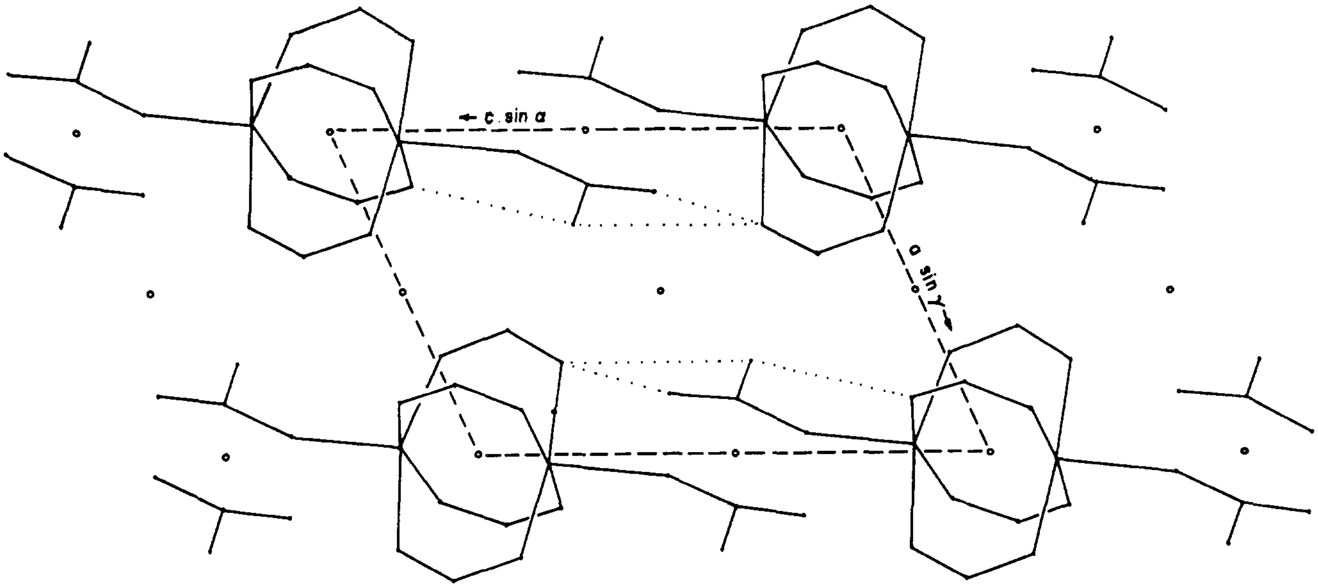

Figure 3.—Projection of the structure of copper(II) formate monourea onto a plane perpendicular to the [010] direction.

tabulated in Table V and the more plausible hydrogen-bonding interactions are illustrated in Figures 2 and 3.

Acknowledgments.—We thank Mr. Terry Fickies for preparing the crystals used in this study. The support of the National Science Foundation for this work is gratefully acknowledged. Computation was supported in part by an NSF institutional grant to the University of California, Irvine, Calif.

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The Crystal and Molecular Structure of the Acetylacetonimine Adduct of Ytterbium Acetylacetonate, $Yb(C_5H_7O_2)_3(CH_3COCH{=}C(NH_2)CH_3)$

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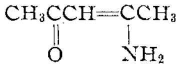
The crystal structure of tris(acetylacetonato)(4-amino-3-penten-2-one)ytterbium, $Yb(C_5H_7O_2)_3(CH_3COCH{=}C(NH_2)CH_3)$, has been determined from three-dimensional X-ray diffraction data. A total of 1301 independent nonzero reflections were collected by counter methods. Four formula units crystallize in a monoclinic unit cell with dimensions a = 18.070 (7), b = 8.538 (10), c = 15.938 (6) Å; β = 99.13 (10)°. The observed and calculated densities are both 1.56 g/cm^3; the space group is $P2_1/c$. The structure was refined by full-matrix least-squares methods to a conventional R factor of 0.073. The ytterbium atom is seven-coordinate, being bonded to six acetylacetonate oxygen atoms and the oxygen atom from the acetylacetonimine molecule. The coordination polyhedron is a capped trigonal prism, with an acetylacetonate oxygen as the capping atom. The NH_2 group in acetylacetonimine is hydrogen bonded to the acetylacetonate oxygen atoms in a glide-related molecule, thus linking the molecules in chains parallel to (100). The metal–acetylacetonate rings are folded about the O–O lines, at angles ranging from 10.1 to 19.6°. The Yb–O(acetylacetonimine) distance of 2.24 (2) Å is practically the same as the average of the six Yb–O(acetylacetonate) distances, 2.23 (2) Å.

In recent studies of rare earth acetylacetonates (Ln(acac)$_3$),[2] it was found that an acetylacetonimine (Hacim) solvate, with the formula Ln(acac)$_3$·Hacim, is fairly easily obtained for Yb and Lu by the ordinary Stites, McCarty, and Quill preparation method.[3] Both the Yb and Lu compounds can be recrystallized unchanged from acetylacetone and a variety of other solvents.[2] Infrared spectra[2] suggest that the Hacim exists in the amine tautomeric form, 4-amino-3-penten-2-one (**1**). The crystal structure of the Yb compound has been determined in order to discover what structure



$$\underset{\displaystyle O}{\overset{}{CH_3\underset{\|}{C}}}CH{=}\underset{|\atop NH_2}{C}CH_3$$

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[2] M. F. Richardson, D. E. Sands, and W. F. Wagner, *J. Inorg. Nucl. Chem.*, **31**, 1417 (1969).

[3] J. G. Stites, C. N. McCarty, and L. L. Quill, *J. Amer. Chem. Soc.*, **70**, 3142 (1948).

features give the adduct such great stability. Another group of workers[4] has also examined the structure of Yb(acac)$_3$·Hacim. However, the solution and refinement of the structure were hindered because the compound was initially incorrectly formulated as hydrated ytterbium acetylacetonate.[4b]

Experimental Section

Yb(acac)$_3$·Hacim was prepared as described previously[2] and recrystallized from benzene. The crystals were examined under a polarizing microscope and a rectangular prism 0.05 × 0.10 × 0.17 mm, parallel to a, b, and c, respectively, was chosen for the single-crystal study. The crystal was sealed in a thin-walled glass capillary with the 0.17-mm dimension parallel to the capillary. Preliminary oscillation and Weissenberg photographs ($hk0$–$hk3$) indicated the monoclinic space group P2$_1$/c ($0k0$ absent for k odd, $h0l$ absent for l odd). The crystal was transferred to a General Electric X-ray spectrometer equipped with a single-crystal orienter and scintillation counter with pulse height analyzer. The crystal was oriented about the [$\bar{1}$02] axis. The unit cell dimensions were determined accurately from slow θ–2θ scans of the $\bar{h}$,0,2h, $0k0$, and $00l$ reflections: $a = 18.070 \pm 0.007$, $b = 8.538 \pm 0.010$, $c = 18.938 \pm 0.006$ Å. The standard deviations given were derived from the variance of the measurements made of each parameter. The monoclinic angle was measured directly from the observed angle between the $h00$ and $00l$ rows: $\beta = 99.13 \pm 0.10°$. The measured density (by flotation in CHCl$_3$–hexane) is 1.56 g/cm^3; the density calculated for four molecules in the cell is 1.56 g/cm^3.

