this is not completely clear. However, one might speculate about the cause using the empirical rules of Cobble[14] for estimating the entropies of complex ions. If one metal–ligand bond in a complex of a polydentate ligand were broken and the site were then occupied by a water molecule, the resultant entropy change would account for about −0.59 unit of log β_n. This would be sufficient to account for the inversion in the relative stabilities of the two series of complexes. A change in the dentate character of the α,β,β'-trihydroxyisobutyrate ligand seems plausible.

Acknowledgment.—The authors wish to thank Mr. H. R. Burkholder for preparation of the α,β,β'-trihydroxyisobutyric acid used in the experiments.

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Contribution from the Department of Chemistry, Massachusetts
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The Crystal and Molecular Structure of Bis(dipivaloylmethanido)zinc(II)[1]

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A single crystal, three-dimensional X-ray study of bis(dipivaloylmethanido)zinc(II) has been carried out. The results confirm an earlier deduction from space group requirements that the metal atoms lie at positions of $\bar{4}$ symmetry and are thus in "tetrahedral" (strictly D_{2d}) complexes. The space group also requires that each chelate ring be precisely symmetrical. The important bond lengths and angles in the chelate ring (standard deviations in parentheses) are: Zn–O, 1.962 (0.007) Å.; C–O, 1.274 (0.012) Å.; C–C, 1.405 (0.012) Å.; ∠OZnO, 94.7° (0.6); ∠OCC, 125.8° (1.1); ∠CCC, 127.0° (2.8). The remaining ∠OZnO angles are 114.2° (0.6). These dimensions are compared with those in some other β-ketoenolate complexes. The considerable distortion of the immediate environment of the cobalt atom, in the isostructural cobalt(II) complex, from perfect tetrahedral symmetry can be considered as an important cause of the somewhat anomalous characteristics of the visible absorption spectrum of that compound.

Introduction

Interest in the molecular structures of β-ketoenolate complexes of metal ions in this laboratory has mainly centered around those of Co(II),[3,4] Ni(II),[5–7] and Cu(II)[8] and has been generated chiefly in the attempt to understand the electronic structures and bonding and thus to interpret the electronic spectra of such compounds. While acetylacetonates themselves have been most frequently studied, the dipivaloylmethane derivatives have played a crucial role in understanding Co(II) and Ni(II) β-ketoenolate complexes and continue to offer novel and even unique opportunities for study of such compounds. It has been, or will become, necessary, in order to exploit these opportunities properly, to have precise knowledge of the crystal and molecular structures of these compounds and thus a program of X-ray crystallographic investigation has been undertaken. A future paper will report on the isomorphous Cu(II) and Ni(II) compounds, which contain planar molecules. This paper reports the structure of the Zn(II) compound, which is isomorphous[3] with that of Co(II). It has already been reported[3] that the space group and unit cell contents of these compounds appear to require that the molecules have D_{2d} (or, roughly, "tetrahedral") structures and some of the consequences of that for the Co(II) compound have been discussed.[3,4] The complete X-ray study described here fully confirms the earlier report and provides fairly precise values for the various interatomic distances and bond angles. We elected to make this study on the zinc compound chiefly because of its greater convenience both in the preparation and the preservation of single crystals.

Experimental

Single crystals in the form of square prisms with pyramidal ends, or distorted octahedral exhibiting faces of the form {111} (crystal class 4/mmm), were prepared by slow sublimation under vacuum at ~90° by Dr. Roger Soderberg. Using a crystal mounted along the prism axis, precession photographs were taken with Mo Kα radiation. The unit cell was found to be tetragonal with the following dimensions: $a = 10.67 \pm 0.01$ and $c = 21.76 \pm 0.015$ Å. The following systematic absences were observed: for hkl, $h + k + l \neq 2n$; for $hk0$, $h(k) \neq 2n$; $00l$, $l \neq 4n$. These uniquely fix the space group as $I4_1/a$ (No. 88). The corresponding cobalt compound was found to be isomorphous (virtually indistinguishable precession photographs) with unit cell dimensions of $a = 10.67$ and $c = 21.87$ Å. The density (by flotation) was found to be 1.15 ± 0.02 g./cm.^{3}. Taking the molecular weight as 431.4, the calculated value of Z is 3.99 ± 0.07. The density of the cobalt compound was measured as 1.13 ± 0.02 g./cm.^{3} giving for Z, 3.98 ± 0.07.

Intensities were recorded photographically by the equiinclination Weissenberg method, using a crystal about 0.5 × 0.5 × 0.7 mm. and Cu Kα radiation. Layers $hk0$ and $h0l$–$h6l$ were recorded using the multiple film technique and the intensities estimated visually by comparison with a set of timed exposures of a reflection from the same crystal. No corrections were made for absorption in view of the low value of the absorption coefficient (μ = 13.7 cm.$^{-1}$). Absorption corrections for a spherical specimen at 0 and 45° differ by less than 4%. It was calculated that *ca.* 500 independent reflections are accessible with Cu Kα radia-

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[1] Supported by the United States Atomic Energy Commission.

[2] Alfred P. Sloan Foundation Fellow.

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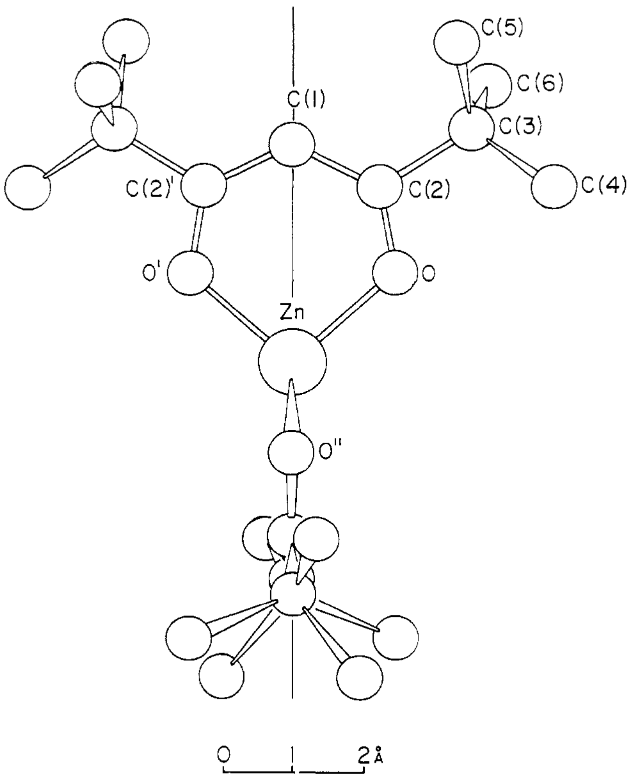

Fig. 1.—One molecule of bis(dipivaloylmethanido)zinc(II) projected onto the plane of one of the chelate rings.

tion in the range $0 < \sin\theta < 2^{-1/2}$ and measurements were restricted to the corresponding region of reciprocal space.

