Indium(III) complexes with *o*-iminobenzoquinone in different redox states†‡

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The indium(III) complexes containing 4,6-di-*tert*-butyl-*N*-(2,6-di-*iso*-propyl-phenyl)-*o*-iminobenzoquinone (**imQ**) in dianion *o*-amidophenolate (AP) (**1**) or radical-anion *o*-iminobenzosemiquinolate (imSQ) (**3**) form and iodide ligands (one in the case of **1** or two in the case of **3**) have been obtained in the presence of donor agent (tetramethylethylenediamine (TMED)). The 4,6-di-*tert*-butyl-*N*-(2,6-di-*iso*-propyl-phenyl)-*o*-amidophenolate-ethyl-indium(III) (**2**) was obtained by the exchange reaction of disodium *o*-amidophenolate ($APNa_2$) with I_2InEt. Structures of complexes **1**, **2** and **3** were determined by X-ray diffraction analysis.

Introduction

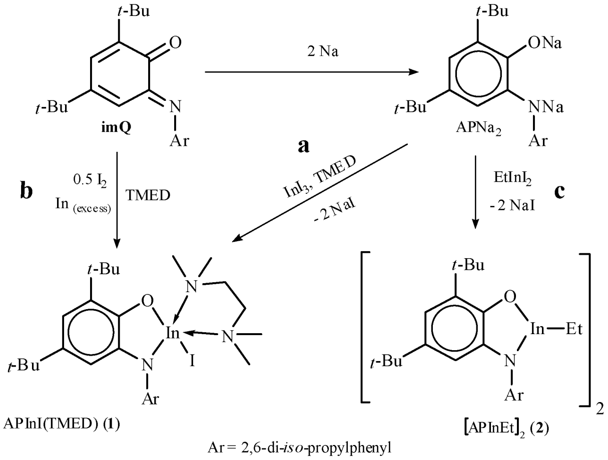
Indium complexes with *o*-quinones are well known. They were detected using EPR spectroscopy for the first time.[1] A number of indium catecholates and *o*-semiquinolates were synthesised by Tuck's research group subsequently.[2] Recently some examples of indium derivatives with α-diimine type ligand were obtained and described.[3] *o*-Iminoquinones are direct analogs of *o*-quinones and α-diimines. The complexes of non-transition metals with *o*-iminoquinone ligands have attracted attention for the last few years. This interest is due to the redox chemistry of such compounds, which is unusual for the main group elements.[4a–d] At the moment a number of non-transition metal complexes with sterically hindered *o*-iminoquinoid ligands with neutral,[5] radical-anion (*o*-iminosemiquinolate)[6a–d] or dianion (*o*-amidophenolate)[4a,b,6d,7] forms of the ligand are known. Previously[8] we described the synthesis of indium(III) derivatives based on the neutral or radical-anion (imSQ) form of 4,6-di-*tert*-butyl-*N*-(2,6-di-*iso*-propyl-phenyl)-*o*-iminobenzoquinone (**imQ**). Our attempts to obtain the indium(III) complex with dianion of the **imQ** by the exchange interaction of *o*-amidophenolate disodium derivative ($APNa_2$) with InI_3 in nonpolar solvents were not successful. The product of this reaction was the paramagnetic compound bis-[4,6-di-*tert*-butyl-*N*-(2,6-di-*iso*-propyl-phenyl)-*o*-iminobenzosemiquinolate]-iodo-indium(III) ($imSQ_2InI$). Thus the In(III) moiety oxidizes a coordinated *o*-amidophenolate ligand to give a *o*-iminobenzosemiquinolate one. The presence of electron acceptor halogen substituents increases the acceptor ability of In(III) moiety and the redox process takes place. On the other hand it is suggested that the introduction of electron donor substitutes to the metal center should prevent oxidation of **imQ** dianion and allows amidophenolate indium(III) complexes to be obtained.

Results and discussion

There are two ways to decrease the electron acceptor ability of In(III) moiety in the case of such compounds. The first route is the coordination of the neutral donor ligand (such as tetramethylethylenediamine (TMED)) to the metal. And the second one is a substitution of the electron acceptor iodide ligand with electron donor alkyl.

