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One-Electron Transfer Processes in the Reaction of Indium(I) Halides with Substituted *o*-Quinones

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Indium(I) halides (InX; X = Cl, Br, I) react with 3,5-di-*tert*-butyl-*o*-quinone (TBQ) in toluene/tmen solution to give the corresponding semiquinone–indium(III) derivatives (TBSQ)InX$_2$·tmen (tmen = *N,N,N',N'*-tetramethylethanediamine). Related species have been prepared by the reaction between Na$^+$TBSQ$^-$ and InX$_3$, and the presence of the semiquinone has been confirmed by X-ray crystallography in the case of (TBSQ)InBr$_2$·2CH$_3$C$_5$H$_4$N·0.5(*N,N*-dimethylformamide), which is monoclinic, with $a = 31.479$ (8) Å, $b = 10.941$ (4) Å, $c = 21.962$ (8) Å, $\beta = 125.06$ (2)°, $V = 6191.5$ (3) Å^3, $Z = 8$, and space group $C2/c$; $R = 0.0529$ and $T = 21$ °C. This molecule has a distorted-octahedral InO$_2$N$_2$Br$_2$ kernel, and the C–O distances with the ligand confirm the presence of the semiquinone. The reaction of InX and TBQ in toluene/pyridine gives species analyzing as (TBSQ$^•$)InX·2py (X = Cl, Br), identified as dimeric indium(II) derivatives. These systems have also been investigated by electron spin resonance spectroscopy. The reaction mechanism proposed involves an initial one-electron transfer process, followed by dimerization and rearrangement reactions, and is in good agreement with both preparative and spectroscopic work. Studies with InX and phenanthrene-9,10-quinone give less detailed but similar results.

Introduction

Recent developments in the experimental techniques for handling indium(I) compounds have allowed certain aspects of the nonaqueous solution chemistry of these otherwise intractable substances to be studied,[1] and among the reactions investigated are oxidation to the appropriate indium(III) species by reagents such as iodine, diphenyl disulfide, and diphenyl diselenide.[2,3] The tentative mechanism proposed to explain these reactions can be applied in essence to the oxidative addition of In^{I}X to M–X bonds.[4-6] Indium(I) halides also react with tetrahalogeno-*o*-quinones (Y$_4$C$_6$O$_2$-*o*; Y = Cl, Br) to give the corresponding indium(III)-substituted catecholate–halogeno complexes InX(O$_2$C$_6$Y$_4$-*o*), which have been stabilized as neutral or anionic complexes with suitable donors.[7] The conditions under which these latter experiments were performed prevented any detailed study of the reaction mechanism, but we now report preparative and spectroscopic studies of the oxidation of indium(I) halides by the substituted *o*-quinones 3,5-di-*tert*-butyl-*o*-benzoquinone (TBQ) and phenanthrene-9,10-quinone (PQ). There is clear evidence of successive one-electron transfer reactions in these systems.

The reactions in question are parallel to those reported elsewhere between stannous halides and *o*-quinones.[8,9] We should also note that indium metal reacts with 3,5-di-*tert*-butyl-*o*-benzoquinone to give the corresponding indium(I) semiquinonate,[10] and with Y$_4$C$_6$O$_2$-*o* (Y = Cl, Br).[11] The spectroscopic properties of the products of these reactions and their derivatives are critical in the discussion of the present spectroscopic results. We should also note the work of Razuvaev et al.,[12] who reported that indium trichloride reacts with substituted *o*-quinones to give semiquinone species, which were identified from the electron spin resonance (ESR) spectra.

Experimental Section

General Data. Indium(I) halides were prepared by heating the metal and trihalide together in a sealed tube,[13] and the trihalides were obtained by direct reaction of metal and halogen.[14] 3,5-Di-*tert*-butyl-*o*-benzoquinone, phenanthrene-9,10-quinone (Gold Label quality), 3,5-di-*tert*-butylcatechol, 4-methylpyridine (γ-picoline), and *N,N,N',N'*-tetramethylethanediamine (tmen) were used as supplied (Aldrich).

Indium analysis of reaction products was by atomic absorption spectrophotometry, and halogen analysis by the Volhard titrimetric method. Infrared spectra were recorded on a Nicolet 5DX instrument, using KBr disks, and ^{1}H and ^{13}C NMR spectra were run on Varian EM 360 or Bruker AC-300 L instruments. All preparative work was carried out in an atmosphere of dry nitrogen.

Throughout this paper, we use the abbreviations TBQ $\xrightarrow{e}$ TBSQ$^{•-}$ $\xrightarrow{e}$ TBC^{2-}, and PQ $\xrightarrow{e}$ PSQ$^{•-}$ $\xrightarrow{e}$ for the *o*-quinone, *o*-semiquinone, and *o*-diolato anionic derivatives of 3,5-di-*tert*-butyl-*o*-benzoquinone and phenanthrene-9,10-quinone, respectively.

Reactions of InX (X = Cl, Br, I) with 3,5-Di-*tert*-butyl-*o*-benzoquinone. (i) InX (3.3 mmol) (X = Cl, Br, I) was suspended in toluene (25 mL) and cooled to about −40 °C, and tmen (2 mL, 13.2 mmol) syringed into the mixture to give the red color characteristic of solutions of indium(I) halides in such media.[1] An equimolar amount of 3,5-di-*tert*-butyl-*o*-benzoquinone (0.66 g, 3.3 mmol) in toluene (25 mL) was added dropwise over a period of 1 h, and the mixture stirred at this temperature for a further hour, at which point the solution was green. The cooling bath was then slowly removed and the mixture allowed to reach room temperature, after which traces of solid impurities were removed by filtration, and the volume of the filtrate reduced by half in vacuo. Addition of petroleum ether (25 mL) afforded a precipitate (pale green, X = Cl, Br; pale brown, X = I) which analyzed as C$_{14}$H$_{20}$O$_2$InX$_2$·tmen. Analogous results were obtained when toluene + tmen was replaced by tetrahydrofuran (thf) (25 mL) + pyridine (py) (2 mL, 24 mmol), in which case the product was the solvate C$_{14}$H$_{20}$O$_2$InX$_2$·2py·0.5thf. The yields were typically 40–45%, based on the quantity of InX used. Analytical results for these and other products are reported in Table I.

(ii) A suspension of InX (X = Cl, Br) (4 mmol) was refluxed for 2 h with an equimolar amount of TBQ in toluene (25 mL), and excess pyridine (2 mL, 24 mmol) was then added. The resultant green solution obtained after ca. 2 h was filtered; slow evaporation of the filtrate yielded a fine crystalline green product which analyzed as C$_{14}$H$_{20}$O$_2$InX·2py. The ESR spectrum of the toluene solution is discussed below.

(iii) Powdered InI (0.52 g, 2.15 mmol) was suspended in a solution of TBQ (0.47 g, 2.15 mmol) and I$_2$ (0.27 g, 1.08 mmol) in toluene (25 mL), and the mixture degassed in vacuo, after which 4-picoline (pic) (1 mL, 0.96 g, 10.3 mmol) was syringed in, and the system again degassed. The mixture was stirred for 2 h at −40 °C and then allowed to reach

