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Indium(III) halide–3,5-di-tert-butyl-*o*-benzosemiquinone systems

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Abstract

The reaction of InX_3 (X = Cl, Br, I) with 2 mol of $Na^+TBSQ^{\cdot -}$ ($TBSQ^{\cdot -}$ = 3,5-di-*t*-butyl-*o*-benzosemiquinonate anion) yields solutions of the diradicals $InX(TBSQ)_2$, whose EPR spectra have been recorded. Addition of pyridine or γ-picoline (= L) to such solutions produces adducts of the 3,5-di-*t*-butylcatecholate–indium(III) halide, of the type $In(TBC)XL_n$. The mechanism of these reactions, and of the related ligand replacement and disproportionation equilibria, is discussed in terms of internal one-electron transfer processes. The compound $In(TBC)(pic)_2 \cdot DMF$ has been the subject of an X-ray crystallographic study. The substance forms monoclinic crystals, space group $P2_1/n$ with $a = 12.992(5)$, $b = 13.923(4)$, $c = 18.491(4)$ Å, $\beta = 98.82(2)°$, $Z = 4$, $R = 0.053$ for 3244 unique reflections. The molecule is dimeric, with a central In_2O_2 ring, involving six-coordinate indium(III).

Keywords: Electron transfer; Crystal structures; Indium complexes; Halide complexes; Benzosemiquinone complexes

1. Introduction

Earlier papers from this laboratory [1–4] have described the reactions between indium(I) or tin(II) halides and substituted *o*-quinones in terms of successive one-electron transfer processes via a semiquinone intermediate to give the appropriate catecholato derivatives of either indium(III) or tin(IV) as the final product. In the course of these studies, we found that a semiquinone derivative of indium(III), $In(TBSQ)^{\cdot})Br_2pic_2$ ($TBSQ^{\cdot -}$ = 3,5-di-t-butyl-*o*-benzosemiquinonate anion; pic = 4-methylpyridine) could be prepared from the reaction of $InBr_3$ with $Na^+TBSQ^{\cdot -}$, followed by complexation by 4-picoline, and the structural and spectroscopic features of this molecule have been discussed elsewhere [4]. In a related series of experiments [5], it was established that 3,5-di-t-butyl-*o*-benzoquinone (TBP) reacts with the metallic elements magnesium, zinc, cadmium or barium (= M) to give $M(TBSQ^{\cdot})_2$ species. These molecules, and their derivatives with donors such as pyridine, 2,2′-bipyridine, etc., are biradicals, whose electron paramagnetic resonance (EPR) spectra have been analysed in terms of the appropriate spin Hamiltonian to yield information on the conformation of the six-coordinate $M(TBSQ^{\cdot})_2L$ complexes present in solution and the solid state. Biradical species of this type are unusual in the chemistry of such elements.

These experiments are part of a series of studies of inter- and intramolecular electron transfer processes in Main Group chemistry [6]. The present paper reports the results of attempts to prepare biradical derivatives of the type $In(TBSQ^{\cdot})_2X$ (X = Cl, Br, I). The results show that such species exist in solution, but the products obtained on crystallisation are indium(III) derivatives of the substituted catecholate. In the case of the iodo compound, this product is a dimer, based on an In_2O_2 ring, and similar to a complex identified in earlier work [7].

2. Experimental

2.1. General

Indium trihalides, InX_3 (X = Cl, Br, I) were prepared by direct reaction between metal and halogen. All other materials were used as supplied, except that solvents were distilled from, and stored over, the appropriate

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drying agents. All preparative and spectroscopic work was carried out in an atmosphere of dry nitrogen.

Indium analysis of reaction products was by atomic absorption spectrophotometry, and halogen analysis by the Volhard titrimetric method. Elemental analysis was performed by Canadian Microanalytical Services Ltd. IR spectra were run on a Nicolet 5DX instrument, using KBr discs, and ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-300L instrument.

Throughout this paper, we use the abbreviations TBQ↔TBSQ$^{\cdot-}$↔TBC^{2-} for the quinone, semiquinonate and catecholate species derived from 3,5-di-t-butyl-*o*-benzoquinone.