The exchange interaction of disodium *o*-amidophenolate ($APNa_2$) with indium(III) iodide in the presence of TMED in THF results in the formation of diamagnetic indium(III) complex containing *o*-amidophenolate, iodide and neutral TMED ligands APInI(TMED) (**1**) (Scheme 1a). The structure of **1** was confirmed by X-ray diffraction analysis (Fig. 1).

Selected bond lengths and angles of complex **1** are given in Table 1. The indium atom has a distorted trigonal-bipyramidal environment. The N(1), N(2) and I(1) atoms form the pyramid base and O(1), N(3) atoms occupy apical sites. The bond



Scheme 1 The synthesis of compounds **1** and **2**.

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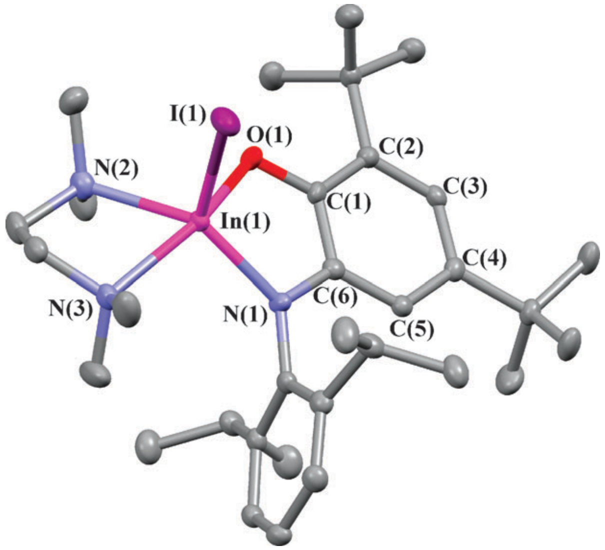


Fig. 1 The molecular structure of **1** with 50% probability ellipsoids. H atoms are omitted for clarity.

Table 1 Selected bond lengths (Å) and angles (°) for the compounds **1–3**

Bond	**1**	**$3\cdot Et_2O$**	Bond	**2**
In(1)–O(1)	2.0978(15)	2.1459(17)	In(1)–O(1)	2.1752(9)
In(1)–N(1)	2.0851(17)	2.271(2)	In(1)–N(1)	2.0732(12)
In(1)–I(1)	2.7459(2)	2.7614(2)	O(1)–C(1)	1.3991(17)
In(1)–I(2)	—	2.8669(2)	N(1)–C(6)	1.3977(18)
In(1)–N(2)	2.314(2)	2.378(2)	C(1)–C(2)	1.3921(19)
In(1)–N(3)	2.3704(18)	2.487(2)	C(2)–C(3)	1.404(2)
O(1)–C(1)	1.351(2)	1.298(3)	C(3)–C(4)	1.3911(19)
N(1)–C(6)	1.402(3)	1.339(3)	C(4)–C(5)	1.400(2)
C(1)–C(2)	1.409(3)	1.433(4)	C(5)–C(6)	1.399(2)
C(2)–C(3)	1.407(3)	1.371(4)	C(6)–C(1)	1.4229(18)
C(3)–C(4)	1.383(3)	1.429(4)	In(1)–O(2)	2.1846(10)
C(4)–C(5)	1.402(3)	1.369(4)	In(1)–C(27)	2.1336(16)
C(5)–C(6)	1.393(3)	1.430(3)	O(2)–C(29)	1.3938(17)
C(6)–C(1)	1.425(3)	1.467(3)	N(2)–C(34)	1.3972(18)
			In(1)···In(2)	3.25511(15)
Angle			Angle	
O(1)–In(1)–N(1)	80.36(6)	75.29(7)	O(1)–In(1)–N(1)	78.43(4)
O(1)–In(1)–I(1)	99.80(4)	169.42(4)	N(1)–In(1)–C(27)	146.35(6)
N(1)–In(1)–I(1)	123.07(5)	95.52(5)	O(1)–In(1)–C(27)	117.41(5)
O(1)–In(1)–N(2)	86.07(6)	91.16(7)	O(1)–In(1)–O(2)	83.77(3)
O(1)–In(1)–N(3)	160.57(7)	81.42(7)	N(1)–In(1)–O(2)	98.09(4)
N(1)–In(1)–N(2)	129.77(7)	166.13(7)	N(1)–In(1)–In(2)	86.93(3)
N(1)–In(1)–N(3)	103.22(7)	99.06(7)	C(27)–In(1)–In(2)	125.25(4)
I(1)–In(1)–N(2)	106.79(5)	97.70(5)	O(1)–In(1)–In(2)	42.04(3)
I(1)–In(1)–N(3)	94.17(5)	95.13(5)	O(2)–In(2)–O(1)	83.43(3)
N(2)–In(1)–N(3)	76.96(7)	75.61(7)	N(2)–In(2)–O(1)	98.62(4)
O(1)–In(1)–I(2)	—	86.46(5)	O(1)–In(2)–C(55)	115.87(5)
N(1)–In(1)–I(2)	—	95.75(5)	O(2)–In(1)–C(27)	112.44(5)
I(2)–In(1)–N(2)	—	86.13(5)	N(2)–In(2)–In(1)	88.94(3)
I(2)–In(1)–N(3)	—	157.77(5)	C(55)–In(2)–In(1)	126.89(4)
I(1)–In(1)–I(2)	—	99.857(8)	O(2)–In(2)–In(1)	41.83(2)
			In(1)–O(1)–In(2)	96.34(4)