Goniostat settings[5] were calculated for the Mo Kα_1 line (λ 0.70930 Å). The intensities of all independent reflections for which $2\theta \leqslant 40°$ were measured manually using a 40-sec counting period and Zr-filtered Mo Kα radiation at a takeoff angle of 4°. The counter aperture was 3°. Since ϕ is the most critical angle setting for measuring the data manually, the reflections were sorted according to the value of ϕ and all reflections with a given ϕ were measured consecutively. Where possible, a strong reflection in each group was used to obtain the optimum ϕ. This procedure minimizes errors due to small missettings of the ϕ wheel. Conversion factors for obtaining integrated intensities were based on 12 intensities measured by a manual ω scan. These reflections covered the 2θ range 4–34°. Background corrections were made by interpolation of a plot of background *vs.* 2θ which was based on measurements made with the crystal out of reflecting position. A standard reflection ($\bar{2}00$) was measured after every ~50 reflections. A factor of A_0/A was applied to correct for decomposition (which was ~10%) and instrumental fluctuations, where A_0 is the first value of the standard reflection and A is the value obtained by linear interpolation between the two standard reflections which bracket the intensity being measured.

The intensities were converted to structure factors by means of the equation

$$F_o^2 = [(I_{\text{raw}} - B)S]rP$$

where I_{raw} is the raw counts, B is the background, $S = A/A_0$, r is the ratio for converting peak heights to integrated intensities, and P is the Lorentz–polarization correction. An absorption correction ($\mu = 40.9$ cm^{-1}) was then applied to the data. The transmission factors ranged from 0.664 to 0.815. Standard deviations on F_o were calculated by means of eq 1, which is a variation of the method of Smith and Alexander.[6] In this equation, $C = (I_{\text{raw}} - B)$ and s is the estimated variance in the measurement of r.

$$\sigma(F_o) = 0.5F_o\left[\frac{S^2I_{\text{raw}} + I_{\text{raw}}^2S(1 + S)/A + B}{C^2} + \frac{s}{r^2}\right] \quad (1)$$

A total of 2479 intensities, of which 1301 were at least twice the standard deviation and are therefore classified as observed, were obtained. Only the observed reflections were used in the final stages of the structure determination and refinement.

Structure Determination and Refinement

The atomic form factors for Yb^{3+} were taken from Cromer, Larson, and Waber;[7] those for C, N, and O were from the compilation of Ibers.[8] The values for the six oxygen atoms in the three acetylacetonate rings were the average of values for the neutral atom and O$^-$. The real and imaginary components of the anomalous scattering of the Yb were taken from the compilation of Templeton.[9,10]

Trial ytterbium positions were deduced from the three-dimensional unsharpened Patterson function. Further interpretation of the Patterson function was not attempted due to extensive crowding and overlapping of peaks. The ytterbium atoms occupy the P2$_1$/c general positions 4(e): $\pm(x, y, z;\ x, \tfrac{1}{2} - y, \tfrac{1}{2} + z)$ with $x = 0.26$, $y = 0.12$, $z = 0.13$. The ytterbium positional parameters, one scale factor, and the overall temperature factor were refined by the method of least squares. The function minimized was $\Sigma w \cdot (|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$ and F_o and F_c are the observed and calculated structure factors, respectively. The conventional R factor, $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, was 0.47; the weighted R factor, $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2]^{1/2}$, was 0.59 (including unobserved reflections).

A difference Fourier map based on $F_o - F_c$ was calculated with all of the data. This map had seven peaks at approximately the distance from the ytterbium atom expected for the oxygen atoms. In addition, all of the atoms in the acetylacetonimine group and three carbon atoms of an acetylacetonate ring were found. An additional difference Fourier synthesis yielded the remaining 12 carbon atoms. Two cycles of full-matrix least-squares refinement (scale factor, positional parameters, individual isotropic temperature factors) with all of the data, including unobserved reflections, gave $R_1 = 0.21$, $R_2 = 0.14$.

The unobserved data [all reflections with $F_o \leqslant 2\sigma(F_o)$] were then dropped from the refinement, leaving 1301 observed reflections. At the same time, the ytterbium atom was treated anisotropically. The refinement converged at $R_1 = 0.084$, $R_2 = 0.066$.

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[4] (a) E. F. Korytnyi, L. A. Aslanov, M. A. Porai-Koshits, and O. M. Petrukhin, *Zh. Strukt. Khim.*, **9**, 540 (1968); (b) M. A. Porai-Koshits, 8th International Congress of Crystallography, Stony Brook, N. Y., Aug 15, 1969.

[5] Computations were carried out primarily on the IBM 7094 computers at Wright-Patterson Air Force Base. Programs used included Sands' INCOR for converting intensities to structure factors; Busing, Martin, and Levy's ORFFE for function and error analysis; Johnson's ORTEP thermal ellipsoid plotting program; and local versions of Hamilton's GONO9 for the absorption correction, Zalkin's FORDAP for the Fourier syntheses, and Busing and Levy's ORFLS for the full-matrix least-squares refinement.

[6] G. S. Smith and L. E. Alexander, *Acta Crystallogr.*, **16**, 462 (1963).

[7] D. T. Cromer, A. C. Larson, and J. T. Waber, *ibid.*, **17**, 1044 (1964).

[8] "International Tables for X-Ray Crystallography," Vol. III. The Kynoch Press, Birmingham, England, 1962, p 202.

[9] Reference 8, p 216.

[10] The anomalous scattering correction is an integral part of our version of ORFLS; see J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, **17**, 781 (1964).

