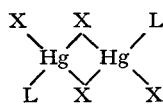


them to be essentially non-electrolytic ( $\Lambda_M \sim 30$  ohm<sup>-1</sup> cm<sup>2</sup> mole<sup>-1</sup>). IR spectra (band positions in cm<sup>-1</sup>) of these complexes are similar to those of 2-methylbenzothiazole complexes with other metal salts<sup>1</sup>, confirming coordination through the nitrogen atom only<sup>1</sup>. In addition to the absorption bands due to coordinated 2-methylbenzothiazole the far IR spectra (Beckman IR-12) of the 1:1 Hg(II) chloride and bromide complexes with this ligand show bands at 267 in the chloro and at 207 in the bromo derivative. The frequencies of these bands are halogen-dependent and are identified as  $\nu$ Hg-Cl and Hg-Br modes, respectively, consistent with terminal Hg-X stretching modes in HgLX<sub>2</sub> complexes<sup>3</sup>, where L=Ph<sub>3</sub>P, pyridine, pyridine-N-oxide or their ring substituted methyl or dimethyl derivatives, which are considered to have halogen-bridged dimeric tetrahedral structures in the solid state. Moreover, the Hg(II) chloride complex shows an additional band at 202 (but not the bromo complex) due to  $\nu$ Hg-Cl involving bridging halogens<sup>3</sup>. The bridging Hg-Br stretching mode expected at  $\sim 150$  could not be recorded with the present range of the spectrophotometer. The observed frequencies of the terminal and bridging Hg-halogen stretching modes in the 1:1 Hg(II) chloride and bromide complexes with 2-methylbenzothiazole lend support to the halogen-bridged dimeric tetrahedral structure (I) for the complexes in the solid state.



I  
X=Cl, Br or SCN

IR spectrum of the 1:1 Hg(II) cyanide-2-methylbenzothiazole complex shows additional absorption bands at 2200, 455 and 360 which are identified as  $\nu$ CN,  $\nu$ Hg-C and  $\delta$  Hg-C-N modes, respectively, due to coordinated cyano groups. Hg(II) cyanide has a linear cyanide-bridged polymeric chain structure<sup>4</sup> in the solid state and absorbs<sup>5</sup> at 2193, 442 and 341 due to  $\nu$ CN,  $\nu$ Hg-C and  $\delta$  Hg C-N modes, respectively. The frequency of  $\nu$ CN suffers a significant negative shift when the cyano bridges break down and Hg(II) cyanide complexes with terminal cyano groups absorb at lower energies<sup>6</sup> than pure mercury cyanide while bridging cyano groups absorb at higher energies<sup>7</sup>. Complexes having both terminal and bridging cyano groups display split bands in each of the  $\nu$ CN,  $\nu$ Hg-C and  $\delta$  Hg CN regions<sup>7</sup>; the one appearing at higher wave number being assigned to the bridging cyano groups while the other at lower wave number to the terminal cyano groups. The observed frequencies of  $\nu$ CN (2200),  $\nu$ Hg-C (455) and  $\delta$  Hg CN (360) are consistent with the presence of only bridging cyano groups. The 1:1 Hg(II) cyanide-2-methylbenzothiazole complex may thus be assigned a cyanobridged polymeric structure in the solid state.

In addition to the ligand bands IR spectrum of the 1:1 Hg(II) thiocyanate-2-methylbenzothiazole complex shows absorption bands at 2133, 2125

and 2090 due to  $\nu$ CN and two bands (770, 690) in the  $\nu$ CS region supporting the presence of both bridging and terminal thiocyanato groups<sup>8</sup> in the complex. On the basis of the stoichiometry and the IR spectral data the 1:1 Hg(II) thiocyanate complex with 2-methylbenzothiazole is tentatively assigned a thiocyanato-bridged dimeric structure in the solid state with two —SCN— bridges and a terminal SCN group bonded through sulphur to each mercury atom.

We thank Prof. O. P. Malhotra for facilities and Dr G. C. Percy, University of Cape Town, for the far IR spectra.

