and undergoes symmetrization to form the triradical metal derivative (Scheme 5b). Possibly, this is related to the fact that the coordination of THF molecules by the indium atom in 3,6-SQInI(Me) is rather weak or absent at all. This is also indicated by the value of constant $a_i(^{115}\text{In})$ for complex **VIII** (13.5 Oe) exceeding the corresponding value for compound **IV** (5.0 Oe). According to the published data [15], this can be explained by a lower coordination number of the metal center in complex **VIII** compared to compound **IV**. Therefore, in THF coordinatively unsaturated complex **VIII** undergoes symmetrization, whereas complex **IV** is stable under these conditions. The second symmetrization products (Scheme 5b) are methylindium iodides MeInI_2 and Me_2InI.

As in the case of compound **VII**, it is impossible to obtain complex **VIII** containing a TMED molecule coordinated by the metal atom. Probably, due to the electron-donor methyl group, the Lewis acidity of the metal center in complex **VIII** is lower than that in 3,6-SQInI$_2$, which considerably weakens its donor-acceptor bonds with the solvent molecules.

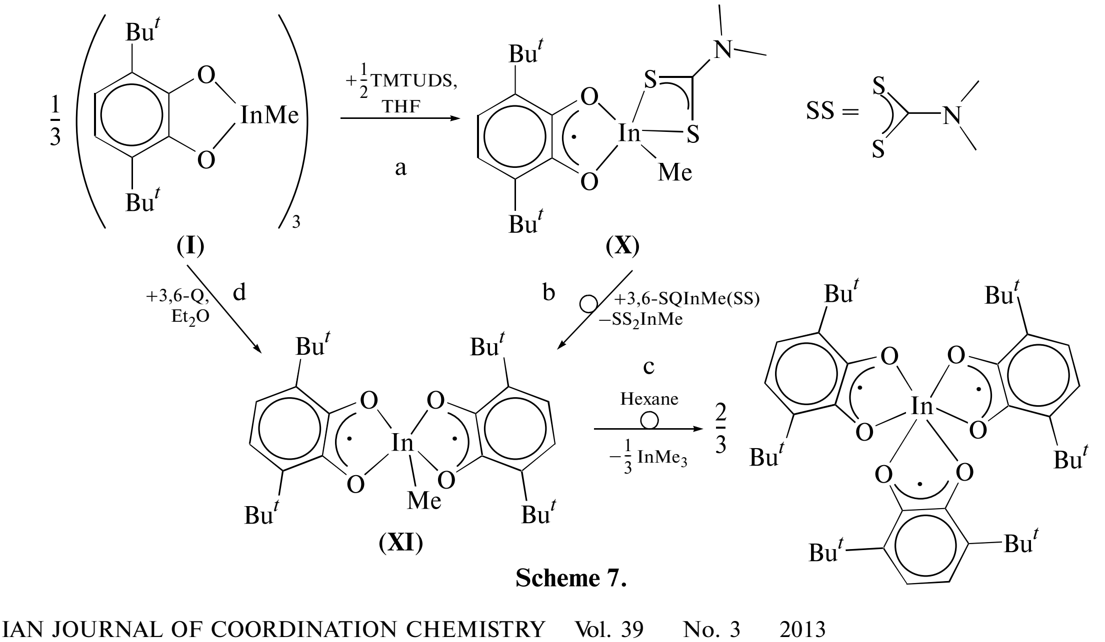
The reaction of compound **III** with TMTUDS is completed within 1 h at ~60°C (Scheme 6a). The formed brown reaction mixture manifests EPR activity. The isotropic EPR signal (Fig. 4) belonging to monoradical complex **IX** is a decet of triplets as in the case of compounds **IV** and **VIII** and characterized by the following parameters: $a_i(2^1\text{H}) = 3.5$ Oe, $a_i(^{115}\text{In}) = 5.2$ Oe, $a_i(^{113}\text{In}) = 4.9$ Oe, and $g_i = 2.0037$.