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Table I. Analytical Results

compound	method of prepn[a]	% found (% calcd)				
		In	C	H	N	halogen
$(C_{14}H_{20}O_2)InCl_2{\cdot}tmen$	i	21.5 (22.0)	46.8 (46.0)	7.65 (6.95)	5.45 (5.36)	13.7 (13.6)
$(C_{14}H_{20}O_2)InBr_2{\cdot}tmen$	i	18.5 (18.0)				26.3 (26.2)
$(C_{14}H_{20}O_2)InI_2{\cdot}tmen$	i	16.4 (15.3)				36.2 (36.0)
$(C_{14}H_{20}O_2)InCl_2{\cdot}2py{\cdot}0.5thf$	i	19.0 (19.1)				11.7 (11.8)
$(C_{14}H_{20}O_2)InBr_2{\cdot}2py{\cdot}0.5thf$	i	16.7 (16.7)	45.4 (45.3)	5.12 (4.97)	3.76 (4.07)	23.0 (23.2)
$(C_{14}H_{20}O_2)InCl{\cdot}2py$	ii	21.8 (21.7)				6.31 (6.71)
$(C_{14}H_{20}O_2)InBr{\cdot}2py$	ii	20.6 (20.0)	50.0 (50.3)	5.43 (5.27)	4.75 (4.89)	14.1 (14.0)
$(C_{14}H_{20}O_2)InCl_2{\cdot}2pic$	iv	19.2 (19.4)				12.1 (12.0)
$(C_{14}H_{20}O_2)InBr_2{\cdot}2pic{\cdot}0.5dmf$	iv	15.9 (16.0)	45.3 (46.0)	5.04 (5.27)	4.87 (4.88)	22.3 (22.3)
$(C_{14}H_{20}O_2)InBr(I){\cdot}2pic$	iii	15.7 (15.8)	43.1 (42.9)	4.73 (4.71)	4.07 (3.85)	
$(C_{14}H_{20}O_2)InI_2{\cdot}3pic{\cdot}0.5tol$	iii	12.6 (12.6)				27.8 (27.8)
$(C_{14}H_8O_2)InCl{\cdot}tmen$	i	24.3 (24.2)	50.4 (50.6)	5.35 (5.06)	5.16 (5.89)	7.45 (7.48)
$(C_{14}H_8O_2)InBr{\cdot}tmen$	i	22.3 (22.1)				15.5 (15.4)
$(C_{14}H_8O_2)InI{\cdot}tmen$	i	20.7 (20.3)				22.5 (22.4)

[a] Refers to text in Experimental Section.

room temperature. After the mixture was further stirred for 2 h, the volume was reduced by ca. 50% and petroleum ether (bp, 35–60 °C) added to precipitate a pale green solid, which was collected by filtration, washed with petroleum ether (two 20-mL portions), and dried in vacuo. This product was identified as $C_{14}H_{20}O_2InI_2{\cdot}3pic{\cdot}0.5$toluene, obtained in 91% yield. In addition to the analytical results, the ligand ratio and the presence of toluene were confirmed by the ^1H NMR spectrum of a solution prepared by treating the product with CF_3COOD: 4-picoline 8.79 (m, 6 H, H 3,3) 8.08 (m, 6 H, H 2,2′), 2.93 (s, 9 H, CH_3); toluene 7.34 (m, 5 H, aromatic), 2.49 (s, 3 H, CH_3); $CATD_2$ 1.47 (s, 9 H, t-C_4H_9 at C5), 1.33 (s, 9 H, t-C_4H_9 at C3) (all in ppm, relative to Me_4Si = 0). We did not observe any resonances corresponding to H4 and H6 of $CATD_2$. The conductivity of $C_{14}H_{20}O_2InI_2{\cdot}3pic{\cdot}0.5$toluene in *N,N*-dimethylformamide (millimolar concentration) was 62 Ω^{-1} cm^2 mol^{-1}, slightly below the normal range for 1:1 electrolytes in this solvent, and we therefore formulate this species as the salt $[C_{14}H_{20}O_2In(I)(pic)_3]I$.

A similar sequence, starting with InBr (0.35 g, 1.8 mmol), TBQ (0.396 g, 1.8 mmol), and I_2 (0.228 g, 0.9 mmol) yielded $C_{14}H_{20}O_2InBr(I){\cdot}2pic$ in 90% yield.

Reaction of InX_3 with $TBSQ^{\bullet-}$. (iv) When 3,5-di-*tert*-butylcatechol (2 g, 4.5 mmol) was treated with sodium hydride (0.11 g, 4.5 mmol) in benzene (24 mL), hydrogen gas evolved and a blue solution of the corresponding sodium semiquinonate was obtained. The mixture was stirred until evolution of hydrogen stopped (30 min), after which $InBr_3$ (1.59 g, 4.5 mmol) or $InCl_3$ (1 g, 4.5 mmol) in benzene (25 mL) was added dropwise to the reaction mixture. An immediate reaction was evident, with the blue solution becoming pale green. The resultant mixture was refluxed for 2 h. The NaX formed (X = Cl, Br) was collected and weighed (X = Cl, found 0.19 g, calcd 0.23 g; X = Br, found 0.40 g, calcd 0.46 g).

A 2-fold excess of either 4-picoline or pyridine (=L) was added to the filtrate, the mixture stirred at room temperature for 1 h, and the volume then reduced by half. Slow evaporation over several days gave a quantitative yield of green crystals, which were collected and dried in vacuo; these solids analyzed as $C_{14}H_{20}O_2InX_2{\cdot}2L$. Recrystallization of the 4-picoline adduct of this complex in *N,N*-dimethylformamide (dmf) gave solvated crystals suitable for X-ray crystallography.

Reaction of InX with Phenanthrene-9,10-quinone. InX (X = Cl, Br, I) (3.3 mmol) and phenanthrene-9,10-quinone (3.3 mmol) were suspended in toluene (50 mL), the suspension was cooled to −40 °C, and tmen (2 mL, 13.3 mmol) was syringed into the mixture, which was stirred at this temperature until the InX had completely dissolved. The cooling bath was then slowly removed. As the solution warmed up, it became cloudy and at room temperature a substantial amount of solid deposit was visible; this was collected, washed with benzene (two 20-mL portions), and dried in vacuo. This material, which analyzed as $C_{14}H_8O_2InX{\cdot}tmen$, is soluble in methylene chloride and tetrahydrofuran.

Electron Spin Resonance Spectroscopy. ESR spectra were obtained with a Varian E12 spectrometer whose sweep was calibrated with an NMR gaussmeter. The klystron frequency was determined from the ESR spectrum of diphenylpicrylhydrazide. Spectra at 77 K were obtained by using a finger Dewar cooled with liquid nitrogen. The preparation of degassed sample solutions, whose solute concentration was typically 10^{-6} mol L^{-1}, followed the methods described previously.[9] All the spectra recorded had g values of 2.0039 unless otherwise noted.

Table II. Summary of Crystal Data Intensity Collection and Structure Refinement for $(t\text{-}Bu_2H_2C_6O_2)InBr_2{\cdot}2(C_6H_7N){\cdot}0.5dmf$

chemical formula	$C_{26}H_{34}N_2O_2Br_2In{\cdot}0.5(C_3H_7NO)$
cell constants	a = 31.479 (8) Å, b = 10.941 (4) Å, c = 21.962 (8) Å, β = 125.06 (2)°
cell volume, Å^3	6191.5 (3)
space group	$C2/c$ (No. 15)
Z; $F(000)$	8; 2732
d (calcd, measd), g cm^{-3}	1.48, 1.51
cryst dimens, mm	0.15 × 0.18 × 0.30
abs coeff, μ, cm^{-1}	32.45
radiation	Mo Kα, λ = 0.710 69 Å
temp, °C	21
total reflecns measd	4001 ($+h$, $+k$, $\pm l$)
unique data used	1697 ($I \geq 3\sigma$)
$R(F_o^2)$	5.29
$R_w(F_o^2)$	5.47
$\Delta\rho_{max}$, ϵ Å^{-3}	0.94

Crystallographic Studies. A suitable crystal of $(TBSQ^{\bullet})InBr_2{\cdot}2pic{\cdot}0.5dmf$ was sealed in a capillary, and mounted on a Syntex $P2_1$ diffractometer. Details of crystal size and other relevant parameters are given in Table II. The intensity of the three monitored reflections decreased approximately 15% during data collection, and this was accounted for by a linear decay correction. A rapid decrease in intensities beyond 2θ = 30° was ascribed to disorder (see below), and most of the reflections beyond 2θ = 30° were therefore rejected in subsequent calculations, so that only 42% of the measured reflections were given "observed" status. The data was further corrected for Lorentz, polarization, and absorption effects. The systematic absence $h, k, l, h + k = 2n + 1$; $h0l, l = 2n + 1$ indicated the space groups $C2/c$ or Cc. The former was used and subsequently assumed to be correct because of the successful refinement of the structure. The structure was solved by the heavy atom method, using the program and methods described previously.

