Figure 1.—A perspective drawing of $Co(NO_2)_6{}^{4-}$. The cobalt and the atoms of one nitrite ion are labeled.

distance of 2.47 A in sodium nitrite is the same as the difference in ionic radii between barium and sodium. Although the structure is, therefore, well described as made up of discrete ions, the change in color of the compounds with change in M' (becoming darker in color down the periodic table in the alkaline earth series, much darker for Pb^{2+}) indicates that there is at least some charge-transfer interaction between the complex and the divalent metal ion, M'.

In the hexanitrocobaltate(II) ion, Figure 1, the nitrites are monodentate and coordinated through the nitrogen. Although the structure shows six nitrogen

atoms octahedrally surrounding the cobalt(II), the actual crystallographic site symmetry of the cobalt(II) is lower than octahedral. The lower symmetry would be of no consequence if a point-charge model were used to discuss the complex; however, any attempt to consider π bonding would involve the nitrogen π orbitals, and the effective symmetry would be S_6.

Since π-bonding effects are probably appreciable in this complex, the lower symmetry may account for the lack of distortion in the cobalt and copper compounds; although an electronic degeneracy remains in both d^7 and d^9 cases in S_6 symmetry, the orbitals do not point directly at the ligands. The orientation of the orbitals with respect to ligands would be similar to the orientation of the T_{2g} orbitals in O_h symmetry, and degeneracies of the T_{2g} orbitals are expected to produce smaller distortions than degeneracies of the E_g orbitals in octahedral symmetry.

Another alternative to explain the lack of distortion would be a dynamic Jahn–Teller effect; however, temperature-dependent magnetic studies[7] showed no unusual featues down to 80°K. Thus, if there is a dynamic effect, it does not appear possible to freeze this into a static effect above 80°K.

(7) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 338 (1959).

Contribution from the Noyes Chemical Laboratory,
University of Illinois, Urbana, Illinois

The Molecular and Crystal Structure of Bis(1-phenyl-1,3-butanedionato)copper[1]

By PING-KAY HON, C. E. PFLUGER, and R. LINN BELFORD

The structure of the *trans* form of bis(benzoylacetonato)copper(II) has been determined from three-dimensional X-ray diffraction data. The crystals are monoclinic, space group $P2_1/c$ with $a = 4.475$ A, $b = 10.640$ A, $c = 18.486$ A; $\beta = 97° 40'$, $Z = 2$. The crystal is made up of discrete monomers. In each molecule the four oxygens and the copper atom are exactly coplanar. The copper–oxygen distances are 1.94 and 1.91 A. The carbon–oxygen distances are 1.24 and 1.29 A. The carbon–carbon distances agree with the usual acceptable values. The standard deviation is 0.005 A for Cu–O bonds and 0.010 A for C–O and C–C bonds.

Introduction

A structure determination of vanadyl bisbenzoyl-acetonate[2] showed differences among the V–O bond

lengths. The variation was attributed to inductive and resonant effects of the phenyl group. For a comparison, and for analysis of a proposed crystal spectroscopic study, we undertook the determination of the crystal

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

structure of bis(benzoylacetonato)copper(II) (Cu-(bzac)₂, bis(1-phenyl-1,3-butanedionato)copper), represented by the following formula.
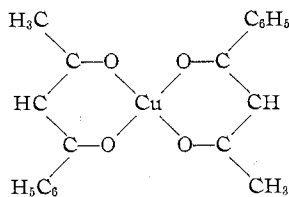
This paper reports the results of the study, which shows that the metal–oxygen bond distances are shortest for the O atom closest to the phenyl group, as in VO(bzac)₂.

Experimental Section

The compound precipitated from a solution consisting of stoichiometric amounts of an aqueous solution of copper sulfate and an ethanol solution of benzoylacetone, neutralized with dilute ammonium hydroxide. It was filtered and washed with water and ether; the bluish gray powder, recrystallized from chloroform, yielded hairy small crystals. *Anal.* Calcd: C, 62.34; H, 4.70. Found: C, 61.79; H, 4.65.

