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Labile 1,10-Phenanthroline N-Oxide Complexes with Tin(II) and (IV) Halides

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Following earlier synthetic and characterization studies of 3d metal chloride, perchlorate and nitrate chelates with 2,2′-bipyridine and 1,10-phenanthroline N-oxides (N-bipyO and N-phenO, respectively) [1], these laboratories reported recently on the preparation and characterization of SnX_4 (X = Cl, Br, I) chelates with N-bipyO [2]. These tin chelates were easily precipitated by combining CCl_4 solutions of salt and ligand at ambient temperature [2]. The same preparative method is inapplicable in the case of N-phenO, owing to its insolubility in CCl_4. Thus, during our attempts at the syntheses of SnX_2 and SnX_4 (X = Cl, Br, I) complexes with N-phenO, we employed the following synthetic method: 0.1 *M* solutions of N-phenO in ethanol, SnX_2 in methanol and SnX_4 in CCl_4 were prepared and dried overnight over molecular sieve 4A (Fisher, 14–30 mesh; 1 g of sieve per 50 ml of solution) [2, 3]. Then, aliquots of the ligand and Sn^{2+} or Sn^{4+} salt solutions were combined at the desired molar ratio (1:1 or 3:1 ligand to tin) [2, 4]. Precipitation was immediate in all cases. During our earlier synthetic work, we allowed the precipitations to remain under the mother liquor overnight, hoping that precipitation would go to completion [2], and then proceeded to their separation by filtration. However, this allowed the initially formed adducts of the $Sn(N\text{-phenO})_mX_n$ (n = 2 or 4; m = 1, 2) type to react with the supernatant, and solid decomposition products were isolated instead. It was established later that, initially, the authentic $Sn(N\text{-phenO})_mX_n$ adducts are indeed formed, as expected [1, 2, 5–7], these adducts can be recovered intact only if they are separated by filtration from the supernatant within 1–2 minutes after the combination of the N-phenO and tin salt solutions; if the contact of the original precipitate with the mother liquor is extended to a period exceeding 5 min., the $Sn(N\text{-phenO})_mX_n$ adduct becomes contaminated with substantial amounts of decomposition products. We have now isolated the authentic adducts in a satisfactorily pure state for characterization, and are reporting on these studies in a separate communication; the present letter deals with the reactions of these adducts with the mother liquor, following their precipitation, and with the solid reaction products isolated.

Table I shows the analyses of the latter products, along with their most likely compositions, suggested by the analyses and the i.r. evidence, which is summarized in Table II. All of the products herein discussed consist of mixtures of N-phenO complexes with tin-containing species and the HX salt of N-phenO (X = Cl, Br, I). Initially, the alcohol (R = C_2H_5, CH_3) is assumed to attack the $Sn(N\text{-phenO})_mX_n$ chelates as follows [8, 9]:

$$Sn(N\text{-phenO})_mX_n + ROH \rightarrow Sn(N\text{-phenO})_mX_{n-1}(OR) + HX \qquad (1)$$

The HX liberated in reaction (*1*) apparently attacks the $Sn(N\text{-phenO})_mX_{n-1}(OR)$ complex, with formation of $[N\text{-phenO}\cdot\cdot H^+]X^-$ [10]. At the same time, HX may also react with the original adduct and force the tin into anionic halotin(II) or (IV) species [10, 11], *e.g.*:

$$Sn(N\text{-phenO})_mX_2 + HX \rightarrow [N\text{-phenO}\cdot\cdot H^+]\,[SnX_3]^- \qquad (2)$$

$$Sn(N\text{-phenO})_mX_4 + HX \rightarrow [N\text{-phenO}\cdot\cdot H^+]\,[SnX_5]^- \qquad (3)$$

$$\text{or } Sn(N\text{-phenO})_mX_4 + 2HX \rightarrow [N\text{-phenO}\cdot\cdot H^+]_2\,[SnX_6]^{2-} \qquad (4)$$

The possibility that Sn^{2+} was partially or completely oxidized to Sn^{4+} in the presence of HX and either alcohol [12] or the N-oxide ligand [13], or even by atmospheric oxygen [14], was also considered but ruled out on the basis of analyses of the Sn^{2+} products (total tin and stannous tin determination by ceric ion titration [15, 16] showed less than 1% Sn^{4+}).

