of the sodium nitrite. It was found that both the absorption and CD spectra of the solution were identical with those obtained for the dinitro species isolated from the preparative solutions. This suggests that the isolated dichloro and dinitro species have identical geometric and absolute configurations.

3. Conclusion

The CD sign patterns for the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition of these complexes are very similar to those observed for the corresponding *cis*-β-Co(trien)X_2^+ complexes[8] (trien = triethylenetetraamine); the only significant difference is in the chloro complexes of the two ligands where the relative intensities of the two CD bands are reversed. This suggests that the two series of complexes have the same absolute configurations. If this is so, then the two bnpic complexes have the absolute configuration shown on the left of Figure 1 and therefore the nitrogen atoms are in the optically active and not the *meso* configuration. This conclusion is supported by studies on the relative stabilities of the two nitrogen configurations in the trien series[9] and by a recent crystal structure of the *cis*-β-Co(trien)ClH_2O^+ ion.[10]

4. Experimental Section

(+)-2,3-Butanediamine.—(±)-2,3-Butanediamine was resolved using (+)-tartaric acid.[11] After five recrystallizations of the less soluble diastereoisomer from ethanol–water (3:1), the salt had a constant rotation α_D +0.89° (5% aqueous solution). It was basified with strong sodium hydroxide solution and the top layer of the diamine was extracted continuously with ether for 10 hr. After distillation 4.5 g of (+)-2,3-butanediamine was obtained.

(+)-Bis-N,N′-2-picolyl-2,3-diaminobutane.—(+)-2,3-Butanediamine (4.5 g) was treated with freshly distilled pyridine-2-carboxaldehyde (18 g) by the method described for ethylenediamine.[12] The product was fractionally distilled yielding 1.6 g of the desired compound as a viscous yellow oil (bp 170° (0.03 mm)) and about 3.5 g of a lower boiling clear liquid which was identified by nmr as the half-reacted species N-2-picolyl-2,3-diaminobutane. This was treated once more with pyridine-2-carboxaldehyde (12 g) to give a further 3 g of the quadridentate ligand (total yield 35%); $[\alpha]_D$ +15° in water, 5.3% solution.

cis-β-**[Co(bnpic)Cl_2]ClO_4.**—A stream of air was bubbled through a solution of the ligand bnpic (2.2 g) and cobalt chloride hexahydrate (2.0 g) in water (75 ml) for 4 hr. To the now dark brown solution was added hydrochloric acid (1 ml; 11 *N*) and concentrated perchloric acid (2 ml) and the resulting red solution was evaporated on a steam bath to a volume of 10 ml. On standing at room temperature for 10 days the violet-red crystals which slowly formed were collected, washed with a little ice water followed by acetone, and dried over $CaCl_2$; yield 1.2 g (35%). The rotation of the substance in methanol was too small to detect on a visual polarimeter. The conductivity rapidly increased in water solution although an extrapolated value of about 115 cm^2 ohm^{-1} mol^{-1} is consistent for a 1:1 electrolyte. *Anal.* Calcd for $C_{16}H_{22}N_4Cl_3O_4Co$: C, 38.45; H, 4.45; N, 11.2; Cl, 21.3. Found: C, 38.4; H, 4.5; N, 11.2; Cl, 21.1

cis-β-**[Co(bnpic)$(NO_2)_2$]$ClO_4 \cdot H_2O$.**—Sodium nitrite (0.114 g) in water (5 ml) was added to a hot solution of *cis*-β-[Co(bnpic)Cl_2]ClO_4 (0.40 g) in water (10 ml). The solution was boiled for 0.5 min and filtered into a solution of sodium perchlorate (1 g) in water (5 ml), and on cooling to 0° the golden yellow crystals were collected and washed with a little iced water; yield 0.3 g (70%); $[\alpha]_D$ −270° in methanol 1% solution; molar conductivity 110 cm^2 ohm^{-1} mol^{-1} (1:1 electrolyte). *Anal.* Calcd for $C_{16}H_{24}ClO_9Co$: C, 35.6; H, 4.5; N, 15.6; Cl, 6.6. Found: C, 35.9; H, 4.5; N, 15.3; Cl, 6.7.

Instrumentation.—The nmr spectra were recorded on a Varian HA-100 spectrometer using 15% solutions at 29° with TMS as a reference. The absorption spectra were recorded with a Unicam SP800 spectrophotometer and the CD spectra were obtained by means of a Roussel-Jouan Dichrograph (sensitivity 1.5×10^{-4}).