Most of the larger crystals are twinned and have a spine shape. Their diffraction patterns superficially appeared to be orthorhombic but corresponded to none of the space groups. The single crystal used in this study was a clear section cleaved from a large crystal. This section had the dimensions $1.55 \times 0.12 \times 0.09$ mm and was found to be monoclinic, indicating that the aforementioned orthorhombic symmetry was caused by twinning. The needle axis is defined as **a**.

The diffraction zones $(0kl)$, $(1kl)$, $(2kl)$, $(3kl)$ were recorded on multiple films by an integrating Weissenberg camera using the equiinclination geometry. Of the possible 1486 independent reflections within the Cu Kα sphere, a total of 1131 showed above background as measured on a modified Nonius microdensitometer utilizing the peak maximization method. Each unobserved reflection (excepting systematic absences) was arbitrarily assigned an intensity equal to 25% of the weakest measured reflection on the same film.

Unit Cell and Space Group

Unit cell dimensions were obtained from precession and rotation methods with sodium chloride calibration: $a = 4.47_5 \pm 0.005$ A, $b = 10.64_0 \pm 0.005$ A, $c = 18.48_6 \pm 0.010$ A, $\beta = 97° 40' \pm 5'$.

Systematic extinctions indicated the space group to be P2₁/c; $h0l$ absent for $l = 2n + 1$, $0k0$ absent for $k = 2n + 1$. Based on two molecules per unit cell, the calculated density is 1.469 g/ml, which agrees closely with the experimental value, 1.460 g/ml. The space group symmetry and the number of molecules per unit cell require the molecule to have *trans* configuration and the copper atom to be at a center of symmetry.

Determination of the Structure

After correcting all the intensities for the Lorentz-polarization factors (but not for absorption), we calculated the first two-dimensional [100] Fourier projection from the $(0kl)$ reflections with all signs positive. (Comparison to the final calculated structure factors showed this assumption correct for 76% of the reflections, accounting for 88% of the sum of the structure factors.) The resulting map revealed all the atoms with overlapping appearing only for adjacent oxygen and carbon

atoms. Two additional Fourier syntheses reduced the residual R, $(\Sigma||F_o| - |F_c||)/\Sigma|F_o|$, for this layer down to 0.29. This value was still somewhat high because no thermal motion refinements had been carried out; however, the molecular orientation was defined and confirmed.

The first three-dimensional Fourier synthesis, using all the 1486 reflections and signs based on the copper atom alone, defined the molecular orientation in space. The third atomic position (*i.e.*, the x coordinate) for each atom was readily obtained from this three-dimensional map used in conjunction with the quite accurate two-dimensional map. At this moment the crystal structure of this compound was essentially solved and was ready for refinements.

Refinement of the Structure

Refinement at the first stage relied upon three-dimensional Fourier syntheses using 13 isotropic atoms. The following temperature factors were assigned: 2 to the copper, 3 to the oxygens, and 3.7 to the carbons. At the point when the over-all R factor dropped to about 0.28, the least-squares method, as programmed by Gantzel, Sparks, and Trueblood,[3] was employed. Only the 1131 stronger reflections were used in the first stage of least-squares refinement of the atomic positions. The successive refinements included isotropic temperature factors as well as the atomic coordinates until R reached 0.12. The next stage of refinement utilized anisotropic temperature coefficients, first for some and then for all of the atoms. R at this point was 0.084. The final least-squares refinement using all 1486 reflections included the hydrogen atoms which were obtained from a three-dimensional difference map and produced a final R of 0.084 for 1486 reflections and 0.073 if the unobserved reflections were omitted. All the reflections were equally weighted. We did not examine the result of different weighting schemes. The arbitrary weighting formula was used to generate standard deviations. When refinement terminated, atom shifts were much smaller than the corresponding standard deviations.