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS

H	L	FO	FC
K 0			
-17	0	64	48
-17	2	71	48
-16	0	91	64
-16	2	64	46
-16	4	51	46
-16	6	56	56
-16	8	73	64
-15	0	66	55
-15	6	92	76
-15	8	69	67
-14	0	82	75
-14	4	78	70
-14	6	70	73
-14	8	118	108
-14	10	69	55
-13	0	57	47
-13	2	74	67
-13	4	67	62
-13	6	101	103
-13	10	113	106
-12	0	111	107
-12	2	68	55
-12	4	96	94
-12	6	84	85
-12	8	108	115
-12	12	129	104
-11	0	59	43
-11	2	129	134
-11	4	73	73
-11	6	130	139
-11	10	98	102
-11	12	53	35
-10	0	120	112
-10	2	73	57
-10	4	123	117
-10	6	49	52
-10	8	133	138
-10	12	140	128
-9	2	202	212
-9	4	35	31
-9	6	199	207
-9	10	148	163
-9	14	143	124
-8	0	89	74
-8	2	58	44
-8	4	201	195
-8	6	68	68
-8	8	157	179
-8	12	157	159
-7	0	78	64
-7	2	186	193
-7	4	111	110
-7	6	205	214
-7	8	42	15
-7	10	172	176
-7	14	117	105
-6	0	96	97
-6	2	94	92
-6	4	207	219
-6	8	132	146
-6	10	38	5
-6	12	136	136
-5	0	121	103
-5	2	234	223
-5	4	85	90
-5	6	222	217
-5	10	176	179
-5	14	129	121
-4	0	180	171
-4	2	40	43
-4	4	189	191
-4	6	61	40
-4	8	202	203
-4	10	37	9
-4	12	107	110
-3	0	53	18
-3	2	180	176
-3	4	52	39
-3	6	246	238
-3	8	97	90
-3	10	178	177
-3	12	45	19
-3	14	134	126
-2	0	428	409
-2	2	58	56
-2	4	306	262
-2	6	111	117
-2	8	215	207
-2	10	39	33
-2	12	109	113
-1	0	56	29
-1	2	436	382
-1	4	105	79
-1	6	239	240
-1	8	103	99
-1	10	137	152
-1	14	140	130
0	2	58	52
0	4	318	294
0	6	65	65
0	8	224	239
0	10	53	35
0	12	125	130
0	14	53	10
1	2	302	303
1	4	31	19
1	6	217	216
1	8	33	15
1	10	121	127
1	14	152	148
2	2	134	134
2	4	239	232
2	6	44	31
2	8	159	168
2	10	44	41
2	12	138	141
2	14	67	48
3	2	153	148
3	4	57	59
3	6	182	181
3	8	40	8
3	10	129	135
3	12	45	23
3	14	113	114
4	2	53	56
4	4	167	179
4	6	44	36
4	8	166	191
4	12	118	131
4	14	65	55
5	2	148	150
5	4	48	51
5	6	166	169
5	10	88	99
6	4	123	117
6	6	34	46
6	8	137	152
6	10	52	49
6	12	103	96
7	2	121	120
7	4	88	85
7	6	109	113
7	8	39	54
7	10	62	66
8	2	68	77
8	4	116	118
8	8	93	103
8	10	66	74
8	12	89	78
9	2	147	148
9	4	63	59
9	6	103	115
9	10	90	77
10	2	68	57
10	4	92	86
10	8	84	86
10	10	65	54
11	2	150	152
11	4	47	55
11	6	60	64
11	8	59	71
11	10	74	60
12	2	73	69
12	4	65	66
13	2	107	100
14	2	64	57
14	4	63	59
15	2	75	61
16	2	68	53
K 1			
-17	4	64	39
-16	1	57	42
-16	5	73	64
-16	6	58	61
-15	7	74	69
-15	8	86	66
-14	1	62	68
-14	2	52	44
-14	5	84	92
-14	6	75	77
-14	9	58	61
-14	10	79	74
-13	0	54	50
-13	3	70	61
-13	4	86	79
-13	7	76	65
-13	8	84	86
-12	0	51	53
-12	1	100	97
-12	2	87	93
-12	4	57	56
-12	5	86	88
-12	8	84	81
-11	0	93	93
-11	1	38	39
-11	2	49	54
-11	3	99	98
-11	4	89	95
-11	5	49	47
-11	6	55	50
-11	7	68	59
-11	8	92	96
-11	9	54	44
-11	11	59	47
-11	12	98	98
-10	0	38	50
-10	1	112	120
-10	2	107	111
-10	3	55	53
-10	4	59	69
-10	5	76	78
-10	6	123	126
-10	9	61	68
-10	10	95	108
-10	13	66	74
-9	0	109	110
-9	1	84	90
-9	3	62	76
-9	4	141	143
-9	5	56	57
-9	6	50	59
-9	7	76	80
-9	8	127	130
-9	9	51	46
-9	11	53	56
-9	12	106	108
-8	0	39	42
-8	1	65	71
-8	2	138	141
-8	3	70	68
-8	4	76	76
-8	5	66	76
-8	6	151	153
-8	7	37	25
-8	9	81	82
-8	10	120	124
-8	11	51	54
-8	13	99	85
-8	14	112	101
-7	0	151	153
-7	1	84	86
-7	3	93	99
-7	4	157	157
-7	5	46	45
-7	6	87	89
-7	7	73	78
-7	8	103	109
-7	9	72	61
-7	11	74	72
-7	12	93	89
-7	13	61	49
-7	14	54	15
-6	0	46	46
-6	1	49	42
-6	2	141	143
-6	3	106	102
-6	4	64	62
-6	5	90	89
-6	6	199	181
-6	7	59	58
-6	8	33	9
-6	9	94	94
-6	10	99	102
-6	11	63	61
-6	12	46	20
-6	13	84	79
-6	14	94	88
-5	0	243	228
-5	1	108	115
-5	2	28	24
-5	3	144	142
-5	4	149	158
-5	5	35	45
-5	7	117	118
-5	8	141	145
-5	9	79	77
-5	10	40	6
-5	11	99	109
-5	12	68	72
-5	13	83	78
-4	0	41	38
-4	1	84	76
-4	2	222	205
-4	3	110	96
-4	4	30	5
-4	5	114	105
-4	6	207	198
-4	7	130	125
-4	8	32	25
-4	9	105	105
-4	10	114	123