distances in chelated rings are typical for the metal complexes containing *o*-amidophenolate form of **imQ**.[6d,7,9] Thus O(1)–C(1) and N(1)–C(6) bonds are 1.351(2) and 1.402(3) Å, respectively. These values exceed the corresponding bond lengths in paramagnetic $imSQ_2InI$ complex (O–C and N–C bonds are 1.269(5)–1.290(6) and 1.344(6)–1.346(6) Å, respectively).[8] On the contrary, the In(1)–O(1) (2.0978(15) Å) and In(1)–N(1) (2.0851(17) Å) are shorter than corresponding bonds in $imSQ_2InI$ (2.125(4)–2.126(3) Å for In–O and 2.176(4)–2.177(4) Å for In–N).[8] These facts are also indicative for the dianion nature of **imQ** ligand. The In–N bonds (In(1)–N(2) (2.314(2) Å) and In(1)–N(3) (2.3704(18) Å)) have donor–acceptor nature.

The complex **1** was also obtained by the reaction of **imQ**, I_2 and In excess in THF in the presence of TMED (Scheme 1b).

Another *o*-amidophenolate indium(III) derivative was obtained by an exchange reaction of $APNa_2$ with I_2InEt in diethyl ether (Scheme 1c). The product was characterized by NMR spectroscopy and X-ray diffraction analysis as a dimeric complex (**2**) of 4,6-di-*tert*-butyl-*N*-(2,6-di-*iso*-propyl-phenyl)-*o*-amidophenolato-ethyl-indium(III) ($[APInEt]_2$). The absence of a strong bifunctional donor ligand in **2** leads to the aggregation of indium amidophenolate moieties in comparison with complex **1**.

Selected bond lengths and angles of complex **2** are given in Table 1. In accordance with X-ray diffraction data (Fig. 2) each indium atom in dimer has a distorted tetrahedral environment. The N(1), O(1), O(2) and C(27) atoms occupy vertex of the first tetrahedron and the N(2), O(2), O(1) and C(55) form the second tetrahedron. The C–O (1.3938(17)–1.3991(17) Å) and C–N (1.3972(18)–1.3977(18) Å) distances are close to the corresponding bond lengths in complex **1** and are typical for the metal complexes containing *o*-amidophenolate form of imQ.[6d,7,9] The distances In(1)–O(1), In(2)–O(2), In(1)–O(2) and In(2)–O(1) are equalized and lie in the range of 2.1752(9)–2.1931(10) Å. The In(1)–N(1) (2.07232 Å) and In(2)–N(2) (2.0750 Å) are similar to In–N bond in **1**. The In(1), In(2), O(1) and O(2) atoms form a rectangle. The C_6H_2ON moieties of *o*-amidophenolate ligands are planar and they are practically parallel to each other; dihedral angle between them is 3.5° only. The indium atoms are deviated from the five-membered metallocycles for 0.574 and 0.475 Å (for In(1) and In(2), respectively). Probably, it is caused by nonbonding repulsion between the indium atoms which are separated from each other by 3.25511(15) Å (the covalent radius of In atom is 1.43 Å and its van der Waals radius is 2.2 Å).[10] It is necessary to note that the coordination number of In(1) and In(2) atoms is four and there are no solvent molecules in structure of **2**.