In all the above calculations the atomic scattering factors were taken from Hanson, *et al.*,[4] for the copper and hydrogen and from the International Tables for X-Ray Crystallography[5] for the oxygen and carbon. All computations employed the IBM 7094 at the Computer Center of the University of Illinois.

Results and Discussion

The final observed and calculated structure factors are listed in Table I. Table II lists the atomic coordinates and the temperature factors. The bond lengths and bond angles are shown in Figure 1 and listed with the estimated standard deviations in Table III.

(3) P. K. Gantzel, R. A. Sparks, and K. N. Trueblood, ACA Computer Program No. 317 for IBM 709 or 7090 (UCLA LS1), University of California, Los Angeles, Calif.

(4) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, **17**, 1040 (1964).

(5) "International Tables for X-Ray Crystallography," Vol. III., The Kynoch Press, Birmingham, England, 1962.

Table I
Observed and Calculated Structure Factors

The copper atom and the four oxygens which form a parallelogram centered on copper are completely planar. The bond lengths are of the same order of magnitude as those found in other copper complexes of this type (Table IV). The differences in the Cu–O bond dis-

tances appears to be significant ($>3\sigma$). Conceivably, incomplete refinement—*e.g.*, neglect to try various weighting schemes, uncertain hydrogen locations, and neglect of absorption—could account for this observed variation; however, it is interesting to note that the

TABLE II
ATOMIC COORDINATES AND TEMPERATURE COEFFICIENTS[a]

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
							$10^5 \times$		
Cu	0.00000	0.00000	0.00000	3667	885	257	−485	−60	−6
	0	0	0	104	13	4	58	27	13
O_1	0.19505	0.15040	−0.02872	229	812	267	−506	−336	98
	98	45	25	295	47	15	178	97	44
O_2	0.25282	−0.00944	0.09193	2173	840	214	−674	−63	61
	104	48	23	328	48	14	204	96	46
C_1	0.55019	0.31329	−0.03104	6946	788	332	−1389	−176	275
	221	78	46	708	77	28	359	213	77
C_2	0.42182	0.20115	0.00531	2418	641	228	72	410	91
	163	65	37	546	62	21	256	158	58
C_3	0.57381	0.16124	0.07285	3875	642	199	−507	−104	−46
	172	66	36	543	62	20	270	153	57
C_5	0.62664	0.03797	0.18968	3146	640	164	−107	−83	−97
	164	62	34	506	59	19	251	142	52
C_6	0.81926	0.12541	0.22795	3874	999	277	−1033	−464	−22
	190	79	42	587	85	25	338	179	75
C_7	0.94234	0.10135	0.29869	5716	1273	251	−1164	−1064	6
	214	89	43	684	103	26	408	204	83
C_4	0.47382	0.06372	0.11419	1466	702	213	26	114	−61
	158	64	35	478	64	20	256	138	58
C_8	0.87968	−0.00951	0.33144	5890	1352	233	907	−306	198
	212	97	42	680	106	24	452	186	90
C_9	0.69206	−0.09736	0.29593	5044	1078	267	−30	−235	255
	206	84	44	649	91	26	371	193	79
C_{10}	0.56130	−0.07336	0.22370	5011	883	238	−762	−107	78
	197	76	40	609	79	24	337	177	69

Hydrogen atoms, with isotropic temperature factor $\exp(-B \sin^2 \theta / \lambda^2)$

	H_1	H_2	H_3	H_4	H_5	H_6	H_7	H_8	H_9
x	0.737	0.855	0.021	0.977	0.636	0.433	0.355	0.715	0.702
y	0.202	0.198	0.148	−0.021	−0.172	−0.133	0.347	0.255	0.335
z	0.094	0.210	0.305	0.372	0.317	0.203	0.026	−0.073	−0.014
B, Å^2	1.0	2.5	6.2	5.1	1.2	1.5	5.0	7.1	3.6

[a] Estimated standard deviations are in next line. The form of the anisotropic temperature factor is $\exp(-B_{11}h^2 - B_{22}k^2 - B_{33}l^2 - B_{12}hk - B_{13}hl - B_{23}kl)$.