-4	11	88	82
-4	13	74	62
-4	14	105	95
-4	15	97	80
-3	0	130	126
-3	1	111	106
-3	3	149	140
-3	4	162	159
-3	5	98	87
-3	6	65	54
-3	7	138	132
-3	8	161	164
-3	9	125	126
-3	10	42	18
-3	11	99	88
-3	12	96	98
-3	13	107	103
-2	1	68	65
-2	2	179	178
-2	3	50	45
-2	4	35	22
-2	5	136	129
-2	6	155	157
-2	7	202	190
-2	8	59	46
-2	9	82	74
-2	10	145	139
-2	11	91	88
-2	13	53	43
-2	14	65	61
-2	15	71	66
-1	0	297	273
-1	1	123	121
-1	2	85	76
-1	3	147	141
-1	4	142	143
-1	5	86	84
-1	6	79	70
-1	7	96	92
-1	8	156	164
-1	9	111	104
-1	10	42	27
-1	11	74	66
-1	12	128	122
-1	13	97	80
0	1	241	225
0	2	242	236
0	3	133	128
0	4	42	32
0	5	88	85
0	6	144	147
0	7	173	165
0	9	43	42
0	10	111	105
0	11	96	92
0	14	100	91
0	15	64	55
1	1	156	155
1	2	36	35
1	4	147	142
1	5	103	94
1	6	40	29
1	7	114	105
1	8	112	115
1	9	88	88
1	11	55	46
1	12	114	107
1	13	76	70
2	1	156	148
2	2	133	128
2	3	125	127
2	4	41	28
2	5	92	99
2	6	91	90
2	7	111	116
2	9	36	29
2	10	84	77
2	11	87	92
2	12	53	41
2	14	96	81
3	1	101	100
3	2	181	189
3	3	78	73
3	4	154	155
3	5	92	92
3	7	107	103
3	8	103	103
3	9	87	89
3	10	42	38
3	11	41	33
3	12	88	85
3	13	63	63
4	1	246	221
4	2	136	131
4	3	98	97
4	4	64	71
4	5	125	120
4	6	124	133
4	7	88	95
4	9	44	49
4	10	78	78
4	11	65	76
4	14	67	68
5	1	168	167
5	2	66	71
5	3	61	65
5	4	121	117
5	5	117	117
5	7	69	69
5	8	125	126
5	9	97	97
5	12	61	58
6	2	120	123
6	3	106	107
6	4	67	74
6	5	79	84
6	6	98	98
6	7	105	105
6	8	40	36
6	10	67	65
6	11	60	55
7	1	112	119
7	2	88	94
7	4	86	91
7	5	100	108
7	8	95	91
7	9	46	58
7	10	48	53
8	1	67	51
8	2	90	90
8	3	98	102
8	4	70	77
8	6	101	106
8	7	56	56
8	10	66	68
8	11	59	40
9	1	120	127
9	2	47	50
9	4	103	100
9	5	70	79
9	8	78	74
9	9	59	65
10	2	105	105
10	3	89	98
10	6	80	86
10	10	73	69
11	1	110	106
11	4	73	71
11	5	56	65
11	8	57	60
12	2	88	94
12	3	62	66
12	6	59	55
13	1	64	60
13	4	60	60
14	2	69	57
14	3	59	46
15	1	50	31
K 2			
-15	5	103	94
-14	3	93	86
-14	5	49	43
-14	7	109	111
13	1	98	98
-13	5	110	115
-13	7	58	45
-13	9	92	93
-12	0	40	36
-12	3	125	128
-12	5	42	42
-12	7	99	99
-12	9	61	57
-12	11	102	99
-11	1	111	108
-11	3	54	51
-11	5	128	134
-11	7	57	55
-11	9	107	107
-10	0	39	52
-10	1	67	78
-10	3	138	151
-10	4	39	30
-10	5	71	69
-10	7	125	128
-10	9	56	63
-10	11	116	115
-10	13	99	79
-9	1	91	101
-9	2	33	39
-9	3	81	85
-9	5	157	167
-9	6	46	42
-9	7	79	79
-9	9	99	104
-9	11	71	59
-9	13	135	119
-8	0	37	47
-8	1	96	95
-8	3	129	135
-8	4	73	76
-8	5	99	103
-8	7	116	121
-8	8	38	32
-8	9	83	85
-8	11	128	125
-8	13	103	97
-7	0	33	40
-7	1	144	152
-7	2	48	57
-7	3	113	115
-7	4	38	36
-7	5	155	161
-7	6	39	31
-7	7	84	86
-7	8	36	25
-7	9	103	109
-7	11	83	88
-7	13	112	102
-6	0	39	36
-6	1	119	120
-6	3	170	170
-6	4	30	28
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The assignments of the N(1), O(7), and C(20) atoms in the acetylacetonimine molecule were in doubt, although the structure could be interpreted most logically in terms of the assignment made initially (which was the structure finally accepted; see Figure 2). To check the assignment, the N(1) and O(7) assignments were reversed and the structure was refined through two additional least-squares cycles. The atom coordinated to the Yb atom (now assumed to be nitrogen) had $B = 1.2$ Å^2, while the other atom (now assumed to be oxygen) had $B = 8.4$ Å^2. These values are somewhat unusual in comparison with the other B's in the structure, thus indicating that the original assignment was probably correct and the nitrogen is not coordinated. Similarly, reversal of the N(1) and C(20) assignments led to a relatively small value (1.8 Å^2) of B for "N(1)" (now assumed to be carbon) and a large value (7.8 Å^2) for "C(20)" (now assumed to be nitrogen).