As has been reported,[8] the exchange interaction of sodium *o*-iminobenzosemiquinolate (imSQNa) with InI_3 leads to the complex $imSQ_2InI$ irrespective of the molar ratio of initial reagents (1 : 1 or 2 : 1). However, if the reaction between imSQNa and InI_3 in molar ratio 1 : 1 is carried out in presence of TMED, the product is the paramagnetic indium(III) complex **3** containing one *o*-iminosemiquinolate, two iodide ligands and coordinated TMED molecule (Scheme 2). Complex **3** can be also obtained by the oxidation of complex **1** with 0.5 equivalents of diiodine. The structure of **3** was determined by X-ray diffraction analysis (Fig. 3).

Selected bond lengths and angles of complex **3** are given in Table 1. The unit cell of complex includes one molecule of solvent (diethyl ether). The indium atom has a distorted octahedral environment. The N(1), N(2), N(3) and I(2) form the base of octahedron and O(1), I(1) atoms occupy apical sites. The In(1)–N(1) (2.271(2) Å), In(1)–O(1) (2.1459(17) Å)

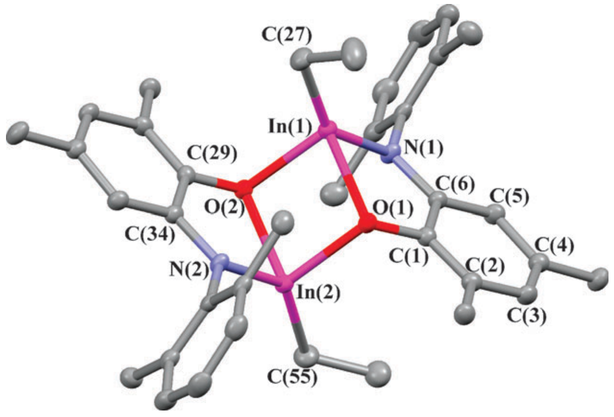
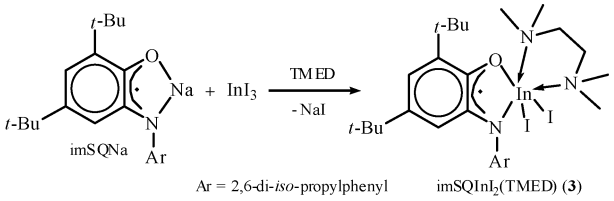


Fig. 2 The molecular structure of **2** with 50% probability ellipsoids. H atoms and methyl groups of *iso*-propyl and *tert*-butyl substituents are omitted for clarity.



Scheme 2 The synthesis of compound **3**.

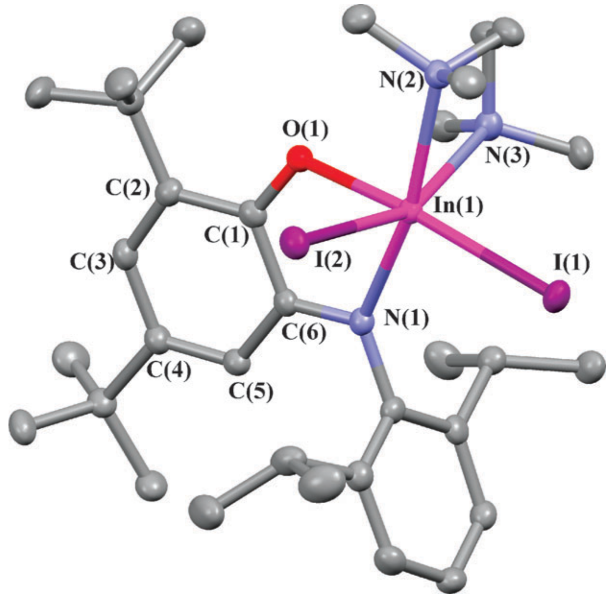


Fig. 3 The molecular structure of **3** with 50% probability ellipsoids. H atoms are omitted for clarity.

bonds are significantly longer while C(1)–O(1) (1.298(3) Å), C(6)–N(1) (1.339(3) Å) bonds are shorter than the corresponding distances in complexes **1** and **2**, but these values lie in the same range as for $imSQ_2InI$ compound. This indicates the radical-anion nature of **imQ** ligand in **3**. The In(1)–N(2) (2.378(2) Å) and In(1)–N(3) (2.487(2) Å) bonds have donor–acceptor nature.

