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Infrared and Nuclear Magnetic Resonance Studies of Some Tin Phthalocyanines and Hemiporphyrazines[1]

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The nmr spectra of $PcSi(OSi(C_2H_5)_3)_2$, $PcSn(OSi(C_2H_5)_3)_2$, and $hpSn(OSi(C_2H_5)_3)_2$ have been studied and further evidence for the nonaromaticity of the hemiporphyrazine ring was thus gathered. In addition, the infrared spectra of a series of simple tin hemiporphyrazines and phthalocyanines have been studied and assignments for absorptions associated with the *trans* group substituents made.

Introduction

In a previous paper[2] the nmr spectra of triethylsiloxygermanium phthalocyanine and triethylsiloxygermanium hemiporphyrazine and the infrared spectra of a series of simple germanium phthalocyanines and hemiporphyrazines were described and discussed. The present paper gives the results of an extension of the nmr work to the corresponding silicon and tin phthalocyanines and the corresponding tin hemiporphyrazine. It also gives the results of infrared work on a series of simple tin hemiporphyrazines. Some work which extends infrared studies made earlier on the tin phthalocyanines[3] is also given.

Experimental Section

hpLiH.—A mixture of 6.21 g of hpH_2, 0.30 g of LiH, and 140 ml of 1,2,4-trimethylbenzene was refluxed for 5 hr and filtered. The resultant γ form of hpLiH weighed 5.81 g.

γ-hpLiH.—Extraction of the synthesis product with 1,2-dichlorobenzene gave an extract containing blue-black crystals. *Anal.* Calcd for $C_{26}H_{15}N_8Li$: C, 69.96; H, 3.39; N, 25.10; Li, 1.55. Found: C, 69.81, H, 3.48; N, 24.91; Li, 1.36.

β-hpLiH. Vacuum sublimation of the synthesis product at 325° yielded blue-black crystals. *Anal.* Found: C, 69.77; H, 3.48; N, 24.97; Li, 1.31.

Since both PcLiH and $PcLi_2$ are known,[4] an attempt was made to prepare $hpLi_2$. In this attempt 1.68 g of hpH_2, 0.21 g of LiH, 70 ml of 1,2,4-trimethylbenzene, and a reflux period of 4 hr were used. The product was, however, hpLiH.

$hpNa_2$.—A 1:2 mole ratio mixture of hpH_2 and NaH (52% oil dispersion) in phenyl ether was refluxed for 1.5 hr and filtered. (The use of a more inert solvent would probably have been preferable.)

Crystallization of the product twice from dimethylformamide gave an orange crystalline solvate. This was heated at 175° under vacuum for 75 min. The resultant desolvated product was a brown hygroscopic powder. *Anal.* Calcd for $C_{26}H_{14}N_8Na_2$: C, 64.46; H, 2.91; N, 23.13; Na, 9.49. Found: C, 64.16; H, 3.51; N, 22.83; Na, 9.32.

hpK_2.—This compound was synthesized in a manner analogous to that used for $hpNa_2$. Purification was achieved through recrystallization of its dimethylformamide adduct (red-orange) as for the sodium compound. It was a brown hygroscopic powder. *Anal.* Calcd for $C_{26}H_{14}N_8K_2$: C, 60.44; H, 2.73; N, 21.69; K, 15.14. Found: C, 60.06; H, 3.48; N, 21.43; K, 14.74.

hpSn.—Under a nitrogen atmosphere a mixture of 4.00 g of $hpNa_2$, 1.57 g of stannous chloride, and 200 ml of quinoline was refluxed for 20 min, cooled, and filtered. The resultant product weighed 4.60 g.

This was extracted under nitrogen with 1,2,4-trimethylbenzene and the product from the extract was then extracted under nitrogen with 1,2-dichlorobenzene. From this extract blue-black-reflecting, brown-transmitting crystals were obtained. *Anal.* Calcd for $C_{26}H_{14}N_8Sn$: C, 56.05; H, 2.53; Sn, 21.30. Found: C, 56.10; H, 2.75; Sn, 21.21.

$hpSnCl_2$.—A mixture of 5.00 g of stannous chloride in 30 ml of pyridine, 5.76 g of 2,6-diaminopyridine, 6.76 g of phthalonitrile, and 500 ml of 1-chloronaphthalene was refluxed for 3.3 hr, cooled, and filtered. This yielded 10.35 g of product.

