

The strong bands appearing in the region 1616-1600 cm^{-1} in the Schiff bases and attributable to $\nu\text{C}=\text{N}$ appear in the region 1653-1639 cm^{-1} in the adducts 1-4 (Table 1), indicating that the coordination has taken place through the azomethine nitrogen.

The assignment of this band in the adducts 5 and 6 (Table 1) is rather cumbersome. In these Schiff bases IIa and IIb, one can expect a band due to δNH . As it is a band of weak intensity, it is rather difficult to locate this band amidst the high intensity $\text{C}=\text{N}$ and aromatic $\text{C}=\text{C}$ vibrations. In these bases a high intensity band is observed at 1598 cm^{-1} and is assigned to the mixture of $\text{C}=\text{N}$ and first high intensity band of aromatic $\text{C}=\text{C}$ vibration. In the complexes 5 and 6, we notice clear resolution of this band; one appearing in the region 1626-1616 cm^{-1} and the other in the region 1590-1587 cm^{-1} . The high frequency band in the complexes is attributed to $\nu\text{C}=\text{N}$.

The band around 3400 cm^{-1} in the bases IIa and IIb is assigned to νNH . This band in the complexes 5 and 6 does not show any split or shift indicating that NH is not involved in coordination.

The non-electrolytic behaviour of the complexes in acetonitrile, the spectral observations and the possibility of coordination numbers six and eight in silicon(IV)^{7,8} make us believe that silicon may assume coordination number eight in the complexes 1-4 and coordination number six in the complexes 5 and 6.

One of the authors (N.S.H.) is thankful to the CSIR, New Delhi, for the award of a junior research fellowship.

References

1. WANNAGAT, U., *Adv. inorg. Chem. & Radiochem.*, **6** (1964), 225; WANNAGAT, U., HARZIG, J., SCHMIDT, P. & SCHULZE, M., *Mh. Chem.*, **102** (1971), 1817; WANNAGAT, U. & METER, S., *Z. anorg. allg. Chem.*, **392** (1972), 392.
2. PAUL, R. C., KAPILA, B., AGGARWAL, V. K. & NARULA, S. P., *Indian J. Chem.*, **9** (1971), 997; PAUL, R. C., DHINDSE, K. S., AHLUWALIA, S. C. & NARULA, S. P., *J. inorg. nucl. Chem.*, **34** (1972), 1813.
3. OROLOVA, L. V., GARNOVSKII, A. D., OSIPOV, C. A. & KUKISHKINA, I. I., *Z. obshch. Khim.*, **38** (1968), 1850; *Chem. Abstr.*, **69** (1968), 113055q.
4. BIRADAR, N. S. & KULKARNI, V. H., *Rev. Roumaine Chim.*, **15** (1970), 1993.
5. WEISSBERGER, A. & PROSKAUER, R. S., *Organic solvents techniques of organic chemistry*, Vol. VII (Interscience, New York), 1955.
6. GEARY, W. J., *Coord. Chem. Rev.*, **7** (1971), 81.
7. BEATTIE, I. R., *Q. Rev.*, **17** (1963), 382.
8. STONE, F. G. A. & SEYPERTH, DIETMER, *J. inorg. nucl. Chem.*, **1** (1955), 112; TROST, W. R., *Can. J. Chem.*, **30** (1952), 835, 842.

Chelated Antimony Compounds*

(MRS) SARADA GOPINATHAN & C. GOPINATHAN
National Chemical Laboratory, Poona 411008

Received 9 August 1976; accepted 24 January 1977

Monochelated antimony(V) tetrachlorides have been prepared from antimony pentachloride and organic bidentate chelating ligands salicylaldehyde, 8-hydroxy-

quinoline, N-benzoyl-N-phenylhydroxylamine, dehydroacetic acid and acetoacetanilide. Bis-chelated triphenylantimony(V) compounds have been obtained from triphenylantimony(V) dibromide and sodio-derivative of bidentate ligands. Tris(salicylaldehydato)-antimony(III) has also been prepared. The spectral and other properties of the new compounds have been studied.