After application of Lorentz-polarization corrections by a graphical method[9] and, when necessary, corrections for extension of spots on upper layer photographs,[10] all reflections were placed on the same relative scale by correlating intensities of $0kl$ reflections on the $h1l$–$h6l$ films with those on the $h0l$ layer. They were then placed on an approximate absolute scale by Wilson's method,[11] which gave an average temperature parameter, B, of 3.2 Å.^{2}.

Determination of Structure

From the space group symmetry and the consequent molecular symmetry ($\bar{4}$), it seemed probable that the orientation of the chelate rings with respect to the x and y crystal axes would be available from the Patterson projection onto (001), as in this projection there might be expected a buildup of vector density due to the overlap of zinc–oxygen, zinc–carbon, and some carbon–carbon vectors arising from atoms in any one chelate ring. The projection computed using the thirty nonzero $hk0$ reflections available with copper radiation showed one high peak at a distance of *ca.* 1.4 Å. from the origin, and a lesser peak at *ca.* 2.5 Å. from the origin, both lying on a common line from the origin, inclined at 24° to the y axis. This angle was taken as the inclination of the chelate ring.

A set of trial coordinates was then calculated for the six carbon atoms and the oxygen atom comprising the asymmetric unit, using as dimensions for the chelate ring, the bond distances and angles observed in ferric acetylacetonate[12] (Fe–O, 1.95 Å.; C–O, 1.28 Å.; C(ring)–C(ring), 1.39 Å.; C(ring)–C(aliphatic), 1.53 Å.). In obtaining coordinates for the three methyl carbon atoms of the *t*-butyl group, consideration of a molecular model suggested that in order to minimize steric conflict with the hydrogen atom on the γ-carbon atom, these would be arranged such that one would lie in the same plane as the chelate ring, but directed away from the γ-carbon atom, and the two others, adjacent to the hydrogen atom, would lie on either side of the ring plane. All coordinates so derived were referred to the centrosymmetric origin, which in the space group $I4_1/a$ is at 0, $^1/_4$, $^1/_8$ in relation to the $\bar{4}$ position.

Since it is impossible to distinguish from the (001) projection between one ring orientation and an alternative one at 90° to the first, it was necessary to calculate structure factors for the two orientations to determine the correct one. Examination of the trigonometric expressions in the structure factors for the different classes of reflection in $I4_1/a$ indicates that the structure amplitudes of reflections with odd l indices will differ for the two orientations, while those for reflections with even l index will be the same. Calculations for the two orientations, using all the three-dimensional data, gave residuals, $R = (\Sigma|F_c - F_o|)/\Sigma|F_o|$, of 0.59 and 0.38, clearly indicating that the orientation corresponding to the latter is the correct one. The atomic scattering factors used in these and subsequent computations were those of Freeman and Watson[13] for zinc(II), corrected for the real part, $\Delta f'$, of anomalous dispersion,[14] and those of Hoerni and Ibers[15] for carbon and oxygen.

A three-dimensional Fourier synthesis was now computed[16] using the phases obtained in the above structure factor calculation. This confirmed the positions for zinc, the ring atoms, and the central carbon atoms of the *t*-butyl groups, but suggested the need for significant shifts in the methyl carbon atoms. The new set of coordinates was used in a new structure factor calculation which gave a residual of 0.27. After a cycle of least squares refinement[17] in which only the individual isotropic temperature parameters and the over-all scale factor were permitted to vary (resulting in significant changes), the residual dropped to 0.16. Two more cycles, in which the variables were positional and isotropic thermal parameters for all atoms, as well as a scale factor for each individual equiinclination level (a total of 33 variables), dropped the residual successively to 0.144 and 0.135. In these cycles, the scale factors did not vary relative to one another by more than 4%.

Weighting of the data now appeared appropriate.

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TABLE I
FINAL ATOMIC PARAMETERS[a,b]

				× 10^4			× 10^4					
Atom	x	y	z	σ_x	σ_y	σ_z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zn	0.0	−0.25	−0.125	...	..	...	63	63	11	...	...	...
C_1	0.0	−0.25	0.0207	...	..	7	71	71	21	−21	...	...
O	0.1256	−0.3029	−0.0659	6	6	3.5	77	76	13	21	−10	3
C_2	0.1087	−0.2959	−0.0081	9	8	5	96	27	15	−27	−11	5
C_3	0.2173	−0.3417	0.0309	11	10	5	114	89	19	−23	−26	10
C_4	0.3377	−0.3578	−0.0076	16.5	16	7.5	22	353	45	36	−20	9
C_5	0.2428	−0.2542	0.0864	14	14	7	234	130	33	−20	−59	−21
C_6	0.1792	−0.4742	0.0545	12	12	6	197	39	48	−7	−26	16
				B								
$H_1(C_1)$	0.0	−0.25	0.068	3.3								
C_4 H_2	0.314	−0.408	−0.074	8.4								
H_3	0.357	−0.274	−0.026									
H_4	0.405	−0.395	0.022									
C_5 H_5	0.188	−0.157	0.079	7.2								
H_6	0.193	−0.288	0.127									
H_7	0.325	−0.213	0.092									
C_6 H_6	0.099	−0.466	0.089	5.8								
H_9	0.257	−0.523	0.079									
H_{10}	0.147	−0.536	0.023									

[a] σ_i represents the estimated standard deviation in the parameter i obtained from the final least squares refinement cycle and calculated according to Cruickshanks formula.[18] [b] β_{ij} represents the ij^th coefficient of the anisotropic thermal parameters in the expression exp $-(\beta_{11}h^2 + \beta_{12}hk + \beta_{22}k^2 + \beta_{13}hl + \beta_{23}kl + \beta_{33}l^2)$.

This was done using Cruickshank's scheme[18] modified to give the greatest weight to structure factors of intermediate magnitude (20–40), which are believed to be those most reliably measured from the films. After one cycle (33 variables) with weighting, the residual stood at 0.130.