Recrystallization from 1-chloronaphthalene yielded blue-black-reflecting, yellow-green-transmitting crystals. These were refluxed with benzene to remove traces of 1-chloronaphthalene. *Anal.* Calcd for $C_{26}H_{14}N_8SnCl_2$: C, 49.72; H, 2.25; Sn, 18.90; Cl, 11.29. Found: C, 49.75; H, 2.42; Sn, 18.54; Cl, 11.52.

The dichloride was also prepared by the reaction of $hpNa_2$ with $SnCl_4$. In one experiment, a mixture of 500 mg of $hpNa_2$, 0.15 ml of $SnCl_4$, and 25 ml of quinoline was refluxed under nitrogen for 20 min and filtered. The yield was 467 mg.

$hpSnBr_2$.—A mixture of 1.00 g of hpSn, 0.15 ml of Br_2, and 30 ml of 1-chloronaphthalene was heated to 70–75° for 1 hr, cooled, and filtered. This gave 1.17 g of product.

Recrystallization from 1-chloronaphthalene yielded blue-black-reflecting, yellow-green-transmitting crystals. *Anal.* Calcd for $C_{26}H_{14}N_8SnBr_2$: C, 43.56; H, 1.97; Sn, 16.55; Br, 22.29. Found: C, 43.66; H, 2.14; Sn, 16.87; Br, 22.46.

$hpSnI_2$.—A mixture of 2.00 g of hpSn, 1.18 g of iodine, and 200 ml of 1-chloronaphthalene was refluxed for 2 min, cooled to ~40°, and filtered. This gave 2.23 g of $hpSnI_2$ in the α form.

α-$hpSnI_2$.—Recrystallization of the synthesis product from 1-chloronaphthalene yielded blue-black-reflecting, yellow-green-transmitting crystals. *Anal.* Calcd for $C_{26}H_{14}N_8SnI_2$: C, 38.51; H, 1.74; Sn, 14.63; I, 31.30. Found: C, 38.49; H, 1.96; Sn, 14.30; I, 31.71.

β-$hpSnI_2$.—Substitution of phenyl ether for 1-chloronaphthalene in the synthesis led to the β polymorph ($hpSnI_2$ is less soluble in phenyl ether and crystals of it were present in the refluxing reaction mixture). Extraction of the product with 1-chloronaphthalene yielded an extract containing the β form as blue-black-reflecting, yellow-green-transmitting crystals. *Anal.* Found: C, 38.65; H, 1.93; Sn, 14.82; I, 31.17.

$hpSn(OCH_3)_2$.—A 1.27-g sample of $hpSn(OH)_2$ prepared by the hydrolysis of $hpSnI_2$ with a refluxing 1:1 pyridine–ammonium hydroxide solution was refluxed with 125 ml of methanol for 8 hr and filtered. This gave 1.14 g of $hpSn(OCH_3)_2$ in the β form.

β-$hpSn(OCH_3)_2$.—Extraction of the synthesis product with methanol yielded an extract containing blue-black-reflecting, yellow-green-transmitting crystals. *Anal.* Calcd for $C_{28}H_{20}$-

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[2] J. N. Esposito, L. E. Sutton, and M. E. Kenney, *Inorg. Chem.*, **6**, 1116 (1967).

[3] W. J. Kroenke and M. E. Kenney, *ibid.*, **3**, 696 (1964).

[4] P. A. Barrett, D. A. Frye, and R. P. Linstead, *J. Chem. Soc.*, 1157 (1938).

N_8SnO_2: C, 54.31; H, 3.26; Sn, 19.17; N, 18.10. Found: C, 54.16; H, 3.58; Sn, 19.00; N, 17.98.