PREPARATION and structures of several organo antimony compounds have been described in literature¹⁻⁶. Results obtained from the reaction between stannic chloride or organotin chlorides with organic chelating ligands⁷ prompted us to prepare similar antimony compounds.

Preparations were carried out using absolutely dry solvents under moisture-free conditions; filtrations were done using a positive pressure of dry nitrogen gas.

Tris(salicylaldehydato)antimony(III) — Antimony trichloride (2.28 g; 0.01 mole) was dissolved in benzene (50 ml) and reacted with sodio-derivative of salicylaldehyde (0.04 mole; prepared via sodium methoxide) by refluxing for 2 hr. The reaction mixture was concentrated, sodium chloride and the excess sodio-salicylaldehyde filtered off, and remaining benzene removed under reduced pressure. The product was washed with hexane and solvent removed under reduced pressure. The yellow product, m.p. 180°, weighed 4.36 g (90% yield) [Found: Sb, 25.10; C, 52.01; H, 3.12. Calc. for $\text{C}_{21}\text{H}_{15}\text{O}_6\text{Sb}$: Sb, 25.11; C, 51.96; H, 3.09%]. Molecular weight: (1) by ebullioscopy in benzene, 490 and (2) by differential vapour pressure method, 482; calc. 485.

8-Hydroxyquinolino)antimony tetrachloride — Antimony pentachloride (2.99 g; 0.01 mole) and 8-hydroxyquinoline (1.45 g; 0.01 mole) were mixed in carbon tetrachloride (50 ml) and refluxed for 2 hr to remove all HCl. The solvent was removed under reduced pressure, the product washed with hexane and dried *in vacuo*. The orange hygroscopic solid, insoluble in benzene, m.p. 170°, weighed 3.3 g (80% yield) [Found: Sb, 29.75; Cl, 34.67; C, 26.66; H, 1.26. Calc. for $\text{C}_9\text{H}_6\text{ONSbCl}_4$: Sb, 29.80; Cl, 34.74; C, 26.47; H, 1.20%].

(Triphenyl)antimony dibromide — It was obtained as a white crystalline powder by the action of bromine on (triphenyl)antimony in glacial acetic acid; it was recrystallized from benzene as needles, m.p. 216° (ref. 8) [Found: Sb, 23.93; C, 42.42; H, 3.01; Br, 31.07. Calc. for $\text{C}_{18}\text{H}_{15}\text{SbBr}_2$: Sb, 23.75; C, 42.14; H, 2.93; Br, 31.18%].

Bis(8-hydroxyquinolino)(triphenyl)antimony — (Triphenyl)antimony dibromide (5.12 g; 0.01 mole) was dissolved in benzene (50 ml) and reacted with the sodio-derivative of 8-hydroxyquinoline (0.03 mole) by refluxing for 2 hr, and the product isolated as in the case of salicylaldehydato complex. The yellow powder, soluble in benzene, m.p. 175°, weighed 5.75 g (90% of theory) [Found: Sb, 19.10; C, 67.62; H, 4.01. Calc. for $\text{C}_{36}\text{H}_{27}\text{O}_2\text{N}_2\text{Sb}$: Sb, 18.99; C, 67.42; H, 4.21%].

Other compounds were prepared similarly (Table 1).

In the presence of a solvent, antimony halides form unstable addition compounds with salicyl-

*Communication No. 2050 from National Chemical Laboratory.

