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A Novel Method for the Synthesis of Cu(II) Complexes of Mixed-aldehyde and β-diketone systems

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There are only a few examples [1–3] of complexes of the type CuAB where A is a β-diketone or a bidentate aldehyde and B is a bidentate aldehyde different from A. The synthetic procedures described for these complexes are specific and are limited to a few *o*-hydroxyaldehydes. None of the above procedures yield a mixed product when pyrrole-2-aldehyde is involved. We wish to report a more general scheme which makes use of the lability of the coordinated methoxide group, consequently replacing it with the desired bidentate aldehyde, ketone or β-diketone. The scheme can be represented as:

$$\mathrm{CuA_2} \xrightarrow[\mathrm{CH_3OH}]{\mathrm{NaOCH_3}} \mathrm{Cu(A)(OCH_3)}$$

$$\xrightarrow[\text{xylene}]{\mathrm{BH}} \mathrm{CuAB + CH_3OH}$$

(A = acac or sal) (BH = bidentate aldehyde, ketone or β-diketone)

Utilizing this scheme we have been able to prepare the various combinations. Examples of each are shown below. Some of the complexes are fully characterized, while others are characterized by copper analysis, infrared and electronic spectra (Table I).

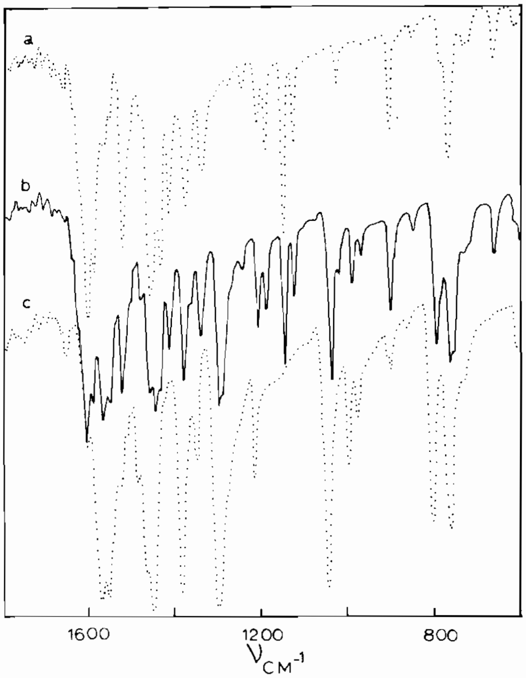

Fig. 1. Infrared spectra (Nujol mull) of a: $\mathrm{Cu(sal)_2}$; b: Cu(sal)(pyrr); c: $\mathrm{Cu(pyrr)_2}$.

Procedure

Freshly prepared [4] and dried $\mathrm{Cu(acac)(OCH_3)}$, 1 mmol, was added quickly to a preheated (≃ 120 °C) solution of 1 mmol of pyrrole-2-aldehyde in xylene. A brisk reaction takes place giving a green solution. The solution was allowed to cool. Shining dark green needle-like crystals were filtered off, washed with xylene followed by a little benzene and dried in a

TABLE I. Characterization of the CuAB Compounds.

Compound	Color and M.P., °C	%C		%H		%N		%Cu		μ_{BM}
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	
Cu(acac)(pyrr)	Dark green needles, 155	46.56	46.40	4.27	4.21	5.54	5.78	24.75	24.66	1.84(293) 1.80(78)
Cu(acac)(sal)	Olive green crystalline powder, 201[a]	50.78	50.77	4.23	4.27	–	–	22.39	22.46	1.87(292) 1.84(78)
Cu(acac)(dbm)	Ochre green crystals, 245							16.46	16.29	
Cu(acac)(*o*-hpr)	Green crystalline powder, 168[a]							20.38	20.31	
Cu(sal)(pyrr)	Ochre green crystals, 158							22.79	22.72	
Cu(sal)(5-Br-sal)	Pale green powder >250							16.52	16.43	

[a] Color changes at these temperatures; m.p. > 250 °C.

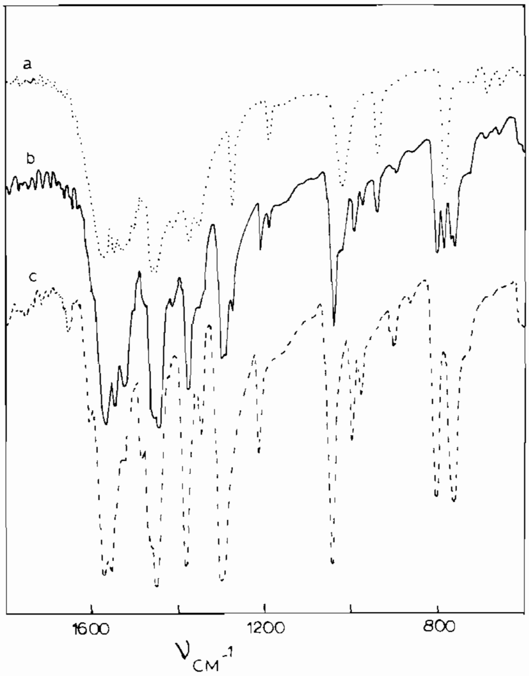

Fig. 2. Infrared spectra (Nujol mull) of a: $Cu(acac)_2$; b: Cu(acac)(pyrr); c: $Cu(pyrr)_2$.

vacuum desiccator at 60 °C for 6 hours. Cu(acac)(sal), Cu(acac)(*o*-hpr) and Cu(acac)(dbm) were prepared as above (*o*-hpr = *o*-hydroxypropiophenone; dbm = dibenzoylmethane). Cu(sal)(pyrr) and Cu(sal)(5-Br-sal) were prepared by a similar procedure using $Cu(sal)(OCH)_3$ as the starting material.

The infrared spectra of the mixed CuAB complexes exhibit all of the features present in the CuA_2 and CuB_2 complexes. Two representative spectra are shown in Figures 1 and 2. The electronic spectra of the complexes exhibit a broad band around 650 nm consistent with the expected [2] planar structure of the complexes. The magnetic data is consistent with the monomeric planar structure.

Acknowledgment

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