0.79 and 1.33 Å from the water oxygen atom. Coordinates of hydrogen atoms that were calculated assuming the known geometry of the water molecule (H–O distance, 0.958 Å; H–O–H angle, 104.5°)[23] and the observed coordinates are shown in Table XIII with the calculated and observed geometries. It appears quite certain that the water molecules are hydrogen bonded to oxygen atoms of the adjacent ligands. The hydrogen bonding contributes to the strength of the linkage between the two trinuclear units, since the two oxygen atoms to which each water molecule is hydrogen bonded are not in the same trinuclear unit.

The geometry of the 1,1,1-trifluoroacetylacetonato ligands is quite close to that given as average for acetylacetonato ligands by Lingafelter and Braun.[24] A small but significant reduction of the C*n*1–C*n*2–O*n*1 angle near the CF_3 group is apparent with a concomitant opening of the O*n*1–C*n*2–C*n*3 angle to maintain the planarity of the chelate ring. The reason for this distortion is not clear, and, unfortunately, there have been no other crystal structure determinations of this ligand for comparison.

The structure of $Ni_6(CF_3COCHCOCH_3)_{10}(OH)_2(H_2O)_2$ is radically different from any other structure found for polymeric acetylacetonates, in that it contains closed triangles of metal atoms. The type of aggregation of octahedral units found in this structure is, of course, only possible in the presence of a moiety which may simultaneously bridge three metal atoms, a role played by the hydroxyl groups in the present case.

Table XIII

Calculated and Observed Positions of Water Hydrogen Atoms

Atom	*X/a* Calcd	Obsd	*Y/b* Calcd	Obsd	*Z/c* Calcd	Obsd
H2a	−0.016	−0.020	−0.104	−0.092	0.066	0.067
H2b	0.116	0.118	0.069	0.075	−0.025	−0.010

Angle	Value, deg Obsd	Calcd	Distance	Value, Å Obsd	Calcd
O2–H2a–O41	156.8	143.5	O2–H2a	0.79	0.958
O2–H2b–O51	176.6	147.8	O2–H2b	1.34	0.958
			H2a–O41	1.95	1.87
			H2b–O51	1.50	1.76

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[23] W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, Inc., New York, N. Y., 1968.

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

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The Crystal and Molecular Structure of Bis(benzoylacetonato)zinc Monoethanolate and X-Ray Data on Related Crystals[1a]

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The crystal structure of bis(benzoylacetonato)zinc monoethanolate has been determined by three-dimensional Fourier methods with the positional and anisotropic thermal parameters refined by least-squares methods to a conventional *R* factor of 0.12 based on 2989 independent nonzero reflections. The data were collected on multiple films by the equiinclination Weissenberg technique. The crystals are monoclinic, space group $P2_1/c$ with $a = 12.28 \pm 0.01$ Å, $b = 8.39 \pm 0.01$ Å, $c = 20.52 \pm 0.02$ Å, and $\beta = 100° 58' \pm 10'$. The density, as measured by flotation, is 1.40 ± 0.01 g/cm^3, in agreement with 1.39 ± 0.01 g/cm^3 calculated for four molecules of $(CH_3COCHCOC_6H_5)_2Zn \cdot C_2H_5OH$ (FW = 433.80 g/mol) in the unit cell. The coordination around the zinc ion is close to square pyramidal with the four chelate oxygen atoms forming the base of the pyramid and being ~1.99 Å from Zn and the ethanol oxygen atom being in the apical position at 2.06 Å from Zn. The benzene rings in each ligand are *cis* to one another, and the molecules are associated in loosely bound pairs in the lattice. Each zinc ion can be considered as forming a weak bond (3.34 Å) to the middle carbon atom of a chelate ring of the second molecule, and this carbon atom is slightly raised (0.078 Å) from the plane of its chelate ring toward the zinc atom to which it is coordinated. These pairs are linked by O–H---O hydrogen bonding to produce stacks of molecules along the *b* direction. The unit cell parameters and space groups of bis(benzoylacetonato)zinc monohydrate and of bis(3-phenylacetylacetonato)zinc monohydrate are also reported; a powder diffraction pattern of bis(benzoylacetonato)magnesium monohydrate suggests that it is isostructural with the corresponding zinc compound. It seems likely that these three complexes also contain five-coordinate metal ions.

Introduction

The metal complexes formed by the acetylacetonato (acac ≡ $CH_3COCHCOCH_3^-$) anion and its derivatives have often shown interesting variation in stereochemistry.

The crystal structures of the 2:1 complexes formed by the benzoylacetonato (benzac ≡ 1-phenyl-1,3-butanedionato ≡ $CH_3COCHCOC_6H_5^-$) anion with the transition metal ions copper,[2] palladium,[3] and vanadyl[4] show several features of special interest; in particular, the phenyl groups are *trans* in the copper and

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[1] (a) Supported by ARPA Contract SD-131 through the Materials Research Laboratory at the University of Illinois, USPH Grant No. GM 12470-04, a predoctoral NDEA Title IV fellowship awarded to N. D. C., and a National Institute of General Medical Sciences senior fellowship (1966–1967) awarded to R. L. B. (b) Taken in part from the Ph.D. thesis of this author to be presented to the University of Illinois, 1969. (c) Alfred P. Sloan Research Fellow.

[2] P.-K. Hon, C. E. Pfluger, and R. L. Belford, *Inorg. Chem.*, **5**, 516 (1966).

[3] P.-K. Hon, C. E. Pfluger, and R. L. Belford, *ibid.*, **6**, 730 (1967).

