requires the bridging atom to take a relatively small ring angle, *i.e.*, in the range 69–87°. From the two structures of copper(I) complexes of trimethylphosphine sulfide, it appears that the sulfur atom exhibits a definite tendency to be tetrahedral. Thus, it forms the less strained six-membered ring instead of the more common four-membered ring, which would be highly strained. Similar considerations were used to explain the formation of a trimeric palladium complex with a mercapto ligand,[25] although the analogous nickel complex was dimeric.[26]

Registry No. $\{Cu[(CH_3)_3PS]Cl\}_3$, 38656-77-8.

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Base Adducts of β-Ketoenolates. V.[1,2] Crystal and Molecular Structures of *cis*-Bis(1,1,1,6,6,6-hexafluoro-2,4-pentanedionato)bis(pyridine)zinc(II) and -copper(II)

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Single crystals of bis(1,1,1,6,6,6-hexafluoro-2,4-pentanedionato)bis(pyridine)zinc(II), $Zn(F_6acac)_2(py)_2$, have been prepared and doped to about 2% with $Cu(F_6acac)_2(py)_2$. Crystals of the pure copper(II) complex also have been prepared and studied. $Zn(F_6acac)_2(py)_2$ crystallizes in space group $C2/c$, $Z = 4$. The monoclinic cell dimensions are $a = 9.2027$ (5), $b = 17.512$ (1), $c = 16.518$ (1) Å, and $\beta = 105.78$ (1)°. Diffractometric data for 2500 symmetry-independent reflections were collected using Cu radiation. Full-matrix, least-squares refinement led to $R_1 = 7.8\%$ and $R_2 = 10.6\%$. The molecule, which is required to have C_2 symmetry, shows a cis octahedral ZnN_2O_4 geometry with alternating long and short bond lengths in the metal ketoenolate rings. The sense of distortions about the metal and in the chelate rings is opposite to that found in $Cu(F_6acac)_2(py)_2$. This copper complex, which crystallizes in space group $P2_1/c$, $Z = 4$, shows also a cis octahedral geometry. The monoclinic cell dimensions are $a = 15.7643$ (4), $b = 10.3651$ (3), $c = 16.8517$ (6) Å, and $\beta = 99.37$ (1)°. Diffractometric data for ~4000 symmetry-independent reflections were collected using Cu radiation. Full-matrix, least-squares refinement produced $R_1 = 6.9\%$ and $R_2 = 9.8\%$. Metal–oxygen distances trans to the metal–nitrogen bonds are for Cu–O 1.998 (4) Å and for Zn–O 2.159 (7) Å, while the axial metal–oxygen bond lengths are for Cu–O 2.283 (6) Å and for Zn–O 2.069 (8) Å. The Cu–N and Zn–N bond lengths are 2.012 (8) and 2.116 (7) Å, respectively. Correlation between the C–O distances and C–O stretching frequencies for some of the adducts of $Zn(F_6acac)_2$ and $Cu(F_6acac)_2$ show that these infrared bands are very sensitive to the extent that metal chelate interactions occur in these complexes.

Introduction

Adduct formation of metal β-ketoenolates with Lewis bases such as ammonia, pyridine, and aniline was reported as early as 1904.[3] Recent work on base adducts of divalent transition metal β-ketoenolate complexes has been reviewed by Graddon.[4] A variety of copper(II) β-ketoenolate base adducts have been isolated[2,5-12] since the first of these compounds was obtained by crystallization of bis(acetylacetonato)copper(II) from quinoline.[12] Comparatively little work has been done on zinc(II) β-ketoenolates and their base adducts. These complexes resemble the copper(II) β-ketoenolates in forming both five- and six-coordinate adducts. The six-coordinate complexes of Zn(II) appear to be rather more stable than those of Cu(II), but for adducts of zinc β-ketoenolates as well as those of Cu(II) the preferred coordination number is 5. Most of these adducts have small formation constants and are somewhat unstable when prepared as solids, decomposing on exposure to the atmosphere with loss of base, leaving a residue of the β-ketoenolate complex. Incorporation into the β-diketone of strongly electron-withdrawing groups increases the strength as a Lewis acid of the complex and gives more stable adducts.[7,8,13] Complexes such as bis(hexafluoroacetylacetonato)copper(II), $Cu(F_6acac)_2$ (the ligand $C_5HF_6O_2^-$ has been abbreviated F_6acac), form 1:1 and 2:1 base adducts in solution. The formation of adducts is essentially complete when stoichiometric molar ratios are attained.[10,14]

A wide variety of physical methods have been used for studying the interaction of bases with copper(II) diketonates. These interactions have been mainly established by their

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effects on the electronic[2,5-11,15] and epr spectra[11,16-23] and by crystal structure determination of a limited number of adducts.[21,24,25] We have been prompted to study the structural and magnetic properties of the pyridine and aquo adducts of $Cu(F_6acac)_2$ because of their exceptional stability toward loss of base as well as their interesting electronic spectra in which the low-energy band is clearly resolved.[2,10]

The crystal structure of the 2,2′-bipyridine adduct of $Cu(F_6acac)_2$[21] provides an interesting example of metal-ligand distances and chelate ring distortions which has been attributed to the Jahn–Teller effect. However, for the anion $Cu(F_6acac)_3^-$ there is no crystallographic evidence[26] for distortions within the chelate rings although the compound shows four short and two long Cu–O bonds. In contrast, for $Mg(F_6acac)_3^-$ which is isomorphous with the Cu complex, the Mg–O distances are equal.[26] The present investigation was undertaken to provide magnetic and structural information for the paramagnetic copper(II) ion in pseudo Jahn–Teller complexes (wherein the ground and excited states can be nearly degenerate) by using zinc compounds as diamagnetic hosts for this ion. Here we report the crystal structures of the bis(pyridine) adducts of $Zn(F_6acac)_2$ and $Cu(F_6acac)_2$.

Experimental Section

Bis(1,1,1,6,6,6-hexafluoro-2,4-pentanedionato)bis(pyridine)zinc(II), $Zn(F_6acac)_2(py)_2$. Crystals of $Zn(F_6acac)_2(py)_2$ doped with copper(II) were obtained by crystallizing the anhydrous $Cu(F_6acac)_2$ and $Zn(F_6acac)_2$ (1:50) from hot neat pyridine. This adduct slowly loses base when exposed to air; however, it can be kept indefinitely under pyridine atmosphere or protected with silicon or paraffin grease. By recrystallizing the above compound using a mixture of CCl_4 and CH_2Cl_2 as solvent, single crystals of a stable adduct were obtained by allowing the solution to evaporate slowly. All calculations throughout the structure determination of this stable adduct were carried out ignoring the presence of the small amount (1–2%) of copper impurity.

The crystals were examined by Weissenberg methods which indicated Laue symmetry of $2/m$. Observed systematic absences were consistent with $C2/c$ or Cc space groups. Final data collection on a Picker four-circle diffractometer was conducted using a crystal sealed in a glass capillary. The crystal was a truncated hexagonal pyramid of maximum dimensions 0.35 × 0.25 × 0.12 mm. Lattice constants obtained were $a = 9.2027$ (5), $b = 17.512$ (1), $c = 16.518$ (1) Å, $\beta = 105.78$ (1)°, and lattice volume $V = 2562$ Å^3. The crystal density was determined by the flotation method with a mixture of $CHCl_3$ and CH_2Br_2. The observed density was 1.660 (5) g cm^{-3}, while the calculated density based on four molecules per unit cell is 1.652 g cm^{-3}. A higher unit cell volume was measured, $V = 2767$ Å^3, for the crystals obtained from pyridine.

Nickel-filtered Cu Kα radiation was used for data collection by the 2θ scan technique; 2500 symmetry-independent reflections to the limit of the copper sphere were collected with the (100) direction chosen to be collinear with the ϕ axis. Backgrounds were obtained on both sides of each reflection with a 20-sec count. The data were corrected for Lorentz polarization effects and a total of 1178 reflections, whose net counts were higher than 2 times their standard deviation,[27] were obtained. After absorption corrections, $\mu = 25.3$ cm^{-1} (transmission factors range from 0.60 to 0.77), 1269 reflections which satisfied the same observability criteria were used at the final stages of refinement.