Since there were still several conspicuously poor agreements in particular structure factors (notably 123), in addition to several low-order reflections which obviously suffered from extinction and which were excluded from the refinement, it was felt that the agreement could probably be improved by including the hydrogen atoms and making an allowance for anisotropic thermal motion. A three-dimensional difference Fourier map was therefore computed. In this, anomalies characteristic of anisotropic vibrational motion were quite evident, especially for the methyl carbon atoms and the zinc atom. Of the ten independent hydrogen atoms, only two, belonging to the *t*-butyl group, were clearly evident. However, from the positions of these, and using a molecular model (C–H, 1.1 Å.), positional parameters were estimated for the other eight, such that intramolecular interactions were minimized. Each hydrogen atom was assigned an isotropic thermal parameter equal to that of the carbon atom to which it was attached. Structure factors calculated including the hydrogen atoms showed several improvements in low-order reflections (especially 123), though the residual dropped only 0.3%. A cycle of least squares refinement was then computed assigning anisotropic temperature factors to the zinc, oxygen, and carbon atoms. The diagonal elements of the temperature factors differed appreciably from the previous isotropic temperature factors and the residual dropped to 0.088. In this cycle, all changes in positional parameters were smaller than the corresponding estimated standard deviations and refinement was thus considered to be complete.

No attempt has been made to analyze or interpret the anisotropic thermal parameters quantitatively. Qualitatively, however, they correspond with the anomalies, mentioned earlier, on the difference Fourier map. The greatest motion of the zinc atom is in the plane perpendicular to the molecular axis and the methyl carbon atoms move mainly in arcs about the threefold axis of the *t*-butyl group.

The final positional and thermal parameters are listed in Table I, and the calculated structure factors given by these parameters are listed, together with the observed values, in Table II. The final residual of 0.081 is calculated giving the accidentally absent reflections half the minimum observed value and omitting those reflections affected by extinction. These are indicated by an asterisk.

Discussion

Figure 1 shows one molecule of the complex projected perpendicular to the mean plane of one of the chelate rings. The atoms in this ring are numbered for reference in Table III which gives the main interatomic distances and interbond angles. Figure 2 shows the contents of one unit cell projected onto the (100) and (010) planes. So far as we have seen, there are no notable intermolecular interactions, all intermolecular internuclear distances being of about the usual van der Waals lengths or greater. The following discussion can therefore be restricted to intramolecular dimensions.

Although several complexes containing β-ketoenolate–metal rings have previously been studied by X-ray

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(18) D. W. J. Cruickshank, *et al.*, in "Computing Methods and the Phase Problem in X-ray Crystal Structure Analysis," R. Pepinsky, J. M. Robertson, and J. C. Speakman, Ed., Pergamon Press, London, 1961, p. 45.