A difference Fourier synthesis was essentially featureless in the neighborhoods of the N(1), O(7), and C(20) atoms. This Fourier synthesis also had a peak 2.3 e$^-$/Å^3 high at the ytterbium position. Subsequent refinement with the scattering factors for neutral Yb and O decreased the R factors very slightly, though not significantly, to $R_1 = 0.083$, $R_2 = 0.066$. Since there seemed to be no basis for choice between neutral atom and ionic scattering factors, the scattering factors for the neutral atoms were used for all subsequent refinements and calculation of F_c. Scattering factors for the neutral atoms seem reasonable in view of the Pauling electroneutrality principle.

An attempt to treat the oxygen atoms anisotropically met with failure, as the temperature factor of O(7) became nonpositive definite. The temperature factor of this atom remained nonpositive definite when the O(7) and N(1) assignments were reversed again.

For correct weights, the value of $w\Delta^2$ should be constant when averaged over various ranges of F_o and $(\sin\theta)/\lambda$, where $\Delta = F_o - F_c$. An analysis showed that the strong planes were overweighted. The average value of $w\Delta^2$ was 1.01 for the $\sim$500 reflections with $F_o > 92.9$, whereas it was 0.51 for the $\sim$800 reflections with $2\sigma(F_o) < F_o < 92.9$. It was thus decided that the weights should be changed. This was done by reestimating $\sigma(F_o)$, in the following manner. Neglecting the term s/r^2 (whose contribution is generally small for the strong reflections), letting $F_o^2 = KC$ (K is a constant), converting $\sigma(F_o)$ to $\sigma^2(F_o^2)$ by $\sigma^2(F_o^2) = 4F_o^2 \cdot [\sigma^2(F_o)]$, and letting $S = 1$ (which is accurate to ±0.1), eq 1 becomes

$$\sigma^2(F_o^2) = K^2\left[I_{\text{raw}} + \frac{2I_{\text{raw}}^2}{A} + B\right] \qquad (2)$$

or

$$\frac{\sigma^2(F_o^2)}{K^2} = \sigma^2\left(\frac{F_o^2}{K}\right) = \sigma^2(C) = \left[I_{\text{raw}} + \frac{2I_{\text{raw}}^2}{A} + B\right] \qquad (3)$$

This equation is remarkably similar to one frequently used by Ibers[11] to estimate standard deviations, namely

$$\sigma^2(I_{\text{net}}) = \left[C_{\text{T}} + (pI_{\text{net}})^2 + 0.25\left(\frac{t_{\text{c}}}{t_{\text{b}}}\right)^2 (B_1 + B_2)\right] \qquad (4)$$

where C_{T} is the total counts, I_{net} is the net intensity (C in eq 1), P is an adjustable parameter, and $0.25 \cdot (t_{\text{c}}/t_{\text{b}})^2(B_1 + B_2)$ is the error contributed by the background measurements. The term $(pI_{\text{net}})^2$ in eq 4 corresponds to the term $2I_{\text{raw}}^2/A$ in eq 3. For very strong reflections, $I_{\text{raw}} \approx I_{\text{net}}$, so that $p \approx \sqrt{2/A}$. The value assigned to p is thus entirely controlled by the standard reflection in our case. The standard reflection had an intensity of ~4000 counts in 40 sec, so that $p \approx 0.02$. The standard deviations and thus the weights were changed by changing the value of p. A trial value of $p = 0.10$ ultimately gave satisfactory weights. In practice, the new standard deviations were obtained by adding $0.0095F_o^4$ to $\sigma^2(F_o^2)$ and converting back to $\sigma(F_o)$.

Refinement with the new weights produced several parameter changes of the order of a standard deviation. A weighting analysis showed that the average value of $\Sigma w\Delta^2$ was 0.47 for the 500 strongest reflections and 0.44 for the 800 weaker reflections. Thus, the new weights represented a significant improvement over the weights previously used. A further indication that the new weighting scheme represented an improvement was given by the decrease in the differences between chemically equivalent dimensions.

After dropping the 611 reflection, since very poor agreement between F_o and F_c indicated a serious error in the measurement, the refinement converged in two cycles to $R_1 = 0.073$, $R_2 = 0.076$. No parameter shift was greater than 0.1 standard deviation on the last cycle. The standard deviation on an observation of unit weight was 0.70. The observed and calculated structure factors (kF_o and F_c) are given in Table I. The positional parameters and temperature factors and the estimated standard deviations (esd's) are given in Table II.

A final difference Fourier synthesis, based on all the observed data, showed that there was still a peak 2 $e^-/Å^3$ high at the ytterbium position; thus, the scattering factors for neutral ytterbium and oxygen did not greatly improve the appearance of the map. There were also several peaks on the order of 1 $e^-/Å^3$ high (~20% of the height of a peak due to carbon). They were not in the neighborhoods of any of the 29 atoms previously found, and they did not generally correspond to plausible hydrogen atom positions. We assume these to be the result of random errors in the data.

TABLE II

ATOMIC PARAMETERS OF $Yb(acac)_3 \cdot Hacim$ WITH ESTIMATED STANDARD DEVIATIONS

Atom	*x*	*y*	*z*	*B*, Å^2
Yb	0.25711 (9)	0.13549 (18)	0.12833 (8)	*a*
O(1)	0.3426 (11)	0.1978 (24)	0.0419 (12)	3.8 (5)
O(2)	0.3574 (12)	0.0021 (26)	0.1776 (12)	4.4 (5)
O(3)	0.1964 (12)	0.1178 (29)	−0.0071 (12)	4.9 (5)
O(4)	0.1492 (13)	0.2569 (25)	0.1290 (14)	4.6 (6)
O(5)	0.2034 (11)	−0.0965 (27)	0.1238 (12)	4.6 (5)
O(6)	0.2400 (11)	0.1035 (27)	0.2633 (12)	4.8 (5)
O(7)	0.3009 (10)	0.3633 (29)	0.1855 (11)	3.5 (4)
N(1)	0.2958 (13)	0.4037 (33)	0.3567 (15)	4.4 (7)
C(1)	0.4494 (19)	0.2799 (43)	−0.0164 (22)	5.7 (10)
C(2)	0.4144 (20)	0.1823 (42)	0.0486 (22)	4.9 (9)
C(3)	0.4569 (18)	0.0896 (42)	0.1113 (21)	4.9 (9)
C(4)	0.4279 (20)	0.0059 (42)	0.1736 (20)	4.4 (8)
C(5)	0.4818 (20)	−0.0930 (53)	0.2335 (23)	7.5 (11)
C(6)	0.1040 (20)	0.0444 (47)	−0.1295 (23)	6.9 (11)
C(7)	0.1228 (19)	0.1101 (44)	−0.0384 (20)	5.0 (8)
C(8)	0.0675 (19)	0.1702 (45)	0.0041 (22)	5.8 (9)
C(9)	0.0848 (20)	0.2464 (38)	0.0867 (22)	4.2 (9)
C(10)	0.0134 (20)	0.3132 (46)	0.1185 (22)	6.6 (10)
C(11)	0.1235 (17)	−0.3213 (42)	0.1380 (19)	4.8 (9)
C(12)	0.1645 (17)	−0.1763 (40)	0.1704 (20)	3.9 (8)
C(13)	0.1592 (16)	−0.1216 (45)	0.2543 (19)	4.1 (7)
C(14)	0.1978 (18)	0.0067 (41)	0.2945 (19)	3.9 (8)
C(15)	0.1989 (19)	0.0300 (47)	0.3932 (22)	6.2 (10)
C(16)	0.3294 (16)	0.5797 (39)	0.1045 (19)	4.2 (8)
C(17)	0.3164 (15)	0.5074 (35)	0.1890 (16)	1.8 (6)
C(18)	0.3230 (14)	0.6057 (36)	0.2582 (16)	2.6 (7)
C(19)	0.3116 (16)	0.5528 (37)	0.3388 (18)	2.8 (7)
C(20)	0.3211 (15)	0.6645 (38)	0.4157 (17)	3.5 (7)

[a] $\beta_{11} = 0.00340$ (7), $\beta_{22} = 0.00879$ (25), $\beta_{33} = 0.00180$ (6), $\beta_{12} = -0.00104$ (19), $\beta_{13} = 0.00128$ (5), and $\beta_{23} = 0.00002$ (17).