[4] P.-K. Hon, R. L. Belford, and C. E. Pfluger, *J. Chem. Phys.*, **43**, 1323 (1965).

palladium complexes but *cis* in the vanadium compound. We therefore decided to determine the crystal structure of a zinc or magnesium benzac complex, in which there are no crystal field effects to influence the molecular structure. Moreover, we found[5] that a small percentage of the molecules in the crystal Zn(benzac)$_2\cdot C_2H_5OH$ can be replaced by those of the corresponding vanadyl complex, making the zinc lattice an ideal host in which to study the epr spectrum of VO(benzac)$_2$. As the information obtainable from the epr data is greatly enhanced if the structure of the host lattice is known, there was an added incentive to examine the structure of Zn(benzac)$_2\cdot C_2H_5OH$. In the early stages of this work, we prepared and surveyed the unit cell parameters and space groups of the similar complexes Zn(benzac)$_2\cdot H_2O$ and Zn(3-phenacac)$_2\cdot H_2O$ [3-phenacac $\equiv$ 3-ϕacac $\equiv$ 3-phenylacetylacetonate anion $\equiv$ 3-phenyl-2,4-pentanedionato $\equiv$ $CH_3COC(C_6H_5)COCH_3^-$] and Mg(benzac)$_2\cdot H_2O$. This paper reports cell data on these potentially pentacoordinate molecules and the crystal structure of Zn(benzac)$_2\cdot C_2H_5OH$ determined by three-dimensional X-ray techniques.

Experimental Section

Preparation of Compounds.—Zn(3-phenacac)$_2$ was prepared by adding an ethanolic solution of the ligand to an aqueous suspension of freshly precipitated zinc hydroxide.[6] Crystallization from 95% ethanol at room temperature yielded colorless single crystals suitable for X-ray work. The analysis was consistent with a monohydrate. *Anal.* Calcd for $C_{22}H_{22}O_4Zn\cdot H_2O$: C, 60.91; H, 5.58. Found: C, 60.81; H, 5.79.

Zn(benzac)$_2$ was prepared in the same manner as above. Crystallization at 5° from 95% ethanol yielded colorless needles which gave an analysis consistent with the monoethanolate adduct Zn(benzac)$_2\cdot C_2H_5OH$. Crystals of suitable size for single-crystal X-ray analysis were also obtained from this recrystallization. *Anal.* Calcd for $C_{20}H_{18}O_4Zn\cdot C_2H_5OH$: C, 60.91; H, 5.58. Found: C, 60.89; H, 5.58.

Slow crystallization of Zn(benzac)$_2$ from 95% ethanol at room temperature yielded colorless crystals which analyses indicate to be the monohydrate and whose sizes were suitable for single-crystal X-ray investigation. *Anal.* Calcd for $C_{20}H_{18}O_4Zn\cdot H_2O$: C, 59.20; H, 4.97. Found: C, 58.90; H, 4.99.

On occasion, room-temperature crystallization produced the monoethanolate compound. Zn(benzac)$_2\cdot C_2H_5OH$ can readily be distinguished from the corresponding monohydrate compound by solution nmr. The proton nmr of Zn(benzac)$_2\cdot C_2H_5OH$ in $CDCl_3$ exhibits quartet and triplet resonances (attributed to the ethanol molecule CH_2–CH_3 coupling) at 3.71 and 1.22 ppm, respectively, downfield from TMS.

Mg(benzac)$_2$ was prepared by the method used above in the preparation of the zinc complexes. Recrystallization from 95% ethanol yielded a product which analysis indicated to be the monohydrate; however, in all crystallization attempts, no single crystals were isolated which were large enough for X-ray analysis. *Anal.* Calcd for $C_{20}H_{18}O_4Mg\cdot H_2O$: C, 65.86; H, 5.53, Found: C, 65.81; H, 5.54.

Unit Cell Dimensions and Space Groups of the Complexes.—The information obtained for single crystals of the complexes is listed in Table I. The unit cell dimensions were determined from precession and rotation photographs using Mo Kα (λ 0.7107 Å) and Cu Kα (λ 1.5418 Å) radiation, respectively. The space groups were uniquely determined by noting systematic extinctions on precession and Weissenberg photographs. Densities were measured by flotation in aqueous potassium iodide solutions.

TABLE I

UNIT CELL DATA OF THE ZINC(II) COMPLEXES

	Zn(3-ϕacac)$_2\cdot H_2O$	Zn(benzac)$_2\cdot$EtOH	Zn(benzac)$_2\cdot H_2O$
Formula	$C_{22}H_{24}O_5Zn$	$C_{22}H_{24}O_5Zn$	$C_{20}H_{20}O_5Zn$
F_w(g/mol)	433.80	433.80	405.75
a(Å)	13.50 ± 0.01	12.28 ± 0.01	23.06 ± 0.03
b(Å)	7.89 ± 0.01	8.39 ± 0.01	7.48 ± 0.01
c(Å)	20.51 ± 0.01	20.52 ± 0.02	22.03 ± 0.01
β	105°45′ ± 10′	100°58′ ± 10′	– – –
V(Å^3)	2103	2076	3800
Space Group	$P2_1/c$	$P2_1/c$	$P2_12_12_1$
$\rho_{Exptl.}$(g/cm^3)	1.39_1	1.39_7	1.41_0
$\rho_{Calc.}$(g/cm^3)	1.369	1.388	1.418
Z	4	4	8

A Debye–Scherrer powder diffraction pattern of Mg(benzac)$_2\cdot H_2O$ was very similar to that of Zn(benzac)$_2\cdot H_2O$, suggesting the two complexes to be isostructural.

Intensity Data.—The crystal [dimensions (1.00 ± 0.05) × (0.225 ± 0.005) × (0.175 ± 0.005) mm measured along b, a, and c^*, respectively] used in the three-dimensional X-ray study of Zn(benzac)$_2\cdot C_2H_5OH$ was mounted in a thin-walled glass capillary and aligned in the direction of the b axis. The well-developed faces were {001} and {100}. The diffraction layers $h0l$–$h7l$ were recorded on multiple films by means of an equiinclination Weissenberg camera with Cu Kα radiation. The intensities of 2898 independent reflections (representing 80% of the possible reflections with $\sin\theta < 0.95$) were estimated visually and were corrected in the usual way for Lorentz and polarization factors and for absorption[7] by the crystal. The linear absorption coefficient μ(Cu Kα) is 19.7 cm^{-1}.[8] The transmission coefficients to be applied to the intensities had a maximum range of 0.60–0.73.