Table I. Fractional Atomic Coordinates and Their Standard Deviations for $Zn(F_6acac)_2(py)_2$

Atom	*x/a*	*y/b*	*z/c*
Zn	0.50000	0.30816 (10)	0.75000
N	0.3706 (10)	0.2297 (5)	0.6620 (5)
O_1	0.3743 (9)	0.4014 (4)	0.6784 (4)
O_2	0.3456 (8)	0.3172 (4)	0.8201 (4)
C_1	0.2965 (14)	0.4464 (6)	0.7079 (7)
C_2	0.2412 (13)	0.4399 (6)	0.7791 (7)
C_3	0.2638 (12)	0.3753 (7)	0.8265 (6)
C_4	0.2597 (27)	0.5202 (8)	0.6523 (15)
C_5	0.1948 (19)	0.3679 (14)	0.8983 (11)
C_6	0.4264 (14)	0.1968 (7)	0.6039 (8)
C_7	0.3461 (16)	0.1476 (8)	0.5411 (8)
C_8	0.1987 (17)	0.1341 (7)	0.5382 (8)
C_9	0.1371 (17)	0.1680 (9)	0.5981 (10)
C_{10}	0.2284 (16)	0.2139 (9)	0.6594 (8)
F_1	0.0961 (20)	0.3176 (11)	0.8838 (9)
F_2	0.1146 (16)	0.4241 (8)	0.9094 (7)
F_3	0.2838 (13)	0.3515 (9)	0.9676 (5)
F_4	0.1673 (13)	0.5115 (5)	0.5855 (5)
F_5	0.1766 (23)	0.5671 (8)	0.6840 (8)
F_6	0.3673 (16)	0.5610 (9)	0.6629 (14)

Bis(1,1,1,6,6,6-hexafluoro-2,4-pentanedionato)bis(pyridine)copper(II), $Cu(F_6acac)_2(py)_2$. Bis(hexafluoroacetylacetonato)bis(pyridine)copper(II) was obtained by preparing a saturated solution of $Cu(F_6acac)_2$ in pyridine and allowing the solution to stand at room temperature several days. The green crystals obtained were in the form of thick hexagonal plates. On exposure to air the crystals lose pyridine slowly; however, they can be kept indefinitely under a pyridine atmosphere. In an effort to obtain stable crystals, the above compound was recrystallized by using two solvents: (1) a mixture of CCl_4 and CH_2Cl_2 and (2) benzene. Crystals obtained from the first solvent, although stable, were found to be twinned. Single crystals suitable for X-ray work were obtained by slow evaporation of the benzene solution. The crystals slowly decompose but can be kept in contact with the solvent.

Both crystallographic forms were examined by Weissenberg methods, which indicated Laue symmetry of $2/m$. The following unit cell volumes were obtained for the crystallographic forms recrystallized from solvents 1 and 2: $V_1 = 2500$ Å^3 and $V_2 = 2717$ Å^3. No density measurements were made because of the instability of the compound obtained from benzene. The larger cell volume for the unstable crystal was considered an indication that some solvent molecules might be trapped into the crystal lattice.

The unit cell dimensions were preliminarily determined from oscillation and zero-level Weissenberg photographs about the b and a crystallographic axes. Observed systematic absences found for zero-level and upper level photographs were consistent with $P2_1/c$ space group. A suitable crystal was selected directly from the benzene solution and rapidly mounted in a thin-walled glass capillary, which was then sealed. Oscillation and zero-level Weissenberg photographs indicated that no decomposition had taken place while transferring the crystal. This was a thick hexagonal prism approximately 0.38 × 0.37 × 0.48 mm. Unit cell parameters, measured on the Weissenberg camera and refined on the Picker four-circle diffractometer using Cu Kα radiation ($\lambda = 1.5418$ Å), were $a = 15.7643$ (4), $b = 10.3651$ (3), $c = 16.8517$ (6) Å, and $\beta = 99.37$ (1)°. The instability of the crystal prohibited density measurement. It was assumed that four molecules of $Cu(F_6acac)_2(py)_2$ were contained in each cell. Nickel-filtered Cu Kα radiation was used for data collection by the 2θ scan technique; ∿4000 reflections were collected out to the limit of the copper sphere with the (100) direction chosen to be collinear with the ϕ axis. The crystal dimensions were very carefully measured and coordinates for the crystal vertices relative to the crystallographic axes were calculated. Absorption corrections were applied ($\mu = 22.39$ cm^{-1}) for those reflections whose net counts were higher than 2 times their standard deviation.[27] Transmission factors

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Table II. Anisotropic Temperature Factors for $Zn(F_6acac)_2(py)_2$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zn	0.02092 (30)	0.00441 (6)	0.00491 (7)	0.00000	0.00199 (10)	0.00000
N	0.0204 (15)	0.0052 (3)	0.0058 (4)	−0.0002 (5)	0.0005 (5)	0.0000 (3)
O_1	0.0292 (15)	0.0057 (3)	0.0058 (3)	0.0010 (5)	0.0016 (5)	0.0004 (2)
O_2	0.0258 (13)	0.0060 (3)	0.0064 (3)	0.0020 (5)	0.0040 (5)	0.0008 (3)
C_1	0.0268 (22)	0.0048 (4)	0.0072 (6)	0.0008 (8)	−0.0034 (9)	0.0000 (4)
C_2	0.0283 (23)	0.0063 (5)	0.0061 (5)	0.0034 (9)	0.0016 (8)	−0.0003 (4)
C_3	0.0213 (18)	0.0073 (5)	0.0056 (5)	0.0033 (9)	0.0004 (7)	−0.0010 (4)
C_4	0.045 (4)	0.0041 (5)	0.0179 (15)	0.0014 (13)	−0.0099 (21)	0.0019 (7)
C_5	0.02_6 (3)	0.0130 (12)	0.0103 (10)	0.0052 (16)	0.0069 (14)	−0.0008 (9)
C_6	0.0267 (22)	0.0066 (5)	0.0096 (7)	0.0002 (9)	0.0035 (10)	−0.0021 (6)
C_7	0.0272 (25)	0.0085 (7)	0.0096 (8)	−0.0022 (11)	0.0020 (11)	−0.0037 (6)
C_8	0.032 (3)	0.0065 (6)	0.0090 (8)	−0.0006 (11)	0.0027 (12)	−0.0004 (5)
C_9	0.029 (3)	0.0100 (8)	0.0099 (8)	−0.0040 (12)	0.0026 (12)	−0.0007 (7)
C_{10}	0.0264 (24)	0.0109 (9)	0.0081 (7)	−0.0056 (12)	0.0046 (10)	−0.0025 (6)
F_1	0.057 (4)	0.0232 (14)	0.0168 (10)	−0.0107 (19)	0.0191 (17)	−0.0023 (9)
F_2	0.061 (3)	0.0189 (10)	0.0149 (7)	0.186 (17)	0.0169 (14)	0.0028 (7)
F_3	0.050 (3)	0.0310 (15)	0.0061 (4)	0.0171 (16)	0.0065 (8)	0.0037 (16)
F_4	0.052 (2)	0.0092 (4)	0.0100 (5)	0.0013 (9)	−0.0038 (9)	0.0036 (4)
F_5	0.119 (7)	0.0099 (6)	0.0131 (8)	0.0179 (19)	0.0089 (19)	0.0032 (6)
F_6	0.048 (3)	0.0119 (7)	0.0383 (20)	−0.0087 (14)	−0.0066 (20)	0.0134 (10)

calculated by ABSCOR ranged from 0.43 to 0.53. The data were corrected for Lorentz and polarization effects and a total of 2681 reflections were obtained.

Solution and Refinement of the Structures.[28] **$Zn(F_6acac)_2(py)_2$.** On the basis of intensity distributions,[29] no clear indication of the presence or absence of a center of symmetry was implied. Since $Z = 4$, the central atom must be placed in a special position if $C2/c$ is chosen. The position assumed, $(0, 0, 0; {}^1/_2, {}^1/_2, 0) + (0, \bar{y}, {}^1/_4; 0, \bar{y}, {}^3/_4)$, requires a C_2 site symmetry for the complex which is consistent with the epr single-crystal data[30] at room temperature, which show that all molecules in the Cu-doped crystal are magnetically equivalent regardless of their relative orientation to the magnetic field. The other special positions require a centrosymmetric complex and that additional reflections be weak (since the Zn would make no contribution), which was not observed. The position chosen for the central atom is also compatible with the general fourfold position of space group Cc with $x = 0$ and $z = {}^1/_4$ arbitrarily chosen for Zn to fix the origin, although no C_2 molecular symmetry would be required for the complex in this case.