2.2. Preparative

In a typical experiment, Na$^+$TBSQ$^{\cdot-}$ was generated by the addition of H_2TBC (0.89 g, 4 mmol) to a suspension of NaH (0.096 g, 4 mmol) in anhydrous tetrahydrofuran (THF; 20 ml). When hydrogen evolution was complete, the resultant blue solution was added dropwise over 1 h to a solution of InX_3 (X = Cl, Br, I) (2 mmol) in THF (20 ml). This mixture was stirred at room temperature for ~2 h, during which time a colourless precipitate formed, and then gently refluxed for 3 h to ensure complete reaction. The precipitate was subsequently removed from the pale green solution by filtration, washed with diethyl ether (2×10 ml), and dried *in vacuo* overnight. This material was identified as NaX, formed in each case in almost quantitative yield (3.7 mmol, 92%).

The EPR spectra of the filtrate (see below) confirmed the presence of the diradical species In(TBSQ$^{\cdot}$)$_2$X, in keeping with the elimination of 2 equiv. of NaX. No solid products separated from these solutions during various periods of standing, or on cooling, but the addition of either pyridine (py) or 4-picoline (pic) in ~ten-fold excess resulted in the formation of crystalline products, which were collected, dried and weighed; yields were of the order of 50%. The chloro compound was recrystallised from 1:1 toluene:tetrahydrofuran (THF), and the iodo derivative from DMF. Analysis and NMR spectra showed that these colourless products are of the form In(TBC)XL$_2$ (solvent) (L = py, pic; solvent = DMF, THF).

In(TBC)Clpic$_2$. Anal. Calc. for $C_{26}H_{34}O_2N_2InCl$: C, 56.0; H, 6.11. Found: C, 56.0; H, 6.11%. ^{1}H NMR (d_6-DMSO), ppm ($Me_4Si = 0$): 8.42 (4H, s, pic), 7.24 (8H, m, pic, TBC^{2-}) 2.31 (6H, s, pic-Me), 1.38 (9H, d, t-Bu), 1.19 (9H, d, t-Bu). ^{13}C (d_6-DMSO), ppm ($Me_4Si = 0$): 149.0 (br), 124.8, 33.8, 31.9, 29.8, 20.5. Significant IR absorptions: 3150–3022 (aromatic γ(C–H)), 2989 (aliphatic γ(C–H)) 1627 (pic), 1511 (aromatic C–H), 1477, 1433, 1421 (γ(C–O)) cm^{-1}.

In(TBC)Brpy$_2$·THF. Anal. Calc. for $C_{28}H_{38}O_3N_2InBr$: C, 52.1; H, 5.93; N, 4.34; In, 17.8; Br, 12.4. Found: C, 51.7; H, 5.71; N, 4.50; In, 17.7; Br, 12.7%. ^{1}H NMR (CF_3COOD): 8.55, 8.32, 7.56 (py), 6.83 (TBC^{2-}), 3.76, 1.83 (THF), 1.32, 1.08 (t-Bu).

In(TBC)Ipic$_2$·DMF. Anal. Calc. for $C_{29}H_{41}O_3N_3InI$: C, 48.3; H, 5.73; N, 5.82; In, 15.9; I, 17.6. Found: C, 48.0; H, 6.02; N, 5.34; In, 16.1; I, 17.7%. ^{1}H NMR (CF_3COOD): 8.70, 7.44 (pic), 2.78, 2.65 (DMF), 2.32 (CH_3, pic) 1.43, 1.22 (t-Bu). Crystals of the iodo compound were subsequently subjected to X-ray crystallographic analysis.

2.3. Electron paramagnetic resonance spectroscopy

The X-band EPR spectra were recorded on a Bruker ESP-300E spectrometer equipped with a Hewlett-Packard microwave frequency counter and a Bruker nuclear magnetometer. Low temperature spectra were taken with use of a liquid nitrogen Dewar insert in the cavity. The spectra were recorded with 5–10 mW of microwave power. The frequency was ~9.80 GHz at room temperature and ~9.44 GHz when the insert Dewar was used.

2.4. Crystallographic studies

A suitable crystal of In(DBC)Ipic$_2$·DMF (**1**), mounted in a glass capillary, was sited in a Rigaku AFC65 diffractometer, using a beam of graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). Details of crystal size and other relevant parameters are given in Table 1. The cell constants, based on 7 reflections in the range $30.33 < 2\theta < 32.71°$, identified a monoclinic

Table 1
Summary of crystal data intensity collection and structure refinement for [In(TBC)Ipic$_2$]$_2$·2DMF, $C_{58}H_{82}O_6N_6In_2I_2$ (**1**)

