2.174 and 2.156 A, both ±0.006 A, observed by Eisenberg and Ibers[20] in di(tetramethylammonium)bis-(maleonitrile dithiolate)nickel(II). The 92.1° N–Ni–S angle as well as the elongated Ni–N and Ni–S distances are consistent with a nonnegligible amount of steric hindrance between the C_1 methyl group and sulfur. The N–C_1, N–C_2, and N–C_3 distances are not significantly longer than the expected N–C bonded distance of 1.47 A. The C–C and C–S distances are also, well within experimental error, "normal" single bonds. The C_1–N–C_2 and C_2–N–C_3 angles are within experimental error of the idealized tetrahedral 109° 28′, but C_1–N–C_3 is significantly less at 105.2 ± 1.2°, again probably due to steric repulsion between C_1 and S. The C_4–S–Ni angle of 100.8 ± 0.5° indicates that the sulfur contributes a p orbital to the Ni–S σ bond and to the S–C bond as well. The Ni–S interaction probably includes some $p\pi$–$p\pi$ interaction, but this is not discernible from the bond lengths and angles.

The dihedral angles between particular planes and the perpendicular displacements of the carbon atoms from the Ni–N_2–S_2 plane are particularly interesting. The dihedral angle between the Ni–N–S plane and the Ni–C_2–N plane is 91.2 ± 0.9° and C_2 is 1.192 A above the plane defined by Ni–N_2–S_2. This means that C_2 is in a stereochemically polar position relative to the NiN_2S_2 plane and effectively blocks any axial chemical attack on the Ni(II) species by another ligand. This is in agreement with the fact that this seems to be a particularly stable complex, relatively inert to attack by other ligands. On the other hand, the dihedral angle between the Ni–N–S plane and the Ni–C_1–N plane is 29.4 ± 1.04° and the C_1 atom is 0.652 A below the NiN_2S_2 plane. Therefore, the C_1 methyl group can be considered as being in an essentially equatorial position relative to the NiN_2S_2 plane. C_3 and C_4 are displaced 0.72 (2) and 0.16 (2) A below this same plane conforming to the expected geometry for the β-mercaptoethylamine group in a metal chelate.

Acknowledgment.—We wish to acknowledge financial support from the National Institutes of Health, Grant No. GM-13985-01,02.

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The Crystal and Molecular Structure of Dimethyltin Bis(8-hydroxyquinolinate)

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The crystal structure of dimethyltin bis(8-hydroxyquinolinate), $(CH_3)_2Sn(C_9H_6NO)_2$, has been determined from three-dimensional X-ray diffraction data. Unit cell constants are a = 9.44 ± 0.02 A, b = 13.28 ± 0.02 A, c = 15.62 ± 0.03 A, and β = 110.0 ± 0.2°. The space group is $P2_1/c$. The density by flotation is 1.57 g/cc. Four molecules in the unit cell give a calculated density of 1.586 g/cc. By visual estimation of film data, the intensities of 1738 independent reflections were obtained. The structure was solved by three-dimensional Patterson and Fourier methods and refined by full-matrix least squares to a final conventional R factor of 7.8%. The arrangement of atoms about the tin atom can be considered to be a highly distorted octahedron with the following bond distances: Sn–C, 2.15 and 2.17 A; Sn–O, 2.10 and 2.11 A; Sn–N, 2.31 and 2.38 A. The bond angles in the distorted octahedron range from 73.4 to 110.7°. The results are discussed in relationship to previous spectroscopic studies of the complex and a qualitative molecular orbital approach to the bonding.

Introduction

In recent chemical literature there have been numerous reports of compounds in which group IV elements are believed to exhibit coordination numbers greater than six. In the case of group IV transition elements the structures of some of these higher coordinate compounds have been determined by X-ray diffraction methods. For example, tetrakis(acetylacetonato)zirconium(IV) has been found to have a square-antiprism structure.[1] However, for the group IV nontransition elements no crystal structures of higher coordinate complexes have been determined. Since a knowledge of the configuration about the metal atoms in higher coordinate group IV complexes could lead to a better understanding of the nature of the bonding, the structures of a number of these compounds will be studied by X-ray diffraction methods.

One of the group IV elements of particular recent interest has been tin. However, even for the lower coordination numbers five and six, crystal structures of tin complexes have not been studied. Before proceeding to a study of the higher coordination numbers, it was considered necessary to examine the configuration about the tin atom in at least one six-coordinate complex. Dimethyltin bis(8-hydroxyquinolinate), $(CH_3)_2Sn(C_9H_6NO)_2$, has been previously studied by spectroscopic techniques,[2-6] and at least two aspects

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[2] M. M. McGrady and R. S. Tobias, *J. Am. Chem. Soc.*, **87**, 1909 (1965).

[3] A. H. Westlake and D. F. Martin, *J. Inorg. Nucl. Chem.*, **27**, 1579 (1965).

[4] W. H. Nelson and D. F. Martin, *ibid.*, **27**, 89 (1965).

[5] K. Kawakami and R. Okawara, *J. Organometal. Chem.* (Amsterdam), **6**, 249 (1966).

[6] W. Kitching, *ibid.*, **6**, 586 (1966).

of the structure have been the subject of conflicting interpretations. First, assuming near-octahedral coordination, the arrangement of groups around the tin atom could lead to either *cis*- or *trans*-methyl groups, and evidence has been offered for both possibilities.[2-6] Second, the strength of the bonds between the tin atom and the nitrogen atoms of the chelating ligands has been a point of concern.[2,6] Since a crystal structure determination could settle both of these points as well as giving the detailed configuration of a six-coordinate tin complex, the crystal structure of dimethyltin bis(8-hydroxyquinolinate) has been determined.

Experimental Section

Crystal Preparation.—The crystals used in this work were kindly supplied by R. S. Tobias and were prepared by the method reported by Tanaka, *et al.*[7]

X-Ray Data.—Dimethyltin bis(8-hydroxyquinolinate) crystallizes in the monoclinic crystal system with four molecules in a unit cell of dimensions $a = 9.44 \pm 0.02$, $b = 13.28 \pm 0.02$, $c = 15.62 \pm 0.03$ A, and $\beta = 110.9 \pm 0.2°$. The reported errors represent the average deviations in the observed cell constants as measured from precession photographs on a camera calibrated with NaCl. A crude flotation measurement of the density in aqueous KI solution gave 1.57 ± 0.01 g/cc. A calculated density of 1.586 ± 0.005 g/cc is obtained, assuming four molecules per unit cell. The systematic extinctions were for $h0l$, l odd, and for $0k0$, k odd, indicating that the space group is $P2_1/c$.