A y parameter of 0.1875 for the Zn atom was determined from the Patterson synthesis along the Harker line $(0, v, {}^1/_2)$. This positional parameter, as well as the scale and the temperature factor obtained from the Wilson plot, was refined by the method of least squares. The y value converged to 0.190 while the unweighted residual index, R, was 32.5% for the 460 more intense reflections ($F_o > 15.0$). An electron density map was calculated using the observed amplitudes ($F_o > 15.0$) with phases calculated with the Zn atoms alone. From this initial Fourier result the position of the diketone ring, as well as of the nitrogen and one of the pyridine's carbons, was clearly resolved. The problem of finding the correct positions for the pyridine ring and CF_3 groups was accomplished by adding the calculated positions for those atoms which were compatible with the electron density maps. After least-squares isotropic refinement of positional parameters for all atoms but the CF_3 groups, which were kept fixed, the R index converged to 25% for 1178 independent reflections.

An expanded electron density map was calculated by using the phases obtained from the above calculation from which the CF_3 groups were omitted. From this map the fluorine and carbon positions were found. However, most of the fluorine peaks were very diffuse and regions of electron density between them were found. Full isotropic least-squares refinement resulted in convergence of the positional parameters while $R = 18.5\%$. At this stage, thermal parameters on the fluorine atoms ranged from 10 to 18 Å^2, suggesting that the CF_3 groups are rotationally disordered about the C-C bonds. Similarly, this disturbing feature for the CF_3 groups has been found in the structure determination of complexes of the same ligand[31] as well as in that of other molecules such as $[PCl(C_6H_5)_3][Au(S_2C_2(CF_3)_2)_2]$.[32]

Further refinement with anisotropic thermal factors for all atoms was undertaken. Two cycles of full-matrix, least-squares refinement led to a conventional R factor of 10%. Introduction of a weighting function obtained by least-squares fitting of mean $\overline{\Delta F_o}^2$ *vs.* mean F_o for groups of similar reflections produced a final converged R factor of 9.3% with a weighted R, $[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} \times 100$, of 13.4%. Absorption corrections were then applied and anomalous dispersions, both real and imaginary parts, for zinc were taken into account. The values of $\Delta f'$ and $\Delta f''$ for Zn and the neutral scattering factors used for all atoms were taken from ref 33a and 33b, respectively. The refinement was continued with these corrections, following the Hughes-type weighting scheme described above, by full-matrix, least-squares analysis until the final parameter shifts were less than one-tenth the standard error. The resulting weighted and unweighted R indices were 10.6 and 7.8%, respectively. The final positional parameters and anisotropic temperature factors are listed[34] in Tables I and II. A final difference Fourier map showed residual electron density of about 1 e/Å^3 between some of the fluorines and indicated, with lower density values, positions which were near those calculated for the hydrogen atoms in the asymmetric unit assuming normal angles and distances.

$Cu(F_6acac)_2(py)_2$. Copper atom positions were found by using a sharpened Patterson function for the space group $P2_1/c$. These positional parameters, as well as the scale and temperature factors (0.75 and 2.948 Å^2) obtained from the Wilson plot, were refined through two cycles by the method of least squares. The coordinates converged to $x = 0.765$, $y = 0.5538$, and $z = 0.0782$, while the unweighted residual index, R, was 44% for the 1600 more intense reflections ($F_o > 30.0$).

An electron density map was calculated using the observed amplitudes ($F_o > 30.0$) with phases calculated with the Cu atoms alone. All atoms but five fluorine and two carbon atoms were found from this initial Fourier result. A second Fourier map was calculated by using the phases obtained from the above positional parameters and 2381 reflections ($F_o > 20.0$). From this map the fluorine and carbon positions were found. However most of the carbon and fluorine peaks of the CF_3 groups were very diffuse. After least-squares isotropic refinement of positional parameters for all atoms, the R index converged to 18.8% for 2496 reflections, whose net counts were higher than three times the standard deviation. At this stage, an attempt to use anisotropic thermal parameters for the CF_3 atoms developed negative thermal values for two of the fluorines.

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(28) Standard crystallographic programs modified for the UNIVAC 1108 were used. A list of these programs is given by J. P. Fackler, *J. Amer. Chem. Soc.*, 94, 1009 (1972).

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Table III. Fractional Coordinates and Their Estimated Standard Deviations for $Cu(F_6acac)_2(py)_2$

Atom	x/a	y/b	z/c
N(1)	0.6573 (4)	0.5293 (6)	−0.0085 (4)
C(11)	0.6063 (6)	0.6304 (9)	−0.0339 (5)
C(12)	0.5302 (11)	0.6137 (10)	−0.0893 (6)
C(13)	0.5074 (6)	0.4930 (11)	−0.1180 (5)
C(14)	0.5608 (6)	0.3896 (10)	−0.0919 (6)
C(15)	0.6351 (6)	0.4125 (8)	−0.0375 (5)
N(2)	0.8397 (4)	0.4663 (6)	0.0076 (4)
C(21)	0.8538 (6)	0.5193 (9)	−0.0609 (5)
C(22)	0.9121 (7)	0.4665 (11)	−0.1053 (6)
C(23)	0.9552 (6)	0.3541 (11)	−0.0800 (6)
C(24)	0.9400 (6)	0.2991 (10)	−0.0090 (6)
C(25)	0.8819 (6)	0.3573 (9)	0.0334 (5)
O(1)	0.7909 (4)	0.7541 (6)	0.0314 (3)
O(2)	0.6914 (4)	0.6471 (5)	0.1455 (3)
C(1)	0.7869 (6)	0.8488 (9)	0.0758 (5)
C(2)	0.7491 (6)	0.8595 (9)	0.1442 (5)
C(3)	0.7035 (6)	0.7602 (9)	0.1719 (5)
C(4)	0.8308 (7)	0.9691 (10)	0.0459 (7)
C(5)	0.6619 (7)	0.7871 (10)	0.2460 (6)
O(3)	0.7338 (4)	0.3741 (6)	0.1460 (3)
O(4)	0.8629 (4)	0.5765 (6)	0.1621 (3)
C(6)	0.7572 (6)	0.3728 (9)	0.2198 (5)
C(7)	0.8221 (6)	0.4473 (11)	0.2671 (5)
C(8)	0.8658 (6)	0.5400 (10)	0.2340 (5)
C(9)	0.7080 (8)	0.2782 (11)	0.2649 (6)
C(10)	0.9350 (8)	0.6112 (18)	0.2908 (7)
$C_b(1)^a$	0.4276 (15)	0.5294 (17)	0.5363 (17)
$C_b(2)$	0.4280 (13)	0.5557 (17)	0.4587 (13)
$C_b(3)$	0.4935 (15)	0.5291 (15)	0.4156 (12)
Cu	0.76199 (7)	0.55442 (11)	0.07501 (6)
F(41)	0.9103 (5)	0.9479 (7)	0.0384 (6)
F(42)	0.8325 (5)	1.0683 (6)	0.0946 (4)
F(43)	0.7921 (7)	1.0035 (9)	−0.0267 (6)
F(51)	0.6864 (8)	1.7086 (10)	0.3035 (4)
F(52)	0.6757 (7)	1.8954 (8)	0.2792 (5)
F(53)	0.5802 (6)	1.7699 (14)	0.2326 (6)
F(91)	0.7317 (7)	1.2723 (11)	0.3405 (5)
F(92)	0.6291 (5)	1.2969 (12)	0.2526 (6)
F(93)	0.7210 (14)	1.1640 (11)	0.2450 (9)
F(101)	0.9406 (5)	1.5871 (12)	0.3641 (4)
F(102)	1.0060 (6)	1.6133 (17)	0.2725 (10)
F(103)	0.9152 (10)	1.7405 (17)	0.2845 (10)

[a] C_b stands for benzene carbon atoms.

