the spectra of the "solvated" chelates should not show any oxine bands and probably would resemble the spectra of the "unsolvated" chelate. The latter is the case for both the thorium(IV) and the uranium(VI) systems as shown in Fig. 1, curve D, and Table I. Thus a structure such as that proposed by Bullwinkel and Nobel[14] appears to be quite reasonable for the uranyl system. For the thorium(IV) system, this may indicate a coordination number of ten.

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# The Infrared Spectra of Some Tin and Lead Phthalocyanines[1]

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The infrared spectra of $PcSnF_2$, $PcSnCl_2$, $PcSnBr_2$, $PcSnI_2$, $PcSn(OH)_2$, PcSn, $\alpha$-$Pc_2Sn$, $\beta$-$Pc_2Sn$, and PcPb are presented in the 286 to 5000 cm.$^{-1}$ region. An interpretation of some features of these spectra is offered.

## Introduction

The infrared spectra of phthalocyanines containing Mg, Fe, Co, Ni, Cu, and Zn recently have been investigated over a wide range by Sidorov and Kotlyar.[2] They confirmed earlier observations that polymorphic modifications of the phthalocyanines can be distinguished by their infrared spectra and showed that certain characteristic bands are shifted by amounts ranging up to 55 cm.$^{-1}$ as one central element is exchanged for another. The present work complements the previous infrared studies of phthalocyanines by giving the spectra of one lead and a number of tin phthalocyanines[3-5] over the 286–5000 cm.$^{-1}$ range. These new spectra are discussed in the light of previous spectra and where appropriate in terms of the factors introduced by the presence of tetravalent tin.

## Experimental

The infrared spectra were recorded with a Perkin-Elmer Model 221 spectrophotometer. Both the KBr disk and Nujol mull techniques were used with each of the compounds. No evidence of band shifting caused by the use of KBr disks was detected. Figure 1 shows the KBr spectra and Table I gives the frequencies obtained from these spectra.

## Discussion

It is reasonable to infer from the structures known for other divalent metal phthalocyanines that both the PcSn and PcPb molecules are planar and possess approximately $D_{4h}$ symmetry. Certainly the similarity of the infrared spectra of these two compounds is consistent with a structural similarity for the molecules. In the event that both have the usual divalent metal phthalocyanine structure, the dissimilarity of the X-ray powder patterns of the two[5] requires that the molecules be packed differently. Simple steric arguments in the case of $PcSn(OH)_2$ and the $PcSnX_2$ series ($X$ = halogen) together with the characteristic phthalocyanino nature of the spectra suggest that these molecules contain octahedrally coordinated tin and accordingly that they all have approximately $D_{4h}$ symmetry (ignoring the hydroxyl hydrogens of $PcSn(OH)_2$). This correlates with previous conclusions.[3,5]

The infrared spectra of the $\alpha$ and $\beta$ polymorphs of $Pc_2Sn$ and the 1-chloronaphthalene solvate are all very similar. However, the $\beta$ form is differentiated from the $\alpha$ form by the presence of a small 1041 cm.$^{-1}$ band and the solvate from both the $\alpha$ and $\beta$ forms by small bands at 970, 791, and 766 cm.$^{-1}$. As in the PcSn–PcPb case, the similarity of the infrared spectra of the polymorphs and the dissimilarity of their X-ray powder patterns[5] suggests that the $Pc_2Sn$ molecules have the same configuration in both cases but are packed differently.

The spectra of the two forms of $Pc_2Sn$ are similar to those of ordinary phthalocyanines except that the 1500 cm.$^{-1}$ region is more complicated. This observation suggests that the rings are not greatly distorted in this unusual compound. Accordingly, the cubic ($D_{4h}$) or square antiprismatic ($D_{4d}$) structures discussed by Fernelius[6] appear to be reasonable. Other structures which do not involve considerable distortion of the ring are also possible, of course. If the choice is between the $D_{4d}$ and $D_{4h}$ arrangements and if this structural variation is not the cause of the polymorphism, then the $D_{4d}$ structure is favored, both because of its

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(2) A. N. Sidorov and I. P. Kotlyar, *Opt. Spectry.*, **11**, 92 (1961).

(3) P. A. Barrett, C. E. Dent, and R. P. Linstead, *J. Chem. Soc.*, 1719 (1936).

(4) M. Whalley, *ibid.*, 866 (1961).

(5) W. J. Kroenke and M. E. Kenney, *Inorg. Chem.*, **3**, 251 (1964).

(6) W. C. Fernelius, "Chemical Architecture," Interscience Publishers, Inc., New York, N. Y., 1948, p. 96.

