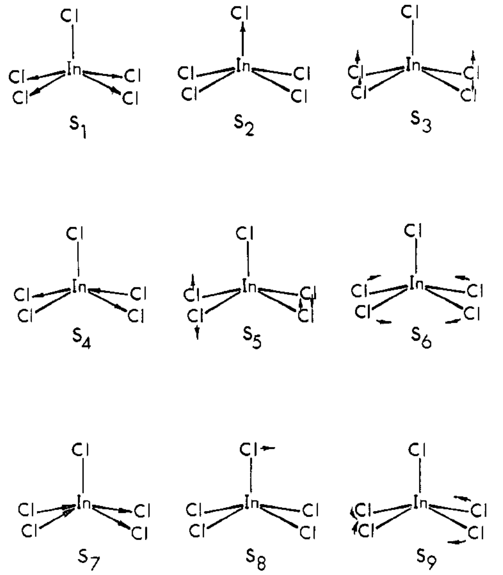

Figure 4.—Approximate symmetry coordinates for $InCl_5^{2-}$ (C_4 symmetry designations). S_1 through S_3 have A symmetry, S_4 through S_6 have B symmetry, and S_7 through S_9 have E symmetry.

(S_9). A similar, but less definite, indication of this effect may be seen from the proposed position of the B modes. Assuming these do fall in the 290–165-cm^{-1} region, either of the two lowest B modes may be attributed to antisymmetric out-of-plane deformation (S_5 of Figure 4), which is the dominant coordinate in the conversion of a square pyramid to a trigonal bipyramid. This places the frequency primarily associated with S_5 fourth or fifth from the lowest for $InCl_5^{2-}$ while it is second from the lowest for BrF_5. The resistance of $InCl_5^{2-}$ to out-of-plane distortion may be due to interionic steric repulsion because we have previously shown that the geometry of $InCl_5^{2-}$ is sensitive to the nature of the cation with which it is associated in the crystal.[5]

Experimental Section

Flat truncated bipyramidal crystals of $[(C_2H_5)_4N]_2[InCl_5]$ approximately 3–4 mm across were grown by slow evaporation of a methylene chloride solution saturated with $[(C_2H_5)_4N]_2[InCl_5]$ and containing an excess of $[(C_2H_5)_4N]Cl$. The C_4 crystallographic axis is perpendicular to the square flat faces as shown by lack of extinction when rotated under a polarizing microscope and by X-ray precession photographs. As usual, the fourfold axis is designated by z. The x and y axes were found to be perpendicular to the edges of the square faces.

Raman spectra were obtained on an instrument which has been described previously.[6] The 5145-Å line of a Coherent Radiation Model 52 Ar ion laser was employed for excitation. The incident beam was attenuated to avoid destruction of the crystal. Alignment of the single crystals was accomplished with the aid of cathetomer. Far-infrared spectra were obtained for Nujol mulls between polyethylene plates using a Beckman IR 11 instrument.

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CONTRIBUTION FROM THE WILLIAM RAMSAY AND
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The Circular Dichroism Spectra of Cobalt(III) Complexes Containing a Stereoselective Quadridentate Ligand

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Recent studies concerned with the relationship between the absolute configurations of metal complexes and the circular dichroism spectra shown by their d–d electronic transitions have largely relied on the use of stereoselective multidentate ligands. The most widely studied of these are the quadridentate systems which appear to provide a direct relationship with the bis-bidentate octahedral complexes and are capable of considerable variation with respect to both the ligand and the occupancy of the two remaining octahedral coordination sites.[2-4] In most of these quadridentate systems, however, work has concentrated on the symmetrical *cis*-α geometry where, at least in principle, there appears to be little ambiguity as to the particular stereoselective preference which the ligand will impart upon complexation. The factors involved in deciding the stereoselective preference are more complicated for the unsymmetrical *cis*-β geometry, and it is the purpose of this note to consider these with respect to the *cis*-β complexes formed by the ligand (shown in Figure 1) (+)-bis-N,N′-2-picolyl-2,3-diaminobutane (bnpic) derived from (+)-2,3-butanediamine.