Empirical formula	$(C_{29}H_{41}O_3N_3InI)_2$
Formula weight	721.37 (monomer)
Crystal colour, habit	green, block
Crystal dimensions (mm)	0.57×0.48×0.35
Crystal system	monoclinic
Cell constants	
a (Å)	12.992(5)
b (Å)	13.923(4)
c (Å)	18.491(4)
β (°)	98.82(2)
Cell volume (Å^3)	3305(3)
Space group	$P2_1/n$ (No. 14)
Z; F(000)	4; 1448
D_{calc} (g cm^{-3})	1.449
Absorption coefficient, μ (cm^{-1})	7.52
Temperature (°C)	23
Total reflections measured	6384
Unique data ($I \geqslant 3\sigma$)	3244
No. variables	309
R	0.053
R_w	0.056
ΔP_{max} (e Å^{-3})	0.42

cell. The systematic absences $h0l$, $h+l \neq 2n$: $0k0$, $k \neq 2n$, and the subsequent successful refinement, identified the space group as $P2_1/n$ (No. 14). The data were corrected for Lorentz and polarisation effects. The structure was solved by direct methods, and all non-hydrogen atoms other than those in the DMF molecule were refined anisotropically.

Convergence was achieved at final values of $R = 0.053$ and $R_w = 0.056$ for 3244 unique observed reflections. The programmes and correction procedures used are listed in Refs. [8–15]; the function minimised was $\Sigma w(|F_o| - |F_c|)^2$. Fig. 1 shows the molecular structure of the dimer $[In(TBC)Ipic_2]_2$, the final atomic coordinates are given in Table 2, and interatomic distances and angles are listed in Table 3. See also Section 6.

3. Results and discussion

3.1. Preparative and spectroscopic

The quantitative elimination of 2 equiv. of sodium halide in reaction (1) identifies the appropriate

$$InX_3 + 2NaTBSQ^{\cdot} \longrightarrow In(TBSQ^{\cdot})_2X + 2NaX \qquad (1)$$

diradical species as being the primary product present in the reaction mixture. The EPR spectrum of a freshly prepared dilute solution (InX_3; X = I) shows the characteristics of a molecule in which $TBSQ^{\cdot -}$ is bonded to an indium(III) centre (Fig. 2). The multiplet centred at $g = 2.0031$ can be resolved into features due to coupling to indium ($I = 9/2$) and one aromatic hydrogen, with hyperfine constants of $A_{In} = 7.2$ G, typical of indium in the +III state, and $A_H = 3.6$ G. Similar values have been reported in earlier work [4]. The frozen solution spectra showed very broad features in the $\Delta M_s = 1$ region due to the extensive but unresolved hyperfine structure of indium. In the case of the iodo compound (Fig. 2) the zero-field splitting parameters were estimated, giving $D = 250 \times 10^{-4}$ cm^{-1} and $E \sim 18 \times 10^{-4}$ cm^{-1}. The relatively high value of D indicates a strongly distorted *cis* configuration of the semiquinone rings in that biradical [5].

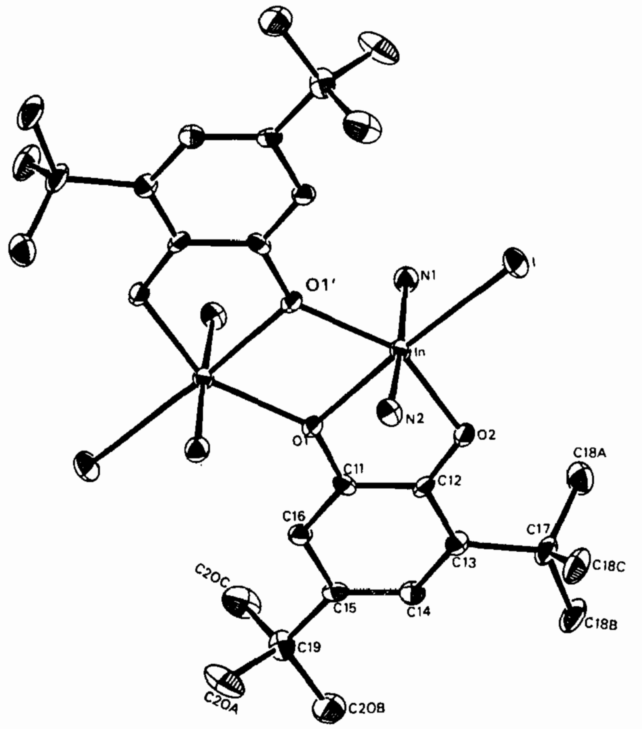


Fig. 1. Molecular structure of $[In(TBC)Ipic_2]_2$ (ORTEP diagram), showing the numbering system; atoms are drawn as 30% probability ellipsoids. The planar picoline rings are identified only by the nitrogen atoms N1 and N2.