Discussion of the Structure

Figure 1 shows a stereographic view of two glide-related molecules of $Yb(acac)_3 \cdot Hacim$, and Figure 2 shows a projection of part of the structure onto (100). The bond lengths and angles of the Yb–acac groupings are given in Table III. Figure 3 presents the average dimensions of an ytterbium–acetylacetonate ring. The dimensions of the ytterbium acetylacetonimine group are shown in Figure 4.

Each ytterbium atom is bonded to seven oxygen atoms, six from the three acetylacetonate ions and one from the acetylacetonimine group. The shortest Yb–N distance in the structure is 4.27 Å (between Yb and N(1) in the same molecule); thus, coordination of nitrogen to ytterbium does not occur. The average metal–oxygen distance of 2.23 (2) Å (not including the acetylacetonimine oxygen atom) is not significantly shorter than the distance of 2.25 Å predicted by Lingafelter and Braun in their study of 16 metal acetyl-

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[11] *E.g.*, see K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, **7**, 1362 (1968).

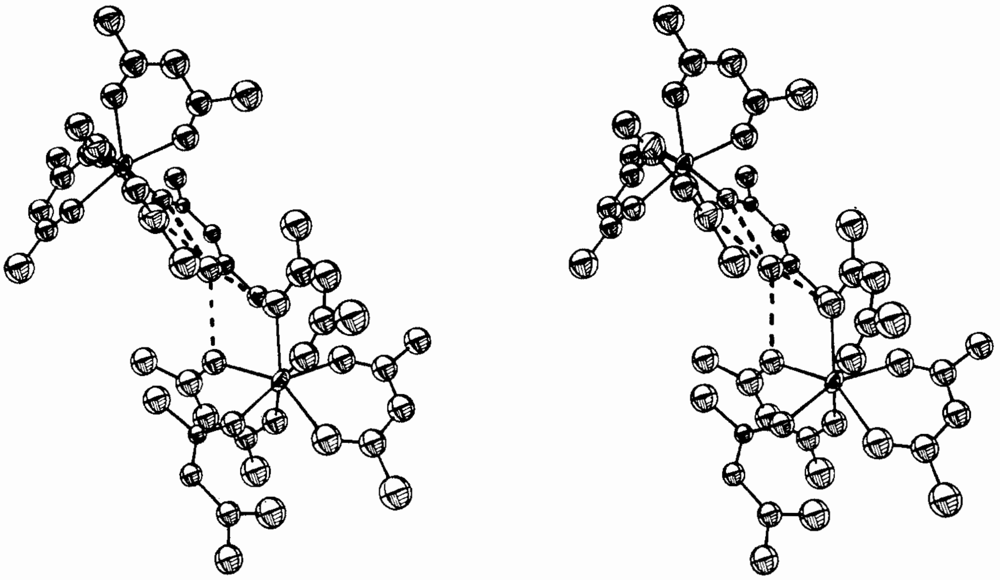

Figure 1.—Stereoview of two glide-related molecules of Yb(acac)$_3$·Hacim, showing the relative orientation of the thermal ellipsoid of Yb. Dashed lines indicate possible hydrogen bonds.

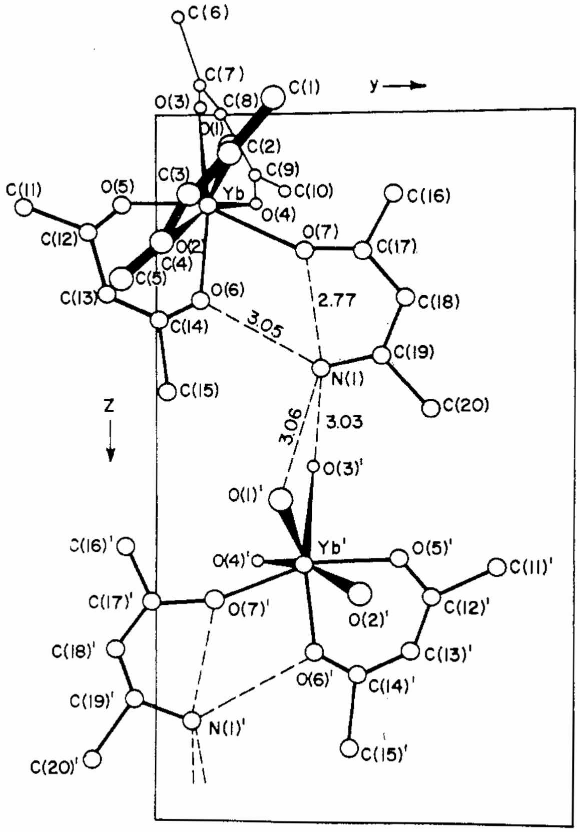

Figure 2.—Projection of part of the Yb(acac)$_3$·Hacim structure onto (100). Primed atoms are related to the unprimed atoms by the glide plane. Possible hydrogen bonds are shown by the dotted lines (esd 0.03 Å). The carbon atoms on the O(1)′–O(2)′ and O(3)′–O(4)′ rings have been omitted for clarity.

TABLE III

INTRAMOLECULAR DISTANCES AND ANGLES FOR THE Yb–acac GROUPINGS[a,b]

	Lengths, Å		
Yb–O(1)	2.29 (2)	C(2)–C(3)	1.40 (4)
Yb–O(2)	2.18 (2)	C(3)–C(4)	1.39 (4)
Yb–O(3)	2.27 (2)	C(7)–C(8)	1.39 (4)
Yb–O(4)	2.21 (2)	C(8)–C(9)	1.46 (4)
Yb–O(5)	2.20 (2)	C(12)–C(13)	1.43 (4)
Yb–O(6)	2.24 (2)	C(13)–C(14)	1.40 (4)
O(1)–O(2)	2.71 (3)	C(1)–C(2)	1.54 (4)
O(3)–O(4)	2.73 (3)	C(4)–C(5)	1.51 (4)
O(5)–O(6)	2.80 (3)	C(6)–C(7)	1.54 (4)
		C(9)–C(10)	1.57 (4)
O(1)–C(2)	1.29 (3)	C(11)–C(12)	1.49 (4)
O(2)–C(4)	1.29 (3)	C(14)–C(15)	1.58 (4)
O(3)–C(7)	1.35 (3)		
O(4)–C(9)	1.25 (3)		
O(5)–C(12)	1.29 (3)		
O(6)–C(14)	1.28 (3)		
	Angles, Deg		
O(1)–Yb–O(2)	74.7 (7)	O(1)–C(2)–C(3)	123 (3)
O(3)–Yb–O(4)	75.0 (8)	O(2)–C(4)–C(3)	122 (3)
O(5)–Yb–O(6)	78.1 (8)	O(3)–C(7)–C(8)	123 (3)
		O(4)–C(9)–C(8)	124 (3)
Yb–O(1)–C(2)	134 (2)	O(5)–C(12)–C(13)	119 (3)
Yb–O(2)–C(4)	138 (2,	O(6)–C(14)–C(13)	128 (3)
Yb–O(3)–C(7)	131 (2)		
Yb–O(4)–C(9)	135 (2)	C(1)–C(2)–C(3)	123 (3)
Yb–O(5)–C(12)	137 (2)	C(3)–C(4)–C(5)	117 (3)
Yb–O(6)–C(14)	129 (2)	C(6)–C(7)–C(8)	122 (3)
		C(8)–C(9)–C(10)	113 (3)
O(1)–C(2)–C(1)	114 (3)	C(11)–C(12)–C(13)	119 (3)
O(2)–C(4)–C(5)	120 (3)	C(13)–C(14)–C(15)	119 (3)
O(3)–C(7)–C(6)	115 (3)		
O(4)–C(9)–C(10)	123 (3)	C(2)–C(3)–C(4)	125 (3)
O(5)–C(12)–C(11)	122 (3)	C(7)–C(8)–C(9)	122 (3)
O(6)–C(14)–C(15)	113 (3)	C(12)–C(13)–C(14)	125 (3)