Structure Determination and Refinement of Zn(benzac)$_2\cdot C_2H_5OH$.—The cell data (Table I) and the space group P2$_1$/c require one zinc atom per asymmetric unit. A three-dimensional Patterson synthesis was computed and the Harker line $P(0, v, {}^1/_2)$ suggested that the zinc atom lay close to $y = {}^1/_4$. The x and z coordinates of this atom could not be assigned unambiguously as the Harker section $P(u, {}^1/_2, w)$ showed vectors corresponding to two possible zinc positions. Since we anticipated problems from the heavy-atom method due to pseudosymmetry and the uncertainty in the zinc position, we employed the symbolic addition procedure for centrosymmetric space groups.[9,10]

Within the total data seven reflections were assigned letter symbols (Table II) on the basis of high E values and a large number of Σ_2-type interactions. Of the group of 357 reflections with $E > 1.4$, 356 were given signs. One combination of signs produced a much smaller number of contradictions than the others (Table II) and this was used to generate an E map. The zinc atom and one chelate ligand molecule could be seen quite clearly on this map and the zinc position was consistent with one of the solutions to the Patterson synthesis. A Fourier map, generated

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[5] M. A. Hitchman and R. L. Belford, *Inorg. Chem.*, **8**, 958 (1969).

[6] D. P. Graddon and D. G. Weeden, *Australian J. Chem.*, **16**, 980 (1963).

[7] For absorption corrections, we used a modification of a program GNABS, suitable for a crystal bound by plane faces. The program was written by C. W. Burnham, Geophysical Laboratory, Carnegie Institute, Washington, D. C.

[8] Calculated from mass absorption coefficients for Cu Kα radiation, "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 162.

[9] This method is reviewed by J. Karle and I. L. Karle, *Acta Cryst.*, **21**, 849 (1966).

[10] The programs used were written by E. B. Fleischer, A. L. Stone, and R. B. K. Dewar of the University of Chicago. One of these (FAME) incorporates statistical tests and calculates normalized structure amplitudes (E's), while another (MAGIC) uses the Karle–Hauptman Σ_2 relationship and the symbolic addition procedure to determine the signs of the E's from a basic set of reflections which are given letter symbols. The phased E's are then used as coefficients in a Fourier synthesis.

TABLE II

SIGN-DETERMINING SYMBOL ASSIGNMENTS

h	*k*	*l*	*E*	Symbol[a]	Number of Interactions	Signs[b]	
						Set 1	Set 2
1	2	−2	2.70	A	35	positive to assign origin	
4	3	−4	5.86	B	38	−	+
2	3	−7	2.68	C	16	positive to assign origin	
1	6	3	2.88	D	14	positive to assign origin	
9	3	0	3.96	E	16	−	+
3	3	−7	3.09	F	21	−	+
2	4	−2	3.72	G	14	not used	
1	4	−2	3.53	H	11	−	−
Percentage of Contradictions among Symbol Equivalences[c]:						0.07	28

[a] From the top twenty-five reflections (and their symmetry equivalents) with the highest E-values, eight reflections were chosen of appropriate parity which had the largest product of E times the number of interactions in the Σ_2 formula. These eight reflections were assigned the symbols A through H. The reflection 2 4 −2 was not used as a starting reflection because of its even-even-even parity. [b] These are the sign-combinations assigned to the set of starting symbols which were used to generate the signs of the remainder of the 356 reflections by the symbolic addition procedure. Only the first two combinations out of the possible sixteen (4^2) are given since the one with the lowest number of contradictions resulted in a structural solution. [c] The number of contradictions in sign-determination is expressed as a percentage of the total number of symbol equivalences found for the group of 356 reflections out of the 357 with $E > 1.40$.

TABLE III

FINAL ATOMIC POISITIONAL PARAMETERS IN FRACTIONS OF THE UNIT CELL EDGE[a]

Atom	*x*	*y*	*z*
Zn.	.4053(1)	.2304(2)	.4515(1)
O1	.3373(6)	.0251(8)	.4817(4)
O2	.3310(5)	.3934(8)	.4987(3)
O3	.5383(5)	.2488(10)	.5212(3)
O2′	.2973(6)	.2908(9)	.3696(3)
O3′	.4966(6)	.1154(9)	.3959(4)
C1	.2555(11)	.0119(17)	.5175(8)
C2	.1506(11)	.0710(22)	.4879(8)
C3	.6652(9)	.3204(13)	.6228(6)
C4	.5545(9)	.3329(13)	.5771(5)
C5	.4727(8)	.4407(15)	.5916(5)
C6	.3676(8)	.4566(11)	.5552(5)
C7	.2820(8)	.5567(12)	.5784(5)
C8	.3103(10)	.6419(13)	.6405(6)
C9	.2232(11)	.7250(17)	.6607(6)
C10	.1179(12)	.7292(17)	.6237(8)
C11	.0908(11)	.6503(17)	.5612(8)
C12	.1757(9)	.5610(15)	.5414(6)
C3′	.5467(12)	−.0295(16)	.3078(6)
C4′	.4669(10)	.0817(13)	.3361(6)
C5′	.3701(9)	.1291(14)	.2927(6)
C6′	.2915(8)	.2303(13)	.3118(5)
C7′	.1895(8)	.2801(13)	.2633(5)
C8′	.1723(11)	.2257(16)	.1963(6)
C9′	.0728(13)	.2677(21)	.1544(6)
C10′	−.0064(12)	.3529(21)	.1748(8)
C11′	.0158(12)	.4151(21)	.2414(8)
C12′	.1126(10)	.3724(17)	.2846(7)