#### References

1. ARTEMENKO, M. V. & SLYUSARENKO, K. F., *Zh. neorg. Khim.*, **10** (1965), 1145; GOODGAME, M. & WEEKS, M. J., *J. chem. Soc., A* (1966), 1156; CHAN, N. N. Y., GOODGAME, M. & WEEKS, M. J., *J. chem. Soc., A* (1968), 2499; DUFF, E. J., HUGHES, M. N. & RUTT, K. J., *J. chem. Soc., A* (1969), 2126; HUGHES, M. N. & RUTT, K. J., *Spectrochim. Acta*, **27** (1971), 924; ARTEMENKO, M. V., CHISTYAKOVA, E. A., SUPRUNENKO, P. A. & KALNAJA, G., *Zh. neorg. Khim.*, **16** (1971), 1082; ARTEMENKO, M. V., SLYUSARENKO, K. F., SUPRUNENKO, P. A. & KALNAJA, G., *Zh. neorg. Khim.*, **18** (1973), 1033.
2. CLARK, R. J. H. & WILLIAMS, C. S., *Inorg. Chem.*, **4** (1965), 350.
3. DEACON, G. B., GREEN, J. H. S. & HARRISON, D. J., *Spectrochim. Acta*, **24A** (1968), 1921; AHUJA, I. S. & RASTOGI, P., *J. chem. Soc., A* (1970), 378, 2161; AHUJA, I. S., *Inorg. nucl. chem. Lett.*, **6** (1970), 879.
4. HVOSLEF, J., *Acta chem. scand.*, **12** (1958), 1568.
5. JONES, L. H., *J. chem. Phys.*, **27** (1957), 665.
6. JAIN, S. C. & RIVEST, R., *Inorg. chim. Acta*, **4** (1970), 291; AHUJA, I. S. & GARG, A., *J. inorg. nucl. Chem.*, **33** (1971), 1515, 2074; AHUJA, I. S. & SINGH, RAGHUVIR, *Inorg. chim. Acta*, **7** (1973), 565; *Inorg. nucl. chem. Lett.*, **10** (1974), 421; AHUJA, I. S. & SAMBASIVA RAO, K., *J. inorg. nucl. Chem.*, **37** (1975), 586.
7. AHUJA, I. S. & GARG, A., *J. inorg. nucl. Chem.*, **34** (1972), 2681.
8. DAVIS, A. R., MURPHY, C. J. & PLANE, R. A., *Inorg. Chem.*, **9** (1970), 423; AHUJA, I. S. & GARG, A., *J. inorg. nucl. Chem.*, **34** (1972), 1929, 2074.

#### Complexes of Organotin(IV) Halides with Neutral Schiff Bases of Salicylaldehyde & 2-Hydroxy-1-naphthaldehyde with 2-Aminopyridine

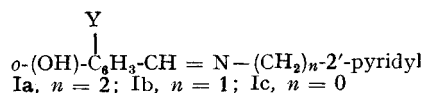
T. N. SRIVASTAVA, A. K. S. CHAUHAN & V. K. AWASTHI  
Chemistry Department, Lucknow University  
Lucknow 226007

Received 14 March 1977; accepted 25 May 1977

Schiff base complexes of the type R<sub>n</sub>SnX<sub>4-n</sub>(SB)<sub>2</sub> (where X = Cl, Br, I, SB = Schiff bases derived from 2-aminopyridine and salicylaldehyde or 2-hydroxy-1-naphthaldehyde) have been synthesized and characterized by elemental analysis, infrared and electronic spectroscopy and conductivity measurements. The ligands behave as monodentate coordinating through azomethine nitrogen atom. An octahedral structure is suggested for the complexes in solid state.

RECENTLY transition metal complexes of N-2-(2'-pyridyl)-ethylsalicylidimines (Ia) have been reported<sup>1</sup>, in which the bases behave as monofunc-

tional terdentate ligands. Oehmke and Bailar<sup>2</sup> studied coordination compounds of N-2-(2'-pyridyl) methylsalicyldimine (Ib, Y = H) with Fe(III), Co(II), Ni(II) and Zn(II) and concluded that the ring nitrogen may or may not take part in coordination depending upon the nature of the central metal atom. In Schiff bases Ic, the steric condition does not seem to be favourable for them to act as terdentate ligands and their anions behave as bidentate in M(II) complexes (M = Cu, Co, Ni, Zn and Pd)<sup>3,4</sup>. The coordination of such bases with organotin(IV) halides has not been investigated and the present note reports the synthesis and structure of the coordination compounds of diphenyltin dihalides, dimethyltin dichloride and phenyltin trichloride with the Schiff bases Ic<sub>1</sub> (Y=H) and Ic<sub>2</sub> (Y=5, 6-benzo).