TABLE I

ABSORPTION FREQUENCIES IN CM.$^{-1}$

| $PcSnF_2$ | $PcSnCl_2$ | $PcSnBr_2$ | $PcSnI_2$ | $PcSn(OH)_2$ | α-$Pc_2Sn$ | β-$Pc_2Sn$ | PcSn | PcPb |
|---|---|---|---|---|---|---|---|---|
| | | | | 3510 | | | | |
| 3030 | 3030 | 3030 | 3030 | 3030 | 3050 | 3050 | 3020 | 3050 |
| 1610 | 1613 | 1610 | 1610 | 1613 | 1608 | 1613 | 1613 | 1608 |
| | | | | | 1550 | 1550 | | |
| | | | | | 1508 | 1508 | | |
| 1475 | 1475 | 1475 | 1475 | 1466 | 1477 | 1477 | 1493 | 1484 |
| 1412 | 1412 | 1412 | 1412 | 1406 | 1427 | 1425 | 1416 | 1404 |
| | | | | | 1383 | 1383 | | |
| 1346 | 1341 | 1339 | 1337 | 1346 | 1333 | 1335 | 1333 | 1330 |
| 1284 | 1287 | 1285 | 1287 | 1285 | 1287 | 1287 | 1285 | 1282 |
| 1164 | 1166 | 1166 | 1167 | 1167 | 1163 | 1166 | 1160 | 1160 |
| | | | | 1130 | | | | |
| 1120 | 1121 | 1121 | 1121 | 1116 | 1115 | 1119 | 1119 | 1114 |
| 1088 | 1085 | 1083 | 1082 | 1085 | 1075 | 1075 | 1074 | 1078 |
| 1060 | 1060 | 1060 | 1060 | 1055 | | | 1062 | 1059 |
| | | | | | | 1041 | | |
| | | | | | 1002 | 1002 | 1001 | 1002 |
| 963 | 965 | 963 | 957 | 959 | 943 | 946 | 952 | 951 |
| 892 | 891 | 890 | 889 | 890 | 891 | 890 | 887 | 881 |
| | | | | | 867 | 866 | 872 | 870 |
| | | | | | 813 | 811 | 820 | 815 |
| 783 | 780 | 777 | 774 | 776 | | | 780 | 780 |
| 774 | 774 | 774 | 770 | 768 | 772 | 772 | 770 | 771 |
| 750 | 750 | 748 | 748 | 750 | 741 | 742 | 745 | 742 |
| 726 | 723 | 720 | 718 | 718 | 720 | 725 | 726 | 723 |
| 688 | 690 | 688 | 686 | 690 | | | | |
| 643 | 645 | 642 | 641 | 642 | 641 | 640 | 642 | 643 |
| | | | | | 625 | 625 | 628 | 626 |
| 573 | 576 | 574 | 574 | 571 | 565 | 565 | 564 | 562 |
| | | | | 563 | | | | |
| 531 | | | | | | | | |
| 497 | 499 | 495 | 497 | 499 | 505 | 504 | 499 | 495 |
| | | | | | 489 | 483 | 489 | 481 |
| 435 | 439 | 437 | 437 | 436 | 429 | 429 | 437 | 438 |
| | | | | | 420 | 420 | | |
| | 346 | | | | | | | |
| | 299 | | | | | | | |

occurrence in other complexes and because of the probable lack of suitable orbitals in tin for the cubic arrangement.[7,8]

Influences of the central metal on the bands directly attributable to the ligand can be detected. For example, the ligand bands in the spectrum of PcPb tend to appear at slightly lower frequencies than the corresponding bands in the spectrum of PcSn. A mass effect is probably important here. It is also interesting in comparing the spectra to note that some of the bands which are relatively metal sensitive here (*e.g.*, those at 1490 and 1410 cm.$^{-1}$) have been reported to be metal sensitive in the Mg, Fe, Co, Ni, Cu, and Zn series of phthalocyanines. Among the ligand bands the following assignments can be made: the 3030 cm.$^{-1}$ band to aromatic C–H stretching vibrations, the 1610 and 1475 cm.$^{-1}$ bands to C–C benzene ring skeletal stretching vibrations, and the 720 cm.$^{-1}$ band to C–H out-of-plane bending vibrations.

The small unique band in the Nujol spectrum of $PcSn(OH)_2$ at 3510 cm.$^{-1}$ can be assigned to a non-hydrogen-bonded O–H stretching vibration. The shoulder at 1130 cm.$^{-1}$ in the spectrum of $PcSn(OH)_2$ and its

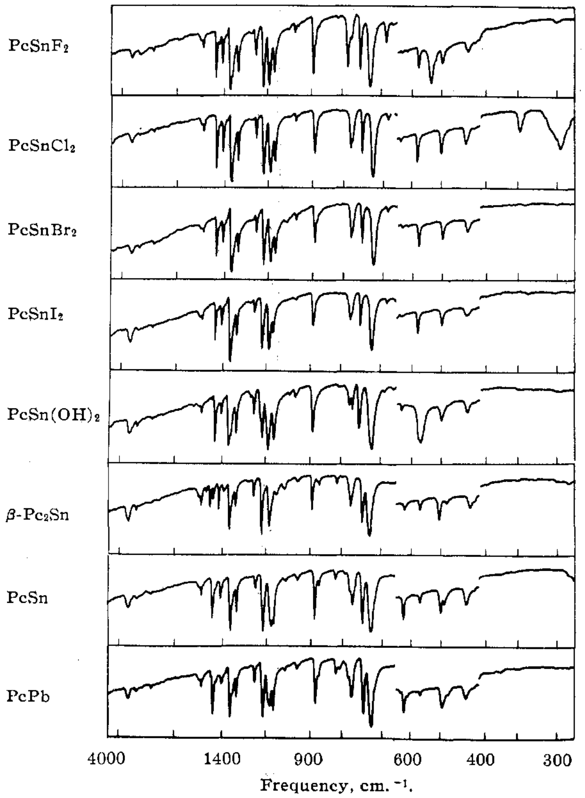

Figure 1.