[a] Chemically equivalent dimensions are grouped together. [b] The standard deviations are those estimated by ORFFE.

acetonates.[12,13] The Yb–O(7) (Hacim) distance of 2.24 (2) Å is the same, within experimental error, as the other Yb–O distances. The average O–O separation in the acetylacetonate groups (the ligand "bite") is 2.75 (3) Å which is the same as the distance found in other ytterbium acetylacetonates[14,15] but somewhat shorter

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[12] E. C. Lingafelter and R. L. Braun, *J. Amer. Chem. Soc.*, **88**, 2951 (1966).

[13] The ionic radius of ytterbium has been taken as 0.86 Å for this calculation.

than the distance of 2.82 Å predicted by Lingafelter and Braun.[12]

The acetylacetonimine group behaves as a monodentate ligand. The "dangling end" of the Hacim is the NH_2 group, which takes part in hydrogen bonding to link the molecules in chains parallel to (100). The planarity of the Hacim molecule (average deviation of the atoms from the unweighted least-squares plane is 0.006 Å) strongly suggests that one of the hydrogen atoms of the NH_2 group is hydrogen bonded to O(7) to give a cyclic molecule (the N(1)–O(7) distance is 2.77 Å; the C(19)–N(1)–O(7) angle is 82°[16,17]). The other hydrogen atom is bonded to either O(1)′ or O(3)′, where the primed atoms are related to unprimed atoms by the glide plane. The N(1)–O(1)′ and N(1)–O(3)′ distances of 3.06 (3) and 3.03 (3) Å and the C(19)–N(1)–O(1)′ and C(19)–N(1)–O(3)′ angles of 116 and 112° are in accord with other known N–H···O hydrogen-bonding parameters.[17] This system of hydrogen bonding is probably the reason that $Yb(acac)_3 \cdot Hacim$ recrystallizes unchanged from acetylacetone; the intermolecular hydrogen-bonding interaction should make $Yb(acac)_3 \cdot Hacim$ less soluble than $Yb(acac)_3 \cdot Hacac$.[18] The latter compound cannot undergo such extensive hydrogen bonding since there is only one proton in the enol form which can form strong hydrogen bonds.

Of interest is the fact that the Yb–O bonds are longer when the oxygens are involved in hydrogen bonding to the NH_2 group. The distances from Yb to the hydrogen-bonded oxygen atoms O(1), O(3), O(6), and O(7) range from 2.24 to 2.29 Å, with an average value of 2.257 (12) Å. The distances from Yb to O(2), O(4), and O(5), which are not involved in hydrogen bonding, range from 2.18 to 2.21 Å, with an average of 2.197 (9) Å. The difference between the hydrogen-bonded and nonhydrogen-bonded Yb–O distances is 0.06 (2) Å. While this difference may not seem significant for a single structure, this regularity has been observed in every known structure of rare earth β-diketonates.[19] It thus seems to be a real and significant phenomenon.

There is a minor problem with the structural assignment given for the Hacim group, and that is that the "double bond" C(18)–C(19) seems to be longer than the "single bond" C(17)–C(18) (see Figure 4). The pertinent distances are 1.41 ± 0.03 and 1.38 ± 0.03 Å, respectively. These values are not significantly different, however, and are not unreasonable in view of the fact that electron delocalization in the conjugated double-bond system, coupled with intramolecular hydrogen bonding between O(7) and N(1), is expected to equalize these bond lengths.

The coordination polyhedron about the ytterbium atom is best described as a capped trigonal prism (Figure 5), with one of the acetylacetonate oxygens O(6) as the capping atom. The angles of the coordination

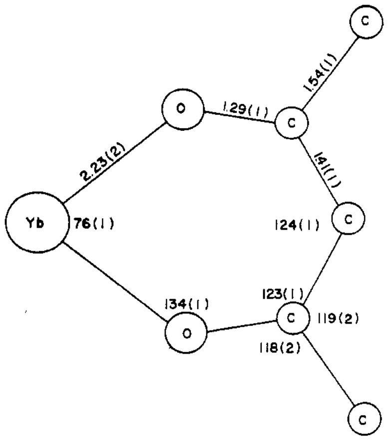

Figure 3.—Average dimensions of an ytterbium–acetylacetonate ring. The standard deviations are calculated for the mean from the formula $\sigma = [\Sigma(\bar{x} - x_i)^2/n(n - 1)]^{1/2}$, where $\bar{x}$ is the mean, x_i is the individual measurement, and n is the number of measurements.

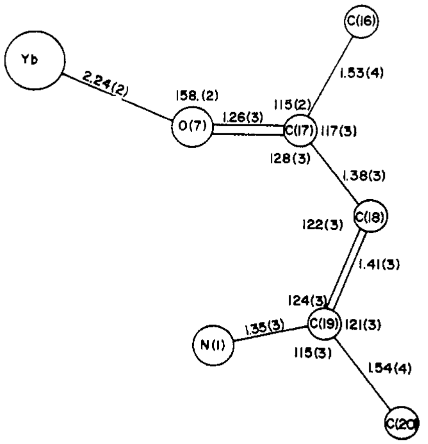

Figure 4.—Dimensions of the ytterbium–acetylacetonimine grouping. The esd's are those estimated by ORFFE.

