

The foregoing kinetic analysis has been for lines separated only by chemical shifts. Such an excursion as that of a methyl group from $\text{Ga}(\text{CH}_3)_3$ to short-lived $\text{Al}(\text{CH}_3)_3$ and back to $\text{Ga}(\text{CH}_3)_3$ will not contribute to line broadening, in accord with the Gutowsky-Holm equation.⁴ If collapse of a spin multiplet were involved, such excursions would contribute to $1/\tau$ and would have to be taken into account. The present method of kinetic analysis can be extended to multistage reactions by assigning a different fraction Q_1, Q_2, \dots, Q_n to each intermediate and solving for the Q 's by means of the equilibrium relationships.

(4) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

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Electron Spin Resonance of Copper Bis(dibenzoylmethane). Superhyperfine Anomalies¹

Sir:

Recently So and Belford² commented on the report of Kuska, *et al.*,³ about the esr spectra of frozen solu-

tions of bis(1,3-diphenyl-1,3-propanedionato)copper $\{\text{Cu}(\text{dbm})_2\}$. Kuska, *et al.*, attributed the complicated "superhyperfine structure" which is observed in frozen chloroform solutions to a delocalization of the unpaired electron over the phenyl groups leading to a substantial interaction with the protons of these rings. So and Belford showed that the same compound exhibits a completely normal esr spectrum if the solutions are prepared with commercial grade chloroform at room temperature. Spectra similarly complicated as those of Kuska, *et al.*, were obtained as soon as the solution was boiled before taking the esr spectrum.

So and Belford postulated from this observation that an unidentified radical species is formed upon boiling the chloroform solution. They also observed a diminution of these extra hyperfine lines when toluene is added to a boiled chloroform solution. They attribute this effect to a sensitivity of the "radical species" toward toluene.

This communication prompted us to reproduce the esr spectra of $\text{Cu}(\text{dbm})_2$ in frozen solutions, since we had observed similar hyperfine structure anomalies in several esr spectra of frozen solutions of low-spin Co(II) complexes.⁴ However, the reason for these anomalies was found to be rather trivial, and we could prove that the anomalous spectra of $\text{Cu}(\text{dbm})_2$ can be explained as follows.

We call the appearance of an unexpected and complicated hyperfine pattern in the esr spectrum of a