The low-frequency i.r. evidence (Table II) is conclusive as far as the presence of N-phenO ligands coordinated to tin ions is concerned. In fact, the products containing $Sn(N\text{-phenO})Cl_2$, $Sn(N\text{-phenO})Cl_4$ and $Sn(N\text{-phenO})_2I_4$ show strong bands that can be attributed to the $\nu_{Sn(II)-O}$ [16–18] or $\nu_{Sn(IV)-O}$ [2, 19, 20] vibrational mode. Likewise, $\nu_{Sn(II)-Cl}$, $\nu_{Sn(IV)-Cl}$ and $\nu_{Sn(IV)-N}$ bands are observed in the

TABLE I. Analyses and Likely Composition[a] of the Solid Reaction Products of N-phenO(L)–SnX_m Complexes[b] with the Mother Liquor.

X_m	Likely Composition	Color[d]	Analysis, Found (Calc.)%				
			C	H	N	Sn	X
Cl_2	$SnLCl_2$ + [LH]Cl	Yellow	46.30 (46.61)	2.34 (2.77)	8.75 (9.06)	19.45 (19.19)	17.49 (17.20)
Br_2	[LH][$SnBr_3$] + [LH]Br	Yellow	34.28 (34.62)	1.86 (2.18)	6.02 (6.35)	13.93 (14.25)	38.75 (38.38)
I_2	[LH][SnI_3] + 2[LH]I	Brown	32.58 (32.15)	2.25 (2.02)	6.28 (6.25)	8.39 (8.83)	46.90 (47.18)
Cl_4	[LH][$SnCl_5$] + [LH]Cl	Yellow	39.49 (39.71)	2.21 (2.50)	7.38 (7.72)	16.04 (16.35)	29.70 (29.31)
Cl_4[c]	$SnLCl_4$ + [LH]Cl	Yellow	41.24 (41.81)	2.18 (2.49)	7.85 (8.13)	16.90 (17.22)	25.42 (25.71)
I_4[c]	SnL_2I_4 + 3[LH]I	Green	35.71 (36.19)	2.32 (2.18)	6.68 (7.03)	5.59 (5.96)	45.11 (44.62)

[a] See text. [b] Formed by interaction of L and SnX_m at a 1:1 molar ratio, unless otherwise indicated. [c] Initial interaction of SnX_4 and L was at a 1:3 molar ratio. [d] The solid products herein reported are uniformly colored, despite the fact that they are mixtures of two components; they all decompose without melting at 273–319 °C. *Note*: A yellow product was also obtained during the decomposition of the 1:1 adduct of L and $SnBr_4$, but its analyses could not be interpreted in terms of any reasonable combination of [LH]Br and a tin-containing complex.

TABLE II. Pertinent Infrared Data (cm^{-1}) for the Reaction Products of N-phenO(L)–SnX_m Complexes with the Mother Liquor.

Product	ν_{N-O} region[a]	ν_{Sn-O}	ν_{Sn-X}	ν_{Sn-N}
$SnLCl_2$ + [LH]Cl	1259m, 1232m, 1200m	331ms	322ms	302m
[LH][$SnBr_3$] + [LH]Br	1232w, 1207s	–	213vs	–
[LH][SnI_3] + 2[LH]I	1233w, 1208vs	–	b	–
[LH][$SnCl_5$] + [LH]Cl	1225w, sh, 1200ms	–	350m, 324ms	–
$SnLCl_4$ + [LH]Cl	1260m, 1231ms, 1209m, 1201m	397s	321vs, 327vs, 320vs, 313ms	240m, 216m
SnL_2I_4 + 3[LH]1	1255w, 1239m, 1210s, 1204m, sh	389s	b	244ms, 226m

[a] ν_{N-O} appears as a doublet at 1269, 1249 cm^{-1} in the spectrum of free N-phenO [6], while compounds of the [LH]X type (X = Cl, Br, I, ClO_4, BF_4) show medium or strong ν_{N-O} absorption, usually appearing as a doublet, with the strongest maximum at 1210–1200 cm^{-1} [29]. [b] ν_{Sn-I} in SnL_2I_4 or the ν_1 mode in $[SnI_3]^-$ occur below the lower limit (200 cm^{-1}) of the range of the ir instrument used (Perkin-Elmer 621 spectrophotometer).