Sheme 6.

Compound **IX** is stable in THF within several days, but in hexane (toluene) it undergoes almost instant symmetrization to (3,6-SQ)$_3$In (Scheme 6b), whose formation is confirmed by its reaction with TMED. The second symmetrization products are indium dithiocarbamatoiodides SSInI_2 and SS_2InI.

The green reaction mixture obtained by the oxidation of catecholate complex **I** with TMTUDS (Scheme 7a) also exhibits EPR activity.



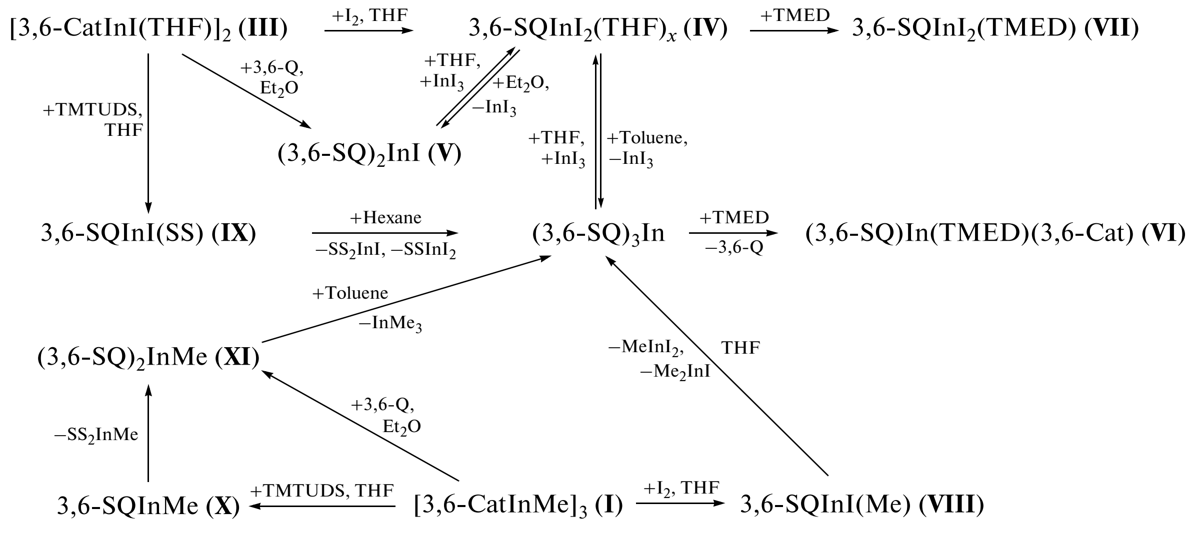
Scheme 7.

In this case, a superposition of two signals is observed, and the ratio of the signals reversibly changes with temperature (Fig. 5). The both spectra represent decets of triplets but differ in the linewidth and hyperfine coupling constants. The signal characterized by broader lines and predominant at elevated temperature has the following parameters: $a_i(2^1\text{H}) = 3.6$ Oe, $a_i(^{115}\text{In}) = 6.3$ Oe, $a_i(^{113}\text{In}) = 6.0$ Oe, and $g_i = 2.0038$. The values of the spectral parameters with narrower lines are as follows: $a_i(2^1\text{H}) = 3.5$ Oe, $a_i(^{115}\text{In}) = 5.1$ Oe, $a_i(^{113}\text{In}) = 4.8$ Oe, and $g_i = 2.0040$. The observed signals belong to the monoradical *o*-benzosemiquinolate indium derivatives formed at the first stage of oxidation having the same composition 3,6-SQInMe(SS) (**X**) (Scheme 7a) but different geometries of the coordination center. The tetrahedral pyramidal structure can be proposed for one of them. In this structure the base of the pyramid is formed by two oxygen atoms of the *o*-semiquinolate ligand and two sulfur atoms of the dithiocarbamate ligand, and the carbon atom of the methyl group occupies the vertex. The structure of the second coordination center can be a trigonal bipyramid, where the base is formed by two oxygen atoms of ligand 3,6-SQ and one of the sulfur atoms of the SS fragment, whereas the second sulfur atom and the carbon atom of the methyl group occupy the apical positions. The observed dynamics of the EPR spectra indicates that the both forms of complex **X** reversibly transform into each other in solution as the temperature changes.