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Correspondence

Electron Spin Resonance of Copper Bisdibenzoylmethane. Superhyperfine Anomalies[1]

Sir:

Several years ago Kuska, *et al.*,[2] reported a quite complicated epr spectrum, very rich in apparent superhyperfine structure, for frozen solutions of bis(1,3-diphenyl-1,3-propanedionato)copper [copper bisdibenzoylmethane, $Cu(dbm)_2$, $(C_6H_5COCHCOC_6H_5)_2Cu$]. They suggested that the unpaired electron in this β-ketoenolate is sufficiently delocalized to interact markedly with the 20 protons of the phenyl rings.[2] However, such extensive delocalization would imply that $Cu(dbm)_2$ is radically different from other copper chelates which are structurally similar and which have very similar visible spectra and other properties. To elucidate this anomalous epr structure and to obtain accurate epr parameters for other purposes, we have studied the epr spectra of copper-doped single crystals of the corresponding palladium chelate, $Pd(dbm)_2$, and have made further observations on various frozen solution spectra of $Cu(dbm)_2$. This note reports our findings. No superhyperfine structure appeared in any of the single-crystal spectra. Structure like that reported by Kuska, *et al.*, appeared in frozen solutions of samples that had been subjected to heating; it is apparent that this structure represents a chemical species other than $Cu(dbm)_2$.

Slow diffusion of ethanol into a chloroform solution of $Pd(dbm)_2$ containing a little ${}^{63}CuCl_2$ produced suit-

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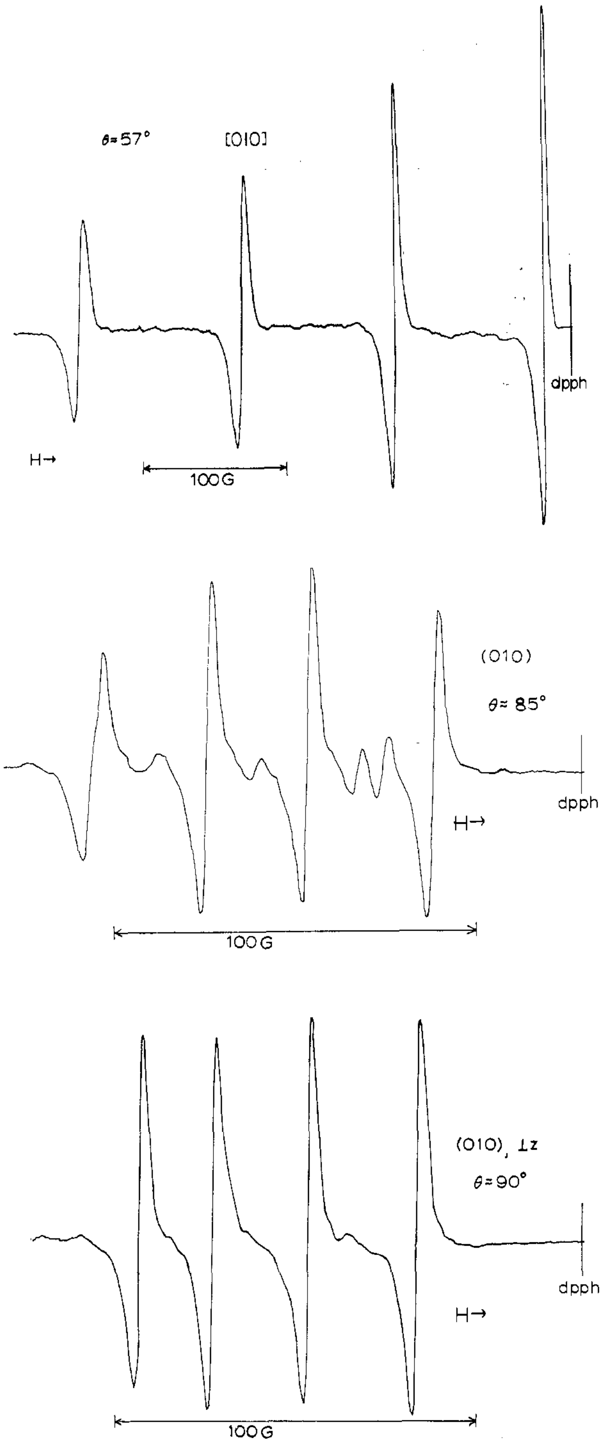

Figure 1.—Samples of electron paramagnetic resonance spectra of Cu^{2+} as dilute substitutional impurity in a $Pd(dbm)_2$ single crystal; first-derivative plots. $\nu_0 \approx 9$ GHz. DPPH marker occurred at $H = 3376$ G. θ denotes the angle between the principal axis of the g tensor and the magnetic field direction.