Expanded difference Fourier maps were calculated by using all atoms except some of the fluorines for which the thermal parameters were either too high (isotropic) or negative (anisotropic). Upon inspection of the electron density maps, some of the fluorines were relocated and three peaks, corresponding to a benzene molecule located with its center at the special position ($^1/_2$, $^1/_2$, $^1/_2$), were found. Isotropic refinement of positional parameters for some of the fluorine atoms and the "new" carbons of the solvent molecule resulted in convergence at $R = 14\%$.

Further refinement in which anisotropic thermal parameters were introduced at different stages was undertaken. Two cycles in which 243 parameters were varied led to a conventional R factor of 11%. A weighting function obtained by a least-squares fitting of mean ΔF_o *vs.* mean F_o for groups of similar reflections ($\Delta F_o = a + bF_o + cF_o^2$) was then applied. Anomalous dispersions, both real and imaginary parts, for Cu were taken into account. The refinement was continued by full-matrix least squares using anisotropic thermal parameters for all atoms but one fluorine. In every cycle 243 parameters were varied from a total of 373 positional and thermal parameters. For one of the fluorine atoms the anisotropic temperature factor was found inadequate and an isotropic value of 19.0 Å^2 was used. The last cycle of refinement was carried out on all atoms of the molecule but the CF_3 groups, which were kept fixed. Final parameter shifts were less than one-thrid the standard error and the unweighted and weighted R factors were 7.3 and 10.3%, respectively. The final positional parameters and anisotropic temperature factors[34] are listed in Tables III and IV, respectively. The structure factor amplitudes[34] were calculated with the hydrogen atoms located at normal angles and distances. Significantly, the R factors were lowered to 6.9 and 9.8% when hydrogen atoms placed in calculated positions were used in the structure factor calculations. A final difference Fourier map showed residual density of about 1.0 e/Å^3 between some of the fluorine atoms and lower density values in some regions where no atomic positions are reasonably expected. Evidently, the approximation of the CF_3 complex motion (or disorder) by anisotropic temperature factors improperly accounts for their behavior.

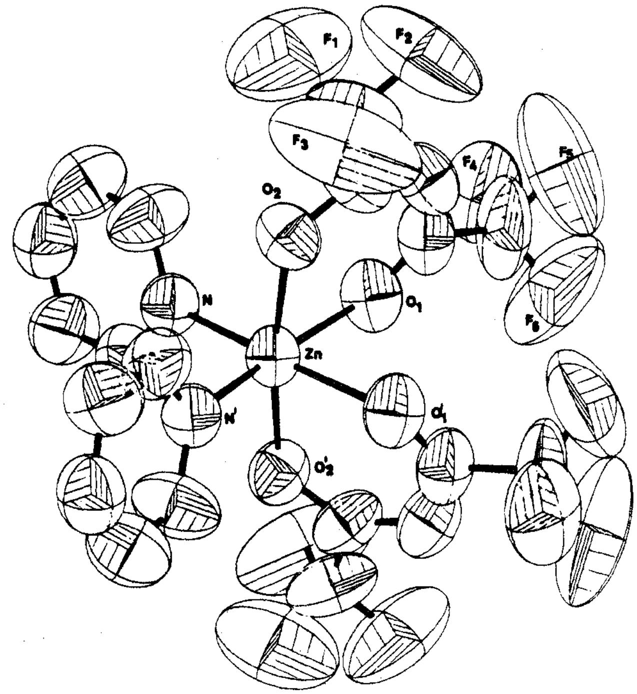

Figure 1. Thermal ellipsoids of the molecule $Zn(F_6acac)_2(py)_2$ composed with ORTEP.

Infrared Spectra. The infrared spectra (4000–625 cm^{-1}) of some of the base adducts were recorded with a Perkin-Elmer Model 257 spectrophotometer. All samples were pressed into KBr disks.

Results

Description of Structures. $Zn(F_6acac)_2(py)_2$. A parallel projection of the molecule composed with ORTEP is shown in Figure 1. Examination of the fluorine thermal ellipsoids shows that the orientation and magnitudes of their principal axes correspond to a pattern of rotational motion of the fluorine atoms around the C–C bonds. An illustration of the unit cell is shown in Figure 2. All contacts between molecules are normal van der Waals distances. These weak intermolecular interactions are consistent with the observation that this compound readily sublimes.

The structure is that of the cis bis(pyridine) adduct to $Zn(F_6acac)_2$. The molecule is required to have C_2 symmetry. The least-squares best plane through the zinc atom and symmetry-related nitrogen and oxygen atoms situated in trans positions (which has been labeled as the equatorial plane) is used in Table V as a reference for reporting dihedral angles. Direction cosines and root-mean-square deviations of fitted atoms from planes are also listed in Table V. Deviations from least-squares planes indicate planarity, within experimental error, for the pyridine and diketone rings. The zinc atom is 0.148 and 0.530 Å out of the pyridine and chelate rings, respectively.

Table VI contains the bond distances and Table VII the bond angles found in the molecule. The bond angles about the zinc differ significantly from the 90° expected for symmetrical octahedral coordination. These distortions about the central atom are illustrated in Figure 3, where selected bond distances are shown. Interestingly, the β-ketoenolate ring is bonded asymmetrically to the central metal ion. An alternation of short and long bond lengths is found in the