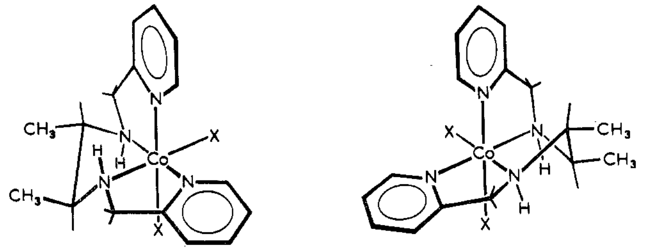

Figure 1.—Two isomers of the *cis*-β-Co(bnpic)X_2^+ complexes derived from (+)-2,3-butanediamine. The figure on the left shows the complex with optically active nitrogen atoms and the one on the right has the nitrogen atoms *meso*. Both absolute configurations of the complexes are those where the methyl groups are equatorially disposed.

The *cis*-octahedral complexes formed by the bnpic ligand have three sources of asymmetry: (1) the configurational asymmetry due to the overall molecular framework, (2) the asymmetry due to the asymmetric carbon atoms on the 2,3-diaminobutane linkage, and (3) the configurations of the two inner nitrogen atoms

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[1] Lash Miller Chemical Laboratories, University of Toronto, Toronto 181, Ontario, Canada.

[2] (a) R. G. Asperger and C. F. Liu, *Inorg. Chem.*, **4**, 1395 (1965); (b) B. Bosnich, *Proc. Roy. Soc., Ser. A*, **297**, 88 (1967).

[3] J. I. Legg, D. W. Cooke, and B. E. Douglas, *Inorg. Chem.* **6**, 700 (1967).

[4] B. Bosnich and A. T. Phillip, *J. Chem. Soc.*, in press.

which can either be racemic or *meso*. A consideration of the interplay of these three aspects of dissymmetry together with the ring conformations is sufficient, in principle, to reach conclusions regarding the stereoselective preference of one antipode of the ligand. In the case of the symmetrical *cis*-α geometry, the configurational asymmetry and the nitrogen atom asymmetry are mutually dependent in the sense that, because of stringent steric requirements, the two terminal chelate arms cannot adopt a *cis*-α arrangement when the nitrogen atoms are *meso* and, furthermore, when the nitrogen atoms are in the racemic configurations, their absolute configurations will exclusively determine the absolute configurations of the terminal chelate arms. The final preferred absolute configuration of the complex is then determined by the most energetically favorable arrangement of the methyl groups in the cobalt–2,3-diaminobutane ring. In the case of the *cis*-β geometry the steric restrictions are not so exclusive and, using only one antipode of the ligand, it is possible to conceive four possible isomers of the complex which depend on the isomerism of the nitrogen atoms and the overall absolute configuration of the complex. If the coordinated nitrogen atoms are in the racemic configuration, the absolute configuration of the terminal chelate arms is fixed by the absolute configurations of the nitrogen atoms. The two isomers then arise from the axial *vs.* equatorial dispositions of the methyl groups attached to the puckered cobalt–2,3-diaminobutane ring.[5] One would expect that the cobalt–2,3-diaminobutane ring would be intrinsically less stable when the methyl groups are axial than when they are equatorial,[5] and, furthermore, molecular models show that there is considerably more interaction between a methyl group and the *cis*-arranged terminal chelate arm when the methyl groups are axial than when they are equatorial. Thus using the ligand derived from (+)-2,3-butanediamine the preferred *cis*-β absolute configuration of the complex containing optically active nitrogen atoms is the one shown on the left of Figure 1. However, when the coordinated nitrogen atoms are in the *meso* configuration, similar arguments to the ones presented above lead to the opposite conclusion as to the preferred overall absolute configuration of the complex using the same absolute configuration of the ligand. The structure drawn on the right of Figure 1 shows the preferred absolute configuration of the complex when the nitrogen atoms are *meso* and the methyl groups equatorial. (In the opposite absolute configuration of the chelate arms the methyl groups are axially disposed.) Thus unlike the case of the *cis*-α complex the configurations of the coordinated nitrogen atoms and the absolute configuration of the ligand must both be known before the absolute configuration of the *cis*-β complex can be inferred from steric considerations alone.