[a] Origin as in "International Tables for X-Ray Crystallography". Estimated standard deviations ($\times 10^4$) in parentheses.

using this zinc position, agreed very well with the E map, except that it contained a pseudomirror plane generated by the proximity of the zinc atom to the plane $y = {}^1/_4$. Eight atoms (six carbons and two oxygens) which were well resolved on both maps and had y coordinates significantly different from ${}^1/_4$ were chosen and a second Fourier map was generated using these and the zinc atom. This effectively destroyed the pseudosymmetry and revealed the positions of all of the atoms (other than hydrogen) except for the ethanol molecule. The carbon and oxygen atoms in the ethanol molecule were revealed on the next Fourier map, which was based on all the other atomic positions. The R factor ($R = \Sigma \left||F_o| - |F_c|\right|/\Sigma|F_o|$) at this stage was 0.37.

The structure was refined by least-squares methods in which all reflections were weighted[11] and the quantity minimized was $\Sigma w\left||F_o| - |F_c|\right|^2$. Four cycles of full-matrix refinement using isotropic temperature factors produced values of $R = 0.16$ and $R_2 = 0.16$, where

$$R_2 = \left\{\frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma w|F_o|^2}\right\}^{1/2}$$

After adjustment of the interlevel scaling factors, such that $\Sigma F_o = \Sigma F_c$ for each level, anisotropic temperature factors were introduced for all of the atoms, and after four cycles of least-squares refinement, the final reliability factors were $R = 0.12$ and $R_2 = 0.12$.

The structure is too large to permit full-matrix anisotropic refinement on the computer available to us. Therefore, the structure was divided into parts for each cycle; each part contained 14 atoms. The first part consisted of the molecule excluding the atoms C6–C12 and C6′–C12′ and the second part consisted of the atoms C6–C12 and C6′–C12′. In the second full cycle of refinement the atoms C6′ and C6 were interchanged with the atoms C1 and C2. The roles of these atoms were then alternately interchanged in each succeeding full cycle. The parameter shifts for all of the atoms in the final cycle were less than 16% of the estimated standard deviations. A final difference Fourier map showed no negative peak larger than 20% of a typical carbon atom and no positive peak greater than 15% of a typical carbon atom.

The final atomic positions and temperature factors are shown in Tables III and IV, and the calculated and observed structure factors are listed in Table V. The calculated values of the unobserved reflections were in every case too small to indicate that they should have been observed, except for a few low-order reflections which were obscured by the beam stop.[12] The scattering

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(11) Using $\sqrt{w} = |F_o|/30.0$ when $|F_o| \leqslant 30.0$ and $\sqrt{w} = 30.0/|F_o|$ when $|F_o| > 30.0$.

(12) The following reflections were obscured by the beam stop: $k = 0$, $hl = 10, 02, 12$; $k = 1, hl = 10, 11, 01, 02, 1-1, 1-2$; $k = 2, hl = 01, 02, -11, -12, 10, 11$; $k = 3, hl = 10, 01, 1-1, 11$; $hkl = 041, 051, 061, 071$.

TABLE IV

FINAL ANISOTROPIC TEMPERATURE PARAMETERS ($\times 10^4$)[a]

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}	$B(\text{Å}^2)^b$
Zn	89(1)	158(2)	31(0)	42(3)	26(1)	3(2)	4.76(.05)
O1	87(7)	95(12)	57(3)	57(14)	69(8)	58(10)	4.6(.2)
O2	70(6)	155(13)	25(2)	69(14)	18(6)	5(8)	4.2(.2)
O3	67(5)	202(15)	34(2)	82(17)	11(5)	29(12)	4.8(.2)
O2′	99(6)	182(14)	22(2)	81(17)	3(6)	−22(9)	4.7(.2)
O3′	83(7)	150(14)	33(3)	71(15)	34(7)	3(10)	4.7(.2)
C1	94(12)	247(30)	76(7)	39(32)	87(16)	123(24)	7.7(.5)
C2	69(11)	400(40)	68(7)	78(36)	29(14)	−49(26)	8.3(.5)
C3	72(9)	157(21)	37(4)	0(22)	−11(9)	19(15)	5.0(.3)
C4	87(10)	112(18)	24(3)	21(22)	19(9)	5(13)	4.3(.3)
C5	63(8)	215(23)	24(3)	31(24)	12(8)	49(14)	4.2(.3)
C6	87(9)	89(17)	27(3)	33(21)	22(9)	12(12)	4.1(.3)
C7	69(9)	124(18)	29(3)	−18(22)	47(9)	19(14)	3.8(.3)
C8	142(13)	129(19)	28(4)	−3(27)	62(11)	10(14)	5.0(.3)
C9	122(12)	210(26)	39(4)	−1(35)	70(12)	11(19)	6.1(.3)
C10	122(13)	201(27)	55(5)	89(35)	86(14)	−7(22)	6.4(.4)
C11	99(12)	200(25)	61(6)	19(31)	41(14)	−23(22)	7.1(.4)
C12	68(10)	195(24)	46(4)	34(26)	27(11)	13(17)	5.3(.3)
C3′	157(15)	225(26)	35(4)	69(33)	52(13)	−51(17)	6.1(.4)
C4′	83(10)	126(20)	35(4)	−45(24)	55(11)	−23(15)	4.0(.3)
C5′	81(10)	144(20)	36(4)	24(24)	40(10)	−6(14)	4.1(.3)
C6′	84(8)	137(19)	29(3)	−56(24)	23(8)	12(14)	3.9(.3)
C7′	83(9)	142(19)	27(3)	25(24)	26(9)	4(14)	4.0(.3)
C8′	141(13)	188(24)	26(3)	−19(32)	3(11)	16(17)	6.0(.4)
C9′	148(15)	314(34)	32(4)	52(44)	12(13)	14(23)	7.6(.4)
C10′	123(14)	308(34)	41(5)	22(38)	−5(14)	68(22)	7.7(.5)
C11′	93(13)	364(38)	44(5)	25(37)	−1(13)	29(24)	7.2(.4)
C12′	82(11)	247(28)	43(5)	48(30)	36(12)	12(19)	5.7(.4)