α-hpSn(OCH$_3$)$_2$.—A hot chlorobenzene solution of pure hpSn(OCH$_3$)$_2$ was added dropwise to *n*-hexane held at 0°. This gave an olive-green powder. *Anal.* Found: C, 54.19; H, 3.55; Sn, 19.36.

hpSn(OH)$_2$.—A 235-mg sample of pure β-hpSn(OCH$_3$)$_2$ was refluxed with 30 ml of 1:1 pyridine–ammonium hydroxide solution for 3 hr. The resultant blue-black-reflecting, yellow-green-transmitting crystals weighed 147 mg. *Anal.* Calcd for $C_{26}H_{16}N_8SnO_2$: C, 52.83; H, 2.73; N, 18.95; Sn, 20.08. Found: C, 52.13; H, 2.70; N, 18.63; Sn, 20.08.

hpSn(OD)$_2$.—A 200-mg sample of pure β-hpSn(OCH$_3$)$_2$ was refluxed with a mixture of 2 ml of D_2O and 10 ml of pyridine for 4 hr and filtered. This gave 177 mg of blue-black-reflecting, yellow-green-transmitting crystals. *Anal.* Calcd for $C_{26}H_{14}D_2N_8SnO_2$: C, 52.65; N, 18.89; Sn, 20.00. Found: C, 52.42; N, 18.98; Sn, 20.14.

(hpSnO)$_x$.—A 202.4-mg sample of pure hpSn(OH)$_2$ was heated at 350° for 30 min under vacuum. A small amount of sublimate and an olive-colored product weighing 193.4 mg were obtained. *Anal.* Calcd for $C_{26}H_{14}N_8SnO$: C, 54.49; H, 2.46; N, 19.55; Sn, 20.71. Found: C, 54.08; H, 2.57; N, 19.32; Sn, 21.03. For the size sample used the calculated weight loss was 6.3 mg. The polymer also was obtained by refluxing a mixture of hpSn(OH)$_2$ and 1-chloronaphthalene and by refluxing a mixture of hpSn and 1,2,4-trimethylbenzene in air.

hpSnF$_2$.—An 800-mg sample of hpSn(OH)$_2$ was evaporated to dryness on a steam bath with 4 ml of 49% aqueous HF and 15 ml of pyridine. The product, after being washed with pyridine, benzene, and ether, weighed 640 mg.

A double recrystallization from 1-chloronaphthalene yielded blue-black-reflecting, yellow-green-transmitting crystals. *Anal.* Calcd for $C_{26}H_{14}N_8SnF_2$: C, 52.47; H, 2.37; Sn, 19.94; F, 6.38. Found: C, 52.10; H, 2.34; Sn, 20.26; F, 6.15.

hpSn(OSi(C$_2$H$_5$)$_3$)$_2$.—A mixture of 591 mg of hpSn(OH)$_2$ and 0.6 ml of triethylsilanol in 25 ml of chlorobenzene was refluxed for 22 hr and filtered. Evaporation of the filtrate yielded 754 mg of product.

α-hpSn(OSi(C$_2$H$_5$)$_3$)$_2$.—The synthesis product was recrystallized twice from cyclohexane and air dried. The resultant crystals were blue-black by reflection and yellow-green by transmission.

β-hpSn(OSi(C$_2$H$_5$)$_3$)$_2$.—The recrystallized α form was heated at 150° for 1 hr under vacuum. *Anal.* Calcd for $C_{38}H_{44}N_8SnSi_2O_2$: C, 55.68; H, 5.41. Found: C, 55.82, 55.61; H, 5.49, 5.61.

In the presence of cyclohexane, or even mineral oil, the β to α conversion occurred readily at room temperature. In a mineral oil mull, conversion was detectable after 0.25 hr and complete after 1.3 hr.

PcSi(OSi(C$_2$H$_5$)$_3$)$_2$.—A mixture of 1.15 g of PcSi(OH)$_2$, 0.7 ml of hexamethyldisilazane, and 70 ml of quinoline was refluxed for 2.5 hr, filtered, and cooled. This gave 1.12 g of product.

Recrystallization from toluene twice gave red-reflecting, blue-transmitting crystals. *Anal.* Calcd for $C_{44}H_{46}N_8Si_3O_2$: C, 65.80; H, 5.77; Si, 10.49. Found: C, 65.91; H, 5.88; Si, 10.51.

PcSn(OSi(C$_2$H$_5$)$_3$)$_2$.—A mixture of 500 mg of PcSn(OH)$_2$, 0.45 ml of triethylsilanol, and 70 ml of chlorobenzene was refluxed for 35 min, filtered, and cooled. The resultant product weighed 432 mg.

A double recrystallization from toluene yielded red-reflecting, blue-green-transmitting crystals. *Anal.* Calcd for $C_{44}H_{46}N_8SnSi_2O_2$: C, 59.13; H, 5.19. Found: C, 58.98; H, 5.13.