A crystal approximately 0.15 × 0.25 × 0.40 mm mounted with the long dimension as the rotation axis was chosen for intensity measurements. Using a Zr filter and brass interleaving sheets, multiple-film Mo Kα Weissenberg photographs were taken of the $0kl$–$9kl$ zones, and multiple exposures were taken of the $hk0$, $h0l$, $h1l$, and $h2l$ zones by the precession method. The relative intensities were estimated by visual comparison with a series of timed exposures of a selected reflection. There were 1738 independent reflections of measurable intensity. The usual Lorentz and polarization corrections were made. Absorption corrections were not made ($\mu = 14.1$ cm^{-1}). A rough estimate[8] of the absorption factors for a given Weissenberg layer indicated a range of less than 10%. The data were placed on a common scale using the interlayer scaling program of Hamilton, Rollett, and Sparks.

Determination of the Structure.—The calculations described above and below were made on the IBM 7040 computer of the Computer Research Center of the University of Missouri. The programs used in this work were A. Zalkin's FORDAP program, W. R. Busing and H. A. Levy's ORFLS least-squares and ORFFE error-function programs, and data-handling programs of W. C. Hamilton and J. A. Ibers.

A three-dimensional Patterson synthesis was prepared. The tin–tin vectors were easily located and indicated that the tin atoms are very nearly repeated by a translation of half the c dimension, the approximate tin atom position being (0.202, 0.250, 0.140) or (0.202, 0.250, 0.390). Although both positions gave reasonable agreement, the latter position was eliminated since chemically reasonable positions for the other atoms could not be obtained from a Fourier phased with the tin in that location. A structure factor calculation after a least-squares refinement of the former tin atom position gave $R = \Sigma(|F_o|^2 - |kF_c|^2)/\Sigma|F_o|^2 = 0.56$ and $r = [\Sigma w(|F_o|^2 - |kF_c|^2)^2/(\Sigma w|F_o|^2)^2]^{1/2} = 0.55$ for all reflections. For $(0.148F_o)^2 \leq 64$, $w = (1/12.8)^2$, and for $(0.148 \cdot F_o)^2 > 64$, $w = [1/0.20(0.148F)^2]^2$. In this and subsequent calculations, scattering factors[9a] for neutral carbon, nitrogen, and oxygen and Thomas–Fermi–Dirac values for neutral tin[9b] corrected for f' and f'' dispersion factors[9c] were used.

Using only even l reflections, a three-dimensional Fourier synthesis was prepared with the phases from the calculated structure factors and the magnitudes from the observed structure factors. From this synthesis which possesses a false mirror plane at $y = 1/4$ it was possible to obtain approximate positions for all of the carbon, nitrogen, and oxygen atoms by taking into account the expected geometry of the ligand and the chemical reasonableness of the other atom positions. The first structure factor calculation based on all 25 atoms (ignoring hydrogens) gave $R = 0.30$ and $r = 0.27$. Three cycles of isotropic refinement of all atoms converged with $R = 0.16$ and $r = 0.20$. This and all subsequent least-squares refinements minimized the numerator of r. Unobserved reflections were not included in any least-squares refinements. Two cycles of refinement with the tin atoms anisotropic converged with $R = 0.13$ and $r = 0.16$. The estimated error in an observation of unit weight was 0.6. The maximum shift in any positional parameter at this stage was less than half the estimated standard deviation of that parameter. The conventional agreement factor $R^* = \Sigma(|F_o| = |kF_o|)/\Sigma|F_o|$ was 0.078. A difference Fourier based on the parameters from this refinement had only four peaks with densities greater than 1 e/A^3 (maximum 2 e/A^3). These were all within 1.1 A of the tin atom and are probably heavy-atom artifacts. The weakest peak observed for any carbon atom on the corresponding Fourier had a density of ~5 e/A^3.

The final positional parameters and temperature factors are given in Table I. The observed and calculated structure factors (×10) from the last described least-squares cycle are in Table II.

Discussion

Distances and Angles.—The individual bond distances and angles are given in Table III and Figure 1. The numbering system is shown in Figure 2. The average Sn–C, Sn–N, and Sn–O bond distances are compared to distances in related compounds in Table IV. The ligand bond distances are compared to those found in other compounds in Table V.

The Sn–C distances (2.15 and 2.17 A) are, within experimental error, equal to those observed for trigonal-bipyramidal $(CH_3)_3SnCN$ and the tetrahedral molecules $(CH_3)_ySnX_{4-y}$ and CH_3SnH_3. The Sn–C distance (2.06 A) in the other six-coordinate structure, $(CH_3)_2SnF_2$, is, however, considerably shorter. The sum of the covalent radii[10] for Sn and C is 2.17 A, in agreement with the observed distances. It is perhaps somewhat surprising that one does not observe a larger change in Sn–C distance with change in coordination number.

In oxinate complexes of known structure, one observes two types of bonding to the metal. In the complexes of copper,[11] zinc,[12] and palladium[13] the metal–nitrogen and metal–oxygen bond distances (Table IV) and, presumably, bond strengths are roughly equivalent. With tin and uranium,[14] however, one finds much shorter metal–oxygen bonds than metal–nitrogen bonds, the difference being about 0.25 A for both the tin complex and the uranium complex. This behavior

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Table I

Positional and Thermal Parameters[a] for $(CH_3)_2Sn(C_9H_6NO)_2$[b]