anticipated regions for SnX_n adducts with N-phenO [2, 16–20]. Regarding the Sn(II)–nitrogen bond, ν_{Sn-N} was expected to occur at above 400 cm^{-1} [21]; however, the only band with possible ν_{Sn-N} character occurs at 302 cm^{-1} in the $SnCl_2$ product. Regarding the products characterized as mixtures of [LH]X with [LH][SnX_3] (X = Br, I) and [LH][$SnCl_5$] (L = N-phenO), it is obvious that they could be alternatively formulated as $[LH]_2[SnBr_4]$, $[LH]_2[SnI_4]$ + [LH]I and $[LH]_2[SnCl_6]$, respectively. The i.r. evidence is, however, in favor of the presence of the $[SnBr_3]^-$ (ν_1 at 213 cm^{-1}) [22] and $[SnCl_5]^-$ (ν_5, e′ at 350 and ν_3, a_2'' at 324 cm^{-1}) [23, 24] anions, while the presence of $[SnI_3]^-$ in the stannous iodide product is assumed by analogy to the corresponding bromide species. In the case of Sn^{2+}, $[SnX_3]^-$ are more common than $[SnX_4]^{2-}$ anions (X = halogen) [25]; $[SnBr_3]^-$ compounds have been characterized [25], while very little information is available on anionic iodotin(II) species [26]. With Sn^{4+}, the hexahalogeno-ions are the common ones; nevertheless, since the highest energy vibration of the $[SnCl_6]^{2-}$ anion reportedly appears at 318–294 cm^{-1} [23, 24, 27, 28], and the i.r. spectrum of the product under study is compatible with the presence of $[SnCl_5]^-$, we consider the formulation proposed above as justified.

Dega-Szafran has characterized several mineral acid salts of N-phenO by i.r. spectroscopy [29]. The ν_{N-O} mode, which appears as a doublet at 1269, 1249 cm^{-1} in free N-phenO [6], usually occurs as a doublet with the strongest maximum at 1210–1200

cm^{-1} in the spectra of various $[\text{N-phenO--H}^+]X^-$ salts ($X = Cl, Br, I, ClO_4, BF_4$) [29]. The same features are observed in the ν_{N-O} region of the spectra of the products characterized as mixtures of [LH]X and [LH] $[SnX_n]$ (n = 3 for X = Br, I; n = 5 for X = Cl), *viz.* a strong maximum at 1208–1200 cm^{-1} and a weaker band at 1233–1225 cm^{-1}. On the other hand, the products consisting of mixtures of [LH]X with adducts of the $SnLCl_2$, $SnLCl_4$ and SnL_2I_4 types, show ν_{N-O} bands attributable to both the species present, as follows: two or three maxima at 1260–1255, 1239–1231 and 1210–1201 cm^{-1}, due to the spectrum of the tin halide adduct [2–7], and one maximum at 1210–1200 cm^{-1}, due to the presence of [LH]X, whose second i.r. absorption in the ν_{N-O} region overlaps with the corresponding band of the tin halide adduct [29].

Prior to concluding, it should be pointed out that the factors favoring the complete decomposition of the adducts initially formed, under our experimental conditions, are not completely understood. In fact, in three of the cases investigated the decomposition was complete, while in the other three cases The final product was a mixture of the adduct with [LH]X. It is likely that of key importance would be the resistance of the adduct to the attack of the hydrogen halide liberated during reaction (*1*). The fact that $Sn(\text{N-phenO})Cl_4$, which is initially formed during interaction of N-phenO and $SnCl_4$ at a 1:1 molar ratio, is completely converted to $[\text{N-phenO--H}^+]$-$[SnCl_5]$, whilst in the final product obtained from the corresponding interaction at a 1:3 molar ratio, $Sn(\text{N-phenO})Cl_4$ is intact, would seem to contradict, *prima facie*, the preceding statement. Nevertheless, during the latter reaction, the product initially precipitated was determined to be $Sn(\text{N-phenO})_2Cl_4$, as anticipated [2, 4]; this adduct apparently loses one N-phenO ligand, when allowed to remain under the mother liquor, but the resulting $Sn(\text{N-phenO})Cl_4$ is not further attacked, probably owing to the absence of sufficient HCl in the mixture. With SnI_4, $Sn(\text{N-phenO})_2I_4$ is initially formed, and part of it remains intact throughout its exposure to the mother liquor. It is also worth noticing, that reactions analogous to those herein discussed must be occurring in solution, during interactions of transition metal perchlorates or tetrafluoroborates and aromatic amine N-oxides in ethanol–triethyl orthoformate. In fact, such solutions have reportedly yielded precipitates containing major or minor amounts of the $HClO_4$ or HBF_4 salt of the N-oxide in several instances [30, 31].

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