Table 2
Final fractional coordinates and isotropic thermal parameters (Å^2) for non-hydrogen atoms of $[In(TBC)Ipic_2]_2 \cdot 2DMF$, with standard deviations in parentheses

Atom	x	y	z	B_{eq}
I	0.36232(6)	0.76823(5)	0.56084(5)	5.21(4)
In	0.41374(5)	0.57979(4)	0.53455(3)	2.76(3)
O(1)	0.4450(4)	0.4270(4)	0.5121(3)	3.1(3)
O(2)	0.2930(4)	0.5082(4)	0.5743(3)	3.3(3)
O(3)	1.136(1)	0.302(1)	0.3399(8)	13.0(4)
N(1)	0.5129(6)	0.5767(6)	0.6494(4)	3.9(4)
N(2)	0.3264(6)	0.5895(5)	0.4187(4)	3.8(4)
N(3)	1.006(1)	0.243(1)	0.3845(9)	11.0(4)
C(11)	0.3758(7)	0.3668(6)	0.5408(4)	3.0(4)
C(12)	0.2988(6)	0.4113(7)	0.5741(4)	2.9(4)
C(13)	0.2302(7)	0.3519(6)	0.6046(5)	3.2(4)
C(14)	0.2424(8)	0.2544(6)	0.6021(5)	3.5(4)
C(15)	0.3175(7)	0.2094(6)	0.5705(5)	3.1(4)
C(16)	0.3866(7)	0.2695(6)	0.5377(5)	3.3(4)
C(17)	0.1388(8)	0.3973(7)	0.6394(6)	4.5(5)
C(18A)	0.183(1)	0.4634(9)	0.7020(6)	5.6(6)
C(18B)	0.0664(9)	0.4548(9)	0.5804(7)	6.4(7)
C(18C)	0.074(1)	0.3208(8)	0.6714(7)	6.6(7)
C(19)	0.3356(9)	0.0985(7)	0.5689(5)	4.3(5)
C(20A)	0.339(1)	0.0656(8)	0.4931(7)	7.8(8)
C(20B)	0.435(1)	0.0735(8)	0.6163(7)	6.8(7)
C(20C)	0.246(1)	0.0477(8)	0.5967(8)	6.9(7)
C(21)	0.6046(8)	0.6217(8)	0.6638(6)	4.6(5)
C(22)	0.656(1)	0.6363(9)	0.7344(7)	6.1(6)
C(23)	0.611(1)	0.608(1)	0.7931(6)	5.8(7)
C(24)	0.518(1)	0.563(1)	0.7780(6)	6.5(7)
C(25)	0.4686(9)	0.5469(8)	0.7067(6)	5.5(6)
C(26)	0.662(1)	0.629(1)	0.8692(7)	8.5(8)
C(31)	0.2355(8)	0.5390(8)	0.3991(6)	4.6(5)
C(32)	0.1837(8)	0.5379(9)	0.3320(7)	5.4(6)
C(33)	0.220(1)	0.5946(8)	0.2758(6)	5.2(6)
C(34)	0.3103(9)	0.6427(9)	0.2949(6)	5.1(6)
C(35)	0.3612(8)	0.6408(7)	0.3667(6)	4.4(5)
C(36)	0.163(1)	0.593(1)	0.1988(6)	8.1(8)
C(41)	1.104(2)	0.270(1)	0.395(1)	10.7(5)
C(42)	0.973(3)	0.207(2)	0.453(2)	22(1)
C(43)	0.924(2)	0.248(2)	0.316(1)	17.3(9)

As pointed out in Section 2, we were not able to obtain crystalline samples of the products $In(TBSQ^{\cdot})_2X$.

