Crystal and Molecular Structure of Deca-μ-acetato-dioxobis(pyridine)-heptazinc(II) and the Electron Paramagnetic Resonance Spectrum of its Copper-doped Crystals

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Crystals of the title complex $[\{Zn_{3.5}O(O_2CMe)_5(py)\}_2]$ (py = pyridine) are orthorhombic, space group *Pbca*, with unit-cell dimensions a = 16.598(3), b = 14.682(4), c = 19.111(9) Å, and Z = 4. The crystal and molecular structure has been determined from diffractometric data by the heavy-atom method and refined by least squares to R 0.076. Seven zinc atoms, bridged by acetate groups, form a heptameric centrosymmetrical unit. In each of the two semi-units a central oxygen is surrounded tetrahedrally by three zinc atoms which are in a tetrahedral arrangement, and by one zinc atom in a tetragonally compressed octahedral environment. The low-temperature e.s.r. spectrum of ^{63}Cu-doped crystals of the complex is reported. The paramagnetic ion is substituted at the compressed tetragonal zinc site. The g, metal hyperfine-coupling, and quadrupole-coupling tensors have been obtained from an analysis of the angular variation of the spectra. In spite of the low site symmetry indicated by the X-ray results, an almost pure d_{z^2} ground state is found to be present. A small 4s admixture is assumed to be responsible for the reduced value of the isotropic part of the copper hyperfine tensor.

As a continuation of our studies of copper(II) complexes of α-nitroketones we have recently investigated the e.s.r. spectra of some of these complexes diluted in the diamagnetic, isomorphous, zinc(II) analogues.[1,2]

During the preparation of single crystals of copper(II)-doped bis(nitroacetonato)bis(pyridine)zinc(II) some solutions yielded, on standing, crystals of a different complex, which was later found to be an oligomeric basic zinc acetate derivative [hereafter referred to as (1)]. It has long been known[3] that, upon alkaline hydrolysis, α-nitroketones readily undergo cleavage of the carbon–carbon bond in the α position with respect to the nitro-group. Thus the formation of the acetate anion starting from a solution containing nitroacetone in the presence of water and pyridine is not surprising. Later, complex (1) was also obtained by appropriate crystallization of zinc acetate dihydrate.

Since the system (1) showed some interesting structural and spectroscopic features, further work has been carried out and we now report the determination of its crystal and molecular structure, together with an e.s.r. study of its copper-doped crystals.

EXPERIMENTAL

Preparation of complex (1).—The complex $[Zn(na)_2(OH_2)_2]$[4] (na = nitroacetonate) or $[Zn(O_2CMe)_2(OH_2)_2]$ (150 mg) was dissolved in a mixture of acetone (10 cm^3) and pyridine (0.3 cm^3), in the presence of *ca.* 1% of $^{63}CuCl_2\cdot 2H_2O$ (purchased from Oak Ridge National Laboratories in the form of copper oxide). n-Heptane (10 cm^3) was added and the container stoppered and set aside at room temperature. Large pale yellow crystals were obtained after *ca.* 1 week.

Small pale green crystals of $[(Cu,Zn)(na)_2(py)_2]$ (py = pyridine) could be obtained after 1 or 2 d when the nitroacetonato-complex was used as starting material. Usually these dissolve again to give crystals of copper-doped (1) after some days.

Starting with $[Zn(O_2CMe)_2(OH_2)_2]$, light blue crystals of $[(Cu,Zn)(O_2CMe)_2(py)]$ could be obtained, together with crystals of copper-doped (1). The yield of the monopyridine derivative could be decreased by using smaller amounts of copper ion (*ca.* 0.1—0.3%).

Crystal Data.—$C_{30}H_{40}N_2O_{22}Zn_7$, M = 1 238.2, colourless orthorhombic prisms, a = 16.598(3), b = 14.682(4), c = 19.111(9) Å, U = 4 657 Å^3, D_m = 1.77 ± 0.01 (by flotation), Z = 4, D_c = 1.77 g cm^3, $F(000)$ = 2 470.76, μ(Mo-K_α) = 37.31 cm^{-1}, space group *Pbca* (D_{2h}^{15}, no. 61) from systematic absences and structure determination.

