between the single crystal and the polycrystalline spectra were observed and we therefore conclude that BCC crystallizes in the *aa* conformation under high pressure at ambient temperature.

The present results for BCC are in sharp contrast with our previous data for the *trans*-1,2-dichloro- and *trans*-1,2-dibromocyclohexane [1] as well as the halo cyclohexanes,[4] since they all crystallize in the same conformation at low temperatures and under high pressure. Thus, for BCC the stabilities of the *ee* and the *aa* crystalline solids are evidently very similar. This is not surprising since this molecule is a hybrid between the dichloro and the dibromo compounds which crystallize [1,4] in *ee* and *aa* conformations, respectively. It is interesting to compare the result for BCC with those obtained [5] for 1,1,2,2-tetrachloroethane giving the *trans* conformation at high pressure and *gauche* at low temperatures. The tetrabromoethane, however, could crystallize in *trans* or *gauche* at low temperatures or high pressure according to the experimental procedure.[5] Using a simultaneous freezing and pressing an *ee* crystal of BCC was obtained, which slowly changed to *aa* at room temperature during the recording.

The spectrum of BCC in the *aa* conformation obtained for the first time were in good agreement with our earlier assignments [1] for this molecule. However, a few discrepancies were observed for bands which were assigned to one conformer and now turn out to be common for both conformers or *vice versa*.

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# Magnetic Properties of (Acyloin oximato)copper(II) Complexes. Studies in Magnetochemistry 26*

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The constitution of (benzoin oximato)-copper(II), first described by Feigl,[1,2] has been discussed in some publications.[3–7] The structure shown in Fig. 1 A has been

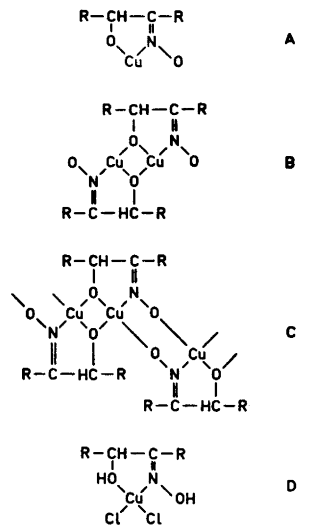


*Fig. 1.* The structures proposed for the copper complexes.

proposed, and some authors [5,7] suggest a polymerisation resulting in four-coordinated copper. However, as the complex is insoluble in all common solvents, it has neither been possible to determine the molecular weight, nor to prepare single crystals for X-ray analyses, and it has so far not been possible to prove these assumptions by X-ray evidence. The X-ray powder photos of the compound show, that the substance is microcrystalline; only very diffuse lines appear.

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We have measured the magnetic susceptibility of the insoluble, dark green (benzoin oximato)copper(II), and we have found $\chi_M^{corr} = 271 \times 10^{-6}$ c.g.s. units at room temperature, corresponding to $\mu_{eff} = 0.80$ $\beta$ for Cu. Earlier Ray and Sen[5] have reported that the magnetic susceptibility of the compound is $1285.5 \times 10^{-6}$ c.g.s. units and for Cu $\mu_{eff} = 1.76$ $\beta$. In spite of several variations in the methods of preparations and the storage conditions we have not been able to obtain a specimen with the same magnetic properties as those reported by Ray and Sen.

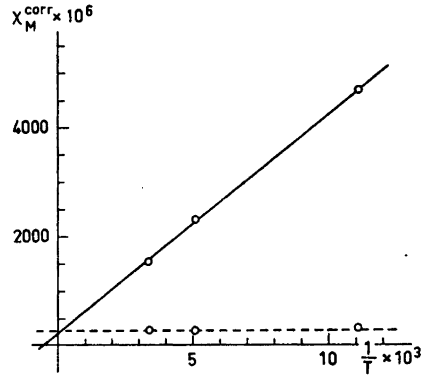


*Fig. 2.* The temperature dependence of $\chi_M^{corr}$, - - - - (benzoin oximato)copper(II); ——— dichloro(benzoin oxime)copper(II).

From the magnetic and the analytical[3] data it cannot be excluded that (benzoin oximato)copper could be a copper(I) compound, the $NH_2OH$ in benzoin oxime could make a reduction of copper(II) possible. By treatment of (benzoin oximato)copper with alcoholic hydrogen chloride a green crystalline salt dichloro(benzoin oxime)-copper is obtained. The composition of this compound can only be explained as a copper(II) compound, and Jennings *et al.*[3] conclude that (benzoin oximato)copper must be a copper(II) compound. We have measured the magnetic susceptibility of dichloro(benzoin oxime)copper(II) $\chi_M^{corr} = 1543 \times 10^{-6}$ c.g.s. units and for Cu $\mu_{eff} = 1.91$ $\beta$ at room temperature (Table 1). These results confirm the conclusion made by Jennings *et al.*

The temperature dependence of the molar magnetic susceptibility $\chi_M^{corr}$ is given in Fig. 2. According to these measurements dichloro(benzoin oxime)copper(II) is a normal paramagnetic compound, while (benzoin oximato)copper(II) only has the temperature independent paramagnetisme.

