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MÖSSBAUER STUDIES OF COMPLEXES OF DIORGANOTIN DIISOTHIOCYANATES WITH TRIDENTATE LIGANDS*

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SUMMARY

Mössbauer and infrared spectra have been obtained for terpyridyl complexes of dimethyl-, di-n-butyl- and diphenyltin diisothiocyanates and the corresponding $[R_2Sn(NCS)\cdot\text{terpyridyl}]^+[BPh_4]^-$ compounds, and for the 8-(2-pyridylmethyleneamino)quinoline, PMAQ, complexes with di-n-butyl- and diphenyltin diisothiocyanates. Infrared spectra of the neutral complexes indicate seven-coordination for tin and the Mössbauer parameters indicate axial C–Sn–C bonds having a greater tin *s*-character than in *trans* octahedral complexes. The largest quadrupole splitting, 4.73 mm/sec, was obtained for the terpyridyl complex with di-n-butyltin diisothiocyanate.

INTRODUCTION

The crystal structure of the 1/2 complex of 2,2′,2″-terpyridyl with dimethyltin dichloride indicates a $[(CH_3)_2SnCl\cdot\text{terpyridyl}]^+[(CH_3)_2SnCl_3]^-$ structure. The cation is a highly distorted octahedron with *trans* methyl groups[1]. Zuckerman and coworkers[2] have obtained the Mössbauer spectra of a number of complexes containing the $[R_2SnCl\cdot\text{Terpy}]^+$ cation and reported ^{119}Sn quadrupole splittings of 3.0–3.6 mm/sec. As the N–M–N bond angles in terpyridyl complexes are about 72° [1,3], it occurred to the authors that seven-coordinate tin complexes of terpyridyl with R_2SnX_2 could be obtained if X is a group having a smaller atom than chlorine bonded to tin. There is evidence for a number of seven-coordinate tin complexes. The crystal structures of monochloro- and monohydroxotris(tropolonato)tin(IV)[4], methyltris(nitrato)tin(IV)[5] and methyltris(*N*,*N*-diethyldithiocarbamato)tin(IV)[6] indicate distorted pentagonal bipyramidal configurations. Mössbauer data include those for $XSnY_3$, where X is a halogen atom and Y is the chelated anion of picolinic acid[7],

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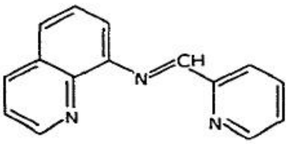
8-hydroxyquinoline[8], and kojic acid[9]. Previous evidence for seven-coordinate tin complexes containing two tin–carbon bonds, however, appears to be lacking.

The present study is concerned with complexes of dimethyl-, di-n-butyl- and diphenyltin diisothiocyanate with terpyridyl, and of the latter two compounds with another tridentate ligand, 8-(2-pyridylmethyleneamino)quinoline, PMAQ,



EXPERIMENTAL

Dimethyl-, di-n-butyl- and diphenyltin dichloride and di-n-butyltin difluoride were obtained from Alfa Inorganics, Inc. 2,2′,2″-Terpyridyl was a G. F. Smith Chemical Co. product. 2,2′-Dipyridyl and *o*-phenanthroline were obtained from Aldrich Chemical Co. Sodium tetraphenylboron was supplied by Fisher Scientific Co.

Dimethyl-, di-n-butyl- and diphenyltin diisothiocyanate were prepared from the dichlorides by the method of Seyferth and Rochow[10]. The 1/1 addition complexes of these compounds with 2,2′,2″-terpyridyl were prepared by adding absolute ethanol solutions of the respective isothiocyanates to a slight excess of terpyridyl in the same solvent. The complexes precipitated immediately. After washing with ethanol they were vacuum dried at 56°. Tetraphenylborate salts of the terpyridyl complexes, $[R_2Sn(NCS)\cdot Terpy]^+[Ph_4B]^-$, were prepared according to the method of Fergusson, Roper and Wilkins[11] by adding each terpyridyl complex in absolute ethanol to an excess of sodium tetraphenylborate in the same solvent. The 1/1 complex of dimethyltin diisothiocyanate with 2,2′-dipyridyl formed when a methanol solution of the diisothiocyanate was added to an excess of dipyridyl in the same solvent. The white powder was washed with methanol.

8-(2-Pyridylmethyleneamino)quinoline, PMAQ, was prepared as described by Lions and Martin[12]. The 1/1 complexes of di-n-butyl- and diphenyltin diisothiocyanate with PMAQ were prepared by adding a solution of the diisothiocyanate in anhydrous diethyl ether to an excess of PMAQ in ether. The dark yellow products precipitated immediately.