All the data were collected on a Syntex $P2_1$ automatic four-circle diffractometer by the θ—2θ scan technique. Only the intensities of the 1 133 independent reflections having $I \geqslant 3\sigma(I)$ were used throughout the refinement. The data were corrected for background and for Lorentz and polarization effects. Given the low value of μ and the dimensions of the crystal (*ca.* 0.1 × 0.2 × 0.2 mm), an absorption correction was not applied. Unit-cell parameters were obtained from a least-squares fit to the angular setting of 15 reflections having $2\theta \geqslant 25°$.

Calculations.—Calculations were made on the Univac 1108 computer at Rome University using the system of programs of the Laboratorio di Strutturistica Chimica del C.N.R. Neutral-atom scattering factors, and corrections for the anomalous dispersion of zinc, were taken from ref. 5.

Determination and Refinement of the Structure.—The solution and refinement of the structure proceeded by standard methods. The three zinc atoms in general positions were located from a three-dimensional Patterson synthesis computed using the full set of observed independent terms. A Fourier map phased on the positions of four zinc atoms, the fourth required to lie on $\bar{1}$ from symmetry considerations, was sufficient to locate all the remaining non-hydrogen atoms. Block-diagonal least-squares refinement was carried out on F. The function minimized was $\Sigma w(|F_o| - k|F_c|)^2$. The weighting scheme $w = (a + bF_o + cF_o^2)^{-1}$, where a = 20.0, b = 1.0, and c = 0.000 01, was used. With individual atoms given isotropic thermal parameters, refinement converged at R 0.103. Refinement was continued using anisotropic thermal parameters until final shifts in the atomic parameters were $< 0.2\ \sigma$ at which stage the final R was 0.076. Final least-squares atomic parameters with standard deviations are in Table 1. Calculated and observed structure factors, and thermal parameters, are listed in Supplementary Publication No. SUP 22342 (9 pp.).* Interatomic distances and angles within the chemical unit are shown in Table 2.

Spectra.—Single-crystal e.s.r. spectra were recorded at the *X*-band frequency using a Varian E-9 spectrometer equipped with a variable-temperature accessory. Magnetic-field intensities were used without corrections, after checking the linearity of the field with a manganese(II)-doped sample of MgO. Diphenylpicrylhydrazyl (dpph) was used as a *g* marker (*g* 2.003 6). The crystal was mounted on a quartz rod by means of apiezon grease and measurements were carried out around three arbitrary rotation axes. In each plane, spectra were recorded at 10° intervals at *ca.* 110 K.