Diphenyltin dihalides were prepared by the reported method<sup>5-7</sup>. Dimethyltin dichloride and phenyltin trichloride (Alfa Inorganics, USA), 2-aminopyridine (J. T. Baker) and 2-hydroxy-1-naphthaldehyde (Fluka) were used without further purification. Salicylaldehyde (BDH) was distilled before use. The Schiff bases Ic<sub>1</sub> (m.p. 70°) and Ic<sub>2</sub> (m.p. 172-73°) were synthesized by condensation of the amine with the aldehydes<sup>8</sup>.

*Preparation of the complexes*—To a stirring solution of a Schiff base (5 mmol) in *n*-hexane or dichloromethane (25 ml) was added dropwise a solution of Lewis acid (2 mmol) in the same solvent. The complexes were precipitated immediately. In a few cases the desired product was obtained by distilling off the excess solvent followed by cooling. The solid product was filtered, washed with the same solvent and dried *in vacuo*. The complexes of Ph<sub>2</sub>SnI<sub>2</sub> and PhSnCl<sub>3</sub> with Ic<sub>1</sub> are hygroscopic and were handled in a dry nitrogen atmosphere. The analytical data are reported in Table 1.

The complexes are intense yellow to red in colour, soluble in common organic solvents except ether and have sharp melting points. The analytical data show that the bases form adducts of 1:2 stoichiometry, in which they behave as neutral monodentate ligands coordinated to tin irrespective of the halogen atom attached to the metal and the nature and the number of the organic moieties  $\sigma$ -bonded to tin(IV).

Electronic spectrum (400-200 nm, Perkin-Elmer 202) of Ic<sub>1</sub> shows four absorption bands at 226, 270, 301 and 344 nm and that of Ic<sub>2</sub> consists of three bands at 234, 257 and 316 nm. The intense band of shortest wavelength is associated with the imino substituted pyridine ring<sup>8</sup>. The band at  $\sim 265$  nm can be assigned to the N $\rightarrow\pi^*$  and  $\pi\rightarrow\pi^*$  transitions of the pyridine and *o*-hydroxyaldehyde moieties<sup>9,10</sup>. The spectra of the adducts in methanol are similar to corresponding ligands indicating considerable dissociation of the complexes in solution. Molar conductance values 10<sup>-3</sup>M solution of complexes in methanol measured at 20° on a Phillips conductivity bridge are of the same order as those reported for the corresponding Lewis acids in the same concentration range<sup>11</sup>, indicating the presence of same conducting species in solution and thus supporting the conclusion derived from UV spectral studies that the complexes in solution are largely dissociated into parent components. This is in agreement with previous reports on some analogous derivatives of other Schiff bases<sup>11,12</sup>.

The IR spectra of the free and coordinated ligands do not substantially differ in the 3000 cm<sup>-1</sup> region. The bands in the spectra of the adducts located in the region 3200-3030 cm<sup>-1</sup> correspond to the weak broad band of Schiff bases at 3055  $\pm$  5 cm<sup>-1</sup> due to H-bonded (OH)<sup>13-15</sup>. The strong band appearing in the spectra of the ligands around 1275 cm<sup>-1</sup> due to phenolic C-O stretching mode<sup>16</sup> shows negligible shift, indicating that *o*-hydroxy group of the bases has not taken part in complex formation. The analytical data support the above statement.