TABLE III
BOND LENGTHS AND BOND ANGLES AND THE ESTIMATED STANDARD DEVIATIONS (ESD)

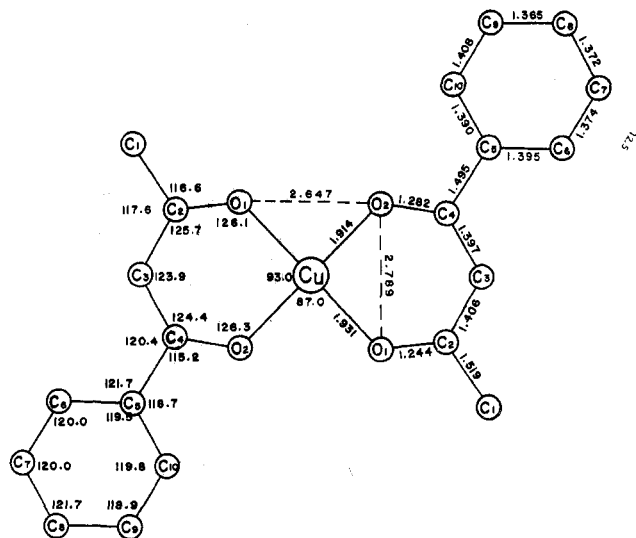|	Length, A	Esd, A		Angle, deg	Esd, deg
Cu–O_1	1.931	0.005	O_1–Cu–O_2	93.0	0.2
Cu–O_2	1.914	0.005	O_1–Cu–O_2'	87.0	0.2
O_1–C_2	1.244	0.008	Cu–O_1–C_2	126.1	0.3
O_2–C_4	1.282	0.008	Cu–O_2–C_4	126.3	0.3
C_2–C_3	1.406	0.010	O_1–C_2–C_1	116.6	0.7
C_3–C_4	1.397	0.010	O_2–C_4–C_5	115.2	0.6
C_1–C_2	1.519	0.011	O_1–C_2–C_3	125.7	0.4
C_4–C_5	1.495	0.009	O_2–C_4–C_3	124.4	0.5
C_5–C_6	1.395	0.011	C_2–C_3–C_4	123.9	0.6
C_6–C_7	1.374	0.011			
C_7–C_8	1.372	0.013	C_1–C_2–C_3	117.6	0.6
C_8–C_9	1.365	0.013	C_3–C_4–C_5	120.4	0.5
C_9–C_{10}	1.408	0.011			
C_{10}–C_5	1.390	0.010	C_4–C_5–C_6	121.7	0.6
			C_4–C_5–C_{10}	118.7	0.5
C_3–H_1	0.89	0.08			
C_6–H_2	0.86	0.09	C_6–C_5–C_{10}	119.4	0.5
C_7–H_3	0.61	0.12	C_5–C_6–C_7	120.0	0.5
C_8–H_4	0.82	0.11	C_6–C_7–C_8	120.0	0.6
C_9–H_5	0.93	0.08	C_7–C_8–C_9	121.7	0.9
C_{10}–H_6	0.91	0.08	C_8–C_9–C_{10}	118.9	0.5
C_1–H_7	0.96	0.11	C_9–C_{10}–C_5	119.8	0.5
C_1–H_8	1.21	0.12			
C_1–H_9	0.75	0.10			

Figure 1.—Bond lengths and bond angles; for standard deviations see Table III.