Atom	x	y	z	B
O(1)	0.038 (1)	0.358 (1)	0.068 (1)	3.0 (3)
N(1)	0.048 (1)	0.270 (1)	0.223 (1)	3.1 (3)
C(1)	0.050 (2)	0.225 (1)	0.301 (1)	3.5 (4)
C(2)	−0.047 (2)	0.246 (2)	0.345 (1)	4.4 (4)
C(3)	−0.156 (2)	0.317 (2)	0.311 (1)	3.9 (5)
C(4)	−0.276 (2)	0.445 (1)	0.186 (1)	3.7 (4)
C(5)	−0.276 (2)	0.491 (2)	0.108 (1)	4.1 (5)
C(6)	−0.165 (2)	0.463 (1)	0.068 (1)	3.5 (4)
C(7)	−0.057 (2)	0.387 (1)	0.106 (1)	2.2 (3)
C(8)	−0.061 (2)	0.341 (1)	0.187 (1)	2.8 (4)
C(9)	−0.169 (2)	0.370 (1)	0.227 (1)	3.3 (4)
C(10)	0.350 (2)	0.290 (2)	0.064 (2)	5.2 (6)
O(2)	0.361 (1)	0.187 (1)	0.258 (1)	3.0 (3)
N(2)	0.313 (1)	0.387 (1)	0.238 (1)	2.9 (3)
C(11)	0.283 (2)	0.486 (1)	0.222 (1)	3.8 (4)
C(12)	0.372 (2)	0.556 (2)	0.286 (1)	4.2 (5)
C(13)	0.483 (2)	0.527 (2)	0.366 (1)	4.1 (5)
C(14)	0.628 (2)	0.381 (1)	0.462 (1)	3.7 (4)
C(15)	0.649 (2)	0.278 (1)	0.470 (1)	4.0 (5)
C(16)	0.561 (2)	0.212 (1)	0.401 (1)	3.3 (4)
C(17)	0.447 (1)	0.241 (1)	0.323 (1)	2.4 (3)
C(18)	0.423 (2)	0.354 (1)	0.314 (1)	2.8 (4)
C(19)	0.516 (2)	0.422 (1)	0.382 (1)	3.3 (4)
C(20)	0.086 (2)	0.111 (1)	0.086 (1)	3.4 (4)
Sn	0.2029 (1)	0.2496 (2)	0.1380 (1)	...

	$\beta(11)$	$\beta(22)$	$\beta(33)$	$\beta(12)$	$\beta(13)$	$\beta(23)$
Sn	0.0106 (1)	0.00404 (5)	0.00349 (4)	0.0027 (2)	0.0028 (1)	−0.0001 (2)

[a] The anisotropic temperature factors for the Sn atom are of the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.
[b] Standard deviations are in parentheses.

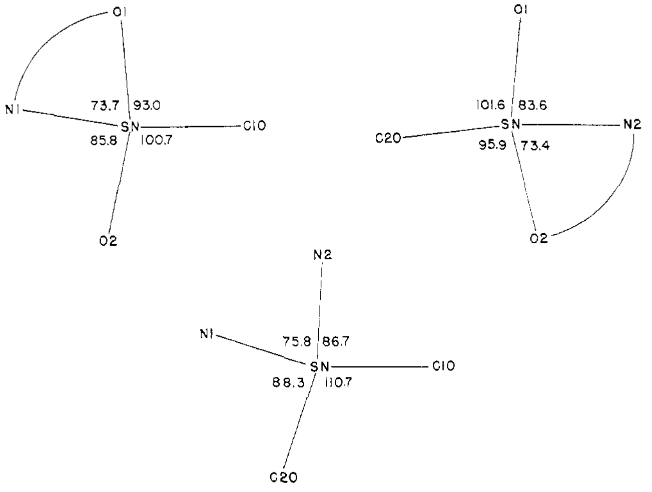

Figure 1.—Bond angles around the tin atom in $(CH_3)_2Sn(C_9H_6NO)_2$.

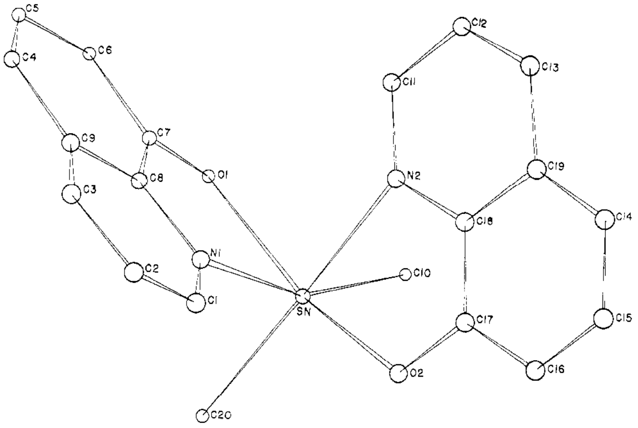

Figure 2.—Perspective view of the molecular structure of $(CH_3)_2Sn(C_9H_6NO)_2$.

can be rationalized from Pearson's hard and soft acid–base concept.[15] Since the nitrogen is a softer base than the oxygen, it is not so strongly attracted to the hard acids tin(IV) and uranium(VI). The nitrogen is, however, strongly attracted to the softer acids Cu(II), Zn(II), and Pd(II).

The ligand bond distances (Table V) are in reasonable agreement with the average values determined by other workers[11–13] for Cu, Zn, and Pd oxinate complexes and with those from a Hückel LCAO–MO calculation for quinoline by Pullman and Pullman.[16] A definitive check on the magnitude of the alternation in C–C and C–N distances in quinoline-type systems awaits a more accurate structure determination. The average C–C distance in $(CH_3)_2Sn(C_9H_6NO)_2$ is 1.41 ± 0.02 A and the average C–N distance 1.35 ± 0.01 A.

The deviation of ligand bond angles from 120° cannot be considered significant in light of the large standard deviations. Weighted least-squares planes through the 11 ligand atoms for the O(1) ligand and for the O(2) ligand in monoclinic coordinates have, respectively, the equations

$$8.39x + 0.72y - 11.8z - 0.12 = 0$$

and

$$4.50x + 9.27y + 5.19z - 3.86 = 0$$

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(15) R. C. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).

(16) B. Pullman and A. Pullman, "Quantum Biochemistry," Interscience Publishers, Inc., New York, N. Y., 1963, p 812.