TABLE II
OBSERVED AND CALCULATED STRUCTURE FACTORS

h	k	l	$F_o/2$	$F_c/2$
0	0	4	48.00	45.90
0	0	8	23.10	20.73
0	0	12	2.97	-0.80
0	0	16	37.11	39.87
*0	1	1	39.12	-78.99
0	1	3	3.52	1.75
0	1	5	31.35	33.07
0	1	7	13.30	11.70
0	1	9	14.75	-14.93
0	1	11	8.89	-10.84
0	1	13	29.67	28.50
0	1	15	31.97	29.55
0	1	17	29.90	-29.63
0	1	19	25.71	-25.91
*0	2	2	53.53	-77.78
0	2	4	31.30	29.38
0	2	6	15.03	16.02
0	2	8	52.50	-56.69
0	2	10	13.85	-11.89
0	2	12	19.09	20.10
0	2	14	8.76	-8.18
0	2	16	30.93	-32.41
0	2	18	2.88	5.86
0	3	1	11.40	8.98
0	3	3	28.51	29.44
0	3	5	1.90	-0.18
0	3	7	43.99	-42.40
0	3	9	43.70	48.16
0	3	11	5.27	6.24
0	3	13	31.77	-29.13
0	3	15	18.74	-18.76
0	3	17	14.66	14.15
0	4	2	35.95	34.66
0	4	4	46.46	-59.00
0	4	6	17.20	-15.27
0	4	8	28.21	27.36
0	4	10	1.94	-1.18
0	4	12	29.15	-28.41
0	4	14	21.62	20.82
0	4	16	10.29	8.27
0	5	1	14.19	-14.31
0	5	3	15.55	-15.39
0	5	5	28.40	31.45
0	5	7	16.30	17.26
0	5	9	27.35	-27.92
0	5	11	30.24	-34.25
0	5	13	28.40	30.42
0	5	15	2.63	2.29
0	6	2	20.11	18.86
0	6	4	30.39	30.55
0	6	6	7.57	6.87
0	6	8	31.07	-33.09
0	6	10	9.30	-9.18
0	6	12	17.86	17.97
0	6	14	2.35	0.17
0	7	1	16.86	15.62
0	7	3	16.26	16.47
0	7	5	27.56	-26.70
0	7	7	6.38	-4.34
0	7	9	13.64	12.77
0	7	11	15.33	15.52
0	7	13	9.71	-10.05
0	8	2	12.28	-11.13
0	8	4	20.74	-21.49
0	8	6	3.27	3.53
0	8	8	16.37	17.05
0	8	10	3.27	0.66
0	9	1	20.35	-23.96
0	9	3	15.33	16.65
0	9	5	17.02	16.71
0	9	7	22.40	24.94
*1	1	2	41.91	-62.52
1	1	4	31.41	31.44
1	1	6	36.33	39.08
1	1	8	13.97	16.13
1	1	10	10.73	-11.47
1	1	12	1.84	2.04
1	1	14	35.65	37.98
1	1	16	4.47	-6.64
1	1	18	32.41	-32.95
*1	2	1	61.35	-134.65
1	2	3	10.90	9.54
1	2	5	16.28	-13.64
1	2	7	33.74	-35.98
1	2	9	31.49	-28.92
1	2	11	22.23	21.70
1	2	13	10.46	8.07
1	2	15	27.55	-26.48
1	2	17	17.30	-15.50
1	2	19	9.45	7.73
1	3	2	55.20	56.90
1	3	4	50.00	53.09
1	3	6	43.72	-44.11
1	3	8	4.90	-6.37
1	3	10	17.92	17.74
1	3	12	28.13	-26.00
1	3	14	35.30	-32.47
1	3	16	13.14	13.02
1	3	18	19.28	19.81
1	4	1	53.00	57.93
1	4	3	46.18	53.00
1	4	5	57.52	-54.12
1	4	7	50.61	57.18
1	4	9	21.18	20.78
1	4	11	13.94	-14.38
1	4	13	14.10	-15.20
1	4	15	32.63	30.89
1	4	17	7.02	6.59
1	5	2	18.93	-18.21
1	5	4	15.78	-14.46
1	5	6	41.13	45.36
1	5	8	2.10	-4.25
1	5	10	21.04	-21.67
1	5	12	2.26	3.65
1	5	14	20.77	20.70
1	5	16	6.21	-4.35
1	6	1	40.20	-37.95
1	6	3	23.50	25.50
1	6	5	12.27	12.99
1	6	7	13.30	-15.13
1	6	9	14.62	-15.83
1	6	11	9.35	10.73
1	6	13	9.35	9.25
1	6	15	14.26	-14.61
1	7	2	41.30	39.47
1	7	4	5.82	-3.92
1	7	6	11.62	-10.49
1	7	8	7.27	6.30
1	7	10	15.50	13.90
1	7	12	2.51	4.38
1	8	1	9.44	10.45
1	8	3	28.11	-27.30
1	8	5	10.73	-8.31
1	8	7	17.09	15.04
1	8	9	17.83	17.29
1	9	2	11.18	-12.28
1	9	4	5.42	5.46
1	9	6	18.44	20.61
*2	0	0	45.50	61.60
2	1	1	14.53	-13.40
*2	1	3	46.22	-65.80
2	1	5	38.40	40.29
2	1	7	39.51	38.39
2	1	9	19.50	-18.66
2	1	11	16.37	-16.41
2	1	13	17.32	16.37
2	1	15	19.00	18.16
2	1	17	17.32	-18.61
2	1	19	12.46	-10.59
2	2	0	40.38	-43.42
2	2	2	22.50	-19.88
2	2	4	12.27	12.94
2	2	6	30.18	27.11
2	2	8	41.13	-40.43
2	2	10	17.60	16.36
2	2	12	35.56	38.75
2	2	14	10.08	-8.26
2	2	16	31.62	-32.28
2	2	18	2.94	-3.33
2	3	1	42.64	42.01
2	3	3	51.60	57.29
2	3	5	3.64	-0.51
2	3	7	45.08	-42.78
2	3	9	6.35	4.18
2	3	11	12.55	10.88
2	3	13	37.75	-37.08
2	3	15	4.78	-2.14
2	3	17	12.55	12.15
2	4	0	50.33	57.45
2	4	2	37.61	37.66
2	4	4	22.12	-23.13
2	4	6	29.87	26.97
2	4	8	32.20	34.80
2	4	10	7.52	5.88
2	4	12	34.40	-35.38
2	4	14	19.03	19.70
2	4	16	11.89	10.32
2	5	1	34.18	-34.10
2	5	3	37.80	-35.17
2	5	5	17.99	16.60
2	5	7	30.30	32.89
2	5	9	9.05	-8.71
2	5	11	2.26	-0.70
2	5	13	23.40	21.22
2	5	15	5.89	6.73
2	6	0	59.01	-65.00
2	6	2	33.42	-31.93
2	6	4	10.30	12.01
2	6	6	6.79	-8.49
2	6	8	22.98	-21.93
2	6	10	6.79	4.95
2	6	12	13.58	16.10
2	7	1	30.36	26.77
2	7	3	23.23	22.86
2	7	5	15.90	-16.61
2	7	7	11.25	-9.69
2	7	9	2.94	1.11
2	7	11	8.14	9.75
2	7	13	9.83	-8.37
2	8	0	41.20	45.48
2	8	2	15.53	-18.68
2	8	4	2.94	-1.74
2	8	6	2.94	2.81
2	8	8	22.54	25.97
2	8	10	3.00	2.09
2	9	1	23.16	-23.18
2	9	3	11.64	-11.41
2	9	5	2.94	2.49
3	1	2	34.03	-36.70
3	1	4	11.74	-15.37
3	1	6	42.47	44.67
3	1	8	5.81	-6.30
3	1	10	46.94	-51.12
3	1	12	2.01	-3.02
3	1	14	24.87	24.81
3	1	16	2.35	2.06
3	1	18	7.04	-7.45
3	2	1	41.76	-37.47
3	2	3	4.50	3.06
3	2	5	44.39	45.90
3	2	7	40.00	-42.69
3	2	9	22.66	-21.83
3	2	11	26.92	29.23
3	2	13	5.88	4.57
3	2	15	23.23	-22.08
3	2	17	12.52	-11.52
3	3	2	18.00	15.98
3	3	4	37.48	32.86
3	3	6	60.02	-65.57
3	3	8	15.75	13.72
3	3	10	31.99	35.16
3	3	12	2.39	3.85
3	3	14	26.88	-25.89
3	3	16	8.96	8.82
3	3	18	2.62	4.66
3	4	1	23.78	20.98
3	4	3	2.90	0.47
3	4	5	35.51	-33.56
3	4	7	29.75	27.99