Other Phthalocyanines.—The tin phthalocyanines PcSn(OH)$_2$, PcSnF$_2$, PcSnCl$_2$, PcSnBr$_2$, and PcSnI$_2$ were prepared and purified by methods similar to those previously described.[3]

X-Ray Patterns.—The accompanying calculated *d* spacings and estimated intensities were obtained from Debye–Scherrer photographs. A 114.6-mm camera, nickel-filtered Cu$K\alpha$ radiation, and 0.3-mm glass capillaries were used to produce photographs. **β-hpLiH:** 16.6, w; 12.8, w; 11.6, m; 9.58, w; 6.55, w; 5.82, s; 4.77, m; 4.40, w; 4.16, vs; 3.91, w; 3.74, s; 3.40, s; 3.16, w; 2.50 vw; 2.23, vw; 1.88, w. **γ-hpLiH:** 11.9, vs; 9.96, m; 7.53, w; 6.54, m; 5.99, m; 5.69, vw; 5.13, s; 4.82, w; 4.40, vw; 4.10, w; 3.92, w; 3.76, w; 3.60, s; 3.46 s; 3.24, s; 3.02, w; 2.88, w. **α-hpSnI$_2$:** 10.5, vs; 7.23, vs; 5.92, vw; 5.36, m; 4.57, w; 4.12, m; 3.91, m; 3.72, m; 3.48, w; 3.29, s; 3.04, w; 2.89, w; 2.81, w; 2.58, w; 2.47, vw; 2.33, w; 2.21, vw. **β hpSnI$_2$:** 10.7, s; 9.27, vs; 7.87, s; 6.73, m; 5.52, w; 4.98, w; 4.40, w; 4.28, w; 4.05, w; 3.77, vw; 3.60, w; 3.41, w; 3.30, m; 3.05, vw; 2.76, vw; 2.63, vw. **α-hpSn(OCH$_3$)$_2$:** 9.64, vs; 7.30, vs; 6.66, s; 5.47, m; 4.74, m; 4.35, w; 4.20, w; 3.89, m; 3.54, w; 3.32, s; 3.20, vw; 3.03, w; 2.91, w; 2.82, w; 2.53, vw; 2.41, vw; 2.27, vw; 1.91, s; 1.66 m. **β-hpSn(OCH$_3$)$_2$:** 8.55, vw; 6.27, s; 5.35, m; 4.93, w; 4.71, w; 4.37, w; 4.01, s; 3.78, w; 3.64, w; 3.50, m; 3.35, w; 3.12, w; 3.02, m; 2.92, vw; 2.81, m; 2.68, w; 2.62, w; 2.48, w; 2.39, w; 2.28, w; 2.22, w; 2.15, w; 2.04, vw; 1.91, s; 1.79, vw; 1.66, m. **(hpSnO)$_x$:** 12.0, vs; 6.79, w; 3.67, s; 1.85, w. On the basis of additional powder pattern data it was concluded that hpSn(OH)$_2$ and hpSn(OD)$_2$ are isomorphous and that hpSnCl$_2$ and hpSnBr$_2$ probably are isomorphous.

Infrared Spectra.—Mineral oil mulls and Beckman IR-8, IR-5A CsBr, and IR-11 spectrophotometers were used in obtaining the infrared spectra. Polystyrene, 1,2,4-trichlorobenzene, and water vapor were used for calibration. The range covered for the fluoro, chloro, bromo, iodo, hydroxy, and deuteroxy compounds was 33 to 4000 cm^{-1}.

Nmr Spectra.—A Varian A-60A spectrometer operating at 39° was used to obtain the nmr spectra. Tetramethylsilane was used as an internal standard and carbon tetrachloride as a solvent.