1. Preparations and Structures

The (+)-bnpic ligand was prepared by reaction of (+)-2,3-butanediamine and excess pyridine-2-carboxaldehyde in a reducing solution of zinc and acetic acid. Figure 2 shows the nmr spectrum of the ligand in deuterated dimethyl sulfoxide solution. The integrated intensities are correct if we assume that the pyridine protons occur between τ 1 and 3, the methylene protons between τ 6 and 6.5, and the split methyl protons at τ 9. The CH and NH protons apparently overlap each other at about τ 7.5 and are mixed with absorptions of the protons in DMSO. The validity of this latter assignment has been checked by running the spectra in $CDCl_3$ wherein at 29° the NH protons absorb at τ 7.15 and the CH protons absorb at τ 7.45; the latter were identified by spin decoupling of the methyl protons, and the NH protons (unlike the CH protons) were found to shift to τ 7.10 upon cooling to −5°.

The violet complex *cis*-β-[Co(bnpic)Cl_2]ClO_4 was prepared by aerial oxidation of aqueous cobalt chloride and the ligand, and the *cis*-β-[Co(bnpic)$(NO_2)_2$]ClO_4 complex was prepared from the chloro species by reaction with NO_2^- ions. We have been unable to obtain any information regarding the degree of selectivity of the dichloro complex because, as the conductivity showed, both chlorides are very rapidly dissociated in water to give a mixture of chloroaquo and diaquo species. Attempts to crystallize these highly soluble species fractionally from water proved unsuccessful. Although the dinitro complex is stable in water, fractional crystallization failed to reveal any species having properties different from those of the first isolated complex. The nmr spectrum of the *cis*-β-[Co(bnpic)Cl_2]ClO_4 in deuterated DMSO is shown in Figure 2. It will be seen that there are two split methyl hydrogen resonances of equal intensity at τ 8.66 and 8.88 which suggests that, within the experimental sensitivity (*ca.* 10%), the complex is present as one isomer of the unsymmetrical *cis*-β configuration. Further confirmation of the *cis*-β structure is provided by the nature of the absorptions of the pyridine protons occurring between τ 0.5 and 3.3. The ratio of intensities of the doublet at τ 0.8 and the multiplet at τ 1.7–3.3 is 1:7. This odd ratio of the pyridine protons strongly suggests that the pyridine groups are in inequivalent environments. The complicated absorption region between τ 5.0 and 7.0 integrates correctly if it is assumed that the absorption in this region is due to the NH and CH_2 protons. The CH protons occur under the DMSO absorption (τ ~7.6) and their absorption in this region was confirmed by spin decoupling at around τ 7.6 which led to the successive collapse of the methyl proton doublets into singlets (see Figure 2). The diagnostic features of the nmr spectrum described for the Co(bnpic)Cl_2^+ ion were also found for the Co(bnpic)$(NO_2)_2^+$ complex and we conclude that both complexes are in one form of the *cis*-β geometry. The assignment of the configurations of the nitrogen atoms still remains.

2. Absorption and Circular Dichroism Spectra

In the two complexes, the donor nitrogen atoms of the pyridines and the secondary amines are expected to

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(5) E. J. Corey and J. C. Bailar, *J. Amer. Chem. Soc.*, **81**, 2620 (1959).