3	4	9	19.40	17.97
3	4	11	17.64	-14.89
3	4	13	18.53	-16.55
3	4	15	27.13	27.25
3	4	17	9.24	10.65
3	5	2	49.54	-50.34
3	5	4	2.10	-1.77
3	5	6	15.99	16.11
3	5	8	10.35	8.24
3	5	10	14.25	-14.41
3	5	12	2.47	4.23
3	5	14	25.35	23.33
3	5	16	2.68	1.99
3	6	1	58.49	-53.71
3	6	3	11.49	12.68
3	6	5	2.35	0.84
3	6	7	14.21	-14.73
3	6	9	2.35	-3.80
3	6	11	6.37	6.62
3	6	13	11.54	12.39
3	7	2	31.45	30.13
3	7	4	7.06	-6.64
3	7	6	26.72	-25.87
3	7	8	2.82	-3.61
3	7	10	5.43	7.02
3	7	12	2.82	2.77
3	8	1	31.50	31.45
3	8	3	2.61	1.36
3	8	5	6.95	-4.43
3	8	7	15.64	16.13
3	8	9	11.57	10.98
3	9	2	17.30	-19.34
4	0	0	54.02	49.26
4	1	1	15.14	-15.01
4	1	3	8.33	-7.83
4	1	5	45.55	46.31
4	1	7	29.17	27.89
4	1	9	28.50	-28.32
4	1	11	23.75	-21.55
4	1	13	21.80	24.06
4	1	15	25.43	27.05
4	1	17	2.51	-3.21
4	2	0	10.64	-11.14
4	2	2	8.64	-10.88
4	2	4	31.62	29.00
4	2	6	16.65	16.27
4	2	8	55.84	-57.02
4	2	10	8.64	-8.36
4	2	12	27.86	28.60
4	2	14	9.14	-7.67
4	2	16	8.64	-5.70
4	3	1	9.88	-8.02
4	3	3	20.40	18.10
4	3	5	39.43	-38.92
4	3	7	29.87	-27.20
4	3	9	36.93	36.18
4	3	11	37.48	35.00
4	3	13	25.53	-26.35
4	3	15	2.72	-2.98
4	4	0	40.10	37.18
4	4	2	9.79	8.14
4	4	4	38.99	-37.05
4	4	6	1.88	3.04
4	4	8	31.08	30.80
4	4	10	5.92	3.98
4	4	12	17.42	-16.29
4	4	14	10.78	9.84
4	4	16	12.17	11.20
4	5	1	32.40	-30.75
4	5	3	20.80	-18.78
4	5	5	16.30	14.76
4	5	7	11.78	9.00
4	5	9	22.35	-22.44
4	5	11	13.78	-14.73
4	5	13	13.94	12.26
4	5	15	19.72	20.99
4	6	0	48.17	-43.13
4	6	2	2.09	1.03
4	6	4	21.10	21.19
4	6	6	4.50	-6.12
4	6	8	14.78	-14.31
4	6	10	10.00	-11.56
4	6	12	10.44	10.84
4	7	1	32.58	33.03
4	7	3	2.38	-0.06
4	7	5	11.95	-11.65
4	7	7	11.95	-11.99
4	7	9	9.01	10.02
4	7	11	11.56	10.46
4	8	0	45.35	51.79
4	8	2	6.19	6.23
4	8	4	2.54	-1.49
4	8	6	4.20	-5.63
5	1	2	11.60	-10.62
5	1	4	17.10	15.46
5	1	6	52.59	55.20
5	1	8	13.86	12.22
5	1	10	25.99	-26.11
5	1	12	13.19	10.00
5	1	14	29.62	30.11
5	1	16	2.51	0.04
5	2	1	2.07	-1.02
5	2	3	34.25	32.65
5	2	5	36.62	39.08
5	2	7	39.50	-40.39
5	2	9	16.90	-17.86
5	2	11	16.53	18.68
5	2	13	31.30	31.77
5	2	15	2.94	-1.63
5	3	2	8.53	7.04
5	3	4	4.89	-5.38
5	3	6	55.40	-56.40
5	3	8	6.03	4.76
5	3	10	18.47	16.90
5	3	12	2.61	0.06
5	3	14	27.70	-29.26
5	4	1	14.71	12.90
5	4	3	22.60	-20.03
5	4	5	25.99	-24.54
5	4	7	21.57	21.16
5	4	9	21.60	20.12
5	4	11	17.20	-16.19
5	4	13	17.37	-19.18
5	5	2	27.60	-25.13
5	5	4	13.78	12.31
5	5	6	22.35	21.03
5	5	8	2.47	-3.13
5	5	10	18.77	-19.56
5	5	12	2.68	-2.72
5	6	1	13.58	-13.82
5	6	3	29.56	28.80
5	6	5	7.21	7.19
5	6	7	19.64	-20.99
5	6	9	14.62	-16.10
5	6	11	2.87	-0.60
5	7	2	21.40	23.75
5	7	4	2.63	-2.38
5	7	6	9.47	-11.04
5	7	8	6.89	4.98
5	8	1	16.09	18.49
5	8	3	7.52	-5.37
6	0	0	28.92	30.28
6	1	1	2.51	-1.18
6	1	3	23.75	-23.75
6	1	5	20.65	18.83
6	1	7	42.19	41.11
6	1	9	20.96	-22.88
6	1	11	13.19	-13.77
6	1	13	17.38	16.51
6	1	15	2.51	-0.53
6	2	0	5.88	-3.27
6	2	2	3.76	-6.63
6	2	4	23.16	21.22
6	2	6	2.50	2.62
6	2	8	38.50	-38.75
6	2	10	2.82	-2.39
6	2	12	41.01	41.39
6	2	14	2.94	-3.10
6	3	1	17.65	16.15
6	3	3	11.73	12.17
6	3	5	34.76	-31.76
6	3	7	27.16	-24.22
6	3	9	2.50	0.69
6	3	11	14.66	15.96
6	3	13	21.72	-22.59
6	4	0	29.92	28.42
6	4	2	16.81	-15.17
6	4	4	29.37	-28.03
6	4	6	11.89	13.05
6	4	8	17.03	16.75
6	4	10	2.43	-4.33
6	4	12	23.56	-25.16
6	5	1	22.93	-21.06
6	5	3	2.21	-2.29
6	5	5	32.61	31.59
6	5	7	20.62	19.39
6	5	9	2.63	-3.85
6	5	11	8.41	-7.07
6	6	0	21.67	-18.87
6	6	2	17.18	15.68
6	6	4	14.32	15.20
6	6	6	2.61	-2.25
6	6	8	18.12	-20.69
6	7	1	18.49	22.49
6	7	3	2.61	3.27
6	7	5	2.61	-3.50
7	1	2	20.90	-20.60
7	1	4	17.49	-17.86
7	1	6	37.50	38.70
7	1	8	5.48	-4.02
7	1	10	15.48	-16.87
7	1	12	2.51	-0.55
7	2	1	17.53	-15.48
7	2	3	2.69	3.53
7	2	5	34.30	32.27
7	2	7	28.61	-29.76
7	2	9	2.82	-3.64
7	2	11	12.52	13.24
7	2	13	11.52	8.45
7	3	2	20.91	20.20
7	3	4	2.55	4.56
7	3	6	29.44	-29.22
7	3	8	2.61	-1.91
7	3	10	15.53	17.49
7	3	12	2.72	-1.18
7	4	1	15.32	14.56
7	4	3	20.00	-18.38
7	4	5	5.14	-3.71
7	4	7	10.12	10.28
7	4	9	14.32	15.16
7	5	2	21.04	-21.27
7	5	4	23.14	21.00
7	5	6	22.09	21.80
7	5	8	7.78	7.81
7	6	1	12.01	-13.13
7	6	3	18.12	18.63
7	6	5	6.79	5.49
8	0	0	27.83	29.56
8	1	1	16.43	-15.59
8	1	3	21.85	-20.29
8	1	5	7.27	8.38
8	1	7	10.90	11.34
8	1	9	8.33	-8.27
8	2	0	20.97	-19.40
8	2	2	6.26	-4.30
8	2	4	25.54	26.47
8	2	6	8.58	8.85
8	2	8	8.14	-6.17
8	2	10	2.94	-2.40
8	3	1	12.82	13.69
8	3	3	18.36	18.80
8	3	5	13.14	-14.64
8	3	7	7.30	-8.64
8	3	9	9.23	11.03
8	4	0	23.39	23.46
8	4	2	2.54	-5.27
8	4	4	21.68	-21.79
8	4	6	2.54	-1.18
8	5	1	21.56	-20.79
8	5	3	2.68	-2.53
9	1	2	13.19	-14.19
9	1	4	14.47	-15.96
9	1	6	19.84	21.65
9	2	1	24.10	-27.17
9	2	3	4.50	5.94
9	2	5	6.05	7.12
9	3	2	21.70	24.64