The 1/1 complex of di-n-butyltin difluoride with *o*-phenanthroline precipitated on the addition of a concentrated solution of the difluoride in dimethylsulfoxide to an excess of *o*-phenanthroline in the same solvent. The product was washed with anhydrous diethyl ether. An attempt was made to prepare the 1/1 complex of di-n-butyltin difluoride with terpyridyl by the same method as above. The product crystallized only after most of the solvent evaporated. It gave good carbon and hydrogen analyses and a sharp Mössbauer spectrum ($\delta = 1.49$ and $\Delta E_Q = 4.73$ mm/sec), but the infrared spectrum indicated strong fluorine bridging and a lack of true coordination by terpyridyl.

Infrared and Mössbauer spectra. The former were obtained in KBr disks with Perkin–Elmer spectrometers, Models 421 and 457. Mössbauer parameters for absorbers at 80K were obtained as described previously[13,14], using a barium stannate source at room temperature. The isomer shifts relative to barium stannate and the quadrupole splittings are considered to be accurate to ±0.05 mm/sec with a relative precision of ±0.03 mm/sec.

Conductivity measurements. These were made with a Serfass Conductivity Bridge, Model RCM-15B1, using a Sargent Conductivity Cell, S-29965.

RESULTS

Melting points, analyses, isomer shifts (δ), quadrupole splittings (ΔE_Q) and line widths (Γ) are listed in Table 1. The Mössbauer spectrum of diphenyltin diisothiocyanate·terpyridyl is illustrated in Fig. 1. The slight asymmetry is characteristic of all three neutral terpyridyl complexes. None of the compounds showed resonance absorption at room temperature.

TABLE 1

CHARACTERIZATION AND MÖSSBAUER PARAMETERS (mm/sec) AT 80 K RELATIVE TO $BaSnO_3$

		M.p. (°C)	*Analysis found (calcd.)* (%)		δ	ΔE_Q	Γ_1	Γ_2
			C	*H*				
1	$(CH_3)_2Sn(NCS)_2\cdot$dipyridyl	125–127	39.86 (39.90)	3.56 (3.30)	1.28	4.09	1.24	1.22
2	$(CH_3)_2Sn(NCS)_2\cdot$terpyridyl	213–215	45.92 (45.78)	3.62 (3.41)	1.32	4.29	1.33	1.19
3	$[(CH_3)_2Sn(NCS)\cdot\text{Terpy}]^+[BPh_4]^-$	195–197	66.69 (66.40)	5.12 (4.87)	1.31	3.92	1.24	1.19
4	$(n\text{-}C_4H_9)_2Sn(NCS)_2\cdot$terpyridyl	185–187	51.56 (51.55)	5.19 (4.98)	1.63	4.73	1.14	1.13
5	$[(n\text{-}C_4H_9)_2Sn(NCS)\cdot\text{Terpy}]^+[BPh_4]^-$	145–148	68.06 (68.33)	6.08 (5.81)	1.53	4.01	1.20	1.27
6	$(C_6H_5)_2Sn(NCS)_2\cdot$terpyridyl	208–210	55.62 (55.95)	3.45 (3.38)	1.29	4.18	1.13	1.03
7	$[(C_6H_5)_2Sn(NCS)\cdot\text{Terpy}]^+[BPh_4]^-$	195–197	69.41 (70.67)	4.90 (4.64)	1.27	3.53	0.98	0.87
8	$(n\text{-}C_4H_9)_2Sn(NCS)_2\cdot$PMAQ	119–120	51.45 (51.55)	5.15 (4.98)	1.50	4.35	1.00	1.04
9	$(C_6H_5)_2Sn(NCS)_2\cdot$PMAQ	157–158	54.96 (55.95)	3.67 (3.38)	1.25	3.84	1.28	1.10
10	$(n\text{-}C_4H_9)_2SnF_2\cdot$*o*-phenanthroline	140–144	53.01 (53.21)	5.70 (5.76)	1.30	4.03	1.21	1.35

Equivalent conductances (Λ) in $cm^2\ ohm^{-1}$ of 0.004 *M* solutions in dimethylformamide at 25±2° are 77 for tetramethylammonium bromide, 38, 30 and 28 for the terpyridyl complexes of dimethyl-, di-n-butyl- and diphenyltin diisothiocyanate respectively; and 26 and 22 for the PMAQ complexes with di-n-butyl- and diphenyltin diisothiocyanate.