Table 3
Interatomic distances (Å) and angles (°) with e.s.d.s. in parentheses for $[In(TBC)Ipic_2]_2 \cdot 2DMF$

Bond distances			
I–In	2.769(1)	C11–C12	1.40(1)
In–O1	2.216(6)	C11–C16	1.36(1)
In–O1′	2.146(5)	C12–C13	1.40(1)
In–O2	2.085(6)	C13–C14	1.37(1)
In–N1	2.309(8)	C13–C17	1.57(1)
In–N2	2.268(8)	C14–C15	1.37(1)
O1–C11	1.39(1)	C15–C16	1.43(1)
O2–C12	1.35(1)	C15–C19	1.56(1)
O3–C41	1.24(2)	C17–C18A	1.52(2)
N1–C21	1.34(1)	C17–C18B	1.55(2)
N2–C25	1.35(1)	C17–C18C	1.53(1)
N2–C31	1.37(1)	C19–C20A	1.48(1)
N2–C35	1.33(1)	C19–C20B	1.49(2)
N3–C41	1.31(2)	C19–C20C	1.52(1)
N3–C42	1.49(3)	C21–C22	1.39(1)
N3–C43	1.52(3)	C22–C23	1.36(2)
		C23–C24	1.36(2)
		C23–C26	1.49(2)
		C24–C25	1.39(2)
		C31–C32	1.32(1)
		C32–C33	1.44(1)
		C33–C34	1.35(1)
		C33–C36	1.50(1)
		C34–C35	1.39(1)
Intramolecular bond angles			
I–In–O1	176.6(1)	C16–C15–C19	117.7(8)
I–In–O1	110.9(1)	C11–C16–C15	119.3(9)
I–In–O2	100.2(2)	C13–C17–C18A	109.3(9)
I–In–N1	88.4(2)	C13–C17–C18B	109.6(8)
I–In–N2	90.6(2)	C13–C17–C18C	112.1(8)
O1–In–O1	71.9(2)	C18A–C17–C18B	110.0(9)
O1–In–O2	77.1(2)	C18A–C17–C18C	107.2(9)
O1–In–N1	93.6(2)	C21–N1–C25	117.6(9)
O1–In–N2	87.7(2)	In–N2–C31	120.2(6)
O1–In–O2	148.9(2)	In–N2–C35	122.6(7)
O1–In–N1	88.7(2)	C31–N2–C35	117.2(9)
O1–In–N2	87.6(2)	C41–N3–C42	112(2)
O2–In–N1	90.6(3)		
O2–In–N2	93.8(3)	C20A–C19–C20C	108(1)
N1–In–N2	175.5(3)	C20B–C19–C20C	109(1)
In–O1–In	108.1(2)	N1–C21–C22	123(1)
In–O1–C11	111.1(5)	C21–C22–C23	120(1)
In–O1–C11	140.2(5)	C22–C23–C24	116(1)
In–O2–C12	115.5(5)	C22–C23–C26	121(1)
In–N1–C21	122.0(6)	C24–C23–C26	123(1)
In–N1–C25	118.9(7)	C23–C24–C25	122(1)
C41–N3–C43	130(2)	N1–C25–C24	120(1)
C42–N3–C43	117(2)	N2–C31–C32	123(1)
O1–C11–C12	116.6(7)	C31–C32–C33	120(1)
O1–C11–C16	120.4(8)	C32–C33–C34	117(1)
C12–C11–C16	123.0(9)	C32–C33–C36	120(1)
O2–C12–C11	119.3(7)	C34–C33–C36	123(1)
O2–C12–C13	123.4(7)	C33–C34–C35	121(1)
C11–C12–C13	117.3(8)	N2–C35–C34	122(1)
C12–C13–C14	119.3(8)	C18B–C17–C18C	108.6(9)
C12–C13–C17	119.8(8)	C15–C19–C20A	110.5(8)
C14–C13–C17	120.9(8)	C15–C19–C20B	109.9(9)
C13–C14–C15	124.4(9)	C15–C19–C20C	109.2(9)
C14–C15–C16	116.7(8)	C20A–C19–C20B	110(1)
C14–C15–C19	125.6(8)		

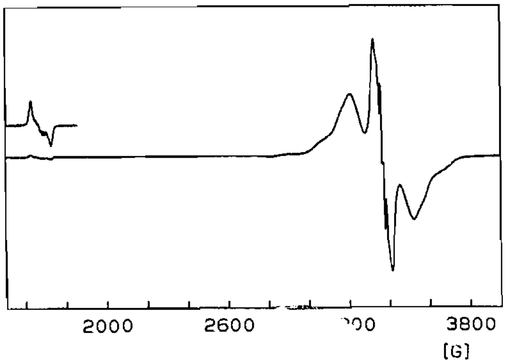


Fig. 2. EPR spectrum of a frozen solution of $In(TBSQ)_2I$ in THF at 77 K, showing the half-resonant-field features.

Addition of 4-picoline gave in each case derivatives of indium(III) with 3,5-di-t-butylcatecholate, and the mechanism of this process is discussed below.