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $(CH_3)_2Sn(C_9H_6NO)_2$

K	L	FO	FC
H= 0			
0	2	1470	1564
0	4	1381	1415
0	8	623	624
0	10	488	528
0	12	401	399
0	14	351	362
0	18	305	281
1	2	1667	1648
1	3	157	138
1	6	1102	1116
1	7	490	469
1	8	214	244
1	10	636	635
1	12	841	858
1	16	380	404
2	0	2502	2501
2	1	1082	1057
2	2	624	586
2	3	129	196
2	4	1083	1096
2	5	276	301
2	6	802	820
2	7	223	280
2	8	599	639
2	10	657	700
2	12	256	265
2	14	343	388
2	18	335	317
3	2	640	642
3	3	142	195
3	5	117	113
3	6	1451	1351
3	7	190	166
3	8	906	825
3	10	688	696
3	12	535	603
3	14	195	306
3	16	301	377
4	0	1814	1731
4	2	414	430
4	4	1539	1471
4	6	877	860
4	7	401	367
4	8	832	831
4	10	509	576
4	12	440	426
4	14	436	519
5	1	484	387
5	2	1373	1224
5	4	587	507
5	6	812	832
5	7	206	266
5	8	483	509
5	10	634	620
5	12	488	551
5	16	300	363
6	0	1374	1382
6	1	517	493
6	4	1210	1201
6	6	607	588
6	8	741	759
6	10	451	501
6	12	325	346
6	14	300	382
7	1	135	92
7	2	938	909
7	4	222	275
7	6	832	881
7	8	166	206
7	10	483	550
7	12	428	467
8	0	1393	1410
8	1	178	195
8	4	961	948
8	6	311	327
8	8	526	575
8	10	409	453
8	14	215	336
9	2	1132	1106
9	6	629	653
9	10	421	493
9	12	400	456
10	0	880	864
10	4	697	728
10	5	302	414
10	6	505	561
10	10	338	354
10	14	277	329
11	2	447	519
11	6	413	398
12	0	456	482
12	4	568	611
12	6	394	401
13	2	467	512
13	6	400	461
14	0	436	466
14	4	360	390
15	2	341	397
16	0	319	354
H= 1			
0	2	1479	1666
0	4	492	458
0	6	1047	994
0	8	762	795
0	10	687	691
0	12	510	539
0	14	391	411
0	16	294	344
0	-2	1280	1477
0	-4	497	510
0	-6	1037	996
0	-8	761	726
0	-10	657	655
0	-12	766	767
0	-14	155	183
0	-16	403	432
0	-20	240	216
1	1	797	833
1	2	610	619
1	3	261	231
1	4	1056	1082
1	6	138	119
1	8	820	832
1	10	458	510
1	12	319	300
1	14	423	439
1	18	207	185
1	-2	1700	1875
1	-3	1035	931
1	-4	1543	1461
1	-6	456	417
1	-8	1072	1029
1	-10	1056	1003
1	-12	206	185
1	-14	569	549
1	-18	354	380
2	0	1008	977
2	1	377	385
2	2	2781	2826
2	3	125	123
2	4	315	303
2	5	359	288
2	6	1234	1344
2	7	207	165
2	8	318	315
2	10	605	595
2	11	197	211
2	12	208	181
2	14	451	461
2	16	275	320
2	-1	255	292
2	-2	1484	1528
2	-3	410	352
2	-4	647	663
2	-6	764	737
2	-8	989	1029
2	-10	375	394
2	-12	762	824
2	-16	402	438
3	0	1982	2015
3	1	420	432
3	2	491	370
3	3	647	553
3	4	1663	1687
3	5	382	396
3	6	365	332
3	7	164	126
3	8	798	773
3	10	194	234
3	12	526	562
3	14	392	423
3	-1	252	192
3	-2	437	442
3	-3	691	609
3	-4	816	840
3	-6	848	789
3	-7	337	240
3	-8	605	528
3	-9	302	220
3	-10	1002	918
3	-12	239	234
3	-14	476	474
3	-18	167	284
4	1	603	605
4	2	1734	1702
4	4	656	581
4	6	1191	1214
4	7	214	267
4	8	211	244
4	10	772	801
4	12	313	308
4	16	200	287
4	-2	944	891
4	-3	125	93
4	-4	845	710
4	-6	625	551
4	-8	980	918
4	-9	158	81
4	-10	389	384
4	-12	789	773
4	-16	362	384
5	0	1148	1083
5	2	274	251
5	3	182	174
5	4	1079	1079
5	5	225	217
5	8	755	840
5	10	222	241
5	12	455	449
5	14	338	361
5	-1	413	418
5	-2	308	289
5	-3	299	295
5	-4	1267	1116
5	-6	1124	1043
5	-8	667	608
5	-9	200	141
5	-10	862	802
5	-12	283	275
5	-14	390	451
5	-18	209	252
6	0	351	344
6	1	174	228
6	2	1521	1469
6	5	241	213
6	6	985	961
6	7	116	157
6	10	620	653
6	12	287	340
6	14	292	267
6	16	238	279
6	-1	171	184
6	-2	1143	1048
6	-4	528	482
6	-6	944	911
6	-8	990	909
6	-10	359	366
6	-12	603	581
6	-16	161	257
7	0	1354	1275
7	1	159	173
7	2	352	290
7	4	1081	1045
7	6	184	176
7	8	477	482
7	12	233	273
7	14	225	284
7	-1	299	201
7	-2	278	846
7	-3	177	217
7	-4	1091	1031
7	-6	762	727
7	-8	440	408
7	-10	661	603
7	-14	377	451
8	0	623	592
8	2	1029	1030
8	6	360	392
8	10	450	506
8	12	306	363
8	14	162	234
8	-1	345	312
8	-2	894	879
8	-3	226	213
8	-4	668	640
8	-6	686	718
8	-8	731	720
8	-10	320	353
8	-12	558	576
8	-16	205	278
9	0	816	797
9	1	183	179
9	4	833	841
9	6	468	490
9	8	456	486
9	10	291	316
9	12	246	310
9	-2	455	487
9	-4	763	746
9	-6	417	397
9	-8	353	348
9	-10	198	267
9	-14	320	385
10	0	307	357
10	2	667	612
10	6	646	672
10	10	459	518
10	12	196	242
10	-2	617	645
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5	-16	413	410
6	0	796	773
6	1	128	59
6	2	286	241
6	4	505	496
6	6	387	393
6	8	358	341
6	10	330	281
6	12	226	169
6	14	298	215
6	-4	1059	1019