Complex **3** is paramagnetic in solid and in solution. The EPR spectrum of **3** in toluene is a wide ($\Delta H \approx 110$ G) unresolved line with $g_i = 2.0042$. The hyperfine structure of this EPR spectrum should be caused by the interaction of unpaired electron with magnetic nuclei of *o*-iminosemiquinolate ligand (^1H, ^{14}N), magnetic isotope ^{115}In and magnetic isotopes of I(2) and N(3) atoms which are situated practically orthogonally to the plane of imSQ ligand. This spectrum should consist of 900 lines. Unfortunately, taking in account the considerable linewidth for such derivatives (≈ 1.5 G[6a]), it is impossible to observe a well resolved EPR spectrum for **3**.

Conclusions

In conclusion, in the course of the present study, indium(III) derivatives containing *o*-iminoquinolate ligand in dianion form were obtained for the first time. The presence of valence-bound substituents or extra ligands with electron donor properties was shown to stabilize amidophenolate type of the redox-active ligand in the coordination sphere of this metal. This prevents the redox process between indium(III) and *o*-amidophenolate dianion. The introduction of TMED molecule into the coordination sphere of indium averts symmetrization processes and allows to obtain the paramagnetic derivative containing one *o*-iminosemiquinolate ligand only.

Experimental

General

Infrared spectra of complexes in the 4000–400 cm^{-1} range were recorded on a Specord M-80 spectrophotometer in Nujol. NMR spectra were recorded in C_6D_6 solution using a Bruker DPX-200 spectrometer (200 MHz) and a Bruker Avance III 400 MHz instrument with Me_4Si as internal standard. EPR investigation were carried out using Bruker EMX (working frequency ~9.75 GHz) spectrometer. The g_i values were determined using DFPH as the reference ($g_i = 2.0037$).

Reagents were purchased from Aldrich. **imQ** was synthesised according to the reported procedure.[11] Solvents were purified following standard methods.[12] All manipulations on complexes were carried out under conditions excluding air oxygen and moisture.

Syntheses

4,6-Di-*tert*-butyl-*N*-(2,6-di-*iso*-propyl-phenyl)-*o*-amidophenolate-iodo-indium(III) APInI(TMED) (1). *First method.* Indium(III) iodide[13a] (0.65 g, 1.32 mmol) was treated with TMED (0.5 ml) and dissolved in 10 ml of THF. The disodium *o*-amidophenolate $APNa_2$[8] (obtained from **imQ** 0.5 g (1.32 mmol)) in the same solvent (25 ml) was added dropwise to this solution at room temperature. The reaction mixture turned orange. THF was replaced with toluene and solution was separated from white deposit of sodium iodide by filtration. The resulting solution was stored at −20 °C overnight. It leads to the formation of orange crystals of **1**. Mother liquor was additionally concentrated and cooled to isolate the product more quantitatively. The total yield of the analytically pure compound is 0.52 g (53.4%).

The second method. The mixture of **imQ** (0.5 g, 1.32 mmol), I_2 (0.1675 g, 0.66 mmol) and In excess was shaken in THF (35 ml) in the presence of TMED (0.5 ml). During the reaction the solution colour changed from wine red to orange. THF was replaced with toluene. The product was isolated by the method described above. The total yield of the analytically pure compound is 0.804 g (82.6%).