Results and Discussion

Nmr Spectra.—The portions of the spectra of PcSi(OSi(C$_2$H$_5$)$_3$)$_2$ and PcSn(OSi(C$_2$H$_5$)$_3$)$_2$ attributable to the macrocyclic ring protons were found to be, as the data in Table I show, very much like the ring proton portion of the spectrum of the previously studied compound PcGe(OSi(C$_2$H$_5$)$_3$)$_2$.[2] Similarly the ring proton portion of the spectrum of hpSn(OSi(C$_2$H$_5$)$_3$)$_2$ was found to be like that of the previously studied compound hpGe(OSi(C$_2$H$_5$)$_3$)$_2$.[5]

Table I

Nmr Phthalocyanine Multiplet Centers (τ)

	3,6 protons	4,5 protons
PcSi(OSi(C$_2$H$_5$)$_3$)$_2$	0.32	1.65
PcGe(OSi(C$_2$H$_5$)$_3$)$_2$	0.30	1.62
PcSn(OSi(C$_2$H$_5$)$_3$)$_2$	0.31	1.62

A marked similarity between the ethyl group portions of the spectra of the three phthalocyanines and between the ethyl group portions of the spectra of the two hemiporphyrazines was also found. Data pertinent to these groups are presented in Table II. The values shown for the tin hemiporphyrazine were obtained with the aid of Rogers' equations[6] and an assumed value of 7.6 cps for the coupling constant.

These data, taken individually and as a whole, provide still more evidence for the aromaticity of the phthalocyanine ring and for the lack of it in the hemi-

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[5] Reproductions of the nmr spectra of both hpGe(OSi(C$_2$H$_5$)$_3$)$_2$ and PcGe(OSi(C$_2$H$_5$)$_3$)$_2$ are shown in ref 2.

[6] P. T. Narasimhan and M. T. Rogers, *J. Am. Chem. Soc.*, **82**, 5983 (1960).

TABLE II

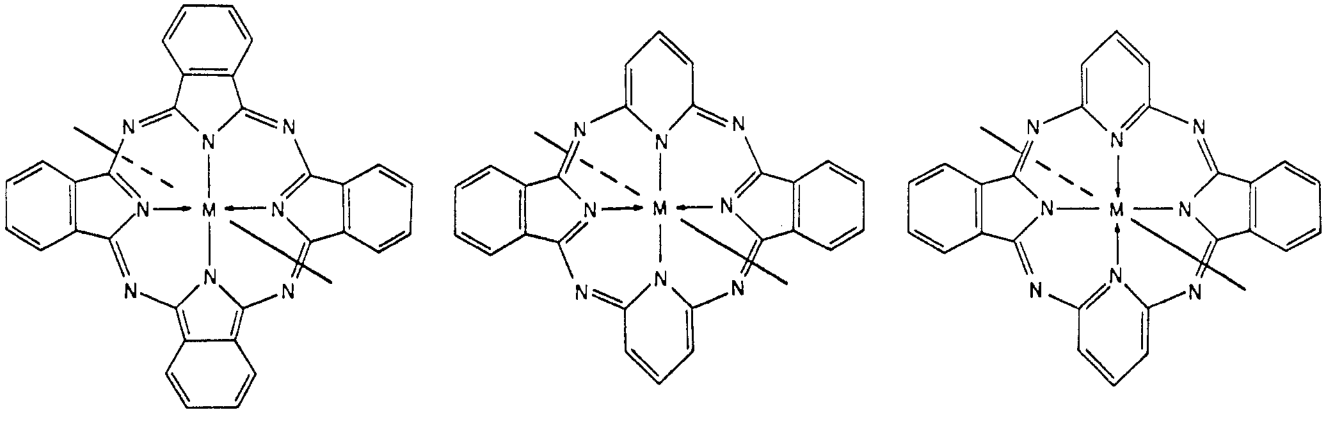
NMR ETHYL MULTIPLET CENTERS (τ)

	CH_3	CH_2	*J*
$PcSi(OSi(C_2H_5)_3)_2$	11.25	12.48	7.6
$PcGe(OSi(C_2H_5)_3)_2$	11.24	12.42	7.6
$PcSn(OSi(C_2H_5)_3)_2$	11.21	12.31	7.6
$hpGe(OSi(C_2H_5)_3)_2$	9.30	9.63	7.6[a]
$hpSn(OSi(C_2H_5)_3)_2$	9.32	9.68	7.6[a]

[a] Assumed.

porphyrazine ring. Further, the similarity of the data for the three phthalocyanines shows that, insofar as the ring current is sensitive to it, the bonding between the central metal and the phthalocyanine ring is much the same for the three. (The small differences observed for the ethyl groups probably can be accounted for in terms of the differences in the bond radii of silicon, germanium, and tin.) This insensitivity of the ring current of the macrocycle to the metal suggests that π bonding between the ring and the metal for silicon, germanium, and tin is either unchanging or unimportant, probably the latter.