6	-7	176	242
6	-8	765	683
6	-10	453	446
6	-12	399	398
6	-14	476	451
6	-18	359	322
7	0	226	189
7	2	611	599
7	4	287	239
7	6	464	437
7	8	335	282
7	10	234	196
7	12	231	195
7	-2	957	920
7	-4	489	463
7	-6	901	802
7	-8	500	430
7	-9	284	325
7	-10	667	569
7	-12	453	430
7	-16	385	346
8	0	682	653
8	1	199	127
8	4	525	504
8	6	307	298
8	8	209	221
8	10	220	203
8	-4	904	822
8	-5	192	155
8	-6	544	494
8	-8	555	507
8	-10	512	493
8	-12	502	487
8	-14	381	367
8	-16	327	235
8	-18	290	266
9	0	286	288
9	2	463	469
9	6	434	432
9	8	189	184
9	-2	683	631
9	-4	148	197
9	-6	381	383
9	-8	387	363
9	-10	420	409
9	-12	503	470
9	-16	320	281
10	0	693	683
10	4	559	531
10	8	309	251
10	10	232	221
10	-3	278	343
10	-4	440	449
10	-5	217	116
10	-8	439	447
10	-10	276	262
10	-12	397	377
10	-14	380	344
11	2	535	511
11	6	362	373
11	-2	652	633
11	-6	447	435
11	-10	393	404
11	-12	379	364
12	0	408	398
12	4	336	349
12	-4	408	433
12	-8	438	434
12	-10	234	211
12	-14	207	249
13	2	363	340
13	6	231	217
13	-2	371	369
13	-6	404	409
14	0	302	306
14	4	254	247
14	-4	344	371
14	-8	346	338
14	-10	232	223
15	2	287	274
15	-2	323	270
15	-6	282	309
16	0	259	254
17	-2	249	250
H= 6			
0	0	317	267
0	2	820	849
0	4	154	108
0	6	434	389
0	8	298	263
0	10	408	334
0	-2	955	1029
0	-6	772	863
0	-8	1176	1204
0	-12	818	789
0	-16	543	556
0	-20	283	304
1	0	920	939
1	4	673	622
1	8	413	336
1	10	214	204
1	12	230	221
1	-1	91	38
1	-2	393	415
1	-3	289	300
1	-4	751	743
1	-6	196	280
1	-7	169	173
1	-8	619	621
1	-9	262	254
1	-10	584	600
1	-14	691	671
1	-18	342	389
2	1	168	135
2	2	748	770
2	4	157	204
2	6	454	413
2	8	212	186
2	10	344	301
2	12	209	229
2	-1	123	115
2	-2	812	929
2	-4	351	394
2	-5	175	205
2	-6	526	592
2	-8	681	695
2	-9	165	84
2	-10	463	460
2	-12	836	790
2	-16	397	414
3	0	935	957
3	4	502	428
3	8	440	395
3	10	198	187
3	-1	159	174
3	-2	556	608
3	-4	567	620
3	-6	456	487
3	-8	686	689
3	-10	469	467
3	-11	239	149
3	-12	531	478
3	-14	639	590
3	-18	342	297
4	2	693	668
4	6	698	597
4	8	251	236
4	10.	274	252
4	-1	137	204
4	-2	1110	1122
4	-4	742	745
4	-6	772	749
4	-7	161	168
4	-8	524	490
4	-10	497	481
4	-11	204	209
4	-12	589	531
4	-16	396	387
5	0	773	768
5	4	585	546
5	8	406	379
5	10	204	160
5	-1	137	180
5	-2	392	404
5	-3	220	304
5	-4	856	808
5	-6	650	589
5	-8	536	541
5	-10	360	360
5	-12	306	322
5	-14	523	446
5	-18	375	335
6	2	637	611
6	4	181	209
6	6	419	355
6	8	214	187
6	10	233	199
6	-2	770	730
6	-3	276	234
6	-4	681	607
6	-6	468	417
6	-7	287	279
6	-8	750	670
6	-9	418	465
6	-10	387	354
6	-12	631	607
6	-16	383	375
7	0	466	448
7	1	207	266
7	3	222	268
7	4	646	623
7	8	327	275
7	-2	281	202
7	-4	383	357
7	-6	350	351
7	-8	379	374
7	-10	475	447
7	-12	328	301
7	-14	606	562
7	-18	389	316
8	2	673	642
8	6	392	341
8	10	267	226
8	-2	726	721
8	-4	271	245
8	-6	433	442
8	-8	599	547
8	-10	233	230
8	-12	534	498
8	-16	288	301
9	0	462	431
9	8	287	243
9	-2	222	207
9	-4	488	481
9	-6	326	295
9	-8	376	353
9	-10	448	432
9	-12	190	190
9	-14	481	491
9	-18	316	310
10	2	459	438
10	6	322	224
10	-2	811	709
10	-4	407	373
10	-6	573	510
10	-8	485	409
10	-10	229	234
10	-12	443	416
11	0	392	435
11	4	355	297
11	8	223	245
11	-4	431	388
11	-6	251	234
11	-8	340	345
11	-10	347	341
11	-12	206	228
11	-14	242	284
12	2	363	348
12	6	300	279
12	-2	431	447
12	-4	317	310
12	-6	401	381
12	-8	346	296
12	-10	229	253
12	-12	262	303
13	0	262	275
13	4	299	243
13	8	266	242
13	-4	318	311
13	-6	249	261
13	-8	284	239
13	-10	262	300
14	2	348	316
14	6	264	207
14	-2	237	253
14	-4	236	187
14	-6	261	267
14	-8	243	254
16	2	267	267
H= 7			
0	0	722	772
0	2	309	310
0	4	520	491
0	8	395	381
0	-2	455	437
0	-4	499	496
0	-6	449	533
0	-8	519	521
0	-10	832	860
0	-14	542	523
0	-18	341	386
1	0	412	382
1	2	693	741
1	6	444	414
1	10	288	188
1	-2	640	721
1	-4	478	513
1	-6	437	508
1	-8	479	486
1	-12	533	528
1	-16	408	454
2	0	756	756
2	2	212	200
2	3	208	166
2	4	330	308
2	8	389	322
2	-2	509	583
2	-3	224	256
2	-4	435	463
2	-6	517	566
2	-8	278	290
2	-10	756	775
2	-14	521	489
2	-18	309	311
3	0	404	388
3	2	674	624
3	6	469	378
3	-1	132	195
3	-2	547	572
3	-3	329	331
3	-4	587	640
3	-6	384	407
3	-8	646	644
3	-10	248	264
3	-12	699	658
3	-16	439	361
4	0	473	487