Anal. calc. for $C_{32}H_{53}IInN_3O$ C, 52.11; H, 7.24; I, 17.21, In, 15.57, N, 5.70%. Found: C, 51.98; H, 7.19; I, 17.10, In, 15.92, N, 5.61%. ^{1}H NMR (200 MHz, C_6D_6, 20 °C, δ (ppm), J/Hz): 1.19 (d, 6H, 6.8, CH_3(*i*-Pr)), 1.30 (d, 6H, 6.8, CH_3(*i*-Pr)), 1.43 (s, 9H, t-Bu), 1.86 (s, 9H, t-Bu), 1.95 (s, 6H, 2CH_3(TMED)), 2.03 (s, 6H, 2CH_3(TMED)), 2.13 (s, 4H, CH_2(TMED)), 3.57 (septet, 2H, 6.8, CH(*i*-Pr)), 6.33 (d, 1H, 2.3, aromatic), 7.05 (d, 1H, 2.3, aromatic), 7.24 (s, 3H, aromatic). IR (Nujol, KBr) cm^{-1}: 1583(w), 1548(m), 1410(s), 1357(s), 1329(s), 1322(s), 1306(s), 1276(s), 1243(s), 1233(s), 1216(s), 1204(s), 1195(s), 1182(m), 1170(m), 1157(m), 1121(m), 1102(m), 1081(m), 1062(m), 1048(m), 1039(m), 1019(m), 1010(m), 996(m), 983(s), 950(m), 929(m), 917(m), 895(m), 879(w), 851(w), 845(m), 825(w), 819(w), 805(s), 796(s), 768(s), 762(s), 737(m), 727(s), 711(m), 694(w), 669(w), 652(w), 642(w), 606(w), 588(w), 579(w), 542(w), 509(w), 491(w).

4,6-Di-*tert*-butyl-*N*-(2,6-di-*iso*-propyl-phenyl)-o-amidophenolate-ethyl-indium(III) [APInEt]$_2$ (2). The APNa$_2$ (obtained from **imQ** 0.5 g, (1.32 mmol)) solution in diethyl ether (25 ml) was added to the ethylindium(III) diiodide [13b] (0.525 g, 1.32 mmol) solution in the same solvent (10 ml). The reaction mixture turned pale yellow and white precipitate of NaI formed. The solution was separated from the sodium iodide by filtration. Slow evaporation of diethyl ether solution resulted in the formation of pale yellow crystals of **2**. The total yield of the analytically pure compound is 0.93 g (67.4%). Anal. calc. for $C_{56}H_{84}In_2N_2O_2$ C, 64.25; H, 8.09; In, 21.93, N, 2.68%. Found: C, 64.98; H, 8.19; In, 21.72, N, 2.51%. ^{1}H NMR (400 MHz, C_6D_6, 20 °C, δ (ppm), J/Hz): 1.01 (d, 3H, 6.8, CH_3(*i*-Pr)), 1.06 (d, 3H, 6.8, CH_3(*i*-Pr)), 1.11 (t, 3H, 7.0, CH_3(Et)), 1.20 (q, 2H, 7.0, CH_2(Et)), 1.23 (s, 9H, t-Bu), 1.38 (s, 9H, t-Bu), 1.38 (d, 3H, 6.8, CH_3(*i*-Pr)), 1.54 (d, 3H, 6.8, CH_3(*i*-Pr)), 3.23 (septet, 1H, 6.8, CH(*i*-Pr)), 4.06 (septet, 1H, 6.8, CH(*i*-Pr)), 6.23 (d, 1H, 2.2, aromatic), 6.70 (d, 1H, 2.2, aromatic), 7.20 (dd, 1H, 1.2, 7.6, aromatic), 7.27 (t, 1H, 7.6, aromatic), 7.39 (dd, 1H, 1.2, 7.6, aromatic). Assignment of NMR signals was defined more exactly using 2D ge-COSY and ge-HSQC NMR. IR (Nujol, KBr) cm^{-1}: 1582(m), 1563(s), 1410(s), 1361(s), 1346(w), 1322(s), 1280(s), 1256(s), 1235(m), 1221(m), 1194(s), 1175(m), 1158(m), 1115(s), 1102(m), 1059(w), 1040(w), 1028(w), 1019(w), 984(s), 946(w), 938(w), 926(w), 916(m), 895(m), 883(w), 861(m), 841(w), 825(w), 812(m), 797(s), 767(m), 759(w), 737(w), 709(m), 654(m), 645(m), 616(w), 574(w), 544(w), 534(w), 516(w), 497(w), 489(w), 470(w).