rather short and the difference between it and the C_4–O_2 bond is greater than the probable uncertainties in these bonds. In bis(3-phenylacetylacetonato)copper(II),[6] the difference between the two C–O bonds is less and about of the same magnitude as the uncertainties in

relative shortening of the Cu–O bond on the phenyl side of the chelate ring is in the same direction as was found in vanadyl benzoylacetonate.[2] The C_2–O_1 bond is

(6) J. W. Carmichael, Ph.D. Thesis, University of Illinois, 1965; J. W. Carmichael, L. K. Steinrauf, and R. L. Belford, *J. Chem. Phys.*, **43**, 3959 (1965).
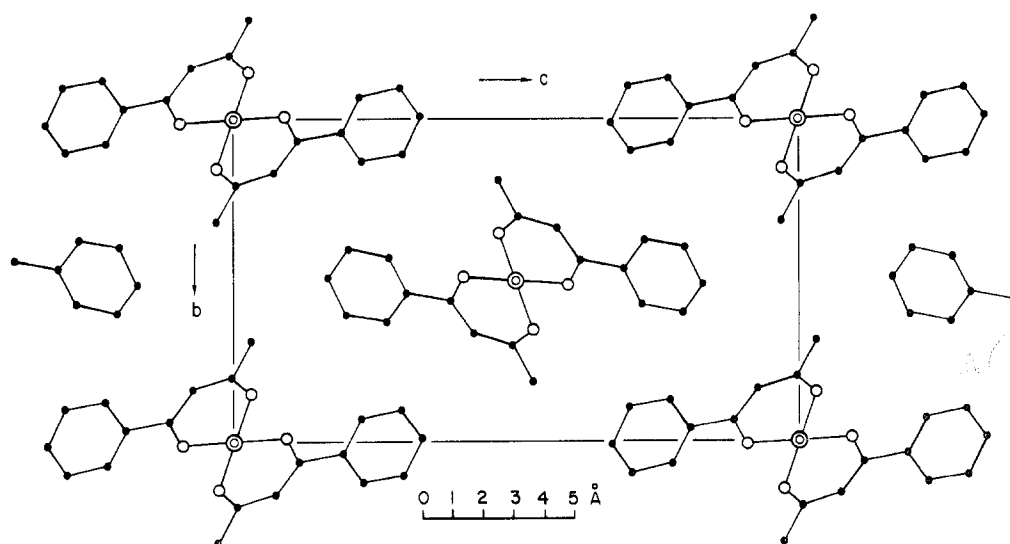
Figure 2.—Copper(II) benzoylacetonate, $Cu(C_6H_5COCHCOCH_3)_2$. Projection along the **a** axis onto the *bc* plane. Hydrogen atoms are omitted.

TABLE IV
COPPER–OXYGEN AND OXYGEN–CARBON BOND DISTANCES

	Cu–O, Å
Bis(benzoylacetonato)copper	1.914
	1.931
Bis(3-phenylacetylacetonato)copper[6]	1.911
	1.902
N,N'-Ethylenebis(acetylacetoneiminato)copper[a]	1.92
	1.96
Bis(acetylacetonato)copper	1.92[b]
	O–C, Å
Bis(benzoylacetonato)copper	1.244
	1.282
Bis(benzoylacetonato)vanadyl[2]	1.292
	1.300
Bis(3-phenylacetylacetonato)copper	1.248
	1.273

[a] D. Hall, A. D. Rae, and T. N. Waters, *J. Chem. Soc.*, 5897 (1963). [b] L. Dahl, unpublished results.