The position of the indium atom was obtained from a sharpened Patterson synthesis, and the remaining non-hydrogen atoms were obtained from subsequent difference Fourier syntheses based on the coordinates of the indium atom. The structure was then refined by full matrix least-squares method, with In, Br, N, and O(1) and O(2) being treated anisotropically and all carbon atoms isotropically. At this stage, the partial dmf of solvation was identified, with the N–CH_3 bond lying on a crystallographic 2-fold axis, and with the formyl group disordered. Refinement was carried out with the carbon and oxygen atoms of the formyl group being assigned 52% and 35% occupancies, respectively, but this gave unreasonable N–C and C–O distances and high thermal parameters. This was corrected by constraining these bond lengths at 1.50 and 1.30 Å, respectively, and by fixing the thermal parameters of O(3). This refinement converged at R = 0.0638 and R_w = 0.0729, at which stage some peaks appeared in the difference map as plausible hydrogen atom locations. No hydrogen atoms were included in the model for the disordered dmf molecule. The remaining hydrogen atoms were subsequently included in idealized position (r(C–H) = 0.95 Å), with isotropic thermal parameters which were given the same values as for the appropriate thermal parameters of the adjacent carbon atoms. Convergence was achieved after six more cycles of refinement, with the final values of R = 0.0529 and R_w = 0.0547 for 1697 unique observed [$I > 3\sigma(I)$] reflections. Figure 1 shows the molecular structure.

The final atomic coordinates for non-hydrogen atoms are given in Table III and important interatomic distances and angles in Table IV. Tables of observed and calculated structure factors, anisotropic thermal parameters, and fractional coordinates for hydrogen atoms and the unit cell packing diagrams are available as supplementary material.

Table III. Final Fractional Coordinates and Isotropic Thermal Parameters (Å^2) for Non-Hydrogen Atoms of (TBSQ)InBr$_2\cdot$2C$_6$H$_7$N$\cdot$0.5dmf, with Standard Deviations in Parentheses

atom	*x*	*y*	*z*	$U_{eq}/U \times 10^3$
In	0.1274	0.2188 (1)	0.1434 (1)	48 (1)
Br(1)	0.1732 (1)	0.2619 (2)	0.0869 (1)	74 (1)
Br(2)	0.0326 (1)	0.2747 (2)	0.0869 (1)	83 (2)
O(1)	0.2019 (3)	0.1625 (9)	0.1613 (5)	46 (7)
O(2)	0.1063 (4)	0.1616 (9)	0.0333 (5)	51 (7)
O(3)	−0.0420 (28)	0.4975 (58)	0.1403 (43)	200
N(1)	0.1435 (5)	0.4097 (11)	0.1180 (7)	50 (10)
N(2)	0.1161 (5)	0.0147 (11)	0.1586 (7)	48 (10)
N(3)	0.0000	0.3866 (32)	0.2500	263 (19)
C(1)	0.1869 (6)	0.4742 (14)	0.1689 (9)	52 (5)
C(2)	0.1951 (6)	0.5931 (15)	0.1561 (9)	65 (5)
C(3)	0.1595 (6)	0.6495 (15)	0.0907 (9)	56 (5)
C(4)	0.1161 (6)	0.5869 (15)	0.0406 (9)	62 (5)
C(5)	0.1094 (6)	0.4697 (16)	0.0540 (10)	67 (5)
C(6)	0.1692 (7)	0.7803 (16)	0.0785 (10)	91 (6)
C(7)	0.1515 (7)	−0.0105 (17)	0.2181 (10)	71 (5)
C(8)	0.1448 (7)	−0.1703 (17)	0.2287 (10)	78 (6)
C(9)	0.0975 (6)	−0.2263 (17)	0.1743 (9)	69 (5)
C(10)	0.0609 (7)	−0.1601 (17)	0.1132 (10)	72 (5)
C(11)	0.0720 (6)	−0.0395 (15)	0.1082 (9)	63 (5)
C(12)	0.0870 (8)	−0.3559 (18)	0.1839 (11)	111 (7)
C(13)	0.1440 (5)	0.1240 (12)	0.0318 (7)	36 (4)
C(14)	0.1393 (6)	0.0816 (14)	−0.0349 (8)	49 (4)
C(15)	0.1832 (5)	0.0528 (13)	−0.0282 (8)	50 (4)
C(16)	0.2348 (5)	0.0578 (13)	−0.0377 (8)	45 (4)
C(17)	0.2401 (5)	0.0938 (12)	0.1030 (8)	46 (4)
C(18)	0.1965 (5)	0.1274 (13)	0.1018 (8)	42 (4)
C(19)	0.0842 (6)	0.0754 (15)	−0.1079 (9)	64 (5)
C(20)	0.0512 (6)	−0.0148 (15)	−0.0841 (9)	78 (6)
C(21)	0.0579 (6)	0.2004 (16)	−0.1300 (10)	86 (6)
C(22)	0.0877 (7)	0.0283 (18)	−0.1712 (10)	103 (7)
C(23)	0.2797 (6)	0.0280 (14)	−0.0339 (9)	57 (5)
C(24)	0.2803 (6)	−0.1082 (15)	0.0240 (9)	82 (6)
C(25)	0.2767 (6)	0.0995 (16)	−0.0278 (9)	84 (6)
C(26)	0.3315 (6)	0.0602 (17)	0.1050 (9)	90 (6)
C(27)	0.0465 (16)	0.3183 (40)	0.2924 (23)	263 (19)
C(28)	0.0016 (33)	0.4724 (51)	0.1988 (39)	216 (43)

[a] U_{eq} for In, Br, N, and O(1) and O(2) atoms is calculated from the refined anisotropic thermal parameters ($U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a^*_i a^*_j a_i a_j$). The remaining atoms were refined isotropically.

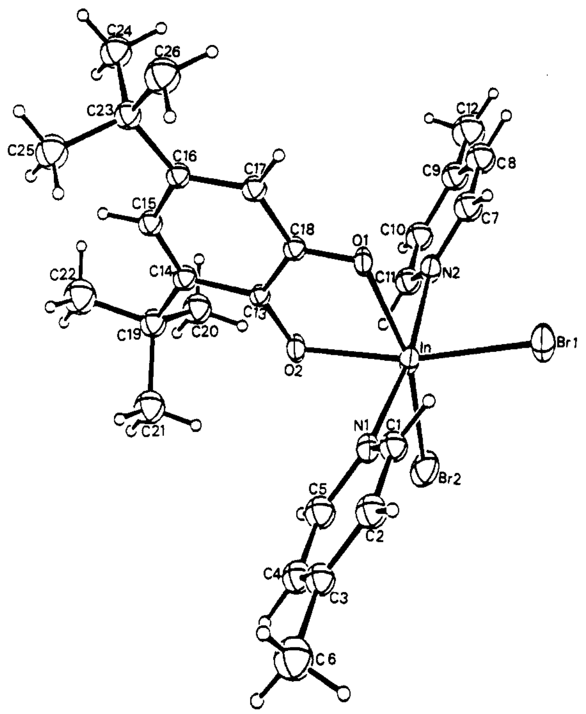


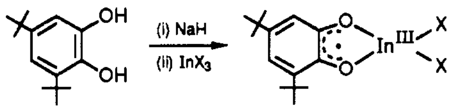
Figure 1. Molecular structure of (TBSQ$^\cdot$)InBr$_2$·2pic, ORTEP diagram with atoms drawn as 30% probability ellipsoids, showing the numbering scheme used.