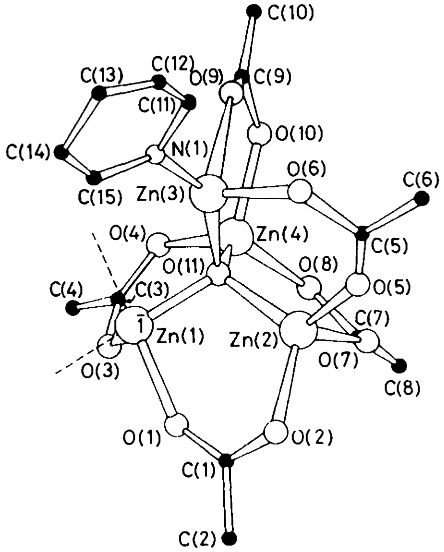

FIGURE 1

TABLE 1

Atom co-ordinates ($\times 10^4$), with standard deviations in parentheses

	x/*a*	*y*/*b*	*z*/*c*
Zn(1)	0	0	0
Zn(2)	456(3)	−2 036(2)	353(2)
Zn(3)	1 353(3)	−326(2)	1 058(2)
Zn(4)	1 668(2)	−829(2)	−542(2)
O(1)	−868(12)	−1 014(12)	−363(8)
O(2)	−707(14)	−2 224(12)	−347(10)
O(3)	302(14)	244(14)	−1 112(9)
O(4)	1 576(13)	52(13)	−1 297(10)
O(5)	897(15)	−2 635(14)	1 171(13)
O(6)	1 565(16)	−1 494(16)	1 635(10)
O(7)	786(19)	−2 821(16)	−417(12)
O(8)	1 680(16)	−2 000(13)	−1 025(8)
O(9)	2 527(17)	−101(17)	874(11)
O(10)	2 777(15)	−629(15)	−191(10)
O(11)	882(12)	840(11)	207(8)
N(1)	1 207(15)	526(14)	1 910(10)
C(1)	−1 148(21)	−1 758(20)	−62(13)
C(2)	−2 010(26)	−2 041(34)	−201(24)
C(3)	891(19)	369(19)	−1 471(14)
C(4)	791(24)	851(27)	−2 159(15)
C(5)	1 391(22)	−2 310(21)	1 602(16)
C(6)	1 883(26)	−2 925(22)	2 069(16)
C(7)	1 290(23)	−2 745(19)	−909(16)
C(8)	1 458(34)	−3 538(26)	−1 394(22)
C(9)	3 038(25)	−320(22)	399(19)
C(10)	3 945(18)	−188(32)	494(20)
C(11)	1 739(20)	315(15)	2 431(10)
C(12)	1 661(23)	751(20)	3 084(18)
C(13)	1 088(23)	1 428(27)	3 156(12)
C(14)	552(23)	1 639(24)	2 593(17)
C(15)	645(20)	1 181(15)	1 981(14)

The theory and the computer programs used to derive principal values and orientations of the various tensors have been described elsewhere.[6] The experimental spectra were fitted to the spin Hamiltonian (1) using second-order perturbation theory. No assumptions were made concerning the relative orientation of the various tensors.

TABLE 2

Bond distances (Å) and angles (°), with standard deviations in parentheses

(*a*) Distances

Zn(1)–Zn(2)	3.157(3)	O(1)–C(1)	1.32(3)
Zn(1)–Zn(3)	3.060(4)	O(2)–C(1)	1.27(4)
Zn(1)–Zn(4)	3.197(4)	O(3)–C(3)	1.21(4)
Zn(1)–O(1)	2.18(2)	O(4)–C(3)	1.27(4)
Zn(1)–O(3)	2.21(2)	O(5)–C(5)	1.26(4)
Zn(1)–O(11)	1.95(2)	O(6)–C(5)	1.24(4)
Zn(2)–Zn(3)	3.215(5)	O(7)–C(7)	1.26(4)
Zn(2)–Zn(4)	3.181(5)	O(8)–C(7)	1.29(4)
Zn(2)–O(2)	1.95(2)	O(9)–C(9)	1.28(5)
Zn(2)–O(5)	1.94(3)	O(10)–C(9)	1.29(4)
Zn(2)–O(7)	1.95(2)	N(1)–C(11)	1.37(3)
Zn(2)–O(11)	1.96(2)	N(1)–C(15)	1.35(4)
Zn(3)–Zn(4)	3.190(4)	C(1)–C(2)	1.51(6)
Zn(3)–O(6)	2.07(2)	C(3)–C(4)	1.50(4)
Zn(3)–O(9)	2.01(3)	C(5)–C(6)	1.51(5)
Zn(3)–O(11)	1.96(2)	C(7)–C(8)	1.52(5)
Zn(3)–N(1)	2.07(2)	C(9)–C(10)	1.53(5)
Zn(4)–O(4)	1.94(4)	C(11)–C(12)	1.41(4)
Zn(4)–O(8)	1.95(2)	C(12)–C(13)	1.38(5)
Zn(4)–O(10)	1.98(2)	C(13)–C(14)	1.43(5)
Zn(4)–O(11)	1.94(2)	C(14)–C(15)	1.36(4)