4	4	432	380
4	8	371	290
4	-2	543	529
4	-4	348	364
4	-6	721	753
4	-8	372	334
4	-10	922	865
4	-14	553	498
4	-18	278	253
5	0	362	318
5	2	600	591
5	6	519	450
5	-2	261	212
5	-4	391	371
5	-6	378	336
5	-8	572	559
5	-10	479	428
5	-12	819	721
5	-16	397	337
6	0	577	614
6	4	552	503
6	8	347	288
6	-2	360	350
6	-4	466	434
6	-6	549	538
6	-8	322	277
6	-10	679	594
6	-14	448	448
7	0	370	343
7	2	590	528
7	6	437	366
7	-2	553	421
7	-4	349	310
7	-6	429	377
7	-8	405	387
7	-12	560	492
7	-16	432	358
8	0	364	406
8	2	257	204
8	4	450	400
8	8	283	224
8	-4	580	521
8	-6	637	554
8	-10	547	432
8	-14	414	373
9	0	280	256
9	2	456	392
9	6	352	285
9	-2	432	436
9	-4	472	455
9	-6	362	344
9	-8	528	453
9	-12	466	379
9	-16	373	300
10	0	319	326
10	4	345	284
10	-2	320	313
10	-4	344	360
10	-6	432	394
10	-10	476	381
10	-14	405	382
11	0	197	210
11	2	297	275
11	-2	368	320
11	-4	448	438
11	-8	393	371
11	-12	357	347
12	0	250	280
12	-2	340	282
12	-4	337	299
12	-6	402	345
12	-10	400	368
13	2	325	265
13	-4	275	256
13	-8	406	382
14	-10	276	273
H= 8			
0	0	509	615
0	2	571	573
0	4	294	292
0	6	301	317
0	-2	264	292
0	-4	495	523
0	-6	245	230
0	-8	417	481
0	-12	267	264
0	-16	326	342
1	0	392	425
1	2	230	220
1	4	332	323
1	8	287	222
1	-2	480	576
1	-4	389	386
1	-6	425	564
1	-10	726	787
1	-12	253	297
1	-14	340	358
1	-18	313	287
2	0	539	571
2	2	431	401
2	4	295	257
2	6	373	350
2	-1	119	119
2	-4	538	642
2	-8	524	614
2	-12	555	597
2	-16	375	371
3	0	330	361
3	4	458	428
3	-2	302	330
3	-4	255	287
3	-6	526	622
3	-10	647	700
3	-14	508	442
3	-18	276	217
4	0	335	327
4	2	347	300
4	4	291	278
4	-2	325	329
4	-4	344	379
4	-8	558	592
4	-12	512	500
4	-16	376	314
5	0	364	356
5	2	192	215
5	4	382	322
5	-2	264	251
5	-4	400	404
5	-6	679	662
5	-10	585	590
5	-14	487	412
6	0	385	380
6	2	439	408
6	-1	265	312
6	-2	325	284
6	-4	458	448
6	-5	235	295
6	-8	560	579
6	-12	389	403
6	-16	300	285
7	0	254	283
7	2	313	266
7	4	360	280
7	-2	446	421
7	-4	361	353
7	-6	544	529
7	-10	654	613
7	-14	423	360
8	0	470	463
8	2	417	398
8	-4	379	396
8	-8	483	459
8	-12	374	308
8	-16	367	268
9	0	231	223
9	2	232	195
9	4	246	233
9	-2	296	286
9	-4	329	316
9	-6	378	408
9	-10	402	410
9	-14	275	277
10	0	301	289
10	2	243	237
10	-4	455	429
10	-8	343	328
10	-12	302	303
11	-2	375	286
11	-6	483	482
11	-10	366	347
11	-14	331	301
12	-4	270	259
12	-8	275	270
12	-12	268	272
13	-6	260	279
13	-10	296	274
H= 9			
0	2	318	343
0	4	300	246
0	-2	278	304
0	-6	582	654
0	-10	523	627
0	-12	410	404
0	-14	185	127
0	-16	237	268
1	0	417	398
1	4	241	249
1	6	301	276
1	-4	420	525
1	-8	505	612
1	-12	466	490
1	-16	272	267
1	-18	341	306
2	0	305	298
2	2	316	298
2	4	309	262
2	6	208	195
2	-1	265	240
2	-2	287	338
2	-4	147	164
2	-6	451	545
2	-10	398	437
2	-12	250	199
2	-14	247	259
3	0	275	241
3	2	207	197
3	4	260	207
3	6	288	235
3	-2	246	269
3	-4	416	547
3	-8	378	436
3	-10	212	228
3	-12	376	405
3	-14	225	214
3	-16	280	264
3	-18	308	239
4	0	219	207
4	2	382	383
4	4	307	251
4	-2	379	413
4	-6	414	493
4	-10	347	397
4	-12	169	190
4	-14	334	294
4	-16	233	230
5	0	386	383
5	2	223	174
5	4	245	212
5	-4	438	474
5	-8	479	509
5	-10	179	199
5	-12	386	387
5	-14	267	249
6	0	218	213
6	2	260	260
6	4	283	204
6	-2	373	411
6	-6	419	406
6	-10	298	306
6	-12	207	197
6	-14	247	268
7	0	344	362
7	2	221	195
7	-4	324	355
7	-8	469	489
7	-10	181	202
7	-12	375	317
8	2	207	200
8	-2	404	372
8	-6	522	547
8	-10	338	346
8	-14	266	222
9	0	303	292
9	-4	338	299
9	-8	425	443
9	-12	336	266
10	-2	328	256
10	-6	393	385
10	-10	336	313
11	0	205	205
11	-4	263	260
11	-8	266	270
11	-12	285	271
12	-2	230	225
12	-6	253	264
12	-10	262	267
13	-4	325	265
14	-2	282	260
H=10			
0	4	257	214
0	-4	431	429
0	-8	385	408
0	-10	286	262
0	-12	376	355
0	-14	319	358
1	0	178	160
1	2	248	258
1	-2	416	437
1	-6	349	426
1	-8	303	326
1	-10	293	302
2	4	298	278
2	-4	414	406
2	-8	348	383
2	-12	296	292
4	0	227	245
6	0	272	266
8	0	236	231
H=11			
0	2	263	239
0	-2	345	343
0	-4	136	129
0	-6	216	251
0	-8	158	198
0	-10	175	178
0	-12	210	252
0	-14	181	152
1	0	283	272
1	4	234	183
1	-4	249	261
1	-8	249	235
1	-14	282	302
2	-2	314	291
2	-6	335	279
2	-8	335	304
3	0	238	236
5	0	204	187
h=12			
0	-4	239	222
0	-6	232	214