Table IV. Interatomic Distances (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses for (DBSQ)InBr$_2\cdot$2(C$_6$H$_7$N)$\cdot$0.5dmf

In–Br(1)	2.558 (3)	N(1)–C(1)	1.36 (2)
In–Br(2)	2.562 (3)	N(2)–C(5)	1.35 (3)
In–O(1)	2.23 (1)	N(2)–C(7)	1.33 (3)
In–O(2)	2.20 (1)	N(2)–C(11)	1.32 (3)
In–N(1)	2.29 (2)	N(3)–C(27)	1.42 (6)
In–N(2)	2.32 (2)	N(3)–C(28)	1.49 (6)
C(18)–O(1)	1.28 (2)	O(3)–C(28)	1.26 (6)
C(13)–O(2)	1.28 (2)		
Br(1)–In–Br(2)	103.6 (1)	In–O(1)–C(18)	113 (1)
Br(1)–In–O(1)	91.5 (4)	In–O(2)–C(13)	115 (1)
Br(2)–In–O(1)	164.9 (4)	In–N(1)–C(1)	122 (2)
Br(1)–In–O(2)	166.1 (4)	In–N(1)–C(5)	123 (2)
Br(2)–In–O(2)	90.2 (4)	In–N(2)–C(7)	123 (2)
O(1)–In–O(2)	74.8 (5)	In–N(2)–C(11)	119 (2)
Br(1)–In–N(1)	94.0 (5)	C(1)–N(1)–C(5)	115 (2)
Br(2)–In–N(1)	91.3 (5)	C(7)–N(2)–C(11)	118 (2)
O(1)–In–N(1)	86.4 (6)	N(1)–C(1)–C(2)	122 (2)
O(2)–In–N(1)	87.6 (6)	N(1)–C(5)–C(4)	124 (3)
Br(1)–In–N(2)	91.9 (5)	C(2)–C(3)–C(6)	119 (2)
Br(2)–In–N(2)	93.8 (5)	C(4)–C(3)–C(6)	123 (2)
O(2)–In–N(2)	84.8 (6)	C(3)–C(4)–C(5)	121 (3)
O(1)–In–N(2)	86.6 (6)	N(2)–C(7)–C(8)	123 (2)
N(1)–In–N(2)	170.9 (6)	N(2)–C(16)–C(10)	124 (3)
C(17)–C(16)–C(23)	124 (2)	C(15)–C(16)–C(23)	120 (2)
C(15)–C(14)–C(19)	125 (2)	O(2)–C(13)–C(14)	125 (2)
C(13)–C(14)–C(19)	117 (2)	O(1)–C(18)–C(13)	119 (2)
O(2)–C(13)–C(18)	118 (2)	O(1)–C(18)–C(17)	120 (2)
4-pic C(1)–C(5)		ring C(13)–C(18)	
mean C–C	1.36 (4)	mean C–C	1.42 (5)
mean C–C–C	121 (3)	mean C–C–C	120 (4)
C(3)–C(6)	1.52 (3)	C(14)–C(19)	1.55 (3)
		C(16)–C(23)	1.50 (3)
4-pic C(7)–C(11)		*t*-Bu C(19)–C(22)	
mean C–C	1.38 (5)	mean C–C	1.54 (3)
mean C–C–C	120 (4)	mean C–C–C	109 (3)
C(9)–C(12)	1.50 (3)		
		t-Bu C(23)–C(26)	
		mean C–C	1.52 (2)
		mean C–C–C	110 (2)

Results

Structure of (TBSQ)InBr$_2\cdot$2CH$_3$C$_5$H$_4$N (1). The preparation and properties of this compound provide a useful starting point for the discussion of this work. The preparative route



implies the formation of an indium(III) semiquinonate derivative, and the quantitative elimination of NaX (X = Cl, Br) in the second stage confirms the reality of these reactions. The structural data obtained by X-ray crystallography is completely congruent with the preparative work, since the structure (Figure 1) is clearly that of a six-coordinate indium(III) species.

The bond distances given in Table IV are in good agreement with those previously reported for molecules with octahedral InO$_2$N$_2$X$_2$ kernels. The average In–O bond distance of 2.22 (1) Å is close to that found in InCl$_2$(acac)(bpy), where the values are 2.124 (3) Å cis to Cl, and 2.164 (3) Å trans.[15] A closer comparison is in the molecule[11] InCl(O$_2$C$_6$Cl$_4$)$\cdot$3CH$_3$C$_5$H$_4$N, in which indium(III) is complexed by the tetrachlorocatecholate ligand, with an average In–O bond length of 2.128 (7) Å. A similar agreement is found between the In–N distances in the present compound (2.31 (1) Å (av)) and those in InCl(O$_2$C$_6$Cl$_4$)$\cdot$3CH$_3$C$_5$H$_4$N, for which the values are 2.265 (9), 2.322 (12), and 2.325 (12) Å; other comparable structures are InCl$_2$(acac)(bpy)

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Table V. Hyperfine Coupling Constants for Various Indium Species (in Gauss)

compound	method of prepn[a]	solvent	A_{In}	A_H
(TBSQ)$InCl_2$·tmen	i	toluene/CH_2Cl_2	7.60	*b*
(TBSQ)$InBr_2$tmen	i	toluene/CH_2Cl_2	7.40	*b*
(TBSQ)InI_2·tmen	i	toluene/CH_2Cl_2	7.10	*b*
(TBSQ)InCl·2py	ii	toluene	10.72	3.31 (C_4)(In^I)
			6.51	3.48 (C_4)(In^{III})
(TBSQ)InBr·2py	ii	toluene	10.14	3.19 (C_4)(In^I)
			6.33	3.53 (C_4)(In^{III})
(TBSQ)InBr·2pic	ii	toluene	9.90	3.20 (C_4)(In^I)
			5.47	3.20 (C_4), 0.37 (C_5)(In^{III})
(TBSQ)$InBr_2$[c]	iii	CH_2Cl_2/pic	5.40	3.20 (C_4)
(TBSQ)InI_2[c]	iii	CH_2Cl_2/pic	3.70	3.60 (C_4)
(TBSQ)$InCl_2$·2py	iv	thf	6.38	3.31 (C_4), 0.31 (C_5)
(TBSQ)$InBr_2$·2py	iv	thf	5.13	3.85 (C_4), 0.34 (C_5)
(TBSQ)$InCl_2$·2pic	iv	benzene	6.11	3.53 (C_4)
(TBSQ)$InBr_2$·2pic	iv	benzene	5.77	3.61 (C_4)
(TBSQ)$InBr_2$·2pic	iv	toluene	5.47	3.20 (C_4), 0.37 (C_5)
(PSQ)InCl·tmen	i	toluene	4.85	2.3 (C_1, 8), 2.3 (C_2, 7), 2.1 (C_3, 6), 1.5 (C_4, 5)
(PSQ)InBr·tmen	i	toluene	4.73	
(PSQ)InI·tmen	i	toluene	4.62	

[a] Refers to text in Experimental Section. [b] Not identifed; see text. [c] Spectra recorded at −60 °C.

and $InCl_2(O_2CC_6H_5)$·2py,[16] where the In–N bond lengths are 2.299 (4) and 2.276 (4) Å and 2.250 (5) and 2.300 (5) Å, respectively. Other reported In–N bond distances are in the range 2.23–2.52 Å, with an average of 2.28 Å proposed as being typical of such bonds.[17] There are relatively few reports of structural determinations of compounds with In–Br bonds, but the present average value of 2.560 (3) Å is within the range of results for $C_2H_5InBr_2$·tmen (2.531 (2), 2.688 (2) Å),[17] $[(CH_3)_2InBr_2]^-$ (2.644 (2), 2.635 (2) Å),[18] and $InBr_6^{3-}$ (av 2.670 (2) Å).[19] In summary, the bonds to indium are typical of those in a variety of other indium(III) compounds, but the parameters of the semiquinone ligand are equally significant. The C—O bonds at C_{13} and C_{18} have a length of 1.28 (2) Å, which is greater than a C=O bond (1.22 Å in *o*-benzoquinone[20]) but smaller than C—O in metal catecholates where the average value is 1.35 Å (see refs 7, 8, and 10 for a discussion of such results). Comparable bond distances in semiquinonate complexes of transition metals[21–23] are in the range 1.27–1.29 Å, so that the crystallographic results confirm the formulation of this compound as a dihalogenoindium(III) semiquinonate species.

The bond angles at indium are conditioned by the presence of the bidentate semiquinonate ligand, for which the bite angle is 74.8 (4)°, slightly below the values of ca. 78° found in indium(III) and tin(IV) catecholato complexes.[8,9,11] The remaining Br-In-N and Br-In-O angles are reasonably close to 90°. The InO_2C_6 system is essentially planar, and the C–C and C–N distances and angles in the 4-picoline ligand, and in the *tert*-butyl groups of the semiquinonate, are all in the normal range for such entities.