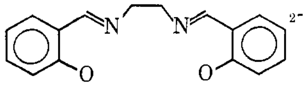
[a] Anisotropic thermal parameters are expressed in the form exp $-(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{12}hk+b_{13}hl+b_{23}kl)$. The estimated standard deviations are given in parentheses. [b] The B values given in the last column are those obtained in the final isotropic refinement before the anisotropic refinement.

factor curves for neutral carbon, oxygen, and zinc were taken from ref 13. No correction was made for anomalous dispersion since the space group is nonpolar and the terms are too small to be of significance in treating our film data.[14] All calculations were performed on IBM 7094 and 360/75 computers at the University of Illinois. The stereoscopic drawings were constructed on a Calcomp plotter by the computer program ORTEP.[15]

Results and Discussion

A stereoscopic view of the molecular structure of $Zn(benzac)_2 \cdot C_2H_5OH$ is shown in Figure 1 together with the bond lengths. The bond angles are illustrated in Figure 2 and the positions of the molecules in the unit cell are shown in Figure 3.

The bonds from the zinc to the four oxygen atoms of the benzac ligands are approximately 1.99 Å (that from Zn to O3 is somewhat shorter (1.962 Å), but as the bond C4–O3 is considerably both longer (1.33 ± 0.01 Å) than the corresponding bonds involving the other benzac oxygen atoms and longer than the similar bond in the copper–, palladium–, and vanadyl–benzac complexes (1.23–1.30 Å),[2-4] it seems likely that atom O3 is slightly misplaced, its true position being somewhat further from Zn and closer to C4). Although the bond between zinc and ethanol oxygen is slightly longer (2.06 Å) than the other zinc–oxygen bonds, it is clear that the ethanol molecule is strongly bonded to the metal ion, as are the coordinated water molecules in the similar (also approximately square-pyramidal) complexes $Zn(acac)_2 \cdot H_2O$[16] and $Zn(ensal) \cdot H_2O$[17] [ensal ≡ N,N′-ethylenebis(salicylideneiminato); see structure I]. In $Zn(acac)_2 \cdot H_2O$ the zinc–water oxygen distance is 2.00 Å while the other Zn–O bonds are 2.02 ± 0.02 Å;[16] in the two-dimensional analysis of $Zn(ensal) \cdot H_2O$[17] the Zn–H_2O distance is reported as 2.0 Å.



I

The coordination around the metal ion in $Zn(benzac)_2 \cdot C_2H_5OH$ is close to square pyramidal, but there is a significant departure from this exact arrangement caused by a twisting of one of the chelate rings. This has the effect of raising one of the oxygen atoms (O3′)

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(13) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, pp 201–209.

(14) For Zn with Cu Kα $\Delta f' = -1.7$ and $\Delta f'' = 0.7$; see ref 13, p 214.

(15) C. K. Johnson, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

(16) H. Montgomery and E. C. Lingafelter, *Acta Cryst.*, **16**, 748 (1963); E. L. Lippert and M. R. Truter, *J. Chem. Soc.*, 4996 (1960).

(17) D. Hall and F. H. Moore, *ibid.*, A, 1822 (1966).

TABLE V

OBSERVED AND CALCULATED STRUCTURE FACTORS[a]

[a] The data are divided into groups of common *k*.

in this chelate ring toward the apex of the pyramid (the ethanol oxygen atom) and lowering the other (O2′), as is shown by the angles O1–Zn–O2′ = 103° and O1–Zn–O3′ = 94°, the angles O1–Zn–O2 and O1–Zn–O3 each being 100° (Figure 2). It should be noted that this does not produce the usual trigonal-bipyramidal distortion, which would involve the lowering of two *trans* chelate oxygen atoms (*e.g.*, O2′ and O3) and the

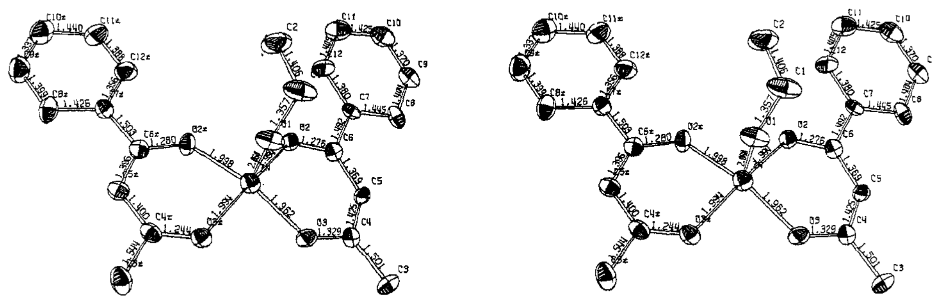

Figure 1.—Molecular structure of $Zn(benzac)_2 \cdot C_2H_5OH$ with the bond lengths. The standard deviations (estimated from the least-squares results) of all zinc–oxygen bond lengths are 0.007 Å; all others range from 0.01 to 0.02 Å.