Infrared spectra of the solid neutral terpyridyl and PMAQ complexes show no absorption at 748 cm^{-1}, a frequency characteristic of the free thiocyanate anion. The high frequency ring vibration at 1578 cm^{-1} in terpyridyl shifts to 1592 cm^{-1} on

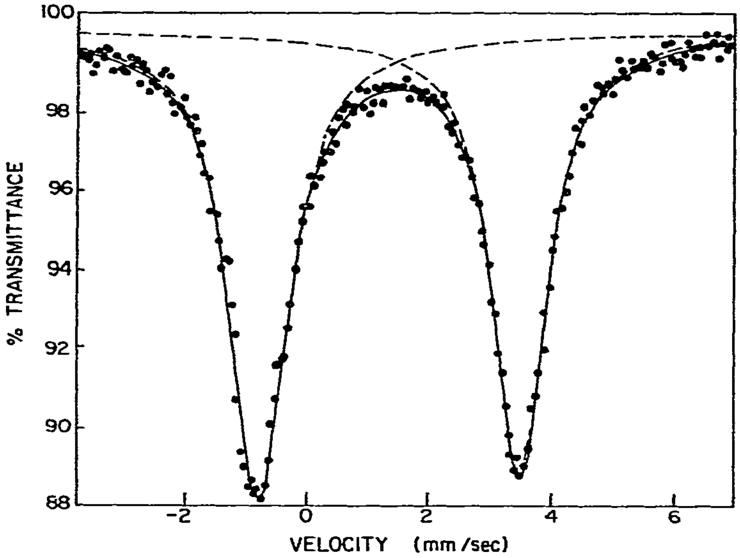


Fig. 1. Mössbauer spectrum of $(C_6H_5)_2Sn(NCS)_2 \cdot$ terpyridyl.

complex formation. An absorption by terpyridyl at 765, very likely associated with a C–H out-of-plane vibration, shifts to 770–772 cm^{-1} in the complexes. The changes in the spectrum of terpyridyl from the free amine to $ZnCl_2 \cdot$ terpyridyl, for which X-ray diffraction studies reveal three nitrogen–metal bonds[3], particularly those in the 1040–1100 cm^{-1} region, are paralleled in the spectra of the tin complexes. Likewise, the changes in the spectrum of PMAQ on complex formation with $ZnCl_2$ and $SnCl_2$[15] are similar to the changes on complex formation with di-n-butyl- and diphenyltin diisothiocyanate. The absorptions in the 2050 cm^{-1} region of the spectra of the neutral complexes of terpyridyl and PMAQ, associated with NCS stretching vibrations, are stronger and much broader than in the spectra of $[R_2Sn(NCS) \cdot Terpy]^+[BPh_4]^-$, indicative of two NCS groups per molecule.

The spectrum of n-$Bu_2SnF_2 \cdot$ *o*-phenanthroline is similar to those of the dichloride and dibromide in the *o*-phenanthroline region, but shows strong absorptions at 470 and 363 cm^{-1}, significantly lower than the frequencies, ~540 cm^{-1}, of Sn–F stretching vibrations in octahedral complexes[16], and differing from the absorptions at 355 and 318 cm^{-1} in fluorine-bridged Bu_2SnF_2. The spectrum of $Bu_2SnF_2 \cdot$ *o*-phen in chloroform shows absorptions at 530 and 470 cm^{-1}.

DISCUSSION

The infrared spectra of the solid neutral terpyridyl and PMAQ complexes indicate seven coordination for tin. The differences in the Mössbauer parameters for $R_2Sn(NCS)_2 \cdot$ terpyridyl and $[R_2Sn(NCS) \cdot Terpy]^+[BPh_4]^-$ are indicative of the presence of two NCS groups bonded to tin in the former (neutral) complexes. The large quadrupole splittings obtained for the complexes indicate axial C–Sn–C bonds. Very recently this has been verified by the determination of the crystal structure of $(CH_3)_2$-$Sn(NCS)_2 \cdot$ terpyridyl in our laboratories by Datta Naik and Professor W. Robert

Scheidt[17]. The C–Sn–C bond angle is 173.7° and the five Sn–N bonds, in the region of the equatorial plane, are all shorter than 2.6 Å, showing seven-coordination for tin. Whereas conductance data reveal appreciable ionization of the complexes in dimethylformamide, the crystal structure, infrared data and sharp Mössbauer spectra indicate no significant partial ionization in the solids. The *trans* arrangement of phenyl groups in the terpyridyl complexes is in contrast to the *cis* arrangement in $Ph_2Sn(NCS)_2 \cdot$dipyridyl[14].