To account for the observed differences in aromaticity between the phthalocyanine and hemiporphyrazine rings, various qualitative arguments can be advanced. For example, it can be pointed out that simple resonance structures can be drawn for the phthalocyanine macrocycle in which rings containing $4n + 2$ π electrons can be traced out, Figure 1a, but that the best that can be done for the hemiporphyrazine macrocycle with such simple structures is a ring with $4n$ π electrons, Figure 1b. Such arguments are, of course, not very satisfactory and full understanding of this point must await detailed theoretical work.



a b c

Figure 1.—Resonance structures for the phthalocyanine and hemiporphyrazine rings.

Infrared Spectra.—In Tables III and IV are given a set of band assignments for the *trans* group vibrations of the tin hemiporphyrazines $hpSn(OH)_2$, $hpSn(OD)_2$, $hpSnF_2$, $hpSnCl_2$, $hpSnBr_2$, and $hpSnI_2$.[7] Also given are a set of assignments for a group of analogous tin phthalocyanines. The assignments for $PcSnBr_2$ and $PcSnI_2$ are new, previous assignments not having been made. Those for $PcSn(OH)_2$, $PcSnF_2$, and $PcSnCl_2$ are in essential agreement with earlier assignments,[3] except that the O–H bending assignment for $PcSn(OH)_2$ has been modified (the earlier assignment not being reasonable in light of the assignments made for $hpSn(OH)_2$ and $hpSn(OD)_2$).

TABLE III

ASSIGNMENTS FOR THE M–O AND M–X VIBRATIONS (cm^{-1})

	PcGe	hpGe	PcSn	hpSn
M–OH asym str	644 m	676 m	564 s	583 s
M–OD asym str	633 m	666 m	...	575 s
M–F asym str	606 s	625 s (α) 629 s (β) 635 s (γ)	534 s	549 s
M–Cl asym str	312 s	347 s	300 s	324 s
M–Br asym str	226 s	256 s	207 s	225 s
M–I asym str	185 s	221 s	157 s	172 s (α) 168 s (β)

TABLE IV

ASSIGNMENTS FOR THE O–H AND O–D VIBRATIONS (cm^{-1})

	PcGe	hpGe	PcSn	hpSn
O–H str	3493 m	3403 m	3510 w	3459 m
O–D str	2585 m	2524 m	...	2556 m
O–H bend	988 m	1050 m	...[a]	955 sh, m
O–D bend	742 m	779 m	...	~710[b] sh, m

[a] May be hidden under ligand band at 890 cm^{-1}. [b] Poorly resolved shoulder on ligand band at 700 cm^{-1}.

For comparison, the previously given assignments for the analogous set of germanium hemiporphyrazines and phthalocyanines[2] are also displayed in Tables III and IV.

Support for the new assignments is found in their general agreement with those made in the literature for comparable tin complexes having hydroxy,[8] fluoro,[8] chloro,[9–11] bromo,[9] and iodo[9] ligands and in the isomer shifts observed for the isomorphous compounds $hpSn(OH)_2$ and $hpSn(OD)_2$. Further support is provided by the consistency between the data for the tin com-

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[7] Reproductions of the spectra of the tin complexes discussed in this paper are shown in the Ph.D. thesis of L. E. S., University Microfilms 67-11571. Plates comparing the spectra of most of the tin and germanium complexes listed in Tables III and IV are shown on pp 36, 37, 41, and 42 of this thesis.

[8] V. H. Kriegsmann and G. Kessler, *Z. Anorg. Allgem. Chem.*, **318**, 277 (1962).

[9] M. F. Farona and J. G. Grasselli, *Inorg. Chem.*, **6**, 1675 (1967).

[10] I. R. Beattie, G. P. McQuillan, L. Rule, and M. Webster, *J. Chem. Soc.*, 1514 (1963).

[11] I. R. Beattie and G. P. McQuillan, *ibid.*, 1519 (1963).

pounds and those for the germanium compounds. In all it is felt that considerable reliance can be placed on both the tin and the germanium assignments.