3.2. Structure of $[In(TBC)I(pic)_2 \cdot 2DMF$ (1)

The most interesting feature of this molecule is its dimeric nature, involving an In_2O_2 four-membered ring, with In–O distances of 2.216(6) and 2.146(5) Å. A similar six-coordinate indium(III) species has been identified in the dianion $[In_2(TBC)_4(NH_3)_2]^{2-}$, obtained in studies of the electrochemical oxidation of indium metal in solutions of H_2TBC in liquid ammonia [16]. Both molecules involve six-coordinate indium(III) bonded to bidentate TBC^{2-} ligands which contribute one bridging oxygen to the In_2O_2 ring; the major difference is that in the dianion each indium atom is also coordinated by a second bidentate TBC^{2-} ligand which plays no part in the bridging. The ring in the dianion is slightly more symmetrical than in **1**, with In–O distances of 2.189(6) and 2.197(6) Å. It may be that a range of such values is possible, since in the case of two related organometallic compounds in which indium(III) is four-coordinate, the reported bond lengths are 2.147(5) and 2.219(12) Å in $(t\text{-}Bu_2InOEt)_2$ [16] and 2.191(2) in $(t\text{-}Bu_2InOOBu\text{-}t)_2$ [17]. An increasing number of molecules of this type is now known in the chemistry of Main Group elements, and such molecules present an interesting challenge in terms of the stabilising factors involved.

The coordination sphere at indium in **1** is completed by an In–I bond of length 2.769(1) Å, which can be compared with values of 2.718(1) Å in $C_2H_5InI_3^-$ [18], 2.717(1) and 2.711(1) in InI_4^- [19], and 2.750(1) (equatorial) and 2.919(1) (apical) in $C_2H_5InI_2 \cdot tmen$ [18]. The In–N bond distances are very similar to those in other species containing monodentate heterocyclic nitrogen donors; for example, r(In–N) in

In(TBSQ$^\cdot$)Br$_2$·2pic is 2.29(2) and 2.31(2) Å, and earlier values are in agreement with these results [4]. The final feature of significance is the C–O bond length in the TBC^{2-} ligand (1.35(1) and 1.39(1) Å) which confirms the formulation of the ligand as a substituted catecholate, and the bite angle at indium (77.1(2)°) which is close to that in related molecules [6,20]. The molecules of DMF present in the lattice play no role in the coordination of indium in this complex.

We also carried out a partial crystallographic analysis of a sample of a material identified as In(TBC)Cl(H$_2$O)py$_2$·2THF. As work on the structure proceeded, it became clear that this was an indium(III) species, with a six-coordinate InCl(O$_2$)N$_2$O′ kernel, whose stereochemical features are very similar to those reported for the molecule In(O$_2$C$_6$Cl$_4$)Clpic$_3$ (O$_2$C$_6$Cl$_4$$^{2-}$, tetrachlorocatecholate anion) [21] and the refinement was therefore discontinued.

3.3. Solution behaviour of InX(TBC) species

The analytical, spectroscopic and crystallographic results show that the products formed by adding strong monodentate donors to In(TBSQ$^\cdot$)$_2$X are indeed neutral diamagnetic adducts of In(TBC)X, correctly formulated as indium(III) halide substituted catecholate species. Despite this, diamagnetic solutions prepared by dissolving these molecules in toluene show strong EPR activity. Fig. 3 shows the spectra obtained from the iodo compound; those from the chloro and bromo species are essentially identical. These spectra are similar to those found in earlier studies [4] of InX/TBQ systems, and can be analysed in terms of the presence of both In^{I}/SQ and In^{III}/SQ species. The hyperfine coupling constants derived from these spectra are given in Table 4.

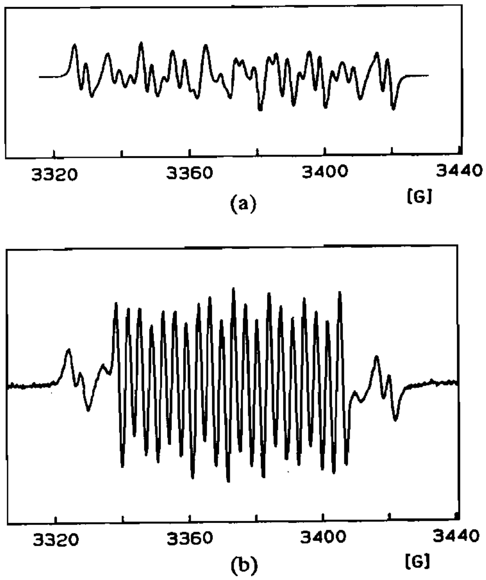


Fig. 3. EPR spectra of a solution prepared by dissolving [In(TBC)Ipic$_2$]$_2$ in toluene, recorded at (a) room temperature and (b) 250 K.