In THF complex **X** undergoes gradual symmetrization, and a signal characteristic of biradical species (Fig. 6) ($D = 241$ Oe, $E = 14$ Oe, and $r = 4.86$ Å) and corresponding to indium bis-*o*-semiquinolate complex **XI** (Scheme 7b) appears in the spectrum of the frozen 2-methyltetrahydrofuran (Me-THF) matrix at 150 K. However, the final symmetrization product in hexane is also $(3,6\text{-SQ})_3\text{In}$ (Scheme 7c). The second symmetrization product of complex **X** was also isolated from the reaction mixture. According to the data of ^{1}H NMR and IR spectroscopy and elemental analysis, this product is SS_2InMe [21] (Scheme 7b).

Biradical complex **XI** is also formed due to the oxidation of compound **I** with an equivalent amount of 3,6-Q in Et_2O (Scheme 7d). The reaction is accompanied by a change in the color of the solution from pale yellow to green and the appearance of the EPR signal in the frozen matrix of diethyl ether, whose parameters ($D = 190$ Oe, $E = 16$ Oe, and $r = 5.30$ Å) are close to the corresponding values that characterize the spectrum detected for complex **XI** in Me-THF. Complex **XI** is stable in Et_2O within several hours but decomposes in a solution during isolation. Therefore, this complex was not obtained in the individual state.

Thus, the compositions and structures of the paramagnetic indium(III) *o*-semiquinolate derivatives formed due to the oxidation of the corresponding catecholate derivatives by various agents depend on the reaction conditions (in particular, on the solvent nature). All mutual transformations listed above can be presented by the following generalized scheme:



Scheme 8.

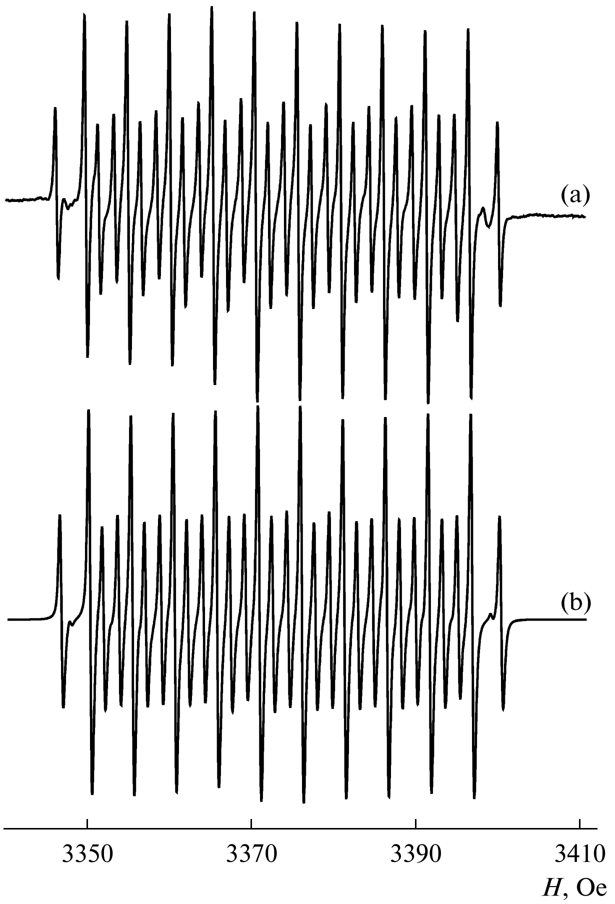


Fig. 4. (a) Experimental and (b) calculated EPR spectra of complex **IX** (diethyl ether, 290 K).