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[7] G. E. Kimball, *J. Chem. Phys.*, **8**, 188 (1940).
[8] J. E. Eisenstein, *ibid.*, **25**, 142 (1956).

Ge,[9] Si,[9] and Al[10] analogs may result from an OH deformation vibration. This band does not appear in the spectra of other phthalocyanines of these metals.

In the 650 to 300 cm.$^{-1}$ region of the tin phthalocyanines investigated it is apparent that bands at 640, 570, 500, and 435 cm.$^{-1}$ are characteristic. A fifth band at approximately 625 cm.$^{-1}$ probably also occurs in all these spectra but is too weak to be seen easily.

Because the Sn–N bonds form 90° angles with the Sn–X bonds in $PcSnX_2$ there should be little transfer of vibrational energy in the separated molecules between the Sn–X bonds and the Sn–N bonds.[11] It seems likely that this situation should not be altered appreciably in the solid phase. Accordingly, the X–Sn–X groups may be assumed to act as essentially independent units and because they have $D_{\infty h}$ symmetry, the asymmetric bond stretching and bond bending modes should be infrared active. The O–Sn–O group in $PcSn(OH)_2$ should behave similarly.

In the appropriate spectra bands are observed which are assignable to Sn–F, Sn–Cl, and Sn–O stretching vibrations. Thus, in $PcSnF_2$ the band at 531 cm.$^{-1}$ can be attributed to the unsymmetrical F–Sn–F stretching vibration. This assignment correlates with assignments of bands at 560 cm.$^{-1}$ to the Sn–F vibration in compounds containing the $SnF_6^{-2}$ ion.[12] Similarly, the 299 cm.$^{-1}$ band in $PcSnCl_2$ can be associated with the unsymmetrical Cl–Sn–Cl stretching vibration. This agrees with the assignment of bands ranging from 330 to 275 cm.$^{-1}$ to Sn–Cl in the $SnCl_4 \cdot 2,2'$-bipyridyl and $SnCl_4 \cdot 1,10$-phenanthroline complexes.[13] The band at 346 cm.$^{-1}$ in the spectrum of $PcSnCl_2$ is apparently a phthalocyanine band which is infrared active only in some phthalocyanines. The band at 563 cm.$^{-1}$ in $PcSn(OH)_2$ is attributed to the O–Sn–O asymmetric stretching vibration. This checks with the assignment of a band at 620 cm.$^{-1}$ in $SnF_5(OH)^{-2}$ partly to an Sn–O vibration[12] and with Poller's prediction of 570 cm.$^{-1}$ as a position where Sn–O vibrations may be expected.[14] No bands attributable to Sn–Br or Sn–I are observed in the spectra of $PcSnBr_2$ and $PcSnI_2$. They probably lie at frequencies beyond the range of the instrument. The fact that the Sn–F, Sn–Cl, and Sn–O stretching vibrations occur in the expected regions provides further evidence for lack of coupling of the X–Sn–X and O–Sn–O groups with the rest of the molecule. If coupling did occur the bands would be expected at much lower frequencies.

An estimate of the position of the symmetric F–Sn–F and O–Sn–O vibrations[15] suggests that these ought to be in the region scanned. This result is consistent with the lack of unaccounted for activity in the spectra of $PcSnF_2$ and $PcSn(OH)_2$ and the postulated structures of these compounds.

Finally, it may be noted that a comparison of the infrared spectra of the tin phthalocyanines in the CsBr region with the spectra of their silicon analogs[16] shows that the tin compounds give simpler spectra, a fact attributable to the size and mass of the tin atom.

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[9] R. D. Joyner, Ph.D. Thesis, University Microfilms No. 61-3317, p. 49.

[10] J. E. Owen, Ph.D. Thesis, University Microfilms No. 61-3309, p. 73.

[11] G. Herzberg, "Molecular Spectra and Molecular Structure II, Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p. 198.

[12] V. H. Kriegsmann and G. Kessler, *Z. anorg. allgem. Chem.*, **318**, 277 (1962).

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

[14] R. C. Poller, *J. Inorg. Nucl. Chem.*, **24**, 593 (1962).

[15] W. J. Kroenke, Ph.D. Thesis, University Microfilms No. 64-13, p. 78.

[16] P. C. Krueger, Ph.D. Thesis, University Microfilms No. 64-14, p. 113