Finally, the magnetic properties of this compound are important in the subsequent discussion. The solid material is ESR-active, but detailed information was obtained from solutions prepared via section iv. After removal of NaX by filtration, the solutions were diluted to a level suitable for ESR spectroscopy; the spectra of (TBSQ•)InX_2·2pic (in benzene), and of (TBSQ•)InX_2·2py in tetrahydrofuran (X = Cl, Br), are those of single species in which TBSQ•⁻ is bound to an indium(III) center, with A_{In} = 5.1–6.4 G and A_H = 3.3–3.8 G, depending on X and on solvent (see Table V for details).

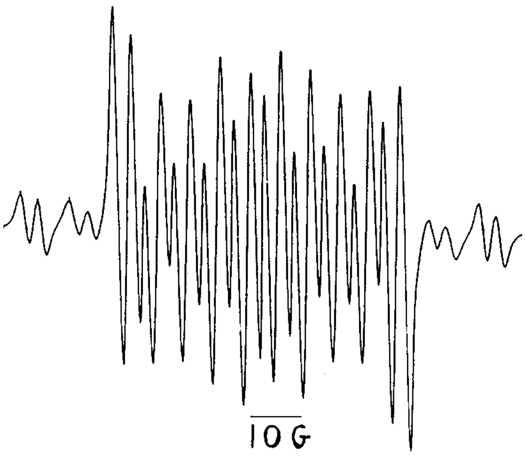

Figure 2. ESR spectrum of a solution of "(TBSQ)InCl·2py" in tetrahydrofuran.

Reaction of TBQ with InX. The reaction between these components in toluene/tmen mixtures yielded a substance analyzing as (TBSQ•)InX_2·tmen, whose structure is presumably analogous to that of (TBSQ•)$InBr_2$·2pic with an $InO_2N_2X_2$ kernel. The compounds obtained from reactions in pyridine/thf media were also of this same type, and in both cases the yield of this indium(III) product was less than 50%, based on the initial quantity of InX. This is undoubtedly due to the coincident formation of indium(I) semiquinone species in the solution phase, as demonstrated by preparative and ESR experiments discussed below.

Under different conditions, namely the reaction of a suspension of InX with TBQ in toluene followed by addition of pyridine, the product analyzed as (TBSQ•)InX·2py, which gave a weak ESR signal in the solid state. Good crystals were grown by the slow evaporation of a solution in thf, but subsequent examination in the diffractometer showed them to be extensively twinned, and we were therefore unable to determine the molecular structure. In the light of our knowledge of indium(III) coordination chemistry, the stoichiometry of this compound can be interpreted in a number of ways, including an indium(III) catecholate monomer (**2**), an indium(II) semiquinonate monomer (**3**), an indium(II) semiquinonate dimer (**4**), or an equimolar mixture of the indium(I) and indium(III) species (**5** and **6**). Structures **3**, **5**, and **6** can be eliminated on the grounds that they would present a strong ESR activity, rather than the weak one actually observed. Compound **4** would give a weak ESR spectrum only if the spins

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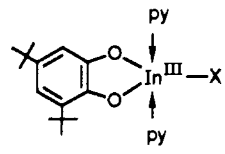

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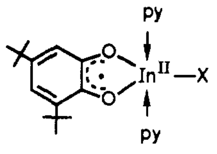

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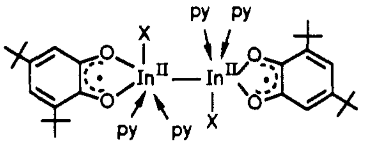

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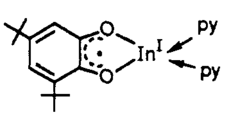

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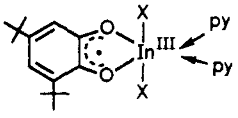

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of the two radical anion ligands were coupled (cf. the discussion of the spectrum of the analogous tin(III) dimer given previously[9]), and structure **2** cannot be ESR active. A solution of (TBSQ)-InX·2py (X = Cl, Br) in thf gives an ESR spectrum (Figure 2) that reveals the presence of both indium(I) and indium(III) semiquinonate species. We conclude that the solid-state species is in the In–In bonded dimer (**4**), whose dissociation in solution gives rise to ESR-active indium(I) and indium(III) semiquinone derivatives (see below).

As noted above, the yield of (TBSQ$^\bullet$)InX$_2$ represents approximately 50% of the initial InX because of the simultaneous formation of (TBSQ$^\bullet$)In^I. When InBr or InI are treated with TBQ and $^1/_2$I$_2$, the product obtained in >90% yield is (TBSQ)InX(I), isolated as the appropriate 4-picoline adduct. In such systems, ESR spectroscopy establishes the absence of (TBSQ$^\bullet$)In^I in the reaction mixture, so that under these conditions, as with the analogous TBQ/SnX$_2$ system,[9] iodine oxidizes In^I to In^{III} but does not affect the semiquinonate ligand.

We have also investigated the TBQ/InBr reaction by NMR spectroscopy. The ^{1}H spectrum of TBQ in toluene-d_8 showed resonances at 0.8 ppm (t-C$_4$H$_9$ at C$_3$), 1.2 ppm (t-C$_4$H$_9$ at C$_6$), 5.9 ppm (H$_6$), and 6.6 ppm (H$_4$), all relative to Me$_4$Si = 0. Solid InBr was added to this solution, and the mixture shaken gently. The NMR spectrum recorded immediately after this showed a broadening of the 0.8 ppm resonance, and the complete disappearance of that at 5.9 ppm. The spectrum was then recorded at 30-min intervals; all the resonances showed considerable broadening, which increased with time, and after 20 h there was no observable NMR spectrum.

ESR Spectroscopy and the Reaction Mechanism. The ESR results clearly indicate that the reaction between InX and TBQ proceeds via a sequence of one-electron oxidation reactions and disproportionation processes. An important point to be emphasized at the outset is that these results refer to concentrations substantially lower than those used in the preparative work.

The ESR spectra of complexes of 1,2-benzoquinone with cations of group II or III metals in aqueous alkaline solution have been studied by Eaton,[24] who reported hyperfine constants in the range 3.65–3.95 G for H$_4$ and H$_5$, and between 0.48 and 0.95 G for H$_3$ and H$_6$, and similar results have been published for substituted *o*-benzoquinones by other workers.[25-27] Previous work[10] in this department has identified the compound (TBSQ$^\bullet$)In^I, for which A_{In} = 9.83 G, A_{H_4} = 3.22 G in toluene. No interaction was detected at H$_6$ in this species, or in the spectrum of the TBSQ$^{\bullet-}$ radical anion,[24] for which A_{H_4} = 3.50 G. The A_{In} constant decreases when oxidation to indium(III) takes place, with values in the range 5–7.5 G, depending on the other ligands present.[10]

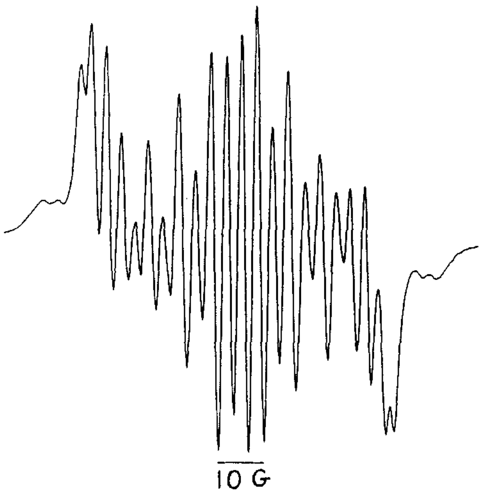

Figure 3. ESR spectrum of a (diluted) solution prepared by refluxing equimolar quantities of InCl and TBQ in tetrahydrofuran.