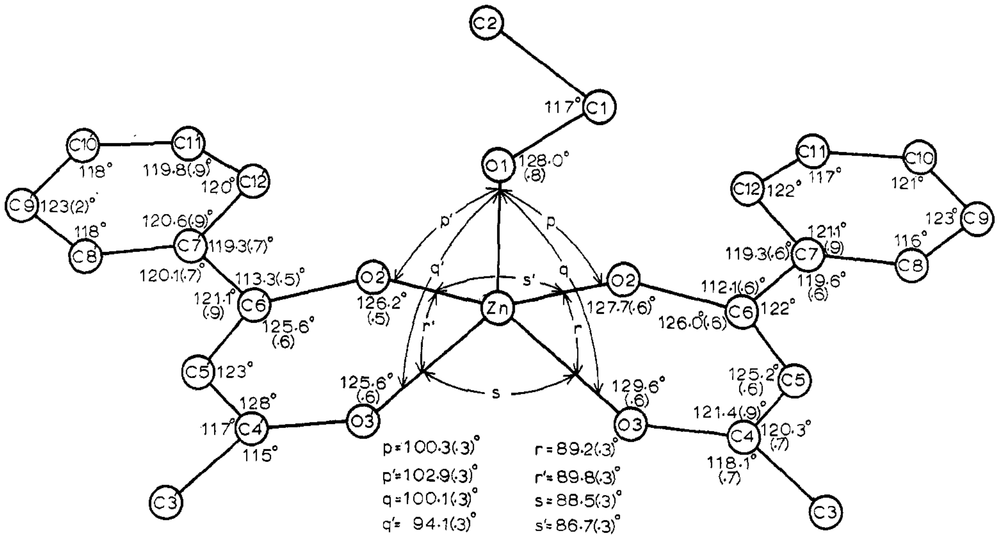

Figure 2.—Bond angles in $Zn(benzac)_2 \cdot C_2H_5OH$. The standard deviations (estimated from the least-squares results) are 1° unless given in parentheses. Other bond angles are O2–Zn–O3′ = 165.6 (0.3)°; O2′–Zn–O3 = 157.0 (0.3)°.

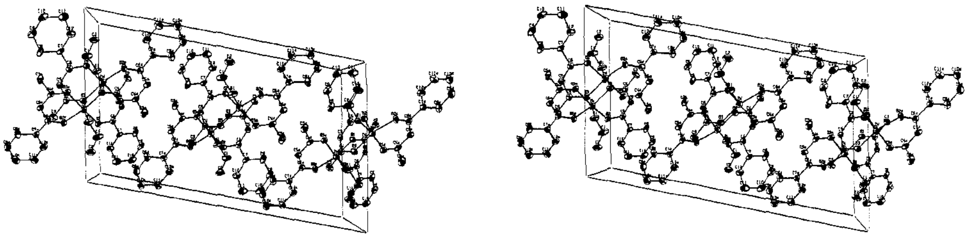

Figure 3.—The unit cell in $Zn(benzac)_2 \cdot C_2H_5OH$ viewed approximately along [010]. The pair of molecules shown in the central portion of the cell exhibit weak Zn- - -C5 contacts; the pairs near the *ab* faces are connected by two hydrogen bonds (not shown explicitly) involving the ethanolic hydrogen (bonded to O1) and O3 of the adjacent molecule.

raising of the other two. In this respect the structure of $Zn(benzac)_2 \cdot C_2H_5OH$ differs from that of $Zn(acac)_2 \cdot H_2O$ in which there is a significant distortion toward a trigonal-bipyramidal configuration.[16]

While the refinement yielded an average standard deviation of 0.017 Å for the 12 C–C distances in the two phenyl rings, the root-mean-square difference between individual C–C distances and their average is 0.033 Å. This discrepancy possibly arises from the partial matrix refinement and indicates that the least-squares esd's are underestimates of the errors. Each phenyl group in $Zn(benzac)_2 \cdot C_2H_5OH$ is approximately coplanar with the rest of the benzac ligand, the angles between the best planes (from a least-squares method using unit weights) being 7.5° for the unprimed ligand (planes 1 and 3 of Table VI) and 3.8° for the primed ligand (planes 2 and 4). The benzene rings in the copper-,[2] palladium-,[3] and vanadyl-benzac[4] complexes are also essentially in the plane formed by the rest of each ligand and it has been suggested[2–4] that conjugation of the π orbitals of the phenyl groups with those of the rest of the ligand may be a factor favoring this coplanarity. The lengths of the C6–C7 and C6′–C7′ bonds in $Zn(benzac)_2 \cdot C_2H_5OH$ do not differ from the normal $C(sp^2)$–$C(sp^2)$ single bond lengths (1.49–1.53 Å)[18] within the accuracy of the analysis.

The carbon atoms of the ethanol molecule have rather high temperature factors (particularly C2; see Table IV) and the measured distances C1–C2 = 1.41 Å and

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(18) O. Kennard, ref 13, pp 275, 276.

Table VI

Best Planes Through Groups of Atoms with Distances[a]

Plane 1	$.2430X + .8100Y - .5337Z = -1.369$ Å					
Atoms	C7	C8	C9	C10	C11	C12
Distances	−.004	.014	−.007	−.013	.022	−.013
Plane 2	$.4318X + .8226Y - .3700Z = 1.101$ Å					
Atoms	C7′	C8′	C9′	C10′	C11′	C12′
Distances	−.017	.012	.016	−.031	.027	−.008
Plane 3	$.3550X + .7479Y - .5609Z = -1.435$ Å					
Atoms	O2	O3	C3	C4	C5	C6
Distances	.015	.007	−.003	−.018	.034	−.035
Plane 4	$.4881X + .7950Y - .3602Z = 1.196$ Å					
Atoms	O2′	O3′	C3′	C4′	C5′	C6′
Distances	.011	−.012	.009	.005	−.009	−.004
Plane 5	$.4903X + .7922Y - .3633Z = 1.181$ Å					
Atoms	O2′	O3′	C4′	C5′	C6′	
Distances	.006	−.009	.012	−.004	−.005	
Plane 6	$.3535X + .7477Y - .5621Z = -1.455$ Å					
Atoms	O2	O3	C4	C5	C6	
Distances	.017	.006	−.021	.032	−.034	
Plane 7	$.3603X + .7625Y - .5374Z = -1.135$ Å					
Atoms	O2	O3	C4	C5*	C6	
Distances	.007	−.006	.007	.078	−.007	
Plane 8	$.4420X + .7991Y - .4075Z = 0.637$ Å					
Atoms	O2	O3	O2′	O3′	Zn*	
Distances	−.090	.054	.080	−.054	−.322	

[a] The (X, Y, Z) axis system is the unit cell system orthogonalized and normalized to 1 Å; *i.e.* $(X, Y, Z) = (x{\cdot}a{\cdot}\sin\beta, y{\cdot}b, z{\cdot}c + x{\cdot}a{\cdot}\cos\beta)$. Atoms marked with an asterisk were not included in the calculation of the plane.