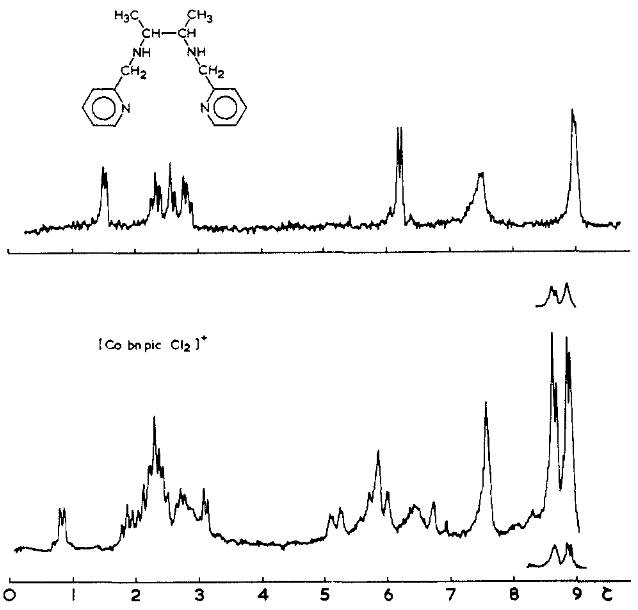

Figure 2.—The nmr spectra of the bnpic ligand (top) and the *cis*-β-Co(bnpic)Cl_2^+ ion.

have very similar ligand fields[6] and thus the overall ligand field exerted on the cobalt d-electron states will be C_{2v}. This will lead to the removal of the degeneracy of the upper state of the first ligand field transition ($^1A_{1g} \rightarrow {}^1T_{1g}$) into three orthogonal components giving rise to the transitions $^1A_1 \rightarrow {}^1A_2$, $^1B_2$, and $^1B_1$ in the C_{2v} point group. It can be shown by a semiempirical molecular orbital calculation that the transitions $^1A_1 \rightarrow {}^1A_2$ and $^1A_1 \rightarrow {}^1B_2$ will be essentially degenerate.[7] Furthermore, in the case of the *cis*-β-Co(bnpic)Cl_2^+ ion the $^1A_1 \rightarrow {}^1B_1$ transition should occur at lower energies than the two component transition, $^1A_1 \rightarrow {}^1A_2$, $^1B_2$, whereas in the *cis*-β-Co(bnpic)$(NO_2)_2^+$ ion the $^1A_1 \rightarrow {}^1B_1$ should be at higher energies than the $^1A_1 \rightarrow {}^1A_2$, $^1B_2$ excitations.[2]

Figures 3 and 4 show the visible absorption spectra and the associated circular dichroism shown by the *cis*-β-[Co(bnpic)Cl_2]ClO_4 and *cis*-β-[Co(bnpic)$(NO_2)_2$]ClO_4 complexes in methanol solution in which the former is stable with respect to dissociation of the chloro groups. It will be seen that for the dichloro species the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition centered at around 19,000 cm^{-1} carries two negative CD components. The weaker energy CD band at around 17,000 cm^{-1} is assigned to the $^1A_1 \rightarrow {}^1B_1$ component and the stronger band at around 20,000 cm^{-1} is assigned to the two component transition $^1A_1 \rightarrow {}^1A_2$, $^1B_2$. The asymmetry of this latter band indicates that the degeneracy has been partly removed probably because of the small difference in ligand fields between the aliphatic nitrogen atoms and those in the pyridine rings. The higher energy bands shown in Figure 3 are probably charge-transfer transitions due to electronic excitations from the chloro groups to the empty levels on the cobalt atom. The *cis*-β-[Co(bnpic)$(NO_2)_2$]ClO_4 complex shows only a single negative CD absorption in