TABLE III
BOND LENGTHS AND ANGLES

Zn–O	1.962 ± 0.007 Å.
C(2)–O	1.274 ± 0.012 Å.
C(1)–C(2)	1.405 ± 0.012 Å.
C(2)–C(3)	1.517 ± 0.016 Å.
C(3)–C(4)	1.547 ± 0.021 Å.
C(3)–C(5)	1.542 ± 0.019 Å.
C(3)–C(6)	1.558 ± 0.017 Å.

O–Zn–O′′	114.2 ± 0.6°	C(2)–C(3)–C(4)	106.8 ± 2.6°
O–Zn–O′	94.7 ± 0.6°	C(2)–C(3)–C(5)	111.9 ± 2.6°
Zn–O–C(2)	121.8 ± 1.1°	C(2)–C(3)–C(6)	106.1 ± 2.6°
O–C(2)–C(1)	125.8 ± 1.1°	C(4)–C(3)–C(5)	110.2 ± 2.8°
C(2)–C(1)–C(2)′	127.0 ± 2.8°	C(4)–C(3)–C(6)	107.2 ± 2.8°
C(3)–C(2)–O	114.7 ± 1.7°	C(5)–C(3)–C(6)	109.6 ± 2.8°
C(3)–C(2)–C(1)	119.6 ± 1.6°		

TABLE IV
COMPARISON OF MOLECULAR DIMENSIONS OF THE CHELATE RINGS IN SOME β-KETOENOLATE COMPLEXES

		Bonds (Å.) in ring			Angles (deg.) in ring				C(ring) to C(aliphatic)	Dihedral angle,[a] deg.
Compound	Ref.	M–O	C–O	C–C	OMO	MOC	OCC	CCC		
$\mathrm{Zr(acac)_4}$[b]	26	2.198	1.270	1.399	75.0	133.1	123.7	122.5	1.517	~158
$\mathrm{VO(acac)_2}$[c,d]	25	1.97	1.285	1.397	87.5	129.1	123.7	123.8	1.52	~168
$\mathrm{Co(acac)_2 \cdot 2H_2O}$[b]	21	2.055	1.275	1.420	92.0	123.4	124.7	127.9	1.48	~164
$\mathrm{Zn(DPM)_2}$[b,e]	...	1.962	1.274	1.405	94.7	121.8	125.8	127.0	1.517	≡180

[a] The angle between the OMO plane and the OCCCO mean plane. [b] Refinement of atomic coordinates included anisotropic therma parameters. [c] Refinement of atomic coordinates used only isotropic thermal parameters. [d] Averaged over all crystallographically inequivalent, but chemically equivalent, bonds or angles. [e] Refinement of atomic coordinates included approximately placed hydrogen atoms; see text.

diffraction,[12,19–28] only a few of the more recent studies have produced molecular parameters of accuracy comparable to that of the present work. In Table IV, some of these more accurate results are presented for comparison with those reported here. There is generally good agreement for the C–O, C(ring)–C(ring), and C(ring)–C(aliphatic) bond lengths in all cases; they correspond, respectively, to the expected distances for bond orders of ~1.3, ~1.5, and ~1.0, due account being taken of the shortening (~0.03 Å.) on going from sp^3 to sp^2 hybridized carbon. The ring formed in the dipivaloylmethanide complex may thus be assumed to involve delocalized π-bonding (or resonance) entirely comparable to that generally postulated for the acetylacetonate rings. It may be noted that in $\mathrm{Zn(DPM)_2}$, the crystal symmetry requires the pairs of C–O and C–C bonds in each ring to be exactly equal in length. Such equality is an expected consequence of the π-delocalization (or resonance) and has been found to exist within experimental uncertainties, though not necessarily precisely, in previous structure determinations on β-ketoenolate complexes.[29]

The bond angles within chelate rings can be seen to vary rather more than the C–O and C–C distances from one compound to another. The angles found in $\mathrm{Zn(DPM)_2}$ are in the same general range as those in the other compounds. The greater variability of the angles seems entirely reasonable and may be attributed to (a) the need for some sort of adjustments in chelate ring shape in order to allow for the various sizes of the metal atoms and (b) the fact that angle deformation force constants are typically much smaller than those for bond stretching and compression. It may be added that the relatively small variations in ring angles will not be likely to have much effect on the π-bonding or resonance energy of the rings. The OMO angle in $\mathrm{Zn(DPM)_2}$ is the largest in Table IV. While the shortness of the Zn–O bonds is to some extent responsible for this, it is most likely due chiefly to the tendency of the zinc atom to form tetrahedrally directed bonds. In the vanadium and cobalt compounds, where the metal atoms are of comparable size, the over-all stereochemistry tends to preferred OMO angles of ~90°. The very low OZrO angle is mainly a consequence of the great size of the metal atom.

Finally, Table IV draws attention to an interesting but previously little discussed feature of the chelate ring structures in β-ketoenolate complexes, namely, a tendency of the OMO plane to be canted at a dihedral angle of ~160° to the mean plane of the ligand atoms. It may be added to the data in Table IV that a similar canting (~165°) has also been found in $\mathrm{Zn(acac)_2H_2O}$[26] though the accuracy here is relatively lower. In all cases, including $\mathrm{Zn(DPM)_2}$, the coplanarity of the OCCCO portions of the rings, as well as the two appended aliphatic carbon atoms, has been established to within the level of significance suggested by the standard deviations. The sum of the angles $O–C_2–C_3$, $C_1–C_2–O$, and $C_1–C_2–C_3$ equals 360.1°. So far as we can see, there is no plain and simple reason for this feature. The results for $\mathrm{Zn(DPM)_2}$, however, show

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(19) H. Koyama, Y. Saito, and H. Kuroya, *J. Inst. Polytech. Osaka City Univ., Ser. C*, **4**, 43 (1953); *Chem. Abstr.*, **48**, 3097*a* (1954) (copper(II) acetylacetonate).