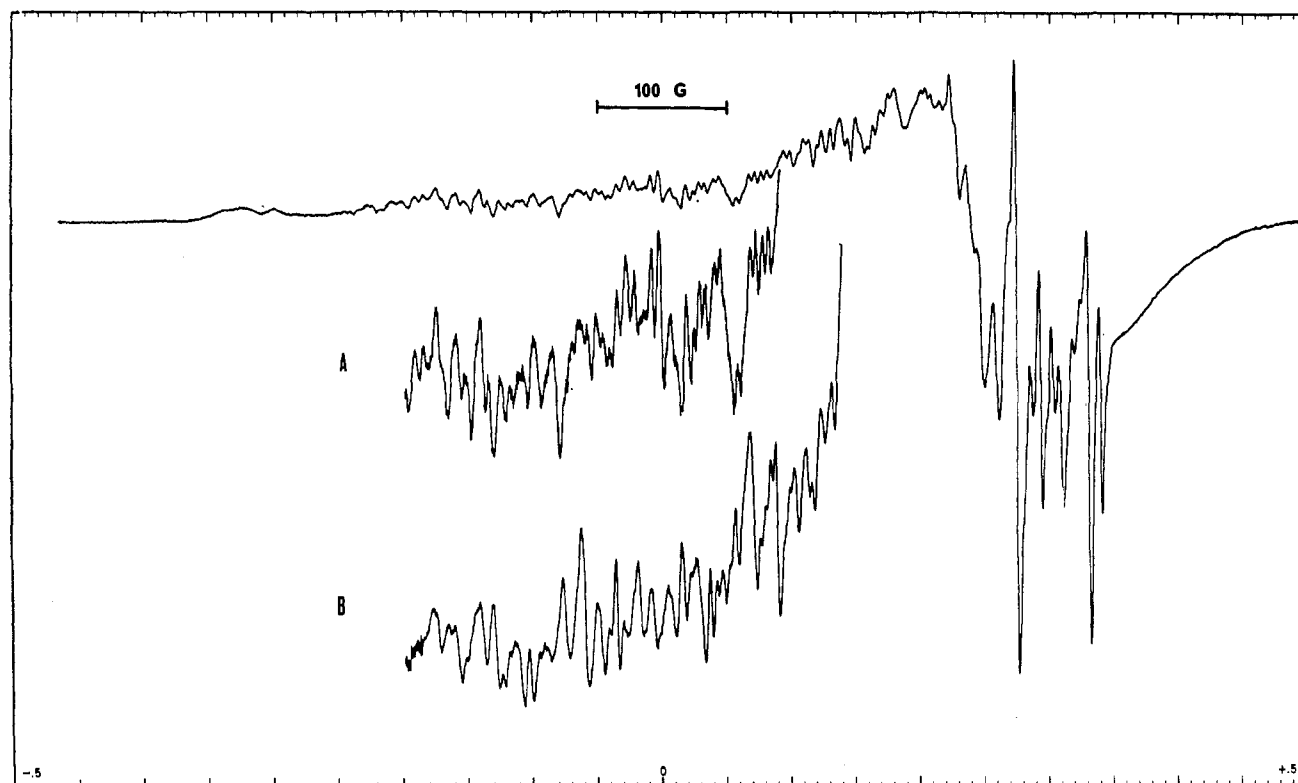


Figure 1.—First-derivative esr spectra of $\text{Cu}(\text{dbm})_2$ frozen solutions at 100°K : A, receiver gain 5 times higher than in the upper spectrum; B, rotation of sample tube *ca.* 90° with respect to orientation of trace A.

(1) Supported by a grant from the Swiss National Foundation for Scientific Research.

(2) H. So and R. L. Belford, *Inorg. Chem.*, **9**, 2194 (1970).

(3) H. A. Kuska, M. T. Rogers, and R. E. Drullinger, *J. Phys. Chem.*, **71**, 109 (1967).

frozen solution in our laboratory jargon the "single-crystal effect." The esr line shape normally observed in frozen solutions or polycrystalline samples is due to

(4) H. Fierz and A. von Zelewsky, to be submitted for publication.

a completely random distribution of all possible orientations of the paramagnetic species.^{5,6} This condition is usually fulfilled in a glassy sample or in a polycrystalline sample consisting of crystallites below a certain size only. If, however, one single crystallite or an orientated domain of the frozen solution exceeds a certain fraction of the total mass of the sample, the contribution of this single crystallite would no longer be infinitesimal. Consequently it will produce additional discrete lines in the esr spectrum. It can be easily estimated that crystallites comprising only 1% of the total sample show lines comparable in intensity with the weak lines of a true powder spectrum. This "single-crystal effect" can be unambiguously proved by a check of the anisotropic behavior of the esr spectra. Clearly the position of the discrete lines of the crystallites will depend on the direction of the magnetic field with respect to the sample, *i.e.*, with respect to the orientated domains.

We have carried out this experiment with a sample of $\text{Cu}(\text{dbm})_2$ showing the "anomalous" hyperfine pattern. Figure 1 shows two spectra of the same sample. Trace B was obtained after a 90° rotation of the sample tube within the cavity. The observed strong directional dependence clearly proves the "single-crystal effect" of this sample.

Another indication that the "single-crystal effect" is responsible for the occurrence of additional lines is the irreproducibility of the detailed pattern of the spectrum. We observed highly different structures after each thawing and refreezing of the sample.

Furthermore, only very unusual radical species with large spin density on the copper atom could give rise to absorptions in this part of the esr spectrum. Organic radicals could not be responsible.

The findings of So and Belford can be rationalized in the following way: A normal spectrum was observed by dissolving $\text{Cu}(\text{dbm})_2$ in commercial grade chloroform. Upon freezing this solution a truly glassy sample is obtained due to impurities in the solvent which inhibit a crystallization of the solution. Upon boiling certain impurities are removed and a purer sample is obtained. This solution crystallizes upon freezing, forming a matrix with a higher degree of order. Now, a number of domains contribute in a nonrandom way to the spectrum, giving rise to the "anomalous" lines. After addition of toluene, a less ordered matrix is obtained. We were able to show that the occurrence of the "anomalous" structure depends only on the purity of the solvent and has no relation to the thermal treatment of the sample. Our samples, prepared with highly purified chloroform, gave always the complicated structure without ever heating the solution above room temperature.