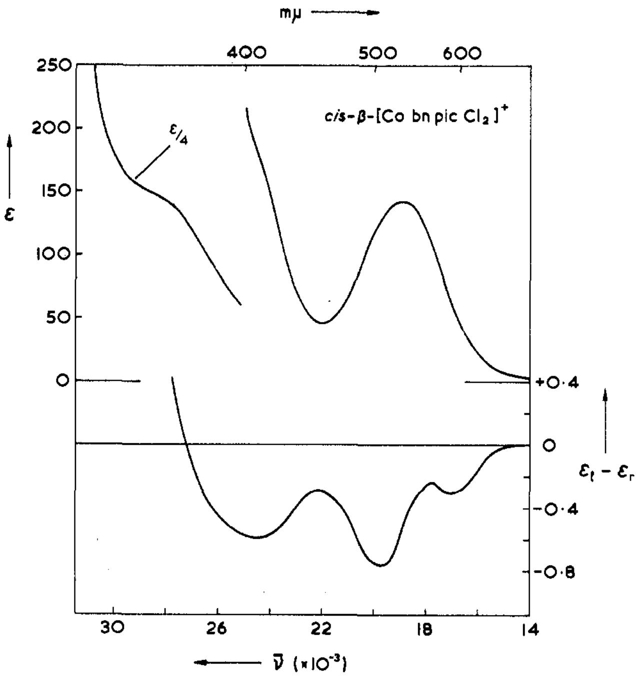

Figure 3.—The absorption and circular dichroism spectra of the *cis*-β-Co(bnpic)Cl_2^+ ion in methanol solution.

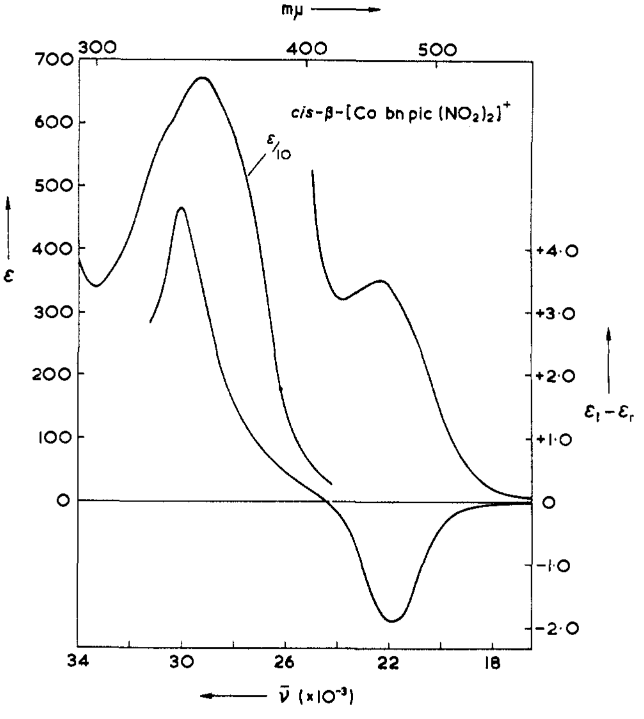

Figure 4.—The absorption and circular dichroism spectra of the *cis*-β-Co(bnpic)$(NO_2)_2^+$ ion in methanol solution.

the region of the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition and probably consists of all three components which are overlapped by the strong positive CD carried by the cobalt to nitro charge-transfer bands centered at around 29,000 cm^{-1}.

We have checked the relative configurations of the dichloro and dinitro complexes by treating the dichloro complex with 2 equiv of sodium nitrite in methanol solution. The reaction is extremely fast at room temperature being essentially complete after the dissolution

[6] C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, London, 1962.

[7] H. Yamatera, *Bull. Chem. Soc. Jap.*, **31**, 95 (1958).

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$_2$O$^+$ 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$_4$·H$_2$O.**—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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(8) A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **4**, 45 (1965).

(9) D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *ibid.*, **6**, 1032 (1967).

(10) H. C. Freeman and I. E. Maxwell, *ibid.*, **8**, 1293 (1969).

(11) F. H. Dickey, W. Fickett, and H. J. Lucas, *J. Amer. Chem. Soc.*, **74**, 950 (1952).

(12) H. A. Goodwin and F. Lions, *ibid.*, **82**, 5021 (1960).

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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(1) Supported by the Advanced Research Projects Agency, SD-131, through the Materials Research Laboratory at the University of Illinois, and by Diamond Shamrock, R. F. Carr, and University of Illinois predoctoral fellowships awarded to H. S.

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