Table 4
Hyperfine coupling constants of solutions of In(TBC)X species in toluene (in gauss)

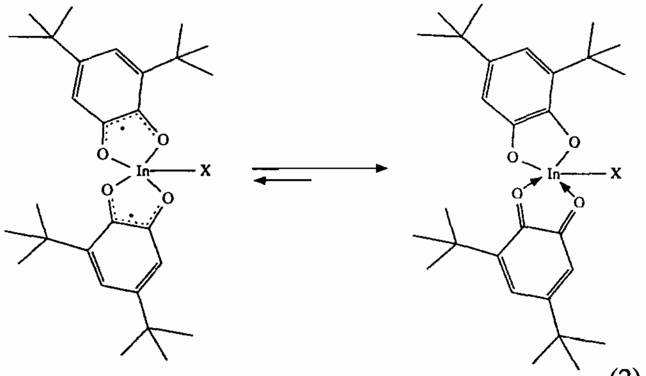
X	A_{In}	A_{H4}
Cl	9.4	3.2
	6.1	3.5
Br	9.6	3.5
	5.9	3.5
I	9.6	3.3
	5.4	3.5

The behaviour of aged solutions of InX(TBSQ$^\cdot$)$_2$ show that similar species are formed by the dissociation of these molecules. The spectrum of a sample of InX(TBSQ$^\cdot$)$_2$ (X = Cl), recorded ~48 h at 250 K after the initial preparation, shows the presence of equimolar quantities of both indium(I) and indium(III) species, with A values of $A_{In}=10.25$ G, $A_H=3.3$ G, $g=2.0032$ (indium(I)) and $A_{In}=7.08$ G, $A_H=3.3$ G, $g=2.0033$ (indium(III)) at 250 K. These values are slightly lower in the room temperature spectrum (e.g. $A_{In}=9.91$ G, $A_H=3.1$ G, $g=2.0033$ for indium(I)).

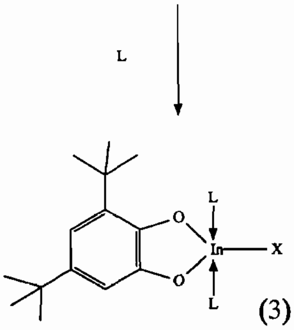
4. Discussion

The preparative, crystallographic and spectroscopic phenomena can be understood in terms of a series of solution equilibria which involve both internal electron transfer and ligand displacement processes. We rely on earlier results on the reactions of InX with *o*-quinones [3,4] and on the reaction of indium metal with tetrahalogeno-*o*-quinones [14] and with TBQ [22] in the interpretation of these results.

As emphasized above, Eq. (1) clearly represents the reaction between InX$_3$ and 2Na$^+$TBSQ$^{\cdot-}$ to yield In(TBSQ$^\cdot$)$_2$X whose presence in the filtrate from this reaction is clearly demonstrated by the EPR data. Such a molecule can equally well be written as the isomer In(TBC)(TBQ)X, formed by internal electron transfer between the two TBSQ$^{\cdot-}$ ligands, and in the presence of a strong base, such as pyridine or 4-picoline (= L), ligand substitution of the neutral *o*-quinone will give In(TBC)XL$_n$. In the case of the chloride system, the product In(TBC)Cl was isolated as colourless crystals forming in a coloured solution. This process, and that with the bromo and iodo compounds, can be represented as



(2)

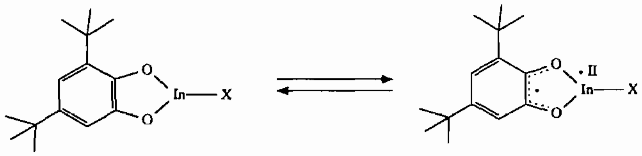


(3)

and the replacement of TBQ by the stronger nitrogen donors (Eq. (3)) is crucial here, and below. The chloro complex is presumably a five-coordinate monomeric species; there is no information on the molecularity of the bromo compound, but the iodide gives rise to the dimeric solid **1** discussed above.