C1–O1 = 1.36 Å are abnormally short. It seems probable that the energy barriers to thermal motion of the ethanol group are low, and this could contribute to the high temperature factors. This motion may result in some artificial bond shortening in the ethanol molecule as determined in the present analysis. It is also possible that some disorder in the positions of the ethanol carbon atoms produces the anomalously short bonds.

The $Zn(benzac)_2 \cdot C_2H_5OH$ molecules occur in loosely bound pairs with every molecule related to its nearest neighbor by an inversion center (*e.g.*, $^1/_2$, $^1/_2$, $^1/_2$). One chelate ring in each molecule experiences rather close intermolecular contacts and these are shown in Figure 4.

Each molecule of each such pair is joined in turn to a molecule of the next pair along the *b*-axis direction by two hydrogen bonds (*e.g.*, across the inversion center at $^1/_2$, 0, $^1/_2$) involving the ethanolic hydrogen atom (*i.e.*, bonded to O1) and the chelate oxygen atom, O3, of the neighboring molecule. The O1–O3 distance is 2.77 Å; the angles C1–O1–O3 = 114°, Zn–O1–C1 = 128°, and Zn–O1–O3 = 116° are reasonable for the ethanol molecule to be both coordinated to zinc and hydrogen bonded to an adjacent molecule. Within a pair, one can describe each zinc atom as very weakly bonded (3.34 Å) to a carbon atom, C5, of a chelate ring of its neighbor. (Other intermolecular contacts are: O2–C4, 3.24 Å; O3–C6, 3.25 Å.) While the chelate ring which does not experience any close intermolecular contacts is planar (Table VI, plane 5), the atom C5 seems to be significantly displaced (0.078, esd = 0.011 Å) from the plane of its chelate ring toward the zinc atom to which it is weakly bonded (plane 6 in Table VI is the plane of the chelate ring including C5, while plane 7 is the plane not including C5). Even if the standard deviations of the atoms of the chelate rings are increased by a factor of 2 (see previous discussion of deviations in the phenyl rings), the χ^2 significance test for plane 6 yields $\chi^2 = 7.4$, while for plane 5, $\chi^2 = 0.8$. If C5 is removed from plane 6, the χ^2 for the resulting plane (7) is 0.6. While these results are not unequivocal, they indicate that plane 6 is planar at only an 0.02 level of significance, while plane 5 is planar between an 0.50 and an 0.90 level of significance. The puckering of this chelate ring can be seen in Figure 1. It should be noted that in several copper keto–enolato[2,19] and acetylacetone–iminato[20] complexes, the metal ion apparently forms weak bonds (3.0–3.4 Å) to the aromatic ring systems of the ligands of neighboring molecules, while in a number of Pt(IV) complexes there is strong coordination to the middle carbon atom of the chelate ring.[21] Indeed, there is an interesting similarity between the loose dimeric units in $Zn(benzac)_2 \cdot C_2H_5OH$ and the strong dimers formed in $Pt(CH_3)_3$(dioxon)[21] (dioxon ≡ 4,6-dioxononyl anion ≡ $C_3H_7COCHCOC_3H_7^-$), the structure of which is illustrated in Figure 5a. The bond from the platinum ion to the acetylacetonato carbon in $Pt(CH_3)_3$(dioxon) is 2.39 Å, and this carbon atom is displaced by 0.25 Å out of the plane of the other four atoms (the equivalents of O_2–O_3–C_4–C_6 in $Zn(benzac)_2 \cdot C_2H_5OH$) of the chelate framework toward the Pt ion.

The complex $VO(benzac)_2$ also packs in loose pairs, very similar to those in $Zn(benzac)_2 \cdot C_2H_5OH$, with each molecule related to its neighbor by an inversion center.[4] In the vanadium complex, however, the distance from the metal ion to the carbon atom in the neighboring chelate ring is 3.85 Å, which is considerably longer than the 3.34 Å found for the zinc complex and is perhaps too far to be considered as even a weak bond. A factor which probably contributes to this is the greater displacement of the vanadium atom from the plane formed by the four chelate oxygen atoms (0.54 Å compared with 0.32 Å for the zinc complex; see plane 8, Table VI). While the angle between the two chelate rings is about the same in the zinc (166°) and vanadium (162°) complexes, the angle between the planes formed by the vanadium atom and each pair of chelate oxygen atoms is 136°, compared with 153° (planes O2′–Zn–O3′

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(19) L. F. Dahl, unpublished results described by T. S. Piper and R. L. Belford, *Mol. Phys.*, **5**, 169 (1962).

(20) D. Hall, A. D. Rae, and T. N. Waters, *J. Chem. Soc.*, 5897 (1963).

(21) A. G. Swallow and M. R. Truter, *Proc. Roy. Soc.* (London), **A254**, 205 (1960), and references therein.