The ESR spectrum of a solution obtained by refluxing equimolar quantities of InX (X = Cl, Br) with TBQ in THF is shown in Figure 3. The spectrum can be simulated by assuming the presence of three indium semiquinone species. That giving the largest hyperfine coupling constant (A_{In} = 9.5 G, A_{H} = 3.3 G) is clearly an indium(I) compound and establishes the presence of (TBSQ$^\bullet$)In^I in the solution. This signal contributes approximately 20% of the total intensity, and the remainder arises from two resonances of approximately equal intensity, with A_{In} = 7.5 G and 7.0 G, respectively, and $A_{\mathrm{H}} \sim$ 3.5 G in both cases. Such solutions are quite stable, in that the ESR spectrum of a sample kept under vacuum over a period of 4 months showed no change. A repetition of this experiment using 2 mol of TBQ per mole of InX (X = Br) gave a similar spectrum, from which we identified one indium(I) (A_{In} = 9.5 G, A_{H} not observed due to increased line width) and two indium(III) species (A_{In} = 7.2 and 6.2 G, $A_{\mathrm{H}} \sim$ 3.5 G). The relative intensities of this latter pair showed an increase in that of the lower (6.2 G) species relative to the comparable component (7.0 G) in the 1:1 mole ratio experiment. Similarly, when an equimolar quantity of TBQ was added to the final solution from the 1:1 experiment, the hyperfine coupling constants were identical with those in the 2:1 case, although the relative intensities were close to those of the 1:1 experiment. A more concentrated 1:1 solution was prepared in benzene, and the ESR spectrum of the frozen material was recorded at 77 K. A weak resonance at 1600 G, with $g \sim 4$, was detected, and the intensity of this signal increased with increasing concentration of the solute species.

The ESR spectra of solutions prepared in the presence of tmen show both indium(I) and indium(III) species present, but in addition there is a major contribution from a radical derived from tmen itself. Further work on this system is required, and we shall not discuss these results in the present paper. The spectrum of the solution obtained from the reaction between equimolar quantities of TBQ and InBr in tetrahydrofuran is changed by the addition of a trace of pyridine, and the resultant spectrum can be satisfactorily simulated by assuming the presence of two components, indium(I) (A_{In} = 10.72 G, A_{H} = 3.30 G, 13% intensity) and indium(III) (A_{In} = 6.36 G, A_{H} = 3.74 G, 87% intensity). The addition of a large excess of pyridine gives the spectrum shown in Figure 4, in which the resolution of the indium(III) species has improved so as to reveal a splitting due to the hydrogen atoms of the *tert*-butyl group at the C$_5$ position. Similar results were obtained in the case of TBQ + InCl, and equally when pyridine was replaced by 4-picoline, except that the *tert*-butyl splittings could not be resolved in this case. As noted above, the spectrum obtained on dissolving "(TBSQ)InBr·2py" in thf (Figure 3) also shows the presence of both indium(I) and indium(III) species, with hyperfine constants and intensities essentially identical with those just quoted.

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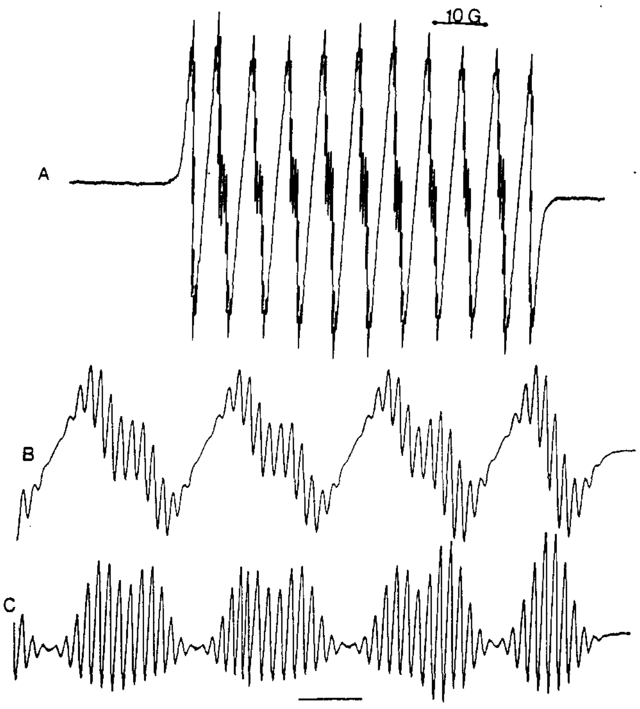
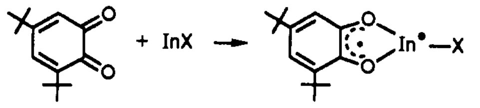


Figure 4. (A) ESR spectrum recorded after the addition of excess pyridine to the solution of Figure 3. (B) Expansion of the right-hand portion of part A. (C) Second derivative of part B.

On the basis of these results, it is clear that the reaction between TBQ and InX yields a mixture of indium(I) and indium(III) semiquinone species. The first step is the transfer of a single electron



(1)

to give an indium(II) semiquinonate monomer; following arguments which have been set out elsewhere,[9,15,28] this monomer will rapidly dimerize to give an indium–indium bonded species. Such molecules have been described earlier,[29-31] and a characteristic reaction in solution is intramolecular halide transfer to give the appropriate indium(I) and indium(III) molecules.[3,32] Reaction 1 is therefore followed by the sequence

$$2(\mathrm{TBSQ}^{\bullet})\mathrm{In}^{\bullet}\mathrm{X} \longrightarrow (\mathrm{TBSQ}^{\bullet})(\mathrm{X})\mathrm{In}\text{—}\mathrm{In}(\mathrm{X})(\mathrm{TBSQ}^{\bullet}) \qquad (2)$$

$$k_3 \Big\downarrow\!\!\Big\uparrow k_{-3}$$

$$(\mathrm{TBSQ}^{\bullet})\mathrm{In}^{\mathrm{I}} + (\mathrm{TBSQ}^{\bullet})\mathrm{InX}_2 \qquad (3)$$

Equilibrium 3 probably lies strongly to the right ($\mathrm{In}^{\mathrm{I}} + \mathrm{In}^{\mathrm{III}}$) in solution, with $k_3 \gg k_{-3}$.

When a solution prepared by reacting InBr and TBQ in $\mathrm{CH_2Cl_2}$ was treated with $\mathrm{I_2}$ (half molar equivalent, room temperature, 2 h, stirring) the ESR spectrum assigned to an equimolar mixture of $(\mathrm{TBSQ}^{\bullet})\mathrm{In}^{\mathrm{I}}$ and $(\mathrm{TBSQ}^{\bullet})\mathrm{InBr}_2$ changed to a simpler spectrum, which was poorly resolved at room temperature. At −60 °C, the resolution was much improved, and the spectrum was identified as that of two indium(III) semiquinone species ($A_{\mathrm{In}} = 5.40$, $A_{\mathrm{H}} = 3.20$ and $A_{\mathrm{In}} = 3.70$, $A_{\mathrm{H}} = 3.60$ G). This is readily interpreted in the light of eqs 1–3; addition of $\mathrm{I_2}$ to $(\mathrm{TBSQ}^{\bullet})\mathrm{In}$ produces $(\mathrm{TBSQ}^{\bullet})\mathrm{InI}_2$ (cf. ref 10) and the mixture of indium(III) semiquinone species then equilibrates

$$(\mathrm{TBSQ}^{\bullet})\mathrm{In} + \mathrm{I}_2 \rightarrow (\mathrm{TBSQ}^{\bullet})\mathrm{InI}_2 \qquad (4)$$

$$(\mathrm{TBSQ}^{\bullet})\mathrm{InI}_2 + (\mathrm{TBSQ}^{\bullet})\mathrm{InBr}_2 \rightleftharpoons 2(\mathrm{TBSQ}^{\bullet})\mathrm{InBr(I)} \qquad (5)$$

as with other indium(III) species.[32] Rapid equilibration between the three species of eq 5 at room temperature will result in poor resolution of the ESR spectrum, but at −60 °C the rate of recombination is sufficiently slowed for the two species to be identified. On the basis of ligand electronegativity, we assign the $A_{\mathrm{In}} = 3.70$ G signal to $(\mathrm{TBSQ}^{\bullet})\mathrm{InI}_2$. On the preparative scale, this reaction gives a solid analyzing as the bis(4-picoline) adduct of (TBSQ)InBr(I), and by analogy with other indium(III) systems, it is likely that this is a single iodo–bromo derivative rather than a mixture of $(\mathrm{TBSQ}^{\bullet})\mathrm{InBr}_2$ and $(\mathrm{TBSQ}^{\bullet})\mathrm{InI}_2$.[32,33]