4,6-Di-*tert*-butyl-*N*-(2,6-di-*iso*-propyl-phenyl)-o-iminoqenzo-quinone-di-iodo-indium(III) imSQInI$_2$(TMED) (3). Indium(III) iodide[13a] (0.65 g, 1.32 mmol) was treated with TMED (0.5 ml) and dissolved in 15 ml of diethyl ether. The imSQNa[8] (obtained from **imQ** 0.5 g, (1.32 mmol)) solution in the same solvent (20 ml) was added to this solution. The reaction mixture turned brown and white precipitate of NaI formed. The solution was separated from the sodium iodide by filtration. The resulting solution was stored at −20 °C overnight. It leads to the formation of brown-green crystals of **3**·Et$_2$O. Mother liquor was additionally concentrated and cooled to

Table 2 The crystal data collection and structure refinement data for the complexes **1–3**

Complex	**1**	**2**	**3·Et$_2$O**
Empirical formula	$C_{32}H_{53}$ IInN$_3$O	$C_{56}H_{84}In_2N_2O_2$	$C_{36}H_{63}I_2In\ N_3O_2$
Formula weight	737.49	1046.89	938.51
T/K	100(2)	100(2)	100(2)
Wavelength/Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Orthorhombic
Space group	$P2_1/c$	$P\bar{1}$	$P2_12_12_1$
Unit cell dimensions			
a/Å	10.4572(2)	11.3746(3)	11.0845(5)
b/Å	21.0844(5)	11.6291(3)	12.5220(5)
c/Å	15.7584(4)	21.8535(6)	30.1245(13)
α (°)	90.00	85.005(1)	90.00
β (°)	106.7190(4)	82.521(1)	90.00
γ (°)	90.00	68.264(1)	90.00
Volume/Å^3	3327.59(13)	2659.96(12)	4181.3(3)
Z	4	2	4
Density (calculated) [g cm^{-3}]	1.472	1.307	1.491
Absorption coefficient/mm^{-1}	1.665	0.907	2.073
Crystal size/mm	0.12 × 0.06 × 0.04	0.29 × 0.19 × 0.12	0.40 × 0.20 × 0.08
Θ range for data collection [°]	1.93–27.50	2.06–26.00	2.12–27.00
Reflections collected	31928	23016	38631
Independent reflections	7635 [R(int) = 0.0364]	10386 [R(int) = 0.0165]	9072 [R(int) = 0.0193]
Completeness (to Θ)	99.8% (27.50)	99.4% (26.00)	99.3% (27.00)
Flack parameter			−0.029(12)
Absorption correction	Semi-empirical from quivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9364 and 0.8252	0.8990 and 0.7789	0.8517 and 0.4911
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	7635/0/343	10386/0/581	9072/12/413
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0292$, w$R_2 = 0.0628$	$R_1 = 0.0249$, w$R_2 = 0.0621$	$R_1 = 0.0193$, w$R_2 = 0.0445$
R indices (all data)	$R_1 = 0.0491$, w$R_2 = 0.0676$	$R_1 = 0.0299$, w$R_2 = 0.0644$	$R_1 = 0.0207$, w$R_2 = 0.0451$
Goodness-of-fit on F^2	0.999	1.076	1.082
Largest diff. peak and hole [e/Å^3]	1.038 and −0.689	1.346 and −0.558	0.818 and −0.306

isolate the product more quantitatively. The total yield of the analytically pure compound is 0.84 g (67.7%). Anal. calc. for $C_{36}H_{63}I_2InN_3O_2$ C, 46.07; H, 6.77; I, 27.04, In, 12.23, N, 4.48%. Found: C, 46.28; H, 6.99; I, 26.90, In, 12.62, N, 4.31%. IR (Nujol, KBr) cm^{-1}: 1587(m), 1562(w), 1520(w), 1436(s), 1361(s), 1354(s), 1335(m), 1319(m), 1255(s), 1227(w), 1216(w), 1199(m), 1179(w), 1169(m), 1112(m), 1101(m), 1057(w), 1041(w), 1026(w), 1008(w), 992(m), 965(w), 937(w), 911(m), 883(w), 872(m), 861(m), 819(w), 798(s), 778(w), 764(m), 743(w), 708(w), 666(w), 648(w), 638(w), 627(w), 607(w), 574(w), 539(w), 527(w).

X-Ray crystallographic study of 1–3

Intensity data for **1–3** were collected at 100 K on a Bruker Smart Apex diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) in the φ–ω scan mode (ω = 0.3°, 10 s on each frame). The intensity data were integrated by SAINT program.[14] SADABS[15] was used to perform area-detector scaling and absorption corrections. The structures were solved by direct methods and were refined on F^2 using all reflections with SHELXTL package.[16] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were found from Fourier synthesis and refined isotropically. The crystal data collection and structure refinement data are listed in Table 2.

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