TABLE 1 — CHARACTERIZATION DATA FOR THE ADDUCTS

Compound	m.p. °C	Found (%) (Calc.)				$\Lambda_M$ ohm <sup>-1</sup> cm <sup>2</sup> mole <sup>-1</sup>	$\nu_{\text{C}=\text{N}}$ (exocyclic) (cm <sup>-1</sup> )
		Sn	C	H	N		
Ph <sub>2</sub> SnCl <sub>2</sub> ·2Ic <sub>1</sub>	148-49	15.92 (16.03)	57.80 (58.41)	3.94 (4.08)	7.65 (7.57)	47.9	1630vs sp 1610m
Ph <sub>2</sub> SnBr <sub>2</sub> ·2Ic <sub>1</sub>	121-23	14.19 (14.31)	51.98 (52.15)	3.62 (3.65)	6.64 (6.76)	54.7	1665s 1624s
Ph <sub>2</sub> SnI <sub>2</sub> ·2Ic <sub>1</sub>	91-92	12.64 (12.86)	46.89 (46.84)	3.34 (3.28)	6.12 (6.07)	52.5	1660vs 1615vs
Me <sub>2</sub> SnCl <sub>2</sub> ·2Ic <sub>1</sub>	138	19.37 (19.26)	50.65 (50.69)	4.22 (4.25)	8.95 (9.09)	56.6	1625vs 1610vs
PhSnCl <sub>3</sub> ·2Ic <sub>1</sub>	160	Hygroscopic compound					
Ph <sub>2</sub> SnCl <sub>2</sub> ·2Ic <sub>2</sub>	180-82	14.26 (14.12)	62.60 (62.89)	4.13 (4.02)	6.71 (6.67)	49.8	1655m 1610s
Ph <sub>2</sub> SnBr <sub>2</sub> ·2Ic <sub>2</sub>	120	12.65 (12.77)	56.52 (56.87)	3.63 (3.69)	5.96 (6.03)	74.4	1670s 1624vs
Me <sub>2</sub> SnCl <sub>2</sub> ·2Ic <sub>2</sub>	176-77	16.56 (16.57)	57.35 (57.02)	4.45 (4.22)	7.94 (7.82)	62.2	1660s 1616vs
PhSnCl <sub>3</sub> ·2Ic <sub>2</sub>	179-80	14.45 (14.86)	57.25 (57.14)	3.80 (3.66)	6.94 (7.01)	40.3	1654vs sp 1612s

The  $\nu\text{C}=\text{N}$  absorption of the pyridine ring<sup>8,17</sup> appears at  $1590 \pm 5 \text{ cm}^{-1}$  in the ligands and remains unaffected on complexation. In-plane and out-of-plane ring deformation modes of pyridine are observed at  $\sim 620$  and  $410 \text{ cm}^{-1}$  respectively in the spectra of the ligands and their adducts, suggesting non-participation of the pyridine N atom in coordination<sup>18</sup>.

The bands appearing at  $1605$  and  $1610 \text{ cm}^{-1}$  in the spectra of the ligands  $\text{Ic}_1$  and  $\text{Ic}_2$  respectively may be attributed to the  $\nu\text{C}=\text{N}$  (azomethine). In the spectra of the complexes these bands appear to be split into two strong peaks at  $1645 \pm 20 \text{ cm}^{-1}$  and  $1618 \pm 6 \text{ cm}^{-1}$ , the former may be assigned mainly to  $\nu\text{C}=\text{N}$  whilst the lower band may be due to  $\nu\text{C}=\text{N}$  coupled with aromatic  $\nu\text{C}-\text{C}$  stretch<sup>15</sup>. The shift of  $20$  to  $60 \text{ cm}^{-1}$ , towards higher frequency suggests coordination through the exocyclic N atom<sup>19-22</sup>.

It is concluded that the Schiff bases behave as monodentate ligand coordinating through azomethine N atom. An octahedral structure is suggested for the complexes in the solid state.

The authors are thankful to the Head of the Chemistry Department, Lucknow University, for providing laboratory facilities and to the Director, Central Drug Research Institute, Lucknow, for his help in collecting the analytical and spectral data. Financial assistance from the CSIR, New Delhi (to A.K.S.C.), is gratefully acknowledged.