(*b*) Angles

O(1)–Zn(1)–O(11)	97.4(7)	Zn(2)–O(2)–C(1)	120(2)
O(1)–Zn(1)–O(3)	87.4(7)	Zn(1)–O(3)–C(3)	139(2)
O(3)–Zn(1)–O(11)	97.3(7)	Zn(4)–O(4)–C(3)	121(2)
O(2)–Zn(2)–O(5)	108.4(9)	Zn(2)–O(5)–C(5)	127(2)
O(2)–Zn(2)–O(7)	101.0(11)	Zn(3)–O(6)–C(5)	138(2)
O(2)–Zn(2)–O(11)	119.7(8)	Zn(2)–O(7)–C(7)	134(2)
O(5)–Zn(2)–O(7)	103.6(10)	Zn(4)–O(8)–C(7)	131(2)
O(5)–Zn(2)–O(11)	113.3(8)	Zn(3)–O(9)–C(9)	136(2)
O(7)–Zn(2)–O(11)	109.2(9)	Zn(4)–O(10)–C(9)	131(2)
O(6)–Zn(3)–O(9)	93.7(10)	Zn(1)–O(11)–Zn(2)	109.4(9)
O(6)–Zn(3)–O(11)	101.0(8)	Zn(1)–O(11)–Zn(3)	103.0(8)
O(6)–Zn(3)–N(1)	95.9(8)	Zn(1)–O(11)–Zn(4)	110.5(8)
O(9)–Zn(3)–O(11)	107.8(8)	Zn(2)–O(11)–Zn(3)	112.3(8)
O(9)–Zn(3)–N(1)	98.8(10)	Zn(2)–O(11)–Zn(4)	111.4(8)
O(11)–Zn(3)–N(1)	147.3(9)	Zn(3)–O(11)–Zn(4)	110.0(9)
O(4)–Zn(4)–O(8)	103.7(8)	O(1)–C(1)–O(2)	121(3)
O(4)–Zn(4)–O(10)	103.1(9)	O(3)–C(3)–O(4)	121(3)
O(4)–Zn(4)–O(11)	120.0(8)	O(5)–C(5)–O(6)	124(3)
O(8)–Zn(4)–O(10)	106.3(10)	O(7)–C(7)–O(8)	122(3)
O(8)–Zn(4)–O(11)	110.4(8)	O(9)–C(9)–O(10)	119(4)
O(10)–Zn(4)–O(11)	112.1(8)	Zn(3)–N(1)–C(11)	111(2)
Zn(1)–O(1)–C(1)	131(2)	Zn(3)–N(1)–C(15)	126(2)

$$H = \mu_b B\,.\,g\,.\,S + S.A.I - g_n\mu_n B.I + I.P.I \qquad (1)$$

DISCUSSION

Description of the Structure.—The most noteworthy aspect of the structure of (1) is shown in Figure 1. Seven zinc atoms bridged by acetate groups form a heptameric centrosymmetrical unit. In each one of the two semi-units a central oxygen is surrounded tetrahedrally by four zinc atoms. Five of the six edges of the resulting tetrahedron are bridged by acetate groups. The sixth one, Zn(1)–Zn(3), is open. There are, therefore, three

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

types of non-equivalent zinc atoms: Zn(1), which lies on the centre of symmetry, has an octahedral arrangement; Zn(3) is tetrahedrally co-ordinated to three oxygen atoms and to the nitrogen atom; Zn(2) and Zn(4) are also tetrahedrally co-ordinated, but to four oxygen atoms. The structure strongly resembles that of $[\mathrm{Zn_4O(O_2CMe)_6}]$ where a closed tetrahedron of zinc atoms surrounds an ' inner ' oxygen.[7]

In the title complex the pyridine molecule opens out one edge of the tetrahedron and, for stoicheiometric reasons, one of the two zinc atoms of the opened edge has to change its co-ordination geometry, by ' duplicating ' its three co-ordination directions. The resulting slightly distorted octahedron of oxygen atoms is therefore tetragonally compressed, the bond distance Zn(1)–O(11) being that relative to a tetragonally co-ordinated oxygen. The Zn–O distances [2.20(2) Å] in the d_{xy} plane containing Zn(1), O(1), and O(3) are actually significantly longer than in the d_{z^2} direction [Zn(1)–O(11) 1.95(2) Å], confirming the description above and the e.s.r. data.