Table IV. Anisotropic Temperature Factors and Their Estimated Standard Deviations for $Cu(F_6acac)_2(py)_2$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.00439 (5)	0.00887 (12)	0.00278 (4)	−0.00075 (7)	0.00084 (3)	−0.00066 (6)
N(1)	0.0044 (3)	0.0089 (8)	0.0029 (2)	−0.0000 (4)	0.0009 (2)	−0.0007 (3)
N(2)	0.0040 (3)	0.0102 (8)	0.0031 (2)	0.0002 (4)	0.0005 (2)	−0.0001 (4)
O(1)	0.0074 (4)	0.0106 (7)	0.0040 (2)	−0.0016 (4)	0.0021 (2)	−0.0006 (3)
O(2)	0.0062 (3)	0.0099 (6)	0.0035 (2)	−0.0015 (4)	0.0017 (2)	−0.0015 (3)
O(3)	0.0072 (3)	0.0114 (7)	0.0032 (2)	−0.0009 (4)	0.0008 (2)	0.0005 (3)
O(4)	0.0052 (3)	0.0157 (8)	0.0034 (2)	−0.0021 (4)	0.0006 (2)	−0.0005 (3)
C(1)	0.0052 (4)	0.0100 (10)	0.0046 (4)	−0.0007 (5)	0.0014 (3)	−0.0001 (5)
C(2)	0.0063 (5)	0.0103 (10)	0.0044 (4)	−0.0009 (6)	0.0015 (4)	−0.0015 (5)
C(3)	0.0056 (4)	0.0118 (11)	0.0033 (3)	0.0005 (6)	0.0015 (3)	−0.0007 (5)
C(4)	0.0083 (6)	0.0119 (13)	0.0073 (6)	−0.0018 (7)	0.0028 (5)	−0.0005 (7)
C(5)	0.0081 (6)	0.0148 (12)	0.0046 (4)	−0.0016 (7)	0.0027 (4)	−0.0022 (5)
C(6)	0.0067 (5)	0.0103 (10)	0.0040 (4)	0.0014 (6)	0.0017 (4)	0.0013 (5)
C(7)	0.0060 (5)	0.0163 (13)	0.0036 (3)	−0.0012 (7)	0.0008 (3)	0.0008 (6)
C(8)	0.0050 (4)	0.0174 (14)	0.0031 (3)	−0.0004 (7)	0.0004 (3)	−0.0016 (6)
C(9)	0.0089 (7)	0.0160 (14)	0.0051 (4)	−0.0019 (8)	0.0007 (5)	0.0037 (6)
C(10)	0.0082 (8)	0.0420 (32)	0.0038 (4)	−0.0051 (13)	−0.0018 (5)	0.0015 (10)
C(11)	0.0057 (5)	0.0115 (11)	0.0042 (4)	0.0007 (6)	0.0013 (3)	0.0012 (5)
C(12)	0.0053 (5)	0.0142 (12)	0.0044 (4)	0.0004 (6)	0.0002 (4)	0.0007 (6)
C(13)	0.0048 (5)	0.0180 (13)	0.0040 (4)	−0.0010 (7)	0.0008 (3)	0.0003 (6)
C(14)	0.0051 (4)	0.0137 (12)	0.0050 (4)	−0.0012 (6)	0.0003 (4)	−0.0007 (6)
C(15)	0.0053 (4)	0.0092 (10)	0.0043 (4)	−0.0004 (5)	0.0007 (3)	−0.0015 (5)
C(21)	0.0065 (5)	0.0125 (11)	0.0035 (3)	0.0003 (6)	0.0014 (3)	0.0000 (5)
C(22)	0.0071 (5)	0.0154 (14)	0.0047 (4)	0.0017 (7)	0.0028 (4)	0.0009 (6)
C(23)	0.0058 (5)	0.0149 (13)	0.0057 (5)	0.0000 (7)	0.0025 (4)	−0.0005 (6)
C(24)	0.0060 (5)	0.0132 (12)	0.0060 (5)	0.0013 (6)	0.0016 (4)	−0.0001 (6)
C(25)	0.0054 (4)	0.0109 (10)	0.0048 (4)	0.0009 (6)	0.0011 (3)	0.0002 (5)
F(41)	0.0102 (4)	0.0192 (10)	0.0157 (7)	−0.0057 (6)	0.0067 (5)	−0.0036 (6)
F(42)	0.0165 (7)	0.0108 (7)	0.0119 (5)	−0.0050 (5)	0.0079 (5)	−0.0025 (5)
F(43)	0.0168 (9)	0.0251 (13)	0.0096 (5)	−0.0047 (9)	0.0017 (6)	0.0074 (7)
F(51)	0.0265 (11)	0.0356 (17)	0.0059 (3)	0.0145 (11)	0.0083 (5)	0.0047 (6)
F(52)	0.0176 (7)	0.0208 (11)	0.0095 (5)	−0.0083 (8)	0.0085 (5)	−0.0085 (6)
F(53)	0.0086 (5)	0.059 (3)	0.0101 (6)	−0.0093 (10)	0.0057 (5)	−0.0150 (11)
F(91)	0.0169 (8)	0.0357 (19)	0.0057 (4)	−0.0093 (10)	0.0022 (4)	0.0051 (6)
F(92)	0.0075 (4)	0.063 (3)	0.0185 (7)	−0.0036 (8)	0.0013 (4)	0.0247 (12)
F(93)	0.0419 (25)	0.0155 (13)	0.0178 (11)	−0.0123 (15)	0.0163 (14)	−0.0020 (10)
F(101)	0.0126 (6)	0.061 (3)	0.0038 (3)	−0.0149 (11)	0.0002 (3)	−0.0029 (7)
F(102)[a]	0.0096 (5)	0.104 (5)	0.0072 (4)	−0.0212 (14)	0.0023 (4)	−0.0129 (12)
$C_b(1)$	159 (16)	157 (22)	183 (17)	−16 (15)	48 (15)	−31 (17)
$C_b(2)$	148 (14)	250 (23)	132 (13)	−66 (15)	4 (12)	−23 (16)
$C_b(3)$	210 (18)	161 (19)	152 (13)	−79 (16)	30 (13)	−51 (13)

[a] F(103) was refined with isotropic $B = 19.1$ Å^2.

Table V. Dihedral Angles, Direction Cosines, and Root-Mean-Square Deviations of Fitted Atoms from Least-Squares Planes $LX + MY + NZ = D^a$ in $Zn(F_6acac)_2(py)_2$

No.	Plane	L	M	N	D, Å	Atoms used in fitting plane[b]	Rms dev, Å	Dihedral angles with plane I, deg
I	Equatorial	0.8431	0.000	−0.5377	−5.371	Zn, N, N′, O(1), O′(1)	0.078	0.0
II	Vertical	−0.3825	0.7079	−0.5938	−3.621	Zn, N, O′(1), O(2), O′(2)	0.059	90.2
III	Vertical	−0.3825	−0.7079	−0.5938	−11.48	Zn, N′, O(1), O(2), O′(2)	0.059	90.2
IV	Diketone	−0.7000	−0.4268	−0.5726	−9.463	O(1), O(2), C(1), C(2), C(3)	0.020	108
V	Pyridine	−0.1307	0.7884	−0.6011	−3.218	C(6)–C(10), N	0.010	75.0

[a] Equation for the plane refers to orthogonal axes *a*, *b*, *c**. [b] Primed atomic symbols stand for symmetry-related atoms.

chelate ring. The Zn–O distance trans to the Zn–N bond is longer by 0.090 Å (nine standard deviations) than the cis Zn–O distance. Differences between observed bond distances from atoms which are normally equivalent in these ligands are listed in Table VI. For the β-ketoenolate ring two different C–O and C–C bond lengths have been found statistically significant (difference = 2σ). This is consistent with the observation of two C–O stretching frequencies (Table VIII) in the infrared spectrum of this compound.

$Cu(F_6acac)_2(py)_2$. The projection of the unit cell structure on a plane normal to the *a* axis is shown in Figure 4. The four molecules shown are related by the twofold screw axes, which are parallel to the *b* axis, and by the *c* glide planes situated at distances of $^1/_4 b$ and $^3/_4 b$ from the origin. In the center of the cell a benzene molecule which corresponds to two asymmetric units is shown. This particular location requires a molecule which possesses a center of symmetry that coincides with the sites ($^1/_2$, $^1/_2$, $^1/_2$) and ($^1/_2$, 0, 0). All contacts between the molecules are normal van der Waals distances. Intermolecular contacts that are less than 3.00 Å occur between some of the fluorine and hydrogen atoms. Minimum distances found are about 2.66 Å.

An ORTEP projection of the molecule which visualizes the vibrational effects is shown in Figure 5. Comparison with $Zn(F_6acac)_2(py)_2$ shows that the same pattern of liberational motion of the fluorine atoms around the C–C bond is found in this molecule. However, for the copper complex, the higher anisotropy of the thermal ellipsoids

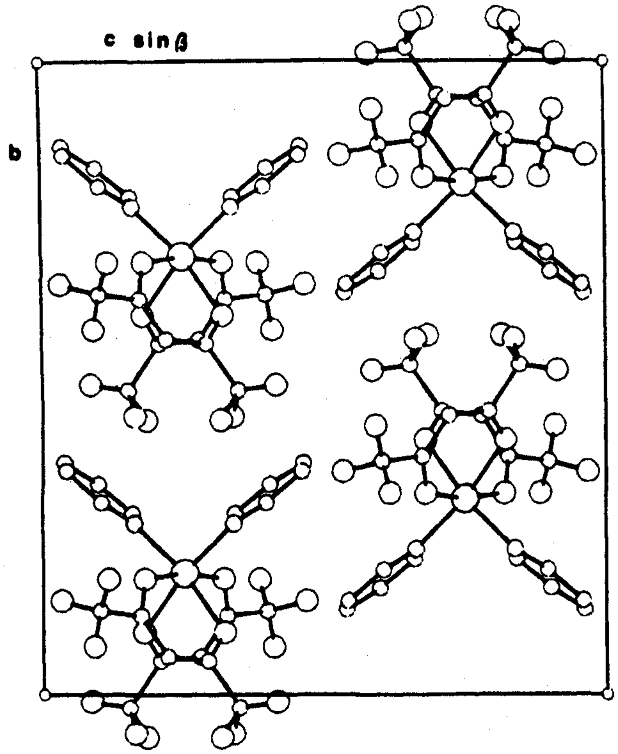

Figure 2. Projection of the unit cell for $Zn(F_6acac)_2(py)_2$ along the *a* axis.