Earlier, in the discussion of the germanium assignments, it was pointed out that the metal–halogen and metal–oxygen stretching bands occur at higher frequencies and the oxygen–hydrogen stretching bands at lower frequencies in the hemiporphyrazine. This led to the suggestion that the substituent–germanium bond is stronger in the hemiporphyrazines than in the phthalocyanines and that the pyridine rings of the hemiporphyrazine macrocycle retain much of their ordinary character in the macrocycle. The newly completed set of assignments for the tin complexes is seen to parallel the set for the germanium complexes and to lead to analogous conclusions. Both sets, then, suggest that the resonance form of Figure 1c is more important than that of Figure 1b for the tin and germanium hemiporphyrazines.

The infrared data also provide evidence supporting the formulation of the dehydration product of $hpSn(OH)_2$, $(hpSnO)_x$, as a polymer. The spectrum of this compound, while similar to that of $hpSn(OH)_2$, shows a broadening of some of the ligand bands and the absence of others. It also shows a relatively strong and broad nonligand absorption at 895 cm^{-1}. These observations all are in keeping with a polymeric formulation for the compound, the broadenings and absences being attributable to coupling and the 895 cm^{-1} absorption (by analogy with $(hpGeO)_x$[2]) to the Sn–O asymmetric vibration. (Using a line of reasoning similar to that applied to $(hpGeO)_x$, further evidence for the polymeric nature of $(hpSnO)_x$ is provided by the prominent 3.67-A line in its powder pattern. Such reasoning also leads to an Sn–O bond length of 1.84 A.)

Finally, it is worth noting that the spectra of the two forms of hpLiH show bands identifiable as N–H bands. For γ-hpLiH bands at 598 and 3419 cm^{-1} can be assigned to the bending and stretching modes, while for β-hpLiH bands at 582 and 3418 cm^{-1} can be similarly assigned. The bands given comparable asignments for hpH_2 are at 574 and 3452 cm^{-1}, respectively.[2]

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Structure Determination and Crystal Preparation of Monoclinic Rare Earth Sesquisulfides

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A method is described by which single crystals of the monoclinic lanthanide sesquisulfides were easily prepared. The crystal structure of one member, Ho_2S_3, was determined using three-dimensional X-ray data. The monoclinic crystals have cell dimensions $a = 17.50 \pm 0.03$, $b = 4.002 \pm 0.005$, $c = 10.15 \pm 0.02$ A, and $\beta = 99.4 \pm 0.2°$. The space group is $P2_1/m$ with 12 Ho atoms and 18 S atoms per cell. All atoms are in the e positions: $x, {}^1/_4, z; \bar{x}, {}^3/_4, \bar{z}$. Half of the holmium atoms are six-coordinated and the others are seven-coordinated, while two-thirds of the sulfur atoms are four-coordinated and the remainder are five-coordinated. Thus the average coordination number of holmium is $6^1/_2$; that of sulfur is $4^1/_3$. These coordination numbers are intermediate between those shown by the sesquisulfides of larger atomic radii (defect Th_3P_4 structure) and those of the smaller atomic radii lanthanides (α-Al_2O_3, Sc_2S_3 structures).

Introduction

The sesquisulfides of the four lanthanide elements Y, Ho, Er, Tm have been prepared previously in single-crystal form and the dimensions of their monoclinic unit cells reported.[1,2] However, the crystal structure of this group has been unknown and forms the largest single gap in our knowledge of the crystal chemistry of the lanthanide sesquichalcogenides. The situation with regard to the sulfides is shown in Table I where the notation is the same as that used in discussing the sesquichalcogenides as a whole.[3] The non rare earth elements Y and Sc are placed in positions corresponding to their ionic radii. Since it was established[4] that Ce_2S_3 has a defect Th_3P_4 structure it has been found that the sesquisulfides of the ten elements from La to Dy crystallize in this structure type. Yb_2S_3 and Lu_2S_3 (E) have the α-Al_2O_3 structure type[5] while Sc_2S_3 (F)[6] is isostructural with a large number of rare earth sesquiselenides and sesquitellurides.

During exploratory synthetic work on the lanthanide sulfides a method was discovered by which single crystals of the structurally unknown group D could be prepared relatively easily, and a crystal structure determination of one member, Ho_2S_3, was undertaken.

Experimental Section

Crystal Preparation.—The anhydrous lanthanide chloride was melted in a carbon boat at 1100° and a slow flow of H_2S was passed

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