From a comparison with data available in the literature, we note that, about the tetrahedral zinc atoms, Zn(2)–O and Zn(4)–O distances are in the narrow range 1.94—1.96 Å (σ 0.02 Å) comparable with those found in $[\mathrm{Zn_4O(O_2CMe)_6}]$ [7] and $[\mathrm{Zn\{SC(NH_2)_2\}_2(O_2CMe)_2}]$,[8] while Zn(3)–O distances are spread over the range 1.96—2.07 Å by the great distortion of the co-ordination tetrahedron owing to the steric hindrance of the pyridine molecule, the six tetrahedral angles around Zn(3) being greatly different from the ideal value of 109.5° [range 96—147° (see Table 2)].

Only two intermolecular contacts shorter than 3.5 Å are present: C(12) · · · O(4) and C(12) · · · O(10), 3.37 and 3.43 Å(σ 0.04 Å) respectively.

E.S.R. Results.—According to the *X*-ray results given above, for a general orientation of the external magnetic field, the e.s.r. spectrum of a crystal of copper-doped (1) is expected to be a superimposition of several copper signals. Apart from possible copper–copper interactions, giving rise to triplet spectra, 28 partly chemically, partly magnetically, inequivalent sites are available for copper substitution. Despite this, the experimental spectra depict a much simpler situation. The major features of the spectrum (Figure 2) can be analyzed by assuming four groups of four signals, coalescing to two sets in the crystallographic planes (Figure 3) and to only one set along the crystallographic axes. On this basis, we assume that copper substitution mainly occurs for only one of the seven possible zinc atoms. The behaviour of the e.s.r. spectra, suggesting an almost pure d_{z^2} ground state, indicates that the paramagnetic ion enters the compressed tetragonal Zn(1) site, which is the only one consistent with such a ground-state orbital.

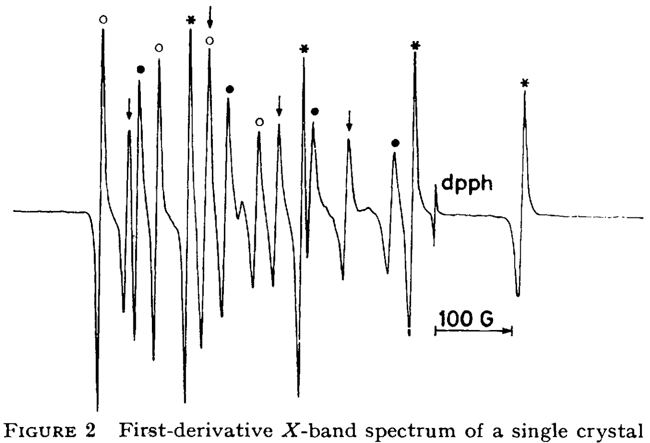

FIGURE 2 First-derivative *X*-band spectrum of a single crystal of copper-63-doped (1) for an arbitrary orientation of the external magnetic field. Absorptions from the four inequivalent sites are indicated

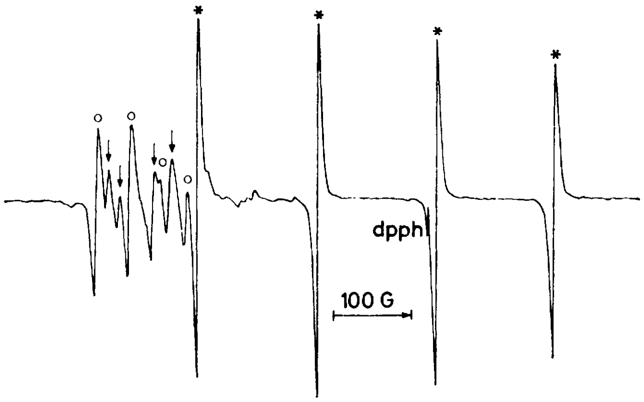

FIGURE 3 First-derivative *X*-band spectrum of a single crystal of copper-63-doped (1). The external magnetic field lies in a crystallographic plane. So-called ' forbidden ' lines are indicated by arrows in the low-field part of the spectrum