Further confirmation is obtained from the ESR spectrum of the product of the reaction TBQ + InI + $^1/_2\mathrm{I}_2$. Only one species is identified, with $A_{\mathrm{In}} = 3.70$, $A_{\mathrm{H}} = 3.40$, and the sequence of reactions in this case is

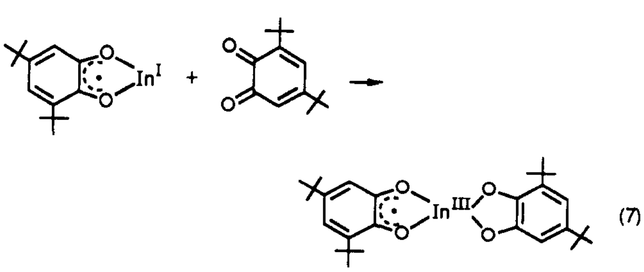
$$\mathrm{TBQ} + \mathrm{InI} \rightarrow (\mathrm{TBSQ}^{\bullet})\mathrm{In}^{\bullet}\mathrm{I} \qquad (1)$$

$$(\mathrm{TBSQ}^{\bullet})\mathrm{InI} + {}^1\!/_2\mathrm{I}_2 \rightarrow (\mathrm{TBSQ}^{\bullet})\mathrm{InI}_2 \qquad (6)$$

Reaction 6 is the analogue of that observed in the $\mathrm{TBQ}/\mathrm{SnX}_2/{}^1/_2\mathrm{I}_2$ system.[9]

The preparative results support these ideas. Reactions in toluene/tmen mixtures produce $(\mathrm{TBSQ})\mathrm{InX}_2\cdot\mathrm{tmen}$, and thf/py mixtures give the analogous $(\mathrm{TBSQ}^{\bullet})\mathrm{InX}_2\cdot 2\mathrm{py}$, but the yields are low (<50%), since a substantial fraction of the original indium remains in solution as solvated $(\mathrm{TBSQ}^{\bullet})\mathrm{In}^{\mathrm{I}}$. When the reaction is carried out in refluxing toluene followed by the addition of excess pyridine and slow evaporation, the favored product is identified as the pyridine adduct of the dimeric species 4, which is biradical. Such a biradical will have both $S = 0$ and $S = 1$ spin states and the absence of a strong ESR signal would indicate that the $S = 0$ state is favored. It should be noted that frozen solutions prepared by refluxing InBr and TBQ in benzene do give an ESR signal with $g \sim 4.0$ ($\Delta M_s = \pm 2$), which indicates that a biradical is present in the solution.

Despite the congruence of the preparative and ESR results, a reaction scheme for TBQ + InX involving only processes 1–3 is quantitatively inadequate, since it predicts equal concentrations of $(\mathrm{TBSQ}^{\bullet})\mathrm{In}^{\mathrm{I}}$ and $(\mathrm{TBSQ}^{\bullet})\mathrm{In}^{\mathrm{III}}\mathrm{X}_2$, whereas a solution containing only InX + TBQ (1:1 mole ratio) has one signal from $(\mathrm{TBSQ}^{\bullet})\mathrm{In}^{\mathrm{I}}$ and two resonances with A values corresponding to indium(III), and furthermore the total intensity of these indium(III) resonances exceeds that due to indium(I) by a significant margin. As noted earlier, the ESR results apply to concentrations lower than those used in the preparative work, and this affects the solute species present, as does the nature of the complexing reactions in solution. The low intensity of the indium(I) resonance can be explained by a secondary reaction between (TBSQ)In and unreacted TBQ, a process which could occur if k_1 is substantially lower than k_2 and k_3, since under these conditions this process (eq 7) can produce



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a second indium(III) species in addition to $(\mathrm{TBSQ}^{\bullet})\mathrm{InX}_2$. It is known from previous work[10] that $(\mathrm{TBSQ}^{\bullet})\mathrm{In}^{\mathrm{I}}$ can be oxidized by

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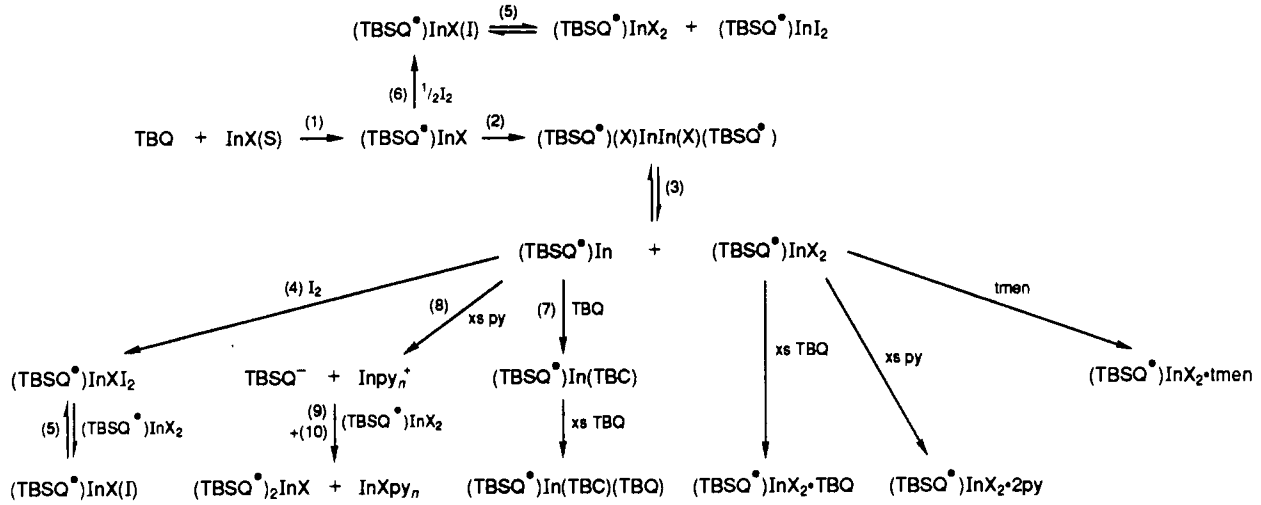
Scheme I[a]



[a] Values in parentheses refer to eqs in text.

o-$O_2C_6Cl_4$ to give (TBSQ•)In^{III}($O_2C_6Cl_4$), and such a reaction would lower the quantity of indium(I) in the final equilibrium solution and produce two indium(III) species. In keeping with this, the addition of an extra molar equivalent of TBQ, or the use of mixtures in which the initial TBQ:InX molar ratio is 2, further reduces the concentration of (TBSQ•)In^{I}, and the changed indium(III) coupling constants suggest that the excess TBQ acts as a bidentate neutral donor to these indium(III) species, as it does to other Lewis acid centers.[34] Confirmation of complexing by TBQ comes from the NMR studies noted above, since TBQ/InX solutions with excess TBQ show a greater broadening of the resonances at C_3 and C_6 relative to those at C_4 and C_5, demonstrating specific intermolecular contact involving the quinone oxygen atoms rather than some generalized effect. Similarly, in thf solution there will be a competition between the basic solvent and unreacted TBQ for the indium(III), so that each system will have a different degree of solvation and/or complexing and, hence, different hyperfine coupling constants.