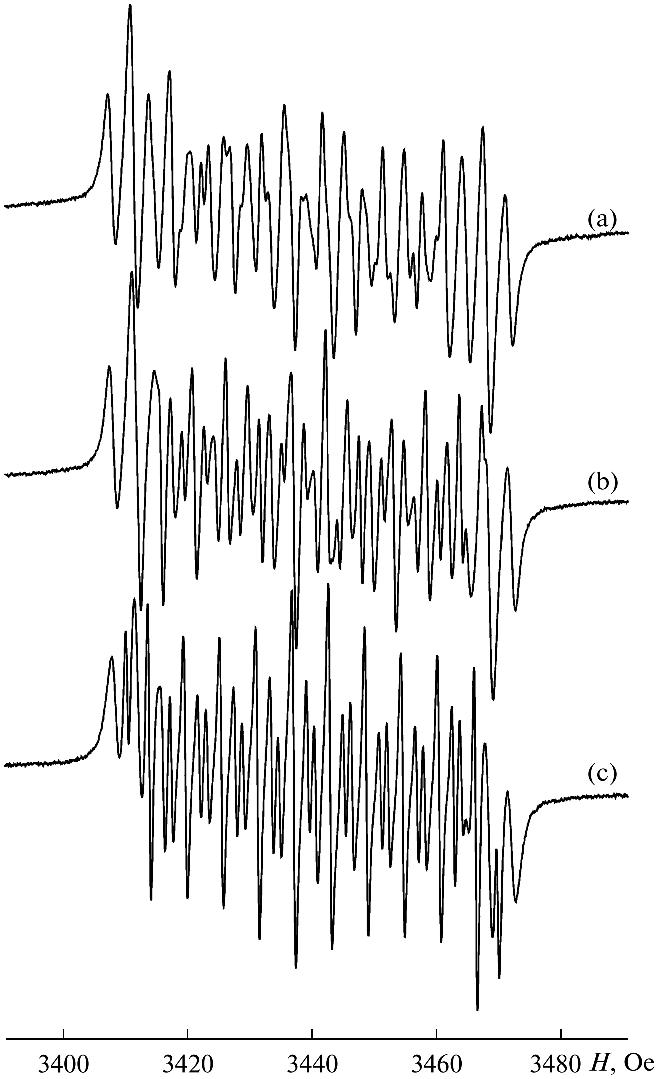


Fig. 5. EPR spectra of complex **X** at (a) 310, (b) 280, and (c) 240 K (toluene).

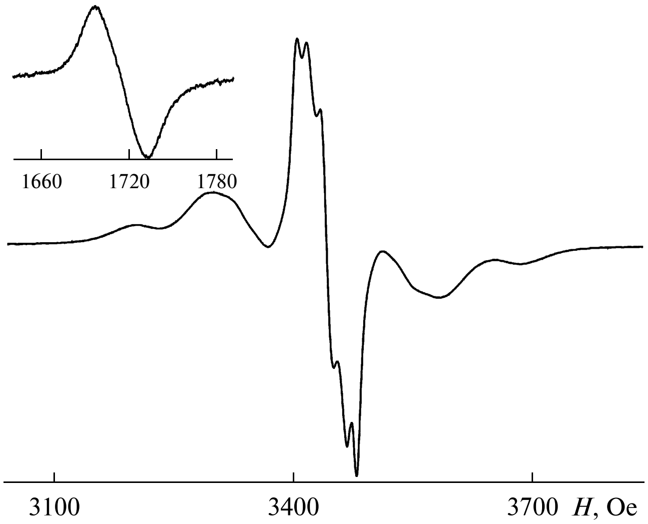


Fig. 6. EPR spectrum of complex **XI** in the frozen Me-THF matrix at 150 K.

ACKNOWLEDGMENTS

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