In addition, other weak signals, due to a chemically different copper ion, can be observed in the spectra. They show clearly resolved hyperfine interaction with one nitrogen nucleus (^{14}N, 100%, $I = \frac{1}{2}$) and are attributed to substitution of some of the copper ions at the Zn(3) tetrahedral site. Since these signals have rather low intensity and have been observed only in few of the several crystals examined, no detailed analysis has been possible and they will not be mentioned further.

Finally, $\Delta M_I > 0$ transitions have been detected. Their intensity results from mixing of spin states with different M_I values by nuclear Zeeman and quadrupole interactions. Keeping in mind that our measurements were carried out at the *X*-band frequency, where nuclear Zeeman effects are small, the high intensity of the forbidden signals points to the presence of a rather large quadrupole coupling tensor. The principal values of the tensors, the angles that their axes make with the crystal axes, and their relative orientations are reported in Table 3. The final values have been obtained by averaging the experimental results for three of the four magnetically inequivalent sites. Extensive overlapping of the signals led to large inaccuracies in the results for the fourth site.

The *g* and hyperfine-coupling tensors are not diagonal in the same axis system; they have one common axis, *i.e.* g_3 and A_1^{Cu}, while the other components, in the perpendicular plane, are rotated by *ca.* 28° with respect to one another. The common axis of the two tensors was located along the tetragonal axis of the molecular frame, *i.e.* along the Zn–O(11) bonding direction. The presence of large distortions in the bonding angles, as shown by the *X*-ray results [O(1)–Zn–O(11) and O(3)–Zn–O(11) are both *ca.* 97°], implies that the other magnetic axes cannot coincide with any simple molecular direction. However, g_1 and g_2 roughly point along the in-plane metal–oxygen bonds.

TABLE 3

Principal values and principal axes of the *g* tensor, the metal hyperfine-coupling, and quadrupole-coupling tensors (10^{-4} cm^{-1}) for copper-doped (1) at 110 K

Principal axis	Principal value	Estimated [a] error	Direction angles [b]		
g_1	2.293 0	0.000 2	73	70.5	16
g_2	2.267 4	0.000 2	54.5	50.8	79.5
g_3	1.996 1	0.000 2	40.5	51	79.8
$g_{av.}$ [c]	2.185 4				
A_1	164.55	0.3	89.7	89.5	179.5
A_2	32.45	0.5	62.5	27.5	89.5
A_3	18.5	0.5	27.5	117.5	90
$A_{av.}$ [c]	37.9				
P_1	3.35	0.05	70	23	102
P_2	−0.80	0.1	97	100	168
P_3	−2.55	0.1	21	110	93
Zn–O(3)			77	81	164
Zn–O(1)			131	133	108
Zn–O(11)			41	129	78

[a] Defined as the largest difference between the corresponding principal values of the magnetically inequivalent sites in the unit cell. [b] The eigenvectors of the *g* tensor and of the metal–oxygen bond distances are given with respect to the crystal-axis system. The direction angles of the *A* and *P* tensors are referred to the *g*-axis system. [c] Average values; $A_{av.}$ was calculated assuming that A_1 is opposite in sign to A_2 and A_3 (see text).

The largest A^{Cu} component is associated with the smallest *g* value, the latter being very close to the free-electron *g* value. These observations indicate that the molecular orbital of the unpaired electron is an essentially d_{z^2} type.[9] Indeed the g_3 value is even smaller than g_e, suggesting negligible mixing with other *d* orbitals. Considering the low symmetry of the metal-ion environment, as revealed by the *X*-ray measurements, this is a rather surprising result. For true d_{z^2} ground states, g_z (or g_3) is expected to be $\leqslant$2.002 3, if higher-order terms of the type $(\lambda/\Delta)^2$ are taken into account[9] [equation (2)]. Small admixtures of other *d* orbitals, mainly $d_{x^2-y^2}$, may raise g_z well above this value.