TABLE 1 — PHYSICO-CHEMICAL DATA OF CHELATED ANTIMONY COMPOUNDS

Reactants		Molar ratio (A: B)	Product	Colour	m.p. (°C)
A	B				
SbCl ₃	Salicylaldehyde	1:4	(C ₇ H ₅ O ₂) ₃ Sb	Yellow	180
do	8-Hydroxyquinoline	1:4	(C ₉ H ₆ ON) ₃ Sb	do	>250(d)
Ph ₃ SbBr ₂	Salicylaldehyde	1:3	(C ₇ H ₅) ₃ Sb(C ₇ H ₅ O ₂) ₂	do	>150(d)
do	8-Hydroxyquinoline	1:3	(C ₉ H ₆) ₃ Sb(C ₉ H ₆ ON) ₂	do	>250(d)
do	N-benzoyl-N-phenylhydroxylamine	1:3	(C ₉ H ₅) ₃ Sb(C ₁₃ H ₁₀ O ₂ N) ₂	Buff	102
do	Dehydroacetic acid	1:3	(C ₈ H ₅) ₃ Sb(C ₈ H ₇ O ₄) ₂	White	155
do	Acetoacetanilide	1:3	(C ₈ H ₆) ₃ Sb(C ₁₀ H ₁₀ O ₂ N) ₂	Pink	173
SbCl ₅	Salicylaldehyde	1:1	C ₇ H ₅ O ₂ SbCl ₄	Yellow	>150(d)
do	8-Hydroxyquinoline	1:1	C ₉ H ₆ ONSbCl ₄	Orange	170
do	N-Benzoyl-N-phenylhydroxylamine	1:1	C ₁₃ H ₁₀ NSbCl ₄	Red	>200(d)
do	Dehydroacetic acid	1:1	C ₈ H ₇ O ₄ SbCl ₄	Yellow	>200(d)
do	Acetoacetanilide	1:1	C ₁₀ H ₁₀ O ₂ NSbCl ₄	Red	>200(d)

Experiments 1-7 carried out using sodio-derivative of the ligand (B).

aldehyde or acetylacetone at room temperature. However, we have observed that when antimony pentachloride is refluxed with salicylaldehyde in carbon tetrachloride, HCl is evolved and (salicylaldehydato)antimony(V) tetrachloride is formed. Other chelating ligands (8-hydroxyquinoline, N-benzoyl-N-phenylhydroxylamine, dehydroacetic acid and acetoacetanilide) behaved similarly. Replacement of the bromine atoms of triphenyl antimony(V) dibromide with chelating ligands was possible by using the sodio-derivative of the chelating ligand. In a similar way tris-chelated antimony(III) compounds were also prepared from antimony trichloride. Tris(salicylaldehydato)antimony(III) reacted quantitatively with bromine to give bis(salicylaldehydato)antimony(III) bromide and not tris(salicylaldehydato)antimony(V) dibromide as expected. Chelated antimony compounds were yellow- to orange-coloured hygroscopic solids; some were moderately soluble in benzene but all were insoluble in hexane. Products which were soluble in benzene were found to be monomeric.

IR spectra — In (salicylaldehydato)antimony tetrachloride, the carbonyl frequency of the hydrogen-bonded ligand (at 1660 cm⁻¹) is shifted to 1610 cm⁻¹, indicating strong coordination of the ligand through the CO group. In bis(salicylaldehydato)triphenyl antimony, the νCO is found at 1620 cm⁻¹, again indicating fairly strong chelation. But in the case of tris(salicylaldehydato)antimony(III), two peaks at 1620 and 1660 cm⁻¹ indicate weak coordination. The comparatively larger shift of νCO observed in the case of (salicylaldehydato)antimony tetrachloride may be attributed to the increased electron affinity of the chlorine atom compared to the phenyl group. The absence of OH stretching frequency in the spectra of all these compounds shows the replacement of hydroxyl proton by antimony atom.

In the N-benzoyl-N-phenylhydroxylamine complexes of antimony, the hydroxylamine group is covalently bonded to antimony and the carbonyl group is intramolecularly coordinated to the metal atom. The νNO found at 920 cm⁻¹ in the ligand is shifted to higher frequencies (950 cm⁻¹) as a result of complexing. In the case of (N-benzoyl-N-phenylhydroxylamino)antimony(V) tetrachloride,

the νCO observed at 1630 cm⁻¹ in the free ligand is lowered to 1580 cm⁻¹ in the complex (probably overlapping with one of the C—C vibrations) indicating strong chelation. However, in bis(N-benzoyl-N-phenylhydroxylamino)triphenyl antimony, the νCO frequency is observed at 1650 and 1680 cm⁻¹, indicating comparatively weaker coordination with the metal.