Table III

Intramolecular Distances and Angles for $(CH_3)_2Sn(C_9H_6NO)_2$

Distance, A		Angle, deg	
Sn–O(1)	2.11 (1)	Sn–N(1)–C(1)	131 (1)
Sn–O(2)	2.10 (1)	Sn–N(1)–C(8)	113 (1)
Sn–N(1)	2.31 (1)	Cl–N(1)–C(8)	116 (1)
Sn–N(2)	2.38 (1)	N(1)–C(1)–C(2)	125 (2)
Sn–C(10)	2.17 (2)	C(1)–C(2)–C(3)	120 (2)
Sn–C(20)	2.15 (2)	C(2)–C(3)–C(9)	120 (2)
C(1)–N(1)	1.36 (2)	C(3)–C(9)–C(4)	125 (2)
C(1)–C(2)	1.36 (2)	C(3)–C(9)–C(8)	115 (2)
C(2)–C(3)	1.36 (3)	C(9)–C(8)–N(1)	124 (2)
C(3)–C(9)	1.46 (3)	C(4)–C(9)–C(8)	120 (2)
C(4)–C(9)	1.39 (2)	C(9)–C(4)–C(5)	120 (2)
C(4)–C(5)	1.37 (3)	C(4)–C(5)–C(6)	120 (2)
C(5)–C(6)	1.44 (3)	C(5)–C(6)–C(7)	122 (2)
C(6)–C(7)	1.42 (2)	C(6)–C(7)–C(8)	116 (1)
C(7)–C(8)	1.41 (2)	C(7)–C(8)–C(9)	122 (2)
C(8)–C(9)	1.43 (2)	C(7)–C(8)–N(1)	114 (2)
C(8)–N(1)	1.36 (2)	O(1)–C(7)–C(8)	122 (1)
C(7)–O(1)	1.31 (2)	O(1)–C(7)–C(6)	122 (1)
C(11)–N(2)	1.35 (2)	Sn–O(1)–C(7)	118 (1)
C(11)–C(12)	1.40 (3)	Sn–N(2)–C(11)	128 (1)
C(12)–C(13)	1.37 (3)	Sn–N(2)–C(18)	111 (1)
C(13)–C(19)	1.43 (3)	C(11)–N(2)–C(18)	121 (1)
C(14)–C(19)	1.42 (2)	N(2)–C(11)–C(12)	119 (2)
C(14)–C(15)	1.39 (3)	C(11)–C(12)–C(13)	122 (2)
C(15)–C(16)	1.40 (2)	C(12)–C(13)–C(19)	119 (2)
C(17)–C(18)	1.51 (2)	C(13)–C(19)–C(14)	125 (2)
C(18)–C(19)	1.43 (2)	C(13)–C(19)–C(18)	116 (2)
C(18)–N(2)	1.35 (2)	C(19)–C(18)–N(2)	122 (2)
C(17)–O(2)	1.27 (2)	C(14)–C(19)–C(18)	118 (2)
		C(19)–C(14)–C(15)	120 (2)
		C(14)–C(15)–C(16)	121 (2)
		C(15)–C(16)–C(17)	125 (2)
		C(16)–C(17)–C(18)	113 (1)
		C(17)–C(18)–C(19)	122 (1)
		C(17)–C(18)–N(2)	116 (1)
		O(2)–C(17)–C(18)	117 (1)
		O(2)–C(17)–C(16)	130 (2)
		Sn–O(2)–C(17)	123 (1)

Table IV

Comparison of Average Bond Distances in $(CH_3)_2Sn(C_9H_6NO)_2$[j] with Those of Related Compounds

	Compound	Distance, A	Ref
Sn–C	$(CH_3)_2Sn(C_9H_6NO)_2$	2.16 ± 0.02	*a*
Sn–C	$(CH_3)_2SnF_2$	2.06 ± 0.01	*b*
Sn–C	$(CH_3)_2SnCN$	2.16 ± 0.03	*c*
Sn–C	$(CH_3)_ySnX_{4-y}$ $X = Cl, Br, or I; y = 1–3$	2.18 ± 0.03	*d*
Sn–C	CH_3SnH_3	2.143	*d*
Sn–O	$(CH_3)_2Sn(C_9H_6NO)_2$	2.11 ± 0.01	*a*
Sn–N	$(CH_3)_2Sn(C_9H_6NO)_2$	2.35 ± 0.04	*a*
U–O	$UO_2(C_9H_6NO)_2(C_9H_7NO)$	2.32 ± 0.04	*e*
U–N	$UO_2(C_9H_6NO)_2(C_9H_7NO)$	2.56 ± 0.04	*e*
Cu–O	$Cu(C_9H_6NO)_2$	1.94 (1.94)	*f, g*
Cu–N	$Cu(C_9H_6NO)_2$	1.96 (1.98)	*f, g*
Pd–O	$Pd(C_9H_6NO)_2$	1.99	*h*
Pd–N	$Pd(C_9H_6NO)_2$	1.99	*h*
Zn–O	$Zn(C_9H_6NO)_2 \cdot 2H_2O$	2.07	*i*
Zn–N	$Zn(C_9H_6NO)_2 \cdot 2H_2O$	2.10	*i*

[a] This work. [b] E. O. Schlemper and W. C. Hamilton, *Inorg. Chem.*, **5,** 995 (1966). [c] E. O. Schlemper and D. Britton, *ibid.*, **5,** 507 (1966). [d] L. E. Sutton, Ed., "Interatomic Distances," The Chemical Society, London, 1958. [e] Reference 14. [f] Reference 11a. [g] Reference 11b. [h] Reference 13; average of values obtained for bis-8-hydroxyquinolinate palladium complexes with 1,2,4,5-tetracyanobenzene and chloranil. [i] Reference 12. [j] C_9H_6NO = 8-hydroxyquinolinate.

Table V

Comparison of Ligand Bond Distances (A) in $(CH_3)_2Sn(C_9H_6NO)_2$ with Those in Related Compounds[a]

	$(CH_3)_2Sn(C_9H_6NO)_2$	Mean[b]	Calcd[c]
N(1)–C(1)	1.35	1.32	1.32
N(1)–C(8)	1.35	1.36	1.35
C(1)–C(2)	1.38	1.40	1.40
C(2)–C(3)	1.36	1.36	1.38
C(3)–C(9)	1.44	1.43	1.41
C(4)–C(9)	1.40	1.39	1.41
C(4)–C(5)	1.38	1.38	1.38
C(5)–C(6)	1.42	1.41	1.41
C(6)–C(7)	1.39	1.39	1.38
C(7)–C(8)	1.46	1.42	1.41
C(8)–C(9)	1.43	1.42	1.42
C(7)–O(1)	1.29	1.32	

[a] The atom-numbering system used is that for the O(1) ligand but the values given for $(CH_3)_2Sn(C_9H_6NO)_2$ are the average of the values obtained for both ligands. [b] Average of values obtained for $Cu(C_9H_6NO)_2$, $Cu(C_9H_6NO)_2 \cdot$tetracyanoquinodimethane, $Cu(C_9H_6NO)_2 \cdot$picryl azine, $Zn(C_9H_6NO)_2 \cdot 2H_2O$, $Pd(C_9H_6NO)_2 \cdot$1,2,4,5-tetracyanobenzene, and $Pd(C_9H_6NO)_2 \cdot$chloranil.[13] [c] Values calculated for quinoline by LCAO–MO method.[16]

The largest deviation of any ligand atom from its respective plane is 0.04 ± 0.02 A. The average deviation of an atom from its plane is 0.01 ± 0.2 A. There is, therefore, definitely no significant observed deviation from planarity for either ligand. If the tin atom is included in the least-squares plane calculations, the deviations of individual atoms from the planes are slightly larger but still not significant.