Other things being equal, a decrease in isomer shift is expected from six- to seven-coordinate tin compounds; this has been observed for a variety of complexes[7,8,9]. However, there is an increase in the isomer shift from a dipyridyl to a terpyridyl complex: 1.28 to 1.32 mm/sec for the dimethyl and 1.40 (ref. 14) to 1.63 mm/sec for the dibutyl complexes. The isomer shift for $Ph_2Sn(NCS)_2 \cdot$terpyridyl, 1.29 mm/sec, is also larger than that expected for a (hypothetical) *trans* dipyridyl complex. (The value is much larger than the shift, 0.81 mm/sec, obtained for the *cis* compound.) This set of comparisons leads the authors to conclude that the axial C–Sn–C bonds in the seven-coordinate complexes have a greater tin *s*-character than in the *trans* octahedral complexes. Solubility limitations prevent the determination of the ^{119}Sn–CH coupling constant for $Me_2Sn(NCS)_2 \cdot$terpyridyl.

The ^{119}Sn–CH coupling constants for $MeSn(S_2CNEt_2)_3$ and $MeSn(S_2CNMe_2)_3$ are 119 and 120 cps, compared to 110 cps for $MeSnCl(S_2CNEt_2)_2$ and $MeSnCl(S_2CNMe_2)_2$[18]. The former pair also show greater isomer shifts than the latter. These data have been interpreted[18] as indicating greater tin *s*-character for the Sn–C bond in each of the seven-coordinate complexes than in the six-coordinate compounds. Similar increases in isomer shift from the six- to seven-coordinate complexes were obtained for the corresponding compounds having butyl–tin and phenyl–tin bonds. The crystal structure of $MeSn(S_2CNEt_2)_3$ reveals an axial C–Sn bond and a significantly shorter distance for the axial Sn–S bond than for the equatorial bonds[6]. This is in contrast to the longer axial bonds in trigonal bipyramidal compounds.

The infrared spectrum of $Bu_2SnF_2 \cdot$*o*-phen suggests seven-coordination for tin, with fluorine bridging. The higher frequencies for the Sn–F stretching vibrations in chloroform suggest that these bridges are broken in solution. The isomer shift for the solid, 1.30 mm/sec, compares with 1.58 mm/sec for the corresponding dichloride[13]. The large quadrupole splitting, 4.03 mm/sec, indicates axial butyl groups. We are unaware of any other report of complexes of dialkyltin difluoride with organic ligands. The preference of tin for –F→Sn dative bonds is illustrated by the evaporation of a pyridine solution of Bu_2SnF_2 at room temperature—there is no trace of pyridine in the solid Bu_2SnF_2 residue.

REFERENCES

1 F. W. B. Einstein and B. R. Penfold, *J. Chem. Soc., A*, (1968) 3019.
2 N. W. G. Debye, E. Rosenberg and J. J. Zuckerman, *J. Amer. Chem. Soc.*, 90 (1968) 3234.
3 F. W. B. Einstein and B. R. Penfold, *Acta Cryst.*, 20 (1966) 924.
4 J. J. Park, D. M. Collins and J. L. Hoard, *J. Amer. Chem. Soc.*, 92 (1970) 3636.
5 G. S. Brownlee, A. Walker, S. C. Nyburg and J. T. Szymanski, *Chem. Commun.*, (1971) 1073.
6 E. O. Schlemper, private communication.
7 D. V. Naik and C. Curran, *Inorg. Chem.*, 10 (1971) 1017.

8 K. M. Ali, D. Cunningham, M. J. Frazier, J. D. Donaldson and B. J. Senior, *J. Chem. Soc. A*, (1969) 2836.
9 D. Naik, J. C. May and C. Curran, *Coordination Chem.*, in press.
10 D. Seyferth and E. G. Rochow, *J. Amer. Chem. Soc.*, 77 (1955) 1302.
11 J. E. Fergusson, W. R. Roper and C. J. Wilkins, *J. Chem. Soc.*, (1965) 3716.
12 F. Lions and K. V. Martin, *J. Amer. Chem. Soc.*, 79 (1957) 2933.
13 M. A. Mullins and C. Curran, *Inorg. Chem.*, 6 (1967) 2017.
14 M. A. Mullins and C. Curran, *Inorg. Chem.*, 7 (1968) 2584.
15 M. A. Doskey and C. Curran, *Inorg. Chim. Acta*, 3 (1969) 169
16 D. Petridis, F. P. Mullins and C. Curran, *Inorg. Chem.*, 9 (1970) 1270.
17 To be submitted for publication.
18 J. C. May, D. Petridis and C. Curran, *Inorg. Chim. Acta*, 5 (1971) 511.