In all the 8-hydroxyquinoline complexes, the IR spectra give evidence of strong chelation. The presence of two bands (at 1587 and 1600 cm⁻¹) in the complexes in place of only one (at 1587 cm⁻¹) in the ligand indicate coordination of nitrogen with the metal and consequent separation of the CN frequency from the C—C frequency in the ring⁸. The spectrum of (8-hydroxyquinolino)antimony tetrachloride also shows two prominent bands at 510 and 390 cm⁻¹ corresponding respectively to νSb—O and νSb—N frequencies which are absent in the parent reactants. The bands at 360 and 345 cm⁻¹ may be attributed to νSb—Cl. These values are very similar to those reported by Meinema *et al.*^{6,11}. Complexes of acetoacetanilide and dehydroacetic acid also gave evidences of fairly strong coordination.

UV spectra — The UV spectra of bis(8-hydroxyquinolino)triphenyl antimony and (8-hydroxyquinolino)antimony tetrachloride in acetonitrile solution show absorptions around 380 and 370 nm respectively. The ligand itself absorbs at 310 nm in the same solvent. This observed shift to longer wavelength regions is a reliable indication for the presence of chelating oxine group. The larger shift observed for (8-hydroxyquinolino)antimony tetrachloride compared to the bis(8-hydroxyquinolino)triphenyl antimony may be due to the increased effective nuclear charge on the antimony atom and hence the formation of stronger chelate in the former case. This is in agreement with the reported results^{10,11}.

NMR spectra — The NMR spectra of the complexes in CHCl₃ or CCl₄ do not show the presence of hydroxyl protons originally present in the free ligands in the hydrogen-bonded state. This indicates the replacement of hydroxyl protons by antimony. The NMR spectra were also recorded in dimethyl sulphoxide. The donation of the lone pair of electrons of nitrogen to antimony during coordina-

tion produced a deshielding of the ligand protons in general. The down field shift of protons has been attributed to strong interaction of the metal atom with the nitrogen of the ligand ring in the complex (8-hydroxyquinolino)antimony tetrachloride^{6,11,13}.

The molar conductivities of the monochelated antimony tetrachloride complexes (of millimolar solutions in nitrobenzene) are of the order $<1 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ which indicates that the complexes are non-electrolytes^{14,15}. Molecular weight of organo- and chloro-antimony chelates, which were soluble in benzene, were determined by differential vapour pressure technique using Mechrolab vapour pressure osmometer, model 301A, at 37°. Molecular weight determinations of these compounds were carried out using a semimicro ebulliometer in boiling benzene also (1%, w/w solution). Results obtained from both these methods indicate that the compounds are monomeric.

References

- DOAK, G. O., LONG, G. G. & FREEDMAN, L. D., *J. organometallic Chem.* **4** (1965), 82.
- SHINDO, M. & OKAWARA, R., *J. organometallic Chem.*, **5** (1966), 537.
- MEINEMA, H. A. & NOLTES, J. G., *J. organometallic Chem.*, **16** (1969), 257.
- MEINEMA, H. A., MACKOR, A. & NOLTES, J. G., *J. organometallic Chem.*, **37** (1972), 285.
- MEINEMA, H. A. & NOLTES, J. G., *J. organometallic Chem.*, **25** (1970), 139.
- MEINEMA, H. A., RIVAROLA, E. & NOLTES, J. G., *J. organometallic Chem.*, **17** (1969), 71.
- GOPINATHAN, S., GOPINATHAN, C. & GUPTA, J., *Indian J. Chem.*, **12** (1974), 626.
- CHRISTIANSEN, W. G., *Organic derivatives of antimony* (Am. Chem. Soc. Monograph Series No. 24), 1925, 170.
- GREENWOOD, N. N., *J. chem. Soc.*, (1960), 1130.
- SONE, K., *J. Am. chem. Soc.*, **75** (1953), 5207.
- MOELLER, T. & PUNDSACK, F. L., *J. Am. chem. Soc.*, **76** (1954), 617.
- MOELLER, T. & COHEN, A. J., *J. Am. chem. Soc.*, **72** (1950), 3546.
- KAWASAKI, Y., *Bull. chem. Soc. Japan*, **49** (1976), 2319.
- CARTY, A. J., *Can. J. Chem.*, **45** (1967), 345.
- LEVER, A. B. P., *J. inorg. nucl. Chem.*, **27** (1965), 149.