The shortest intermolecular distances are given in Table VI. None of them is short enough to suggest any significant deviation from normal van der Waals interactions.

Table VI

Intermolecular Distances (A) in $(CH_3)_2Sn(C_9H_6NO)_2$[a]

O(1)–C(2)	3.56	C(10)–C(13)	3.82
O(2)–C(4)	3.51	C(10)–C(15)	3.73
O(2)–C(5)	3.62	C(10)–C(16)	3.75
O(1)–C(15)	3.88	C(12)–C(16)	3.82
C(1)–C(5)	3.74	C(12)–C(17)	3.73
C(1)–C(6)	3.97	O(2)–C(12)	3.34
C(2)–C(12)	3.93	O(2)–C(13)	3.53
C(5)–C(16)	3.96	O(1)–C(6)	3.67
C(6)–C(15)	3.71	C(5)–C(10)	3.85
C(6)–C(16)	3.75	C(6)–C(10)	3.93
C(7)–C(15)	3.57	C(20)–C(20)	3.93
C(8)–C(15)	3.85	C(13)–C(14)	3.44

[a] All intermolecular distances less than 4.0 A are given.

Nature of the Structure and Bonding.—The oxinate groups are chelating as had been predicted from consideration of the visible–ultraviolet spectrum[17] and the infrared spectrum[5,7] and by the failure to coordinate dimethyl sulfoxide in solution.[6] As predicted by McGrady and Tobias,[2] the Sn–O bonds are shorter (2.11 A) and, presumably, stronger than the Sn–N bonds (2.35 A).

The molecular structure is shown in Figure 2. A

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(17) R. Barbieri, G. Faraglia, M. Giustiniani, and L. Roncucci, *J. Inorg. Nucl. Chem.*, **26**, 203 (1964).

nearly tetrahedral C–Sn–C angle is suggested by the tin–proton coupling constants observed by McGrady and Tobias.[2] Martin and co-workers had postulated a *trans* arrangement of the methyl groups based on their interpretation of the infrared spectrum[3] and their inability to resolve optical isomers.[4] Okawara[5] also preferred the *trans* structure. The observed C–Sn–C angle (110.7 ± 0.8°) is remarkably close to the tetrahedral angle and lends support to the suggested relationship between tin–proton coupling constants and tin orbital hybridization.[18]

An interesting qualitative MO approach to the bonding in tin compounds with coordination number greater than four, not requiring the use of the 5d orbitals, has been postulated.[2,19] For all cases where more than four atoms are bonded to the tin atom by bonds with covalent character, three-center, two-electron bonds can be postulated. For $(CH_3)_2Sn(C_9H_6NO)_2$ the bonding could involve sp^3 hybrid orbitals on the tin participating in normal covalent bonds to the methyl groups and three-center bonds to the oxinate groups. Molecular orbitals constructed from a tin sp^3 hybrid orbital and σ-type orbitals from both nitrogen and oxygen would result in bonding, nonbonding, and antibonding combinations. The four ligand electrons would occupy the bonding and nonbonding orbitals. The angles between the center point of the line connecting N(1) and O(1), the tin atom, and the atoms C(10) and C(20) are 129.8 and 95.8°, respectively. The angles between the center point of the line connecting N(2) and O(2), the tin atom, and the atoms C(10) and C(20) are 94.0 and 133.4°, respectively. The angle between the center point of the line connecting N(1) and O(1), the tin atom, and the center point of the line connecting N(2) and O(2) is 97.5°. The fact that these angles describe a distorted tetrahedral coordination of the tin atom lends some support to the above bonding theory. The fact that the Sn–C bond distances are the same as those observed for tetrahedral tin compounds also lends support to the theory. A larger coefficient for the oxygen orbital in the bonding molecular orbital could account for the shorter Sn–O than Sn–N bond distances and the distortion from tetrahedral coordination observed for the above bond angles. The shorter Sn–C bond in $(CH_3)_2SnF_2$ (Table IV) could be explained by the use of sp hybrid orbitals on the tin for the Sn–C bonds with any covalent bonding to fluorine atoms involving the use of the other two tin p orbitals. The bonds to the fluorine atoms are, however, probably primarily ionic. It is possible that there is some d-orbital contribution to the bonding in $(CH_3)_2Sn(C_9H_6NO)_2$, but the extent of involvement is uncertain. It is also probable that the bonding to the oxinate groups is somewhat ionic. The author plans to examine a complex of the type $R_3Sn(C_9H_6NO)$ as a further test of the above bonding approach and of the relationship between tin–proton coupling constants and the C–Sn–C bond angle.

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[19] I. R. Beattie and G. P. McQuillan, *J. Chem. Soc.*, 1519 (1963).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE RADIATION LABORATORY,[1]
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Electric Dipole Moments and Mössbauer Spectra of Complexes of *o*-Phenanthroline with Di-*n*-butyltin dihalides

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Isomer shifts reveal an order of bond polarity Sn–Cl > Sn–Br > Sn–I in complexes of dibutyltin dihalides with *o*-phenanthroline and with α,α-dipyridyl. The electric dipole moments of the *o*-phenanthroline complexes are 11.3, 12.7, and 12.9 D. for the dichloride, dibromide, and diiodide, respectively, indicating that a portion of the latter two moments is associated with asymmetry in the distribution of unshared halogen electrons. The large moments obtained for these complexes indicate a *trans* arrangement for the butyl groups.

Isomer shifts of compounds of the type R_2SnX_2 and its complexes with donor compounds give an indication of the relative polarity of the Sn–Cl, Sn–Br, and Sn–I bonds and the relative changes in polarity on complex formation. A comparison of the electric dipole moments of these complexes with their Mössbauer spectra offers a means of illustrating the contribution of unshared halogen electrons to the dipole moments.

Bidentate ligands are preferred to monodentate in dipole moment studies because in the event of chelation—the formation of monomer complexes—the number of possible isomers is reduced and the resultant of the dipoles associated with the dative bond is fixed.

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