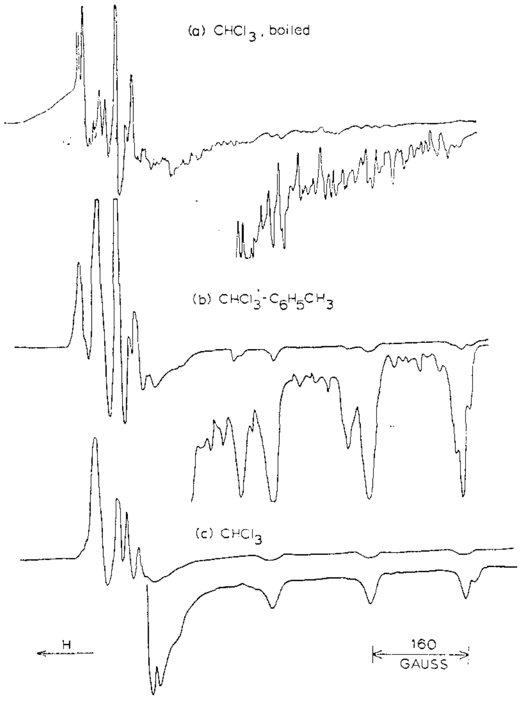

Figure 2.—First-derivative epr spectra of $Cu(dbm)_2$ frozen solutions at 77°K: (a) in $CHCl_3$ after boiling; (b) in $CHCl_3$ after boiling, $C_6H_5CH_3$ added; (c) in $CHCl_3$, prepared at room temperature.

able small crystals. The crystal belongs to space group I2/c and is a needle elongated on [010]. The molecule is effectively planar.[3] Epr spectra (Figure 1) were recorded for magnetic field directions along and perpendicular to [010]. The $g_\parallel$ direction lies 57° from the b axis, while the normal direction to the coordination plane lies 56° from b. The polycrystalline spectrum suggested a small in-plane anisotropy which we have not studied in detail.[4]

The single-crystal epr data, fitted to the usual axial spin Hamiltonian

$$\mathcal{H} = g_\parallel \beta H_z S_z + g_\perp \beta (H_x S_x + H_y S_y) + A S_z I_z + B(S_x I_x + S_y I_y) + Q'(I_z^2 - I(I+1)/3) - g_N \beta_N \mathbf{H} \cdot \mathbf{I} \quad (1)$$

yield these parameters: $g_\parallel = 2.258$, $g_\perp = 2.051$, $A = -0.0178$ cm^{-1}, $B = -0.00236$ cm^{-1}, and $Q' = +3.2 \times 10^{-4}$ cm^{-1}; Q' was determined both from forbidden hyperfine lines and from the allowed lines in the perpendicular spectrum.[4,5]

The g values and hyperfine parameters are quite similar to those of other β-ketoenolate chelates of copper(II)[6,7] and can be interpreted in terms of electronic energy levels and covalency parameters in the usual way, with similar results.[4,7] The quadrupole coupling parameter Q' can be related to metal and ligand charge distributions and will be discussed elsewhere.[4]

$Cu(dbm)_2$ dissolves in $CHCl_3$ at room temperature to give a dilute solution. When frozen, this solution exhibits a normal epr spectrum (Figure 2c), which we attribute to a planar $Cu(dbm)_2$ species with weakly coordinated chloroform (or possibly solvent impurity)

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in the axial positions.[8] However, when the solution is boiled, it yields the complicated type of frozen-solution epr spectrum (Figure 2a) first observed by Kuska, *et al.*[2] After standing several days at room temperature, the same sample again displays a normal spectrum. We surmise that Cu(dbm)$_2$ reacts with either hot chloroform or some impurity in it to produce an unidentified radical species. Several common active impurities in commercial chloroform could react with Cu(dbm)$_2$ to form such a radical species; we have made no attempt to identify the species or its precursors. This species is also sensitive to toluene. On addition of a small amount of toluene to the freshly boiled chloroform solution, the epr spectrum is simplified remarkably (Figure 2b) and now largely consists of two sets of lines. One of them is identical with the lines characteristic of the normal chloroform solution; the other has epr parameters characteristic of a planar species virtually free of axial coordination.[8]

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