Subnormal values for the magnetic moments have been stated for copper carboxylates and several other copper complexes. The structure of some of these compounds have been established by X-ray analyses.[8–10] The complexes are dimeric with a Cu – O – Cu – O-ring or a Cu – Cl – Cu – Cl-ring. The low value of the magnetic moment is a result of an interaction between the Cu-atoms either directly or through bridges. The structure in Fig. 1 A gives by dimerisation the possibility for a Cu – O – Cu – O-ring as shown in Fig. 1 B. We suggest that Cu is four-coordinated as consequence of polymerisation (Fig. 1 C). Polymerisation also accounts for the insolubility of the compound. Concerning the compound dichloro(benzoin oxime)copper(II) we mention that this substance is soluble in a solution of HCl in 99.9 % alcohol without decomposition. The structure shown in Fig. 1 D may explain that dimerisation or polymerisation cannot occur in this case.

Further we have prepared (acetoin oximato)copper(II), (butyroin oximato)-copper(II), (furoin oximato)copper(II). These compounds are dark green and insoluble in common solvents just as (benzoin oximato)copper(II). Feigl[2] classified the (acyloin oximato)copper(II) compounds in two groups according to their solubility in ammonia. For the dried compounds we have only found slightly different solubility in ammonia, so we do not find separation into groups justified.

The results of the measurements of the magnetic susceptibility of the copper compounds and of acetoin oxime and benzoin oxime are in Table 1 together with the results of the chemical analyses of the compounds. The (acyloin oximato)copper-(II) compounds have the same magnetic properties hence we may assume that the structure of the compounds probably are similar.

*Experimental.* The preparation of the compounds was carried out according to the methods given by Feigl *et al.*[1,2] and Jennings *et al.*[3] The (acyloin oximato)copper(II) compounds separate in microcrystalline form. It is difficult to purify these compounds by washing on the filter. Acetoin oxime was prepared from acetoin and hydroxylammonium chloride. After

*Table 1.* Analyses and magnetic measurements. Susceptibility in c.g.s. units.

| | Contents in % | | | | 294 K | | | 195 K | | | 90 K | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | C | H | Cu | $\chi_g \times 10^6$ | $\chi_M^{corr} \times 10^6$ | $\mu_{eff}$ | $\chi_g \times 10^6$ | $\chi_M^{corr} \times 10^6$ | $\mu_{eff}$ | $\chi_g \times 10^6$ | $\chi_M^{corr} \times 10^6$ | $\mu_{eff}$ |
| I | | | | | −0.611 | −63 | | | | | | | |
| II | | | | | −0.664 | −144 | | | | | | | |
| IV | c. | | | 38.6 | 0.990 | 225 | 0.74 | 0.936 | 217 | 0.58 | 0.992 | 227 | 0.41 |
| | f. | | | 38.2 | | | | | | | | | |
| V | c. | 43.5 | 6.8 | 28.8 | 0.714 | 267 | 0.79 | 0.738 | 267 | 0.65 | 0.903 | 303 | 0.47 |
| | f. | 42.7 | 6.8 | 28.5 | | | | | | | | | |
| VI | c. | | | 23.6 | 0.376 | 176 | 0.79 | 0.387 | 179 | 0.53 | 0.487 | 206 | 0.39 |
| | f. | | | 22.6 | | | | | | | | | |
| VIII | c. | 58.2 | 3.8 | 22.0 | 0.440 | 271 | 0.80 | 0.411 | 263 | 0.64 | 0.468 | 279 | 0.45 |
| | f. | 57.3 | 3.9 | 22.0 | | | | | | | | | |
| IX | c. | | | 17.6 | 3.772 | 1543 | 1.91 | 5.829 | 2299 | 1.91 | 12.373 | 4667 | 1.84 |
| | f. | | | 17.5 | | | | | | | | | |

I: Acetoin oxime, II: Benzoin oxime, IV: (Acetoin oximato)copper(II), V: (Butyroin oximato)-copper(II), VI: (Furoin oximato)copper(II), VIII: (Benzoin oximato)copper(II), IX: Dichloro-(benzoin oxime)copper(II).

isolation and recrystallisation from benzene-petroleum ether the melting point of acetoin oxime was found to be 58.0−58.5°C. Acetoin oxime does not seem to be described in the literature.

The copper content in (acetoin oximato)-copper(II) and in (butyroin oximato)copper(II) was determined by titration with iodine-thiosulfate or EDTA after oxidation of organic material with $H_2SO_4-HNO_3$. In (furoin oximato)copper(II), benzoin oximato)copper-(II), and dichloro(benzoin oxime)copper(II) the organic material was destroyed by ignition in a crucible before titration.

The magnetic susceptibilities were measured by means of the Gouy method as described by Asmussen and Soling.[11] The susceptibilities quoted in Table 1 are the mean values of several measurements at four different field strengths ranging from 2600 to 4100 Ørsteds. No sign of field strength dependence of the susceptibilities was found within the limits of the experimental errors. The diamagnetic susceptibilities of acetoin oxime and benzoin oxime were measured directly on the preparates. The results are in Table 1. By means of Pascal's values the diamagnetic susceptibility was calculated for butyroin oxime to $-104 \times 10^{-6}$ c.g.s. units, for furoin oxime to $-75 \times 10^{-6}$ c.g.s. units, and for dichloro(benzoin oxime) to $-182 \times 10^{-6}$ c.g.s. units.


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