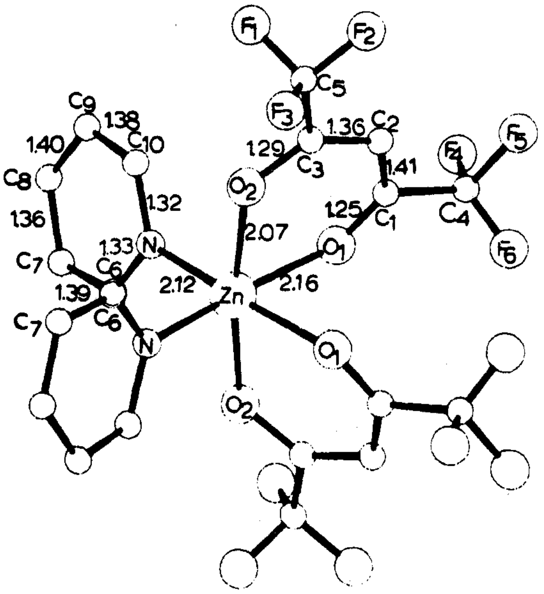

Figure 3. Molecular geometry for $Zn(F_6acac)_2(py)_2$.

Table VI. Bond Lengths (Å) in $Zn(F_6acac)_2(py)_2$. Differences of Normally Equivalent Distances

Atoms	Dist	Diff
Zn-O(1)	2.159 (7)	0.090 (11)
Zn-O(2)	2.069 (8)	
Zn-N	2.116 (7)	
C(1)-O(1)	1.249 (15)	0.039 (20)
C(3)-O(2)	1.288 (14)	
C(1)-C(2)	1.407 (19)	0.048 (25)
C(3)-C(2)	1.359 (17)	
C(6)-N	1.336 (17)	0.010 (24)
C(10)-N	1.326 (17)	
C(6)-C(7)	1.395 (18)	0.012 (38)
C(9)-C(10)	1.383 (20)	
C(7)-C(8)	1.364 (22)	0.035 (33)
C(8)-C(9)	1.399 (24)	
C(1)-C(4)	1.567 (21)	
C(3)-C(5)	1.495 (24)	
C(5)-F(1)	1.24 (3)	
C(5)-F(2)	1.27 (3)	
C(5)-F(3)	1.24 (2)	
C(4)-F(4)	1.21 (2)	
C(4)-F(5)	1.32 (3)	
C(4)-F(6)	1.19 (3)	

Table VII. Bond Angles (deg) in $Zn(F_6acac)_2(py)_2$

Atoms	Angles	Atoms	Angles
N-Zn-O(1)	89.8 (4)	O(1)-C(1)-C(4)	110.3 (1.0)
N-Zn-O(2)	95.1 (4)	O(2)-C(3)-C(5)	112.4 (9)
O(1)-Zn-O(2)	84.3 (3)	C(2)-C(1)-C(4)	119.1 (1.0)
N-Zn-N′	99.0 (4)	C(2)-C(3)-C(5)	119.9 (1.0)
O(2)-Zn-O′(2)	171.2 (3)	F(1)-C(5)-F(2)	98.8 (1.3)
O(1)-Zn-O′(1)	81.7 (3)	F(1)-C(5)-F(3)	106.1 (1.3)
O(1)-C(1)-C(2)	130.5 (8)	F(2)-C(5)-F(3)	107.9 (1.3)
O(2)-C(3)-C(2)	127.7 (8)	F(4)-C(4)-F(5)	95.8 (1.3)
C(1)-C(2)-C(3)	121.0 (8)	F(4)-C(4)-F(6)	124.0 (1.5)
Zn-O(1)-C(1)	122.8 (7)	F(5)-C(5)-F(6)	96.6 (1.4)
Zn-O(2)-C(3)	127.7 (6)		
Zn-N-C(6)	121.2 (7)		
Zn-N-C(10)	121.5 (8)		
N-C(6)-C(7)	124.7 (9)		
N-C(10)-C(9)	122.9 (1.0)		
C(6)-N-C(10)	117.1 (8)		
C(6)-C(7)-C(8)	117.0 (1.0)		
C(8)-C(9)-C(10)	118.7 (1.1)		
C(7)-C(8)-C(9)	119.4 (1.1)		

Table VIII. C-O Infrared Bands and Bond Lengths for Some Copper and Zinc Hexafluoroacetylacetonate Complexes

Compd	Freq,[a] cm^{-1}	C-O dist, Å	Ref
$Cu(F_6acac)_2(dimen)_2$	1675 sp	1.23 (2)	25
$Cu(F_6acac)_2bipy$	1655 b	1.22 (1), 1.26 (1)	21
$Cu(F_6acac)_2(py)_2$	1655 b	1.24 (1), 1.26 (1)	This work
$Cu(F_6acac)_3$	1650 sp	1.26	26
$Cu(F_6acac)_2H_2O$	1644 sp		This work
$Zn(F_6acac)_2(py)_2$	1660 sp, 1645 sp	1.25 (1), 1.29 (1)	This work
$Zn(F_6acac)bipy$	1655 sp, 1640 sp		This work
$Zn(F_6acac)_2py$	1645 sp		This work
$Zn(F_6acac)_2(H_2O)_2$	1645 sp		This work

[a] Key: sp, sharp; b, broad.

suggests that the barrier for rotation of some of the CF_3 groups is probably lower in this adduct than in the zinc complex. Thermal parameters for other atoms suggest similar vibrational motions in the two complexes. The higher amplitudes found for the zinc complex are probably a consequence of the copper impurity doped into the lattice.

It has been found that this complex is the cis bis(pyridine) adduct to $Cu(F_6acac)_2$. $Cu(F_6acac)_2(py)_2$ does not have C_2 symmetry; dihedral angles for least-squares planes show that the relative positions of the pyridine and diketone planes with respect to the equatorial plane Cu-N(1)-N(2)-O(2)-O(4) have small deviations, 10 and 5°, respectively, from the ideal symmetrical angles. Deviations from least-squares planes indicate planarity for the pyridine and benzene rings. Deviations from planarity for the diketone rings and "octahedral planes" are of the same order as those found for the zinc complex. The copper atom is 0.12 and 0.62 Å out of the planes of the pyridine and chelate rings, respectively.

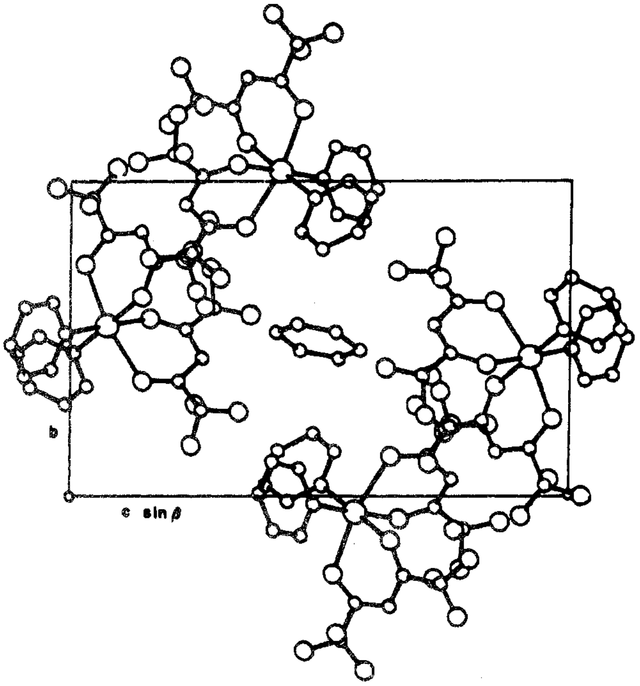

Figure 4. Projection of the unit cell for $Cu(F_6acac)_2(py)_2$ along the *a* axis.

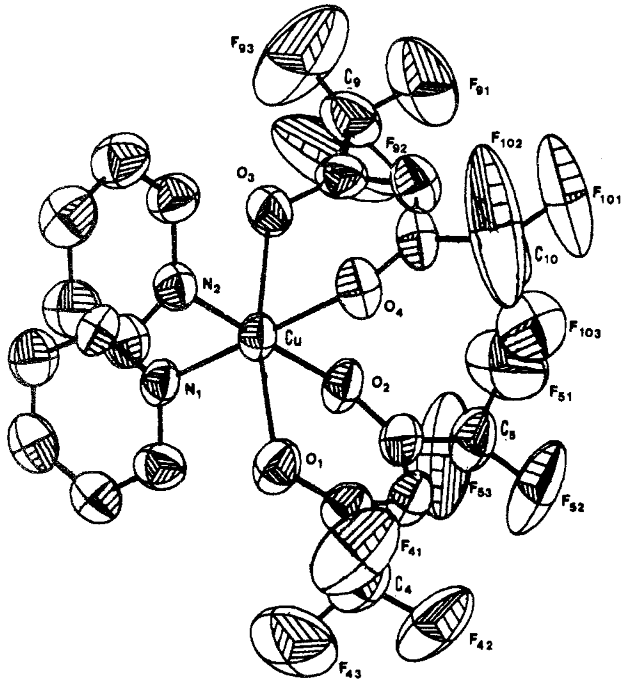

Figure 5. Thermal ellipsoid drawing of $Cu(F_6acac)_2(py)_2$ composed with ORTEP.