Polarographic Determination of Ni(II), Zn(II) & Mn(II) with Sodium Crotonate

A. L. J. RAO, MAKHAN SINGH & ASHOK KUMAR
Department of Chemistry, Punjabi University
Patiala 147002

Received 23 October 1976; accepted 2 January 1977

Polarographic determination of Ni(II), Zn(II) and Mn(II) has been carried out in 0.2M solution of sodium crotonate as the base electrolyte at pH 8.2. Well-defined, diffusion-controlled and irreversible waves are obtained which have been utilized for the determination of small amounts of these metal ions individually and in mixtures.

THE alkali metal salts of many organic acids such as tartaric¹, formic², lactic, malic, salicylic³, malonic⁴ and polyacrylic⁵ acids have been used for the polarographic determination of nickel, zinc and manganese. However, no attempt has been made

so far to use sodium crotonate as a base electrolyte in the determination of these metal ions.

Polarograms of the deoxygenated solutions were recorded at $25^\circ \pm 0.1^\circ$ with a manual Toshniwal polarograph type ClO₂ and pH of the solution was measured with a Philips pH meter. The d.m.e., used in conjunction with SCE connected by a saturated potassium chloride agar bridge, had the following characteristics: $m = 2.08 \text{ mg}^{-1}$ and $t = 3.1 \text{ sec}^{-1}$ in distilled water and in open circuit. Solutions of metal salts (AR) were standardized by classical methods. A freshly prepared solution of crystallized sodium crotonate was used while taking the observations.

A number of polarograms were recorded in various concentrations of sodium crotonate from 0.05M to 0.35M. In the case of Ni(II) and Zn(II), $E_{1/2}$ values shift to more negative potentials with increase in [sodium crotonate], but in the case of Mn(II) the $E_{1/2}$ shifts to positive side at [sodium crotonate] $> 0.2M$. The possible reason for this positive shift may be due to ion pair formation⁶. No maximum was observed in Ni(II) and Zn(II), however, the maxima observed in the case of Mn(II) was suppressed by the addition of 0.001% gelatin.

Polarograms were recorded for different concentrations of the metal ions Ni(II), Zn(II) and Mn(II) in 0.2M sodium crotonate at pH 8.2. The plots of i_d versus [metal ion] were linear passing through the origin, indicating that the polarographic results can be used for the quantitative determination of these metal ions.

The linear plots obtained for i_d versus \sqrt{h} in all the instances indicate that the reduction waves were diffusion-controlled. The values of the slope of the log plot $E_{3/4}-E_{1/4}$ (Table 1) indicate that the waves for all three metal ions studied were irreversible. Because of the irreversibility of the reduction waves, no deductions can be made concerning the composition of metal complexes formed. By comparing the values of i_d with those of some known reduction waves, the values for $n = 2$ were obtained. The values of I , given in Table 1, were calculated by Ilkovic equation.

Procedure for determination of metal ion — A calibration graph was prepared for each metal by recording polarograms for various known concentrations of the metal ion and the diffusion current was plotted against the [metal ion] (range given in Table 1). In the case of Ni(II) and Zn(II), below pH 3.5 the wave mixes with the hydrogen wave but the $E_{1/2}$ values remain constant in the pH range 4-9. But in the case of Mn(II) below pH 7

TABLE 1 — POLAROGRAPHIC CHARACTERISTICS OF Ni(II), Zn(II) AND Mn(II) IN 0.2M SODIUM CROTONATE SOLUTION

Metal	Range of [metal ion] mM	$E_{1/2}$ (V)	$E_{3/4}-E_{1/4}$ (from log plot) mV	I
Ni(II)	0.4-2.0	-0.982	86	2.57
Zn(II)	0.4-2.4	-0.984	100	2.80
Mn(II)	0.4-2.8	-1.490	50	2.90