TABLE V
DEVIATIONS OF ATOMS FROM THE MEAN PLANES (Å)

Atom	Plane 1	Plane 2
Cu	0.046[a]	−0.606
O_1	−0.047[a]	−0.338
O_2	−0.016[a]	−0.372
C_1	0.010[a]	0.254
C_2	−0.013[a]	−0.005
C_3	0.049[a]	0.194
C_4	−0.029[a]	−0.068
C_5	. . .	0.003[a]
C_6	. . .	0.003[a]
C_7	. . .	−0.006[a]
C_8	. . .	0.004[a]
C_9	. . .	0.002[a]
C_{10}	. . .	−0.005[a]

[a] The corresponding atoms used in calculation of the mean plane. Equations of the planes are

(1) $0.67367X - 0.59805Y - 0.43417Z - 0.04598 = 0$

(2) $0.83517X - 0.43553Y - 0.33586Z + 0.60556 = 0$

The angle between these two planes is 14° 19'.

these bonds. (There, the phenyl group is symmetrically located and not in strong conjugation with the chelate ring.) The copper, oxygens, and carbons in the

chelate ring are essentially planar (Table V); however, the copper atom is displaced slightly from the chelate ring plane giving rise to a slight chair structure. The mean plane of the phenyl ring carbons makes an angle of 14° 19' with the mean chelate ring plane. This may be compared with the angles of 6.5 and 19° found for vanadyl benzoylacetonate.[2]

The slight twist of 14° should interfere but little with possible inter-ring conjugation (see discussion in ref 1); it may be significant that the phenyl group and chelate ring are close to coplanar when they are attached to the ring carbon neighboring an oxygen (in both *cis*-$VO(bzac)_2$ and *trans*-$Cu(bzac)_2$) but twisted at a large angle when they are attached to the next carbon (as in bis(3-phenylacetylacetonato)copper[6]). Note that the neighboring methyl groups provide a strong intramolecular steric hindrance to coplanarity in the 3-phenylacetylacetonato chelates, while in the bzac chelates only intermolecular crystal forces are available to modify the electronically favored configuration. However, there are on record an insufficient number of cases to allow safe generalizations, particularly as the demands of efficient crystal packing vary from crystal to crystal.

The hydrogen parameters are not extensively refined. A comparatively large error in the carbon–hydrogen bond distances is expected.

As one can see from the scale projections in Figures 2 and 3 and the perspective view of Figure 4, the molecules are disposed in an infinite chain along **a**. They are linked through long $Cu-C_3'$ intermolecular bonds (3.02 Å) that are essentially perpendicular to the primary $Cu-O_4$ bonds and to the chelate rings. Thus about each Cu atom there are six neighbors forming an elongated octahedron. This arrangement is just the same as in monoclinic copper acetylacetonate,[7] which has intermolecular bonds (3.09 Å) from Cu to the middle chelate carbon atoms of two neighboring molecules.