(20) E. A. Shugam, *Dokl. Akad. Nauk SSSR*, **81**, 853 (1951); *Chem. Abstr.*, **46**, 3894*d* (1952) (copper(II) acetylacetonate).

(21) V. M. Padmanabhan, *Proc. Indian Acad. Sci.*, **47**, 329 (1958) (cobalt(II) acetylacetonate).

(22) L. M. Shkol'nikova and E. A. Shugam, *Kristallografiya*, **5**, 32 (1960) (chromium(III) acetylacetonate).

(23) G. J. Bullen, *Acta Cryst.*, **12**, 703 (1959) (cobalt(II) acetylacetonate dihydrate).

(24) V. Amirthalingam, V. M. Padmanabhan, and J. Shankar, *ibid.*, **13**, 201 (1960) (beryllium(II) acetylacetonate).

(25) G. J. Bullen, R. Mason, and P. Pauling, *Nature*, **189**, 291 (1961) (trimer of nickel(II) acetylacetonate).

(26) E. L. Lippert and M. R. Truter, *J. Chem. Soc.*, 4996 (1960) (zinc(II) acetylacetonate monohydrate).

(27) R. P. Dodge, D. H. Templeton, and A. Zalkin, *J. Chem. Phys.*, **35**, 55 (1961) (oxovanadium(IV) acetylacetonate).

(28) J. V. Silverton and J. L. Hoard, *Inorg. Chem.*, **2**, 243 (1963) (zirconium(IV) acetylacetonate).

(29) The only reported exception to this occurs in the somewhat more complicated case of bis(tropolonato)copper(II) [J. M. Robertson, *J. Chem. Soc.*, 1222 (1951)]. In this case also, equalization of pairs of CO and CC bonds would be expected from π-electron delocalization or resonance and it seems quite possible that the structural study is in error on this point.

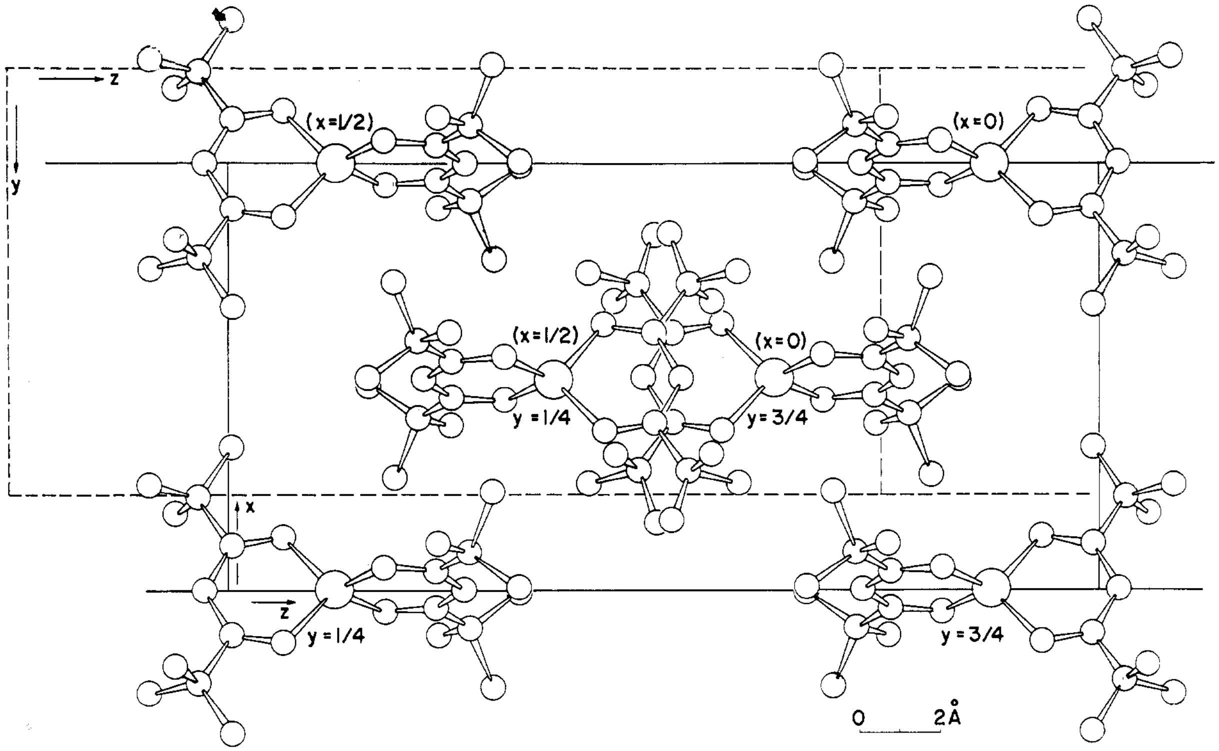

Fig. 2.—The contents of one unit cell, projected onto (010), shown by the full lines, and onto (100), shown by the broken lines. The x and y coordinates of the zinc atoms of the respective molecules are indicated.

that though it is *common*, it is not *essential*. In the case of $Co(acac)_2 \cdot 2H_2O$, the cause could be the formation of intermolecular hydrogen bonds, while in $VO(acac)_2$, it has been suggested[27] that inter-ring conjugation is responsible. It has also been suggested that this or a similar kind of bending of the chelate rings may occur in the formation of polymers by $Co(acac)_2$.[4]

As noted in the Introduction, the primary purpose of this investigation was to obtain structural data bearing on the behavior of the isomorphous and, presumably, molecularly isostructural compound, $Co(DPM)_2$. The results reported here throw some light on the problems raised by the unusual electronic spectrum[3,4] of this compound. These unusual features are (i) the weakness of the visible and near-infrared bands as compared with those in other "tetrahedral" complexes of cobalt(II), (ii) the unusual intensity ratio, $f(\nu_3)/f(\nu_2) \approx 1$, compared to typical ratios of 5–10, and (iii) the apparently low nephelauxetic effect, $\Delta B = -90$ cm.$^{-1}$, as compared to $-200 > \Delta B > -300$ in other "tetrahedral" complexes of cobalt(II).