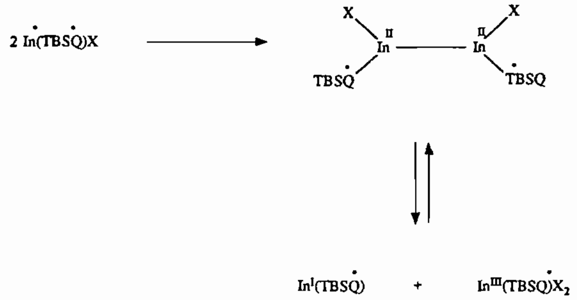
When $\mathrm{In(TBC)XL}_n$ compounds are dissolved in the non-coordinating solvent toluene, or when $\mathrm{In(TBSO^{\bullet})_2X}$ species age in solution, paramagnetic indium(I) and indium(III) species are detected in equimolar quantities. In the case of $\mathrm{In(TBC)XL}_n$, this can be explained in terms of the initial loss of neutral ligand in toluene solution; dissociative phenomena of this type are a common feature of the solution chemistry of indium(III) compounds [23]. Internal electron transfer then allows the indium(III) catecholate species to function as an indium(II) semiquinone

$$\mathrm{In(TBC)XL}_n \rightleftharpoons \mathrm{In(TBC)X} + n\mathrm{L} \tag{4}$$



$\mathrm{In(TBS\dot{Q})X}$ (5)

and following earlier arguments, this indium(II) species can dimerise, and the resultant dimer can then undergo disproportionation to give indium(I) and indium(III) species (Scheme 1).



Scheme 1.

These dimerisation and related processes have been discussed fully elsewhere [3,4]. The essence of Eqs. (5) and (2) is that the detailed electronic behaviour of the In(TBC)X species depends critically on the presence or absence of strong ligands such as pyridine. Strong donation of electron density onto the metal atom by ligation will favour conversion of the $\mathrm{TBSQ}^{\bullet-}$ ligand to TBC^{2-} and the loss of the neutral ligand will equally lead to a reversal of this process, and to the consequent disproportionation to indium(I) and indium(III). The hyperfine coupling constants shown in Table 4 are readily assigned to indium(I) (~9.5 G) and indium(III) (~6 G) derivatives of $\mathrm{TBSQ}^{\bullet-}$. These processes explain the formation of paramagnetic molecules from the diamagnetic InX(TBC) compounds; the dimer $[\mathrm{In(TBC)X(pic)_2}]$ can undergo similar reactions, provided that in this case Eq. (4) is replaced by

$$[\mathrm{In(TBC)XL}_n]_2 \rightleftharpoons 2\mathrm{In(TBC)X} + 2n\mathrm{L} \tag{6}$$

which itself may be rewritten as the sum of separate dimer dissociation and subsequent ligand loss processes.

The formation of indium(I) and (III) species from the slow dissociation of $\mathrm{In(TBSQ^{\bullet})_2X}$ can be understood in similar terms. One isomer of the bis-semiquinone is In(TBC)(TBQ)X, formed by internal electron transfer, and the loss of the neutral *o*-quinone ligand via the equilibrium

$$\mathrm{In(TBC)(TBQ)X} \rightleftharpoons \mathrm{In(TBC)X} + \mathrm{TBQ} \tag{7}$$

then generates the catecholate which in turn can give rise to $\mathrm{In(TBSQ^{\bullet})X}$ by Eq. (5). The sequence of processes discussed above then accounts for the presence of $\mathrm{In(TBSQ^{\bullet})}$ and $\mathrm{In(TBSQ)X_2}$ in these solutions.

5. Conclusions

Attempts to prepare the diradical species $\mathrm{In(TBSQ^{\bullet})_2X}$ were successful insofar as solutions of these compounds were concerned, but solid samples could not be obtained. An understanding of the chemistry of these molecules in the presence of weak or strong bases, and that of the catecholate derivatives In(TBC)XL_n, depends on two principles. The first is that indium(III) complexes are labile in solution in terms of ligand loss and/or substitution. The second is that internal one-electron transfer processes can occur readily in those complexes in which the ligand may be in the form of *o*-quinone, semiquinonate or catecholate, and that the oxidation state of indium can readily accommodate itself to such changes with only a small energy barrier. This type of behaviour has long been accepted in the chemistry of transition element compounds, and must also been taken into account in the solution chemistry of Main Group compounds.

6. Supplementary material

Tables of observed and calculated structure factors, anisotropic thermal parameters, fractional coordinates for hydrogen atoms and least-squares planes for the various rings, are available from the Cambridge Crystallographic Centre.

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