(7) L. Dahl, unpublished results described by T. S. Piper and R. L. Belford, *Mol. Phys.*, **5**, 169 (1962). See also H. Koyama, Y. Saito, and H. Kuroya, *J. Inst. Polytech., Osaka City Univ.*, **C4**, 43 (1953).
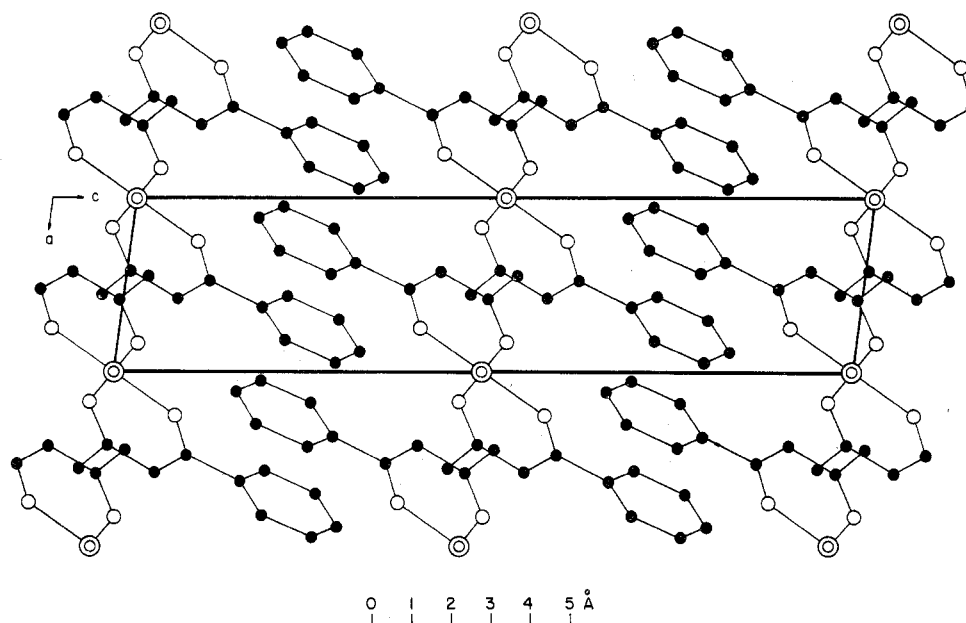
Figure 3.—Copper(II) benzoylacetonate, $Cu(C_6H_5COCHCOCH_3)_2$. The **b** axis projection. Hydrogens are omitted.
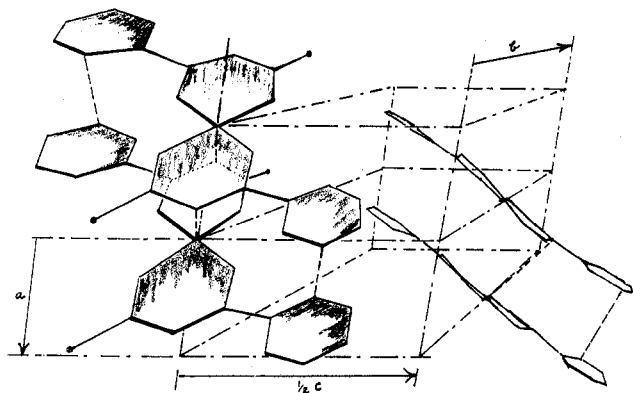

Figure 4.—Perspective view, showing the molecules at 0,0,0; 1,0,0; $0,^1/_2,^1/_2$; $-1,^1/_2,^1/_2$. Solid lines outline molecules, dotted lines outline molecules where hidden behind other molecules, dash–dot lines show coordinate axes, and dashed lines are perpendiculars between corresponding parallel planar segments of neighboring molecules.

In $Cu(bzac)_2$, the phenyl side groups of neighboring molecules in the infinite chain are in contact at 3.74 A, the perpendicular distance between rings coinciding with a line from C_7 of one molecule to C_{10} of the next, as one can visualize from Figure 4. Adjacent infinite chains are related to one another by a shift of $^1/_2\mathbf{b} + ^1/_2\mathbf{c}$

followed by a 180° rotation about **b**. The phenyl ladders of adjacent chains mesh with each other, as may be seen by examination of Figures 2–4.

The two molecules of the unit cell are so situated that their axes (*i.e.*, the $C_3'–Cu–C_3''$ lines or the normals to the chelate planes) make an angle of 36.7° with **b** and 74.4° with each other. Therefore we do not have here the unfortunate situation that arose in $Cu(acac)_2$, in which the corresponding angles are 45 and 90° and the polarized optical spectra therefore were impossible to analyze cleanly.[7]

The molecule has a symmetry of C_i, or C_{2h} if the only intermolecular interaction considered is the $C_3'–Cu–C_3''$ bond and if the slight aplanarities can be ignored. The molecules are clearly resolved as viewed along the **a** and **b** axes (Figures 2 and 3). Optical spectra of the *bc* and *ac* faces should be easy to analyze. An isolated molecule of this compound does not differ very much from bis(3-phenylacetylacetonato)copper(II), and a comparison of their crystal spectra would be valuable in examining the effect of position and twist of the phenyl group. As yet, we have obtained from chloroform, benzene, or carbon tetrachloride solution no single crystals of $Cu(bzac)_2$ of suitable size for polarized optical spectroscopy.