#### References

1. YAMANOUCHI, K. & YAMADA, S., *Inorg. chim. Acta*, **12** (1975), 109.
2. OEHMKE, R. W. & BAILAR (Jr), J. C., *J. inorg. nucl. Chem.*, **27** (1965), 2209.
3. OSIPOV, O. A., MINKIN, V. I., VERKHOVODOVA, D. SH. & KNYAZHANSKII, M. I., *Chem. Abstr.*, **68** (1968), 87107r.
4. YAMADA, S. & YAMANOUCHI, K., *Bull. chem. Soc. Japan*, **42** (1969), 2562.
5. HARADA, T., *Bull. chem. Soc. Japan*, **4** (1929), 266.
6. PEDLEY, J. B., TAKEDA, Y. & KINGAWA, Z., *J. Am. chem. Soc.*, **83** (1961), 538.
7. BULLARD, R. H. & ROBINSON, W. R., *J. Am. chem. Soc.*, **49** (1927), 1368.
8. PRINCE, R. H. & STOTTER, D. A., *Inorg. chim. Acta*, **10** (1974), 89.
9. SHEAT, S. V. & WATERS, T. N., *J. inorg. nucl. Chem.*, **26** (1964), 1221.
10. SONE, K., *J. Am. chem. Soc.*, **75** (1953), 5207.
11. CEFALU, R., PELLERITO, L. & BARBIERI, R., *J. organometal. Chem.*, **32** (1971), 107.
12. KAWAKAMI, K., MIYA-UCHI, M. & TANAKA, T., *J. inorg. nucl. Chem.*, **33** (1971), 3773.
13. YAMANOUCHI, K. & YAMADA, S., *Inorg. chim. Acta*, **11** (1974), 223.
14. PRASAD, R. N. & TANDON, J. P., *J. inorg. nucl. Chem.*, **37** (1975), 35.
15. VIJAY, R. G. & TANDON, J. P., *Syn. React. Inorg. Metal Org. Chem.*, **6** (1976), 231.
16. KOVACIC, J. E., *Spectrochim. Acta*, **23A** (1967), 183.
17. BUSCH, D. H. & BAILAR (Jr), J. C., *J. Am. chem. Soc.*, **78** (1956), 1137.
18. GILL, N. S., NUTIAL, R. H., SCAIFE, D. E. & SHARP, D. W. A., *J. inorg. nucl. Chem.*, **18** (1961), 79.
19. BAMFIELD, P., *J. chem. Soc.*, A (1967), 804.
20. VANDEN BERGEN, A., MURRAY, K. S., O'CONNOR, M. J., REHAK, N. & WEST, B. O., *Aust. J. Chem.*, **21** (1968), 1505.
21. SOKOLOV, V. P., KOGAN, V. A., OSIPOV, O. A. & KOLOMIN, L. G., *Russ. J. inorg. Chem.*, **14** (1969), 1260.
22. VANDEN BERGEN, A., COZENS, R. J. & MURRAY, K. S., *J. chem. Soc.*, A (1970), 3060.

## Nitration & Bromination of Some Binary & Mixed Ligand Schiff Base Complexes of Cu(II)

V. B. MOHANKUMAR, RAKESH K. KOHLI & P. K. BHATTACHARYA

Chemistry Department, Faculty of Science  
M.S. University, Baroda 390002

Received 9 September 1976; accepted 17 June 1977

Nitration and bromination reactions have been carried out on Cu(II) complexes of Schiff bases derived from 2-hydroxybenzophenone and 2-hydroxy-1-naphthaldehyde. In the case of 2-hydroxybenzophenone, the electrophilic substitution takes place in the phenolic ring rather than in the substituent group attached to the azomethine carbon. Dinitration and dibromination take place on each of the ligands resulting in tetranitro and tetrabromo compounds. It is observed that in 2-hydroxy-1-naphthaldehyde moiety, only mono nitration takes place at C-6, and this results in dinitro products in the case of bis-(2-hydroxy-1-naphthalaldiminato)Cu(II) and N,N'-ethylenebis(2-hydroxy-1-naphthalaldiminato)Cu(II) but trinitro products in the case of (2-hydroxy-1-naphthalaldiminato)(salicylaldiminato)Cu(II) and N,N'-ethylene-(2-hydroxy-1-naphthalaldiminato)(salicylaldiminato)Cu(II) complexes. The complexes have been characterized on the basis of elemental analyses, spectral and magnetic studies.

REACTIONS of coordinated ligands have evoked considerable interest in recent years and a number of reports on halogenation, nitration, thiocyanation, acetylation and formylation reactions have appeared<sup>1-19</sup>. In continuation of the work on nitration of Schiff base complexes derived from 2-hydroxyacetophenone, reported earlier from our laboratory<sup>20</sup>, we report here the results of our investigation on nitration and bromination of some Schiff base complexes of Cu(II). Nitration reactions have been mostly performed on Cu(II) complexes, because they are more stable and the ligand does not break easily. The mild nitrating agent acetylnitrate used in the present reaction was formed *in situ* by the reaction of copper(II) nitrate with acetic anhydride. This reagent is especially useful in the case of coordinated ligands because unlike strong nitrating agents ( $\text{N}_2\text{O}_4$ ,  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ ), it does not cause the decomposition of the Schiff base complexes.

N-Bromosuccinimide was used as the brominating agent. It has been used by many workers for brominating coordinated ligands<sup>3,5,8-10</sup>. The brominium ion ( $\text{Br}^+$ ) produced *in situ* acts as an electrophile in the bromination reaction of coordinated ligands.

All the complexes used for the present reactions were prepared according to the published procedure<sup>21,22</sup>. Acetic anhydride (BDH), copper(II) nitrate trihydrate (Riedel), sodium acetate (Pfizer) and N-bromosuccinimide (Riedel) were used as such.

Nitration reactions were carried out on the following Schiff base complexes.