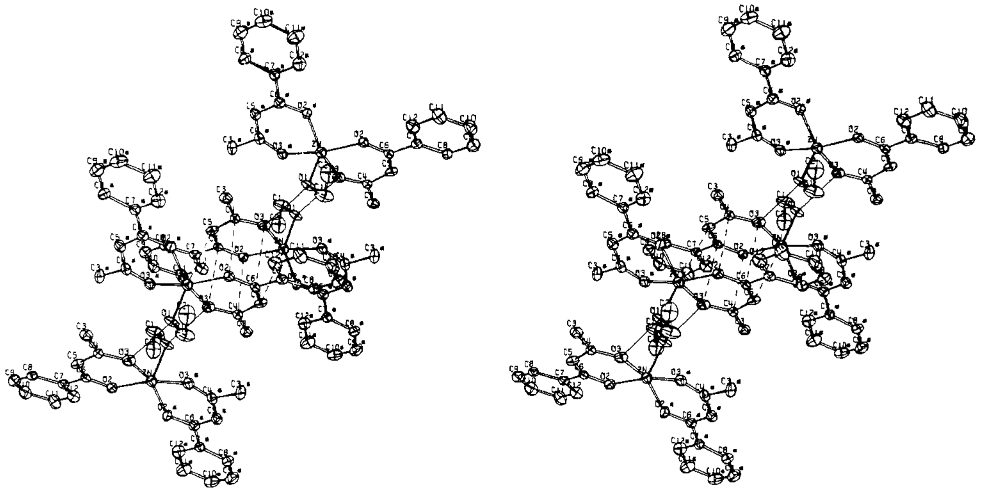

Figure 4.—Stereoscopic view of the intermolecular contacts in the loose dimer of $Zn(benzac)_2 \cdot C_2H_5OH$ and of the hydrogen bonds connecting the dimer to its neighbors.

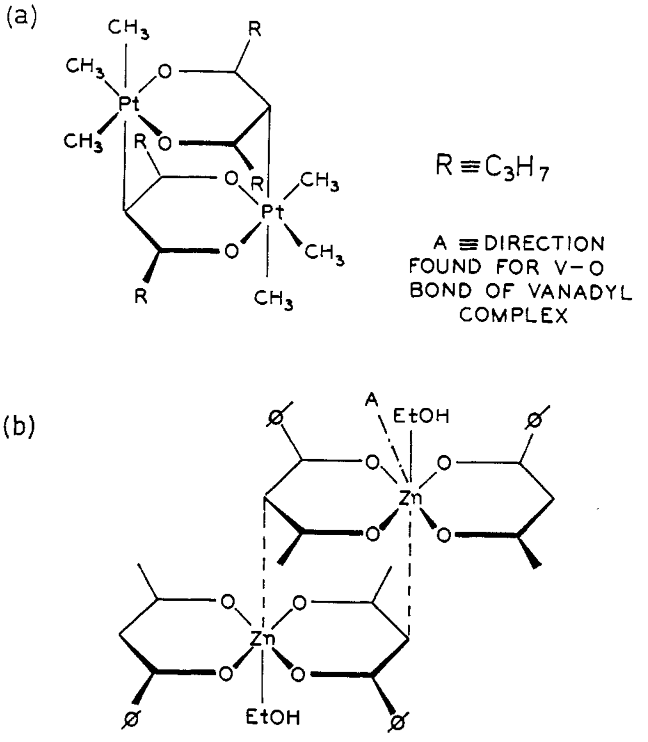

Figure 5.—(a) A diagrammatic representation of the structure of $Pt(CH_3)_3$(dioxon). (b) The position of the vanadyl V–O bond direction of $VO(benzac)_2$ substituted into $Zn(benzac)_2 \cdot C_2H_5OH$.

and O2–Zn–O3) for the corresponding angle in the zinc complex. The epr spectrum of $VO(benzac)_2$ substituted into $Zn(benzac)_2 \cdot C_2H_5OH$ suggests that the vanadium molecules are tilted relative to the corresponding zinc molecules in the lattice,[5] with the vanadyl V–O bond being rotated by ~14°, relative to the Zn–O1 bond, toward the middle of the chelate ring involved in the weak dimerization. This rotation is illustrated in Figure 5b. Without implying any causal relationship, we note that this rotation would allow the distance between vanadium and C5 of the neighboring molecule to attain a value closer to that which it has in the pure $VO(benzac)_2$ crystal.

Considering that substitution of a VO for a ZnC_2H_5-OH group in the crystal eliminates one of the intermolecular hydrogen bonds and provides additional space in the crystal, it is not surprising that some reorientation occurs. It seems likely that these factors are partly responsible for the rotation.

The fact that the benzene rings are *cis* in $Zn(benzac)_2 \cdot C_2H_5OH$, where crystal field effects are absent, suggests that the adoption of the *cis* configuration in the vanadyl–[4] and zinc–benzac complexes is probably caused by crystal-packing effects. It is, perhaps, pertinent in this respect that $Cu(benzac)_2$[2] and $Pd(benzac)_2$[3] both adopt the *trans* centrosymmetric configuration and crystallize with the metal ions on special positions at the center of inversion [each belongs to $P2_1/c$ with $Z = 2$; $Cu(acac)_2$[19] and $Cu(3\text{-phenacac})_2$[22] also belong to $P2_1/c$ with $Z = 2$]. The stoichiometries of $Zn(benzac)_2 \cdot C_2H_5OH$ and $VO(benzac)_2$ preclude centrosymmetric monomer structures. However, in each case the loose dimers do contain a center of inversion, and the only way for this to occur without the benzene rings of one molecule overlying those of the other molecule is for the phenyl groups in each molecule to be in *cis* positions.

The stoichiometries of $Zn(benzac)_2 \cdot H_2O$, $Mg(benzac)_2 \cdot H_2O$, and $Zn(3\text{-phenacac})_2 \cdot H_2O$ make it likely that, by analogy with $Zn(benzac)_2 \cdot C_2H_5OH$, these complexes contain five-coordinate metal ions.

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(22) J. W. Carmichael, Jr., L. K. Steinrauf, and R. L. Belford, *J. Chem. Phys.*, **43**, 3959 (1965).