Leaving this not unimportant point aside for the present, we propose the overall set of reactions summarized in Scheme I, which also shows that the effect of the strong base pyridine can be understood in terms of our earlier work[10] on the behavior of (TBSQ)In^{I} solutions, since in the presence of excess 4-picoline (L), the equilibrium

$$(\mathrm{TBSQ}^\bullet)\mathrm{In}^{I} + n\mathrm{L} \rightleftarrows \mathrm{TBSQ}^{\bullet-} + [\mathrm{InL}_n]^+ \qquad (8)$$

lies strongly to the right. The addition of excess pyridine to a mixture of (TBSQ•)In^{I} and (TBSQ•)InX_2 will therefore bring about the sequence (7)–(9), and as a result two new species are

$$\mathrm{TBSQ}^{\bullet-} + (\mathrm{TBSQ}^\bullet)\mathrm{InX}_2 \rightarrow (\mathrm{TBSQ}^\bullet)_2\mathrm{InX} + \mathrm{X}^- \qquad (9)$$

$$\mathrm{X}^- + [\mathrm{InL}_n]^+ \rightleftarrows \mathrm{InXL}_n \qquad (10)$$

formed. Of these, InXL_n is clearly ESR-silent, and earlier studies[1] of nonaqueous solutions of indium(I) imply that this molecule will be stabilized in solution by excess pyridine. The species (TBSQ•)$_2$InX, or its complex (TBSQ•)$_2$InX·py, is a biradical whose ESR spectrum would not be detectable in solution under our experimental conditions, and in effect therefore, the only ESR-active species in a solution containing excess pyridine will be (TBSQ•)InX_2·2py. Furthermore, ligand exchange will be slowed, since this would require the reversal of eqs 9 and 10, both of which presumably lie strongly to the right, and indeed eq 10 may not be reversible except in the presence of a large excess of halide ion, since this would require replacement of a monodentate by a bidentate ligand, and such processes are not generally thermodynamically favored. In keeping with this argument, the well-resolved ESR spectrum recorded under these circumstances is that of a single species, (TBSQ•)InCl_2·2py, with A_{In} = 6.38 G, lower than the values observed for oxygen donors because of the strong donor power of pyridine. (See Scheme I.)

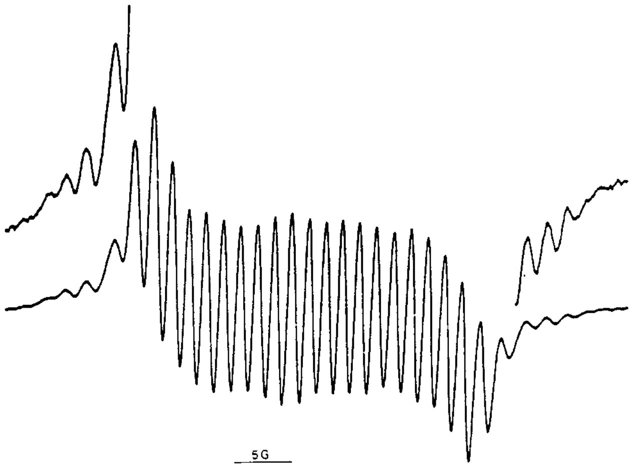
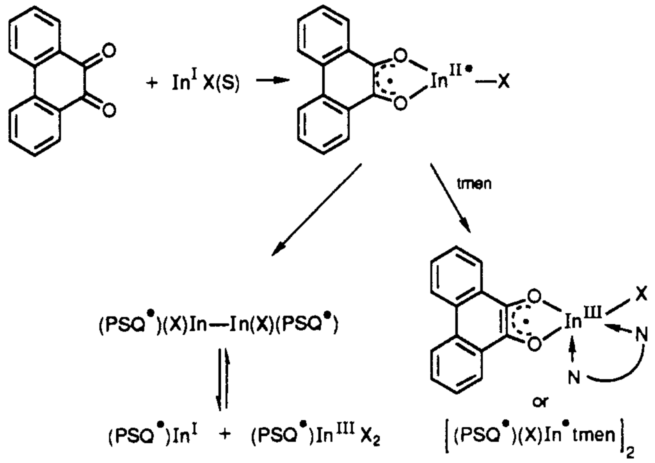


Figure 5. ESR spectrum of a (diluted) solution prepared by reacting InCl and PQ in toluene/tmen solution; the extremities are shown in 4-fold expansion.

Scheme II



Reaction of Phenanthrene-9,10-quinone with InX. When InX reacted with PQ in toluene/tmen solution, the solid product can be formulated as either the catecholatoindium(III) halide adduct or as the adduct of the dimeric (PSQ)In^{II}X species (cf. the discussion of the TBQ case above). A dilute solution of these components gave the ESR spectrum shown in Figure 5 for X = Cl, and one again observes the presence of two indium species. In

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Inorg. Chem. **1990**, *29*, 3943-3952 **3943**

one case, A_{In} = 4.85, implying an indium(III) species, and coupling constants were assigned for each pair of hydrogen atoms of the phenanthrene ring, with values essentially independent of the halide involved. It was not possible to assign values for the indium(I) analogue.

The number of hyperfine constants in this system does not allow for a detailed analysis of the species present in this solution, but the results can be summarized in Scheme II, which invokes a series of reactions which proceed by one-electron transfer. The detailed differences between the TBQ and PQ systems are presumably the result of the differing oxidizing potentials, and/or steric effects, in the two series of compounds.

Discussion

The present work, and earlier studies from this department,[9-11] shows that the oxidation of indium(I) to indium(III), or of tin(II) to tin(IV), by *o*-quinones is not a one-step two-electron transfer process. It has frequently been assumed in discussions of redox reactions in main group chemistry that because the oxidation states identified under normal conditions differ by two electrons, the intermediate states such as tin(III) and indium(II) have no relevance to the overall chemistry of these elements. The fact that most redox reactions in solutions of main group compounds are rapid has hindered any detailed investigation of these processes and has led to the conclusion, in the absence of evidence to the contrary, that two-electron transfers are the norm. The present investigations, involving oxidizing agents in which the successive electron addition processes can be identified spectroscopically, show that one-electron transfer reactions may well be as significant with main group compounds as they are in the more thoroughly studied transition element field. Work on related systems is continuing.

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Supplementary Material Available: Tables of refined anisotropic thermal parameters and fractional coordinates and thermal parameters for hydrogen atoms and cell packing diagram (4 pages); a table of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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Electronic and Structural Properties of the Novel Chain Compound Ta_4Te_4Si

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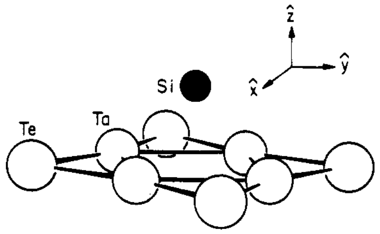
Some interesting aspects of the newly synthesized chain structure Ta_4Te_4Si are discussed in this paper. A fragment analysis shows that both metal-metal bonding and Ta-Si bonding are strong and are responsible for the stabilization of the chain. Band structure calculations suggest that the compound is a metallic conductor. The states that contribute to the conduction bands are derived mostly from the Ta 5d orbitals. The relative stabilities of different structural choices are compared, and possible geometrical distortions are examined. It should be possible to replace the interstitial Si by transition metals, especially Fe or Co. Finally, we examine the possibility of oxidation and reduction of the chain.

Introduction

Molybdenum chalcogenide cluster compounds (e.g., the Chevrel phases)[1] have received much attention from both chemists and physicists, due to their many interesting structural, chemical, and physical properties.[2] These include superconductivity, magnetic ordering at low temperatures, charge density waves, and some anisotropic behavior.[3] In an attempt to make tantalum and niobium ternary phases of the molybdenum analogue, Badding and DiSalvo have recently synthesized a new chain compound, Ta_4Te_4Si, whose single-crystal has been determined by X-ray diffraction techniques.[4] One view of the structure is shown in Figure 1. The basic building unit of this novel material is the square-pyramidal Ta_4Si (**1**) with Ta atoms bridged by telluriums in the same (xy) plane. Such units stack along the c axis in an antiprismatic fashion and form an infinite chain. The chain-chain separation is large, giving a closest Te-Te contact of 3.815 Å. Structurally, this compound is closely related to the binary Ta_2S[5] and the ternary $InMo_3Te_3$,[6] which also contain antiprismatically arranged metal chains: pentagonal and trigonal, respectively. The Si atoms in this compound sit in the center of each square antiprism, forming a nearly equally spaced single-atom chain along the c axis. The situation is similar to what has been observed in another metal-rich ternary tantalum chalcogenide, $Ni_2Ta_9S_6$,[7] where the Ni atoms in the centers of trigonal prisms formed by six Ta atoms generate an entirely symmetric chain.



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Recent synthetic experiments indicate that the central Si atoms may be replaceable by other elements, such as the main-group

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