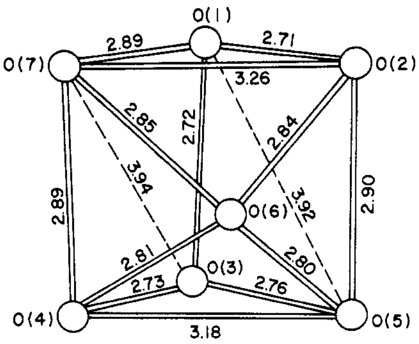

Figure 5.—The coordination polyhedron of $Yb(acac)_3 \cdot Hacim$. The dashed lines between O(1)–O(5) and O(3)–O(7) indicate the slight folding of the O(1)–O(2)–O(3)–O(15) and O(1)–O(3)–O(4)–O(7) faces. The esd's for the O–O distances are 0.03 Å.

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[14] J. A. Cunningham, D. E. Sands, W. F. Wagner, and M. F. Richardson, *Inorg. Chem.*, **8**, 22 (1969).

[15] E. D. Watkins, II, J. A. Cunningham, T. Phillips, II, D. E. Sands, and W. F. Wagner, *ibid.*, **8**, 29 (1969).

[16] A bifurcated hydrogen bond may exist here, as the N(1)–O(6) distance of 3.05 Å is short enough for hydrogen bonding to occur,[17] and the C(19)–N(1)–O(6) angle of 139° gives a favorable geometry to the hydrogen bond. (The O(6) atom lies 0.48 Å from the mean plane of the Hacim molecule.)

[17] G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, p 289.

[18] We have not examined the question of whether or not $Yb(acac)_3 \cdot Hacac$ actually exists in acetylacetone solution, but it is reasonable from the mass action principle that Hacim is displaced from the coordination sphere.

[19] M. F. Richardson, to be submitted for publication.

TABLE IV

ANGLES (DEG) IN THE COORDINATION POLYHEDRON[a]

O(1)–O(5)–O(3)	43.9	O(1)–O(7)–O(3)	43.6
O(3)–O(1)–O(5)	44.8	O(1)–O(3)–O(7)	47.1
O(1)–O(3)–O(5)	91.3	O(3)–O(1)–O(7)	89.2
O(1)–O(5)–O(2)	43.7	O(3)–O(7)–O(4)	43.7
O(2)–O(1)–O(5)	47.7	O(4)–O(3)–O(7)	47.2
O(1)–O(2)–O(5)	88.6	O(3)–O(4)–O(7)	89.1
O(1)–O(7)–O(2)	51.9	O(3)–O(4)–O(5)	55.2
O(1)–O(2)–O(7)	57.0	O(3)–O(5)–O(4)	54.1
O(2)–O(1)–O(7)	71.0	O(4)–O(3)–O(5)	70.7
O(4)–O(5)–O(6)	55.6	O(2)–O(6)–O(7)	69.9
O(5)–O(4)–O(6)	55.3	O(2)–O(7)–O(6)	54.9
O(4)–O(6)–O(5)	69.1	O(6)–O(2)–O(7)	55.2
O(4)–O(6)–O(7)	61.6	O(2)–O(5)–O(6)	59.7
O(6)–O(4)–O(7)	59.9	O(2)–O(6)–O(5)	62.0
O(4)–O(7)–O(6)	58.5	O(5)–O(2)–O(6)	58.3
O(2)–O(1)–O(3)	92.4	O(1)–O(7)–O(4)	87.3
O(2)–O(5)–O(3)	87.6	O(1)–O(3)–O(4)	94.3

[a] Standard deviations (estimated by ORFFE) are 0.5–0.9°.

polyhedron are given in Table IV, and the distances are given in Figure 5. A capped trigonal prism has been found for other seven-coordinate ytterbium chelates.[14,15] Furthermore, the polyhedron is quite similar to that of $Y(bzac)_3 \cdot H_2O$[20] (bzac is the benzoylacetonate anion), although Cotton and Legzdins prefer to call the polyhedron a capped octahedron since the water molecule lies on a pseudo-threefold axis of the complex. The choice of capped trigonal prism in the present case is at least partly dictated by the nearly planar quadrilaterals O(1)–O(2)–O(5)–O(3) and O(1)–O(3)–O(4)–O(7). The former quadrilateral is folded 3.1 (1.2)° about the O(1)–O(5) diagonal; the latter, 3.4 (1.3)° about the O(3)–O(7) diagonal. Description in terms of the tetragonal base–trigonal base polyhedron[21] is also possible, with either the O(1)–O(2)–O(5)–O(3) or the O(1)–O(3)–O(4)–O(7) quadrilaterals as the tetragonal base and the O(4)–O(6)–O(7) or O(2)–O(5)–O(6) triangles as the trigonal base.

The acetylacetonate groups are nearly planar; the average deviation of the carbon and oxygen atoms from the unweighted least-squares planes are 0.016, 0.035, and 0.053 Å for the groups containing O(1)–O(2), O(3)–O(4), and O(5)–O(6), respectively. The distances of the ytterbium atom from these planes are 0.37, 0.58, and 0.28 Å, respectively. Thus, each of the metal–acetylacetonate rings is folded about the O–O line. The ring containing O(1)–O(2) is folded 12.1° toward the acetylacetonimine group. The O(3)–O(4) ring is folded 19.5° toward the O(5)–O(6) ring and away from acetylacetonimine. The O(5)–O(6) ring is folded 10.1° toward the O(3)–O(4) ring.

Other than the hydrogen bonds, the shortest intermolecular contacts within a chain are: O(3)–C(15)′ = 3.40 (3), C(2)–N(1)′ = 3.52 (3), C(1)–N(1)′ = 3.53 (3), C(6)–N(1)′ = 3.54 (3), C(7)–C(15)′ = 3.60 (3), O(3)–C(20)′ = 3.64 (3), and O(1)–C(20)′ = 3.68 (3) Å, where the primed atoms are related to the unprimed atoms by the glide plane. All other contacts within the chain are greater than 3.70 (4) Å. The shortest contacts between chains are: C(12)–C(18)″ = 3.52 (4), O(5)–C(16)″ = 3.62 (3), C(11)–O(4)″ = 3.64 (3), and C(11)–C(10)″ = 3.69 (3) Å, where the primed atoms are related to the unprimed atoms by a unit translation along *y*. All other contacts are greater than 3.70 (4) Å.

Acknowledgments.—We thank Dr. James A. Cunningham for taking the Weissenberg photographs and for assistance in the beginning stages of this work and Mr. Ben Blyton for obtaining the stereographic projection. We also thank the University of Kentucky Computing Center for running some of the minor programs.

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(20) F. A. Cotton and P. Legzdins, *Inorg. Chem.*, **7**, 1777 (1968).

(21) See E. L. Muetterties and C. M. Wright, *Quart. Rev. Chem. Soc.*, **21**, 109 (1967), for a review of the stereochemistry of higher coordination numbers.