A more thorough discussion of the conditions for the appearance of the "single-crystal effect" will be published in a separate paper.⁴

All esr measurements were made with a standard Varian E-9 spectrometer at X-band frequencies at 100°K. Reagent grade chloroform was used as the solvent.

(5) R. H. Sands, *Phys. Rev.*, **99**, 1222 (1955).

(6) F. K. Kneubühl, *J. Chem. Phys.*, **33**, 1074 (1960).

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Anomalous Structure in Electron Paramagnetic Resonance Spectra of Polycrystalline Copper Complexes

Sir:

In the preceding letter,¹ Fierz and von Zelewsky offered an extremely attractive explanation for the complex structure found^{2,3} in frozen-solution epr spectra of boiled chloroform solutions of copper bis(dibenzoylmethane) ($\text{Cu}(\text{dbm})_2$). In their view, the

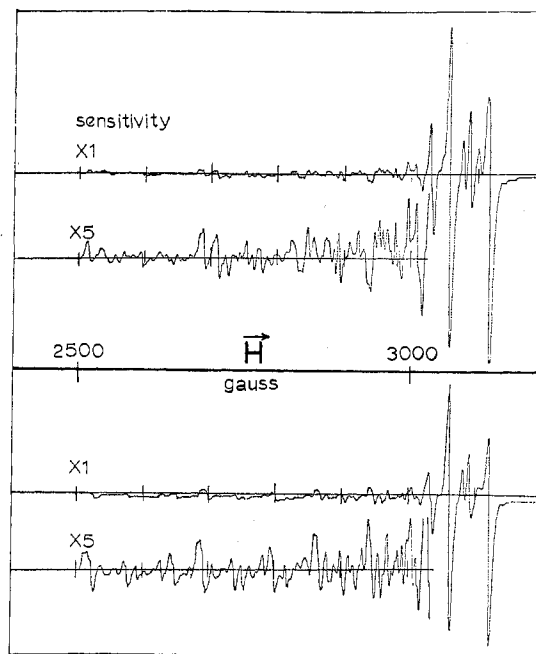


Figure 1. Electron paramagnetic resonance, X-band at -80° , of coarsely powdered $\text{Pd}(\text{dbm})_2$ single crystals with ^{63}Cu as a dilute substitutional impurity. Upper trace: magnetic field perpendicular to axis of sample tube, arbitrarily oriented. Lower trace: conditions identical to those of upper trace but magnetic field rotated about axis of sample tube by 90° .

solvent crystallizes in large grains with the chelate molecules trapped in an oriented, magnetically dilute array, and there are not enough of these granules, randomly oriented, to merge the grain spectra into the classical glassy-state type of spectrum. If this explanation is correct, coarsely ground magnetically dilute $\text{Cu}(\text{dbm})_2$ should produce an epr spectrum of similar appearance and angular variation. We have ground dilute crystals of ^{63}Cu doped into $\text{Pd}(\text{dbm})_2$ ³ to a coarse powder having crystallite sizes ranging from $\sim 10^{-5}$ mm³ downward. Figure 1 shows epr spectra of this sample loosely packed into a quartz tube, for two rotational orientations of the magnetic field. Indeed, the spectra resemble those of the frozen CHCl_3 solutions (boiled^{2,3} or purified¹) and furthermore vary as the sample tube is rotated, as the frozen solutions do.¹ Therefore, we completely concur with the interpretation offered by Fierz and von Zelewsky.¹ This finding has some interesting and possibly practical implications. Since suitable isomorphous diamagnetic host crystals are often unavailable for specified para-

(1) H. Fierz and A. von Zelewsky, *Inorg. Chem.*, **10**, 1556 (1971).

(2) H. A. Kuska, M. T. Rogers, and R. E. Drullinger, *J. Phys. Chem.*, **71**, 109 (1967).

(3) H. So and R. L. Belford, *Inorg. Chem.*, **9**, 2194 (1970).