Selected bond distances and angles for the complex are listed in Tables IX and X, respectively. An elongated tetragonal structure along the Cu-O bonds cis to the coordinated pyridines has been found. A sketch showing the numbering scheme for atoms in the molecule as well as some relevant distances is found in Figure 6. Fluorine atoms are identified by the first number, which belongs to the carbon attached to them, followed by a sequence number. For carbon atoms in the pyridine molecules the first digit stands for the corresponding nitrogen. In the benzene ring, carbon atoms have been labeled as C_b. Bond distances and some angles involving the CF_3 groups and those belonging to the benzene molecule are listed elsewhere.[34] Average values and their estimated standard deviations are given in Table XI for those bond lengths found equal on the basis of the χ^2 test of normal distribution.[35]

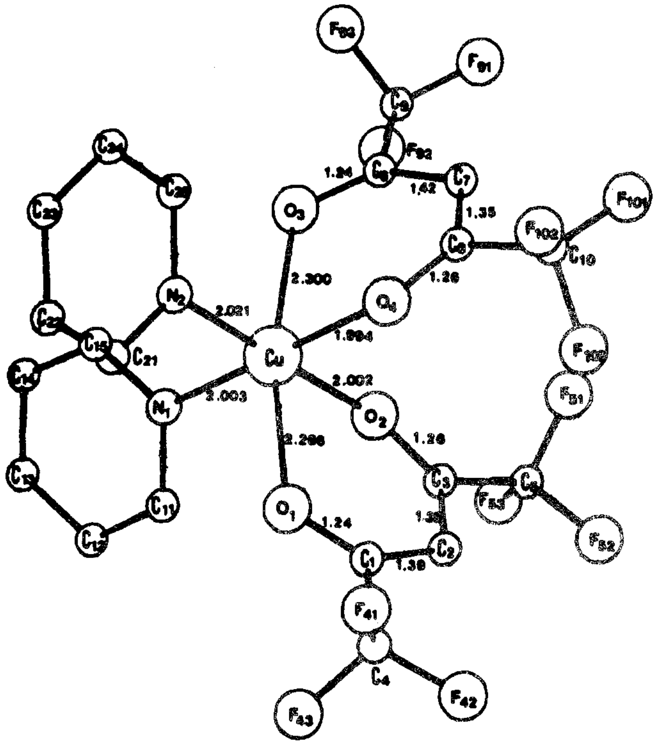

Figure 6. Molecular geometry of $Cu(F_6acac)_2(py)_2$.

Table IX. Bond Lengths (Å) for Copper–Diketone Rings and Copper–Pyridine Atoms in $Cu(F_6acac)_2(py)_2$

Atoms	Dist	Atoms	Dist
Cu-O(1)	2.266 (6)	Cu-N(1)	2.003 (6)
Cu-O(3)	2.300 (6)	Cu-N(2)	2.021 (7)
Cu-O(2)	2.002 (6)	N(1)-C(11)	1.349 (11)
Cu-O(4)	1.994 (5)	C(11)-C(12)	1.405 (10)
C(1)-C(2)	1.386 (14)	C(12)-C(13)	1.369 (15)
C(2)-C(3)	1.378 (13)	C(13)-C(14)	1.390 (14)
C(3)-O(2)	1.257 (11)	C(14)-C(15)	1.385 (12)
C(6)-O(3)	1.238 (10)	N(1)-C(15)	1.331 (10)
C(6)-C(7)	1.418 (13)	N(2)-C(21)	1.329 (11)
C(7)-C(8)	1.353 (15)	C(21)-C(22)	1.388 (15)
C(8)-O(4)	1.263 (10)	C(22)-C(23)	1.381 (15)
C(1)-C(4)	1.548 (15)	C(23)-C(24)	1.380 (15)
C(3)-C(5)	1.529 (14)	C(24)-C(25)	1.389 (15)
C(6)-C(9)	1.528 (15)	N(2)-C(25)	1.347 (11)
C(8)-C(10)	1.520 (16)		

Distortions about the metal and in the β-diketone ring are of the same type as those found[21] in $Cu(F_6acac)_2(bipy)$. An alternation of short and long bond lengths is found in the β-diketone rings. However, the significance of this deformation has only statistical validity. On the basis of the χ^2 test, differences between C-C bonds are found statistically significant although the C-O bonds have been found equivalent. The Cu-O bonds in the equatorial plane are slightly shorter than the Cu-N bonds. Cu-O bond lengths cis to the Cu-N are longer by about 0.28 Å than trans Cu-O distances. The sense of this distortion is opposite to that found

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(35) See ref 27, p 420.

Table X. Bond Angles (deg) for Copper-Diketone Rings and Copper-Pyridine Atoms in $Cu(F_6acac)_2(py)_2$

Atoms	Angle	Atoms	Angle
O(1)-Cu-O(2)	85.0 (3)	N(1)-Cu-N(2)	93.0 (3)
O(1)-Cu-O(3)	167.4 (3)	N(1)-Cu-O(1)	94.3 (3)
O(1)-Cu-O(4)	87.5 (3)	N(1)-Cu-O(2)	90.3 (3)
O(2)-Cu-O(3)	84.7 (3)	N(1)-Cu-O(3)	93.1 (3)
O(2)-Cu-O(4)	87.8 (3)	N(1)-Cu-O(4)	177.2 (3)
O(3)-Cu-O(4)	84.7 (3)	N(2)-Cu-O(1)	93.4 (3)
Cu-O(1)-C(1)	119.6 (5)	N(2)-Cu-O(2)	176.4 (3)
O(1)-C(1)-C(2)	129.5 (6)	N(2)-Cu-O(3)	96.3 (3)
C(1)-C(2)-C(3)	122.6 (7)	N(2)-Cu-O(4)	88.9 (3)
C(2)-C(3)-O(2)	129.3 (6)	Cu-N(1)-C(11)	120.2 (5)[a]
C(3)-O(2)-Cu	126.2 (5)	N(1)-C(11)-C(12)	121.1 (6)
Cu-O(3)-C(6)	118.7 (6)	C(11)-C(12)-C(13)	119.5 (6)
O(3)-C(6)-C(7)	128.9 (7)	C(12)-C(13)-C(14)	118.8 (7)
C(6)-C(7)-C(8)	121.5 (7)	C(13)-C(14)-C(15)	118.8 (7)
C(7)-C(8)-O(4)	131.7 (7)	C(11)-N(1)-C(15)	118.8 (5)
C(8)-O(4)-Cu	124.9 (5)	N(1)-C(15)-C(14)	122.8 (6)
O(1)-C(1)-C(4)	111.8 (6)	Cu-N(1)-C(15)	120.9 (5)
O(2)-C(3)-C(5)	113.5 (6)		
O(3)-C(6)-C(9)	114.5 (7)		
O(4)-C(8)-C(10)	111.6 (7)		

[a] Similar distributions of angles have been found for the second pyridine. Average values for both pyridines are identical (120.1°).

Table XI. Average Values and Their Estimated Standard Deviations for Those Bonds Found Equivalent in $Cu(F_6acac)_2(py)_2$

Type of bond	Av length, Å
C-C (pyridine)	1.386 (4)
C-N	1.339 (7)
C-O	1.250 (6)
$C-CF_3$	1.531 (6)
Cu-N	2.012 (8)
Cu-O (equatorial)	1.998 (4)
C-C (benzene)	1.360 (24)

in $Zn(F_6acac)_2(py)_2$. Reference to Table IX shows that axial metal-oxygen bonds are different by 0.034 (4σ).