$$g_z = g_e - 3[\lambda/\Delta(xz,yz\rightarrow z^2)]^2 \qquad (2)$$

More detailed information can be achieved following the approach of Swalen *et al.*[10] The ground-state orbital wavefunction is written as a linear combination of all the five *d* orbitals. The *g* and A^{Cu} values are then used to derive the five coefficients and the dipolar and isotropic terms. The results of Table 4 show that the experimental *g* values can be reproduced, with reasonable accuracy, by using only three instead of five coefficients. Admixture of the $d_{x^2-y^2}$ and d_{xy} orbitals appears to be unimportant. A small difference in the coefficients and/or energy of the two out-of-plane orbitals, d_{xz} and d_{yz}, is enough to account for the observed in-plane *g* anisotropy.

TABLE 4

d-Orbital mixing coefficient and calculated magnetic parameters for copper-doped (1)

Parameter		Axis	*g*	A^{Cu}
c_{z^2}	0.9983			
$c_{x^2-y^2}$	0			
c_{xy}	0	*x*	2.2940	−21.4
c_{xz}	0.0430	*y*	2.2690	−31.1
c_{yz}	0.0395	*z*	1.9954	164.6
P	369			
K	0.089			

As far as the A^{Cu} principal values are concerned, satisfactory agreement with experiment, together with reasonable values of *P* and *K*, could be obtained only with the choice of signs of Table 4. Different choices invariably led to poor calculated A^{Cu} values or unrealistic, or negative, values of *P* and *K*. However, since the isotropic spectrum could not be measured we do not have experimental support for this result. The calculated *P* value shows almost no reduction with respect to the free-ion value (360×10^{-4} cm^{-1}), whereas the *K* value is much smaller than that usually observed[11] (*ca.* 0.3). It is well known that the isotropic part of the hyperfine splitting is the result of two main contributions of opposite sign, *i.e.* spin polarization of the inner-shell *s* electrons and direct participation of the 4*s* orbital in the ground-state molecular orbital. Although the former is usually the dominating effect, a small 4*s* participation can strongly reduce the observed value of A_{iso}, or even change its sign. In C_{2h} notation the ground state of copper-doped (1) is an A_g-type orbital and hence 4*s* mixing is symmetry-allowed. The effect on the isotropic part of the hyperfine interaction can be quite large, even for a small value of the mixing coefficient. For instance, 5% admixture would raise the calculated *K* value to 0.20.

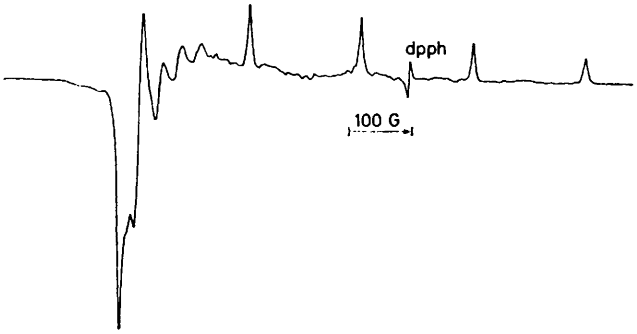

FIGURE 4 *X*-Band powder spectrum of copper-63-doped (1)

Strongly tetragonal systems, such as the one we are dealing with, are expected to give rise to large quadrupole interactions. Compared to other results reported in the literature[12,13] our *P* values appear to be rather small. We believe that this is a consequence of the type of data analysis used. The results of Table 3 were obtained by fitting the line positions of the $\Delta M_I = 0$ transitions with the aid of second-order perturbation expressions. It is well known that, in the presence of large quadrupole effects, this approach may be inadequate to reproduce the positions of the ' allowed ', as well as of the ' forbidden ', lines.[13] Probably accurate P values may be obtained only by exact diagonalization of the energy matrix. However, trial calculations, performed using both the strong-field approximation and the complete spin Hamiltonian, have shown that the other magnetic parameters are rather insensitive to the exact value of the quadrupole-coupling tensor.

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