To a somewhat greater extent than anticipated, $Co(DPM)_2$ is distorted from true tetrahedral symmetry. Instead of six OCoO angles of 109°28′, we have two angles of ~95° and four of ~114°. There may of course be still further distortion in a purely electronic sense because of the anisotropy of metal–ring π-bonding about the Co–O axes. Since the band intensities in "tetrahedral" complexes depend, *inter alia*, on the difference in d–p orbital mixing in ground and excited states,[30] it is not unreasonable that a gross distortion in the geometry of the coordination polyhedron may have a marked effect on the absolute magnitudes of band intensities, although quantitative accounting of this is probably beyond the limits of theory in its present state. Regarding the unusual intensity *ratio*, the work of Ballhausen and Liehr[30] is very apropos, for they have shown that, granting two very reasonable assumptions, the intensity ratio $f(\nu_3)/f(\nu_2)$ is calculable for *strict* tetrahedral symmetry and that distortions will lead to deviations from this calculated ratio. Empirically, it is known that in real, distorted "tetrahedral" complexes of cobalt(II), these deviations are *always* toward lower values of the ratio.[31] It is, therefore, not surprising that in this complex, which has a distortion which is probably greater than that in any of the more normal "tetrahedral" complexes,[29] the deviation in the intensity ratio is greatest. This result is in harmony with the explanation recently proposed for the unusual features of the electronic absorption spectrum of cobalt(II) complexes of the type $Co(R_3MO)_2(NO_3)_2$.[32]

An explanation of the low apparent ΔB for $Co(DPM)_2$ in terms of the observed gross distortion from true tetrahedral symmetry is less secure. In very general terms, it may be connected with a mixing of the states characteristic of a truly tetrahedral field in such a way that the visible transition is now between states separated by nB' where $n > 15$. Thus B' should be given by nB'/n, rather than by $nB'/15$ (as implicitly assumed previously), and it is a large value of n, rather than a large value of B', which is actually being ob-

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(30) C. J. Ballhausen and A. D. Liehr, *J. Mol. Spectry.*, **2**, 342 (1958); **4** 190 (1960).

(31) F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 4690 (1961).

(32) F. A. Cotton, D. M. L. Goodgame, and R. H. Soderberg, *Inorg. Chem.*, **2**, 1162 (1963).

served. It should be emphasized, however, that this is only a plausible hypothesis for which no direct evidence exists at present.

Because of the very favorable orientation of the molecules in the lattice, a study of the polarizations of the absorption bands has been undertaken with the hope of obtaining some direct evidence on the above spectroscopic problems.

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A Series of Phthalocyaninotin Complexes[1]

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Methods of preparing and purifying the compounds $PcSnF_2$, $PcSnBr_2$, $PcSnI_2$, and $PcSn(OH)_2$ are given together with improved procedures for the synthesis and purification of $PcSnCl_2$, Pc_2Sn, PcSn, and PcPb. Pc_2Sn is shown to have two polymorphic modifications and to form a 1:1 solvate with 1-chloronaphthalene. Both polymorphs are found to undergo thermal decomposition at elevated temperatures with the formation of PcSn and PcH_2.

Introduction

The phthalocyanino ring is a planar aromatic system which forms stable coordination compounds with many divalent, trivalent, and tetravalent metals. In the case of phthalocyanines involving trivalent and tetravalent metals appropriate substituent groups are attached to the metal atom in order to maintain electrical neutrality. With these normal phthalocyanino complexes it generally is supposed that the metal atom is located approximately in the plane of the ring and forms bonds with the four pyrrole type nitrogen atoms and that these latter atoms exhibit the approximate symmetry of a square.

An extensive series of phthalocyanines is formed by tin. Members of this series were first investigated by Linstead's group, who succeeded in establishing the existence of PcSn (as well as the analogous PcPb), $PcSnCl_2$, and Pc_2Sn.[2] Recently, Whalley, while obtaining visible spectra of a series of phthalocyanino complexes, verified the composition of Pc_2Sn and demonstrated that it is a distinct homogeneous phase.[3] At the same time Elvidge showed that the oxidation state of the tin in Pc_2Sn is four.[4]

The ratio of two phthalocyanine rings per metal atom makes Pc_2Sn unique among all of the phthalocyanines reported. It has been suggested that the structure of Pc_2Sn may involve tin atoms bonded with eight nearest neighbor nitrogen atoms.[5] The compound thus may be an example of a complex containing a post-transition metal in eight coordination. Infrared data are consistent with this proposed structure.[6]

This investigation of Pc_2Sn and other members of the phthalocyaninotin system is a continuation of our research into the chemistry and properties of the phthalocyanino complexes of the group IV metals. Both this and the earlier investigations show that the phthalocyaninotin system differs markedly from the analogous silicon and germanium systems. This is not surprising because tin is significantly larger than either silicon or germanium and because it is relatively stable in both the +2 and +4 oxidation states.

Experimental

The extractive recrystallizations were carried out in an Ace simplified extraction apparatus in which the usual extractor body was eliminated and the extraction thimble placed directly in the neck of the flask. When high boiling solvents were used, a heating tape was wrapped around the portion of the extractor containing the thimble to ensure that the extractions took place at approximately the reflux temperature of the solvent.

The carbon, hydrogen, and the halogen analyses were made by ordinary microanalytical procedures. Nitrogen was determined by a modification of the Dumas method, in which the compound was decomposed at 1000°. Lead was determined volumetrically by means of a standard method employing ethylenediaminetetraacetic acid as a titrant. Tin was determined iodometrically after an aqueous aluminum reduction.[7]

The thermogravimetric analysis data were obtained with a Stanton HT-D recording thermobalance operating with an argon atmosphere. A heating rate of 3°/min. was used.

For the collection of the differential thermal analysis data an apparatus was used in which the sample and the reference Al_2O_3 were held in two small tantalum crucibles. These had built in thermocouple wells and were placed over thermocouples in the center of a uniform temperature zone. The temperature difference was recorded as a function of the temperature of the Al_2O_3 on a recording millivolt potentiometer. A heating rate of about 10.5°/min. and an argon atmosphere were used.[8]

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[7] Analytical work performed by Schwarzkopf Microanalytical Laboratory.

[8] This equipment belongs to the National Carbon Research Laboratory and the permission of this organization to use the equipment is gratefully acknowledged.