Discussion

Multiple bonding between metal and pyridine or other similar nitrogen bases has been suggested for $Co(acac)_2(py)_2$ and some adducts of $Cu(F_6acac)_2$, on the basis of crystallographic studies[36] and thermochemical experiments,[14] respectively. The Zn-N bond length found in $Zn(F_6acac)_2(py)_2$ is longer than the average distance, 2.061 and 2.04 Å, reported for dichloro(1,10-phenanthroline)zinc[37] and $ZnCl_2(NH_3)_2$,[38] respectively. This rather long distance gives no reason to believe that multiple bonding of the d_π-p_π type between the metal and the pyridine is important in $Zn(F_6acac)_2(py)_2$. However, since there are no other crystallographic studies for pyridine coordinated to zinc in octahedral complexes, no definitive interpretation can be presented. For $Cu(F_6acac)_2(py)_2$, Cu-N bond lengths are very similar to the distances found in other copper complexes with both nitrogen and oxygens coordinated to the copper atom, such as $Cu(CH_3CO_2)_2$,[39] α-$Cu(NH_3)_2C_2O_4$,[40] and α-Cu(γ-hydroxyquinolinate).[41]

An alternative way to assess the type of bonding in these complexes may be made by correlating C-O bond distances and infrared stretching frequencies for some of the adducts of zinc and copper hexafluoroacetylacetonates. The data in Table VIII clearly demonstrate that the strong infrared bands found about 1650 cm^{-1} are very sensitive to the extent that metal-chelate interactions occur in these complexes. This is consistent with normal-coordinate analysis of metal β-diketones[42] and the free ligands[43] which attributes this band to the C-O stretching mode, coupled with ring deformations.

When metal chelates of β-diketones react with Lewis bases, it has been considered unlikely that the metal chelates will be disrupted to accommodate the base.[10] However, the structures of $Zn(F_6acac)_2(py)_2$ and $Cu(F_6acac)_2(py)_2$ show that interaction of Lewis bases with metal diketonates may cause a complete rearrangement of the metal-ligand bonds. Truter and coworkers[25] have found that in bis(hexafluoroacetylacetonato)bis(*N,N*-dimethylethylenediamine)copper(II), $Cu(F_6acac)_2(dimen)_2$, the copper atom is chelated to the base with four short Cu-N distances, while the axial positions of the octahedron are occupied by one oxygen atom from each β-ketoenol ligand with long Cu-O bonds of 2.76 Å. Similarly, we have found[1] that under proper conditions four pyridine molecules can be coordinated with the copper atom by replacing one of the oxygen atoms of the ketoenol ring in $Zn(F_6acac)_2(py)_2$ and $Cu(F_6acac)_2(py)_2$. The high value found for the C-O frequency (1675 cm^{-1}) in $Cu(F_6acac)_2(dimen)_2$ is consistent with the structural data that indicate a more ionic form for the ketoenol ligand. For the dipyridine adduct of $Zn(F_6acac)_2$ the C-O band is clearly split; in contrast, for the monopyridine adduct as well as for the diaquo adduct of $Zn(F_6acac)_2$, sharp C-O bands are found at 1645 cm^{-1}. Presumably, in the five-coordinated adduct the axially coordinated pyridine slightly perturbs the in-plane chelate bonding, as in the case of $Cu(acac)_2$(quinoline),[24] while in the cis adduct the pyridine exerts a considerable lengthening effect on the oxygen atom trans to it. Discussion about whether this interaction between the ligands is due to induced charges through the σ-bonded d_{xy} metal orbital or to competition of electron density from the $d_{x^2-y^2}$ π orbital is unwarranted.

The sense of distortion about the metal and in the chelate rings for $Zn(F_6acac)_2(py)_2$ is opposite to that found in $Cu(F_6acac)_2(py)_2$ and $Cu(F_6acac)_2$bipy. This is probably a consequence of strong Jahn-Teller forces or other concurrent forces present in the Cu(II) ion, such as those suggested by Smith,[44] which constitute the dominant effect. For adducts of $Cu(F_6acac)_2$ sharp C-O bands correspond to undistorted chelates and high vibrational frequencies correlate well with weak metal-chelate interactions. However, for the bipyridine and bis(pyridine) adducts broad C-O bands are found instead of the well-resolved C-O peaks of $Zn(F_6acac)_2(py)_2$ and $Zn(F_6acac)_2$bipy.

The distances and angles involving the atoms of the CF_3 groups vary considerably. No significance can be attached to these values since the approximation of the CF_3 motion by anisotropic temperature factors improperly accounts for their complex motion. Average values for the C-C distances in the pyridine rings, 1.386 (4) and 1.385 (8) Å for the Cu and Zn complexes, respectively, as well as the C-N distances,

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Registry No. $Zn(F_6acac)_2(py)_2$, 38402-93-6; $Cu(F_6acac)_2(py)_2$, 38496-50-3.

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Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

Base Adducts of β-Ketoenolates. VI.[1,2]
Single-Crystal Electron Paramagnetic Resonance and Optical Studies of Copper(II)-Doped *cis*-Bis(hexafluoroacetylacetonato)bis(pyridine)zinc(II), Cu-$Zn(F_6acac)_2(py)_2$

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The epr spectra of Cu(II) doped into $Zn(F_6acac)_2(py)_2$ have been investigated at 4.2°K and in the temperature range 133-300°K. At 4.2°K the spectra are those of three kinds of copper ion, each with approximately axial symmetry about one of the three axes of the octahedron. Two of the epr signals have equal values for their magnetic parameters and intensities. The other, which is the strongest one, corresponds to g and hyperfine tensors nearly equivalent to those found at 133°K, with the z axis nearly perpendicular to the CuN_2O_2 plane. Spectra observed above this temperature show that all molecules in the crystal are magnetically equivalent. A temperature dependence has been observed in the spin-Hamiltonian parameters which are weighted averages of the corresponding values for the static configurations found at 4.2°K. The low- and high-temperature epr spectra are interpreted as due to the static and dynamic Jahn-Teller distortions of the complex. A vibronic energy surface, for which one of the three potential energy minima is slightly more favorable than the other two, has been proposed for the copper-doped complex. This nearly degenerate ground state is interpreted as being a consequence of the axial compression that the copper impurity suffers by crystal packing forces. Single-crystal electronic spectra give further support to this interpretation.

Introduction

The implications of the Jahn-Teller theorem for octahedral inorganic complexes possessing electronically degenerate states have been extensively investigated.[3] Experimental evidence of the theoretical predictions is very often clouded by other concurrent physical effects which can produce the same result as the Jahn-Teller forces. This is particularly true for static distortions which one can attribute to ordinary elastic forces in the crystal or other theoretically acceptable possibilities such as those proposed by Smith[4] for tetragonal Cu(II) and Cr(II) systems.

In contrast to ambiguous illustrations of the Jahn-Teller theorem in structural chemistry, a number of examples have been reported in optical[5,6] and microwave spectroscopy.[7,8] The low-energy band found in the near-infrared region (6-10 kK) has been considered a d-d transition in nearly octahedral Cu(II),[5,9,10] Cr(II), and Mn(III)[6] complexes. This assignment is in accord with predictions of Liehr and Ballhausen,[11] who showed that a Jahn-Teller distortion can result in the splitting of the E_g octahedral degeneracy of about 7.0 kK. Transitions between branches of the E ground state, in complexes for which a regular octahedral configuration has been found, have been interpreted as due to dynamic Jahn-Teller distortions.[6] Complexes having an orbital doublet ground state, such as d^9 and low-spin d^7 octahedral ions, have provided most investigations of Jahn-Teller effects by epr methods. Transitions between high-temperature isotropic to low-temperature anisotropic epr spectra[12,13] have been observed for Cu(II) in octahedral environments. O'Brien[14] has provided the theory for strong vibronic coupling and analyzed the dynamic effects resulting when the complex oscillates between the energy minima corresponding to equivalent elongations along the axes of the octahedron.

For those six-coordinate complexes in which the symmetry of the crystal field is obviously lower than trigonal, one cannot rigorously attribute static distortions or fluxional behavior to the Jahn-Teller theorem. However, because ground-state degeneracy might occur accidentally or because a low-lying excited state is energetically favorable for strong vibronic coupling, a "dynamic" epr spectrum may result, above a certain temperature, from populating higher vibronic levels of the complex.

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