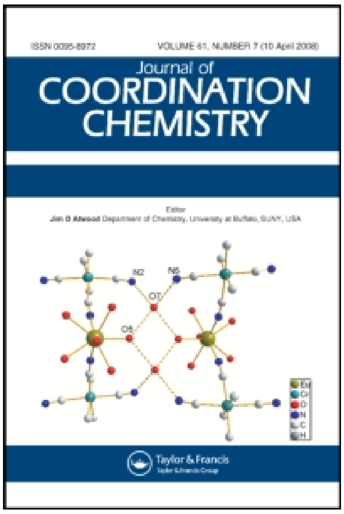

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SOME NEW PENTACOORDINATED COPPER (II) COMPLEXES

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SOME NEW PENTACOORDINATED COPPER (II) COMPLEXES

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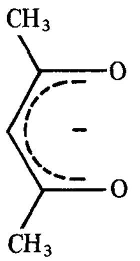
INTRODUCTION

Various pentacoordinated complexes of the general class M(bidentate) (tridentate) have been reported recently, using a simple but little-used strategy for the synthesis of pentacoordinated complexes.[1–5] While nickel (II) and cobalt(II) readily form complexes of the type MAB by the usual[3,4] reactions, copper(II) fails to react in an analogous fashion.[5] We wish to report the synthesis and the probable structure of two CuAB complexes.



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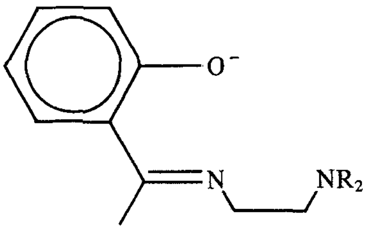

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R=Me; $salNMe_2$
R=Et; $salNEt_2$

EXPERIMENTAL SECTION

Chemicals

Acetylacetone was obtained from the Eastman Organic Chemical Co. The N,N–dialkylethylenediamines were obtained from the Aldrich Chemical Co. Salicylaldehyde and copper(II) acetatemonohydrate were obtained from the J. T. Baker Chemical Co.

Preparation of the Complexes

These complexes were synthesized by the following procedure. Schiff bases were prepared by refluxing 2 mmoles of salicylaldehyde with 2 mmoles of N,N–dimethylethylenediamine or N,N–diethylethylenediamine in 50 ml anhydrous methanol for 2 hours. $Cu(acac)_2$ was prepared by adding with stirring 5 mmoles of copperacetate monohydrate solution (in MeOH/water mixture 1:1) to 10 mmoles of acetylacetone in 100 ml methanol. The blue precipitate of $Cu(acac)_2$ was filtered and suspended in 100 ml methanol. 10 mmoles of sodium metal was dissolved in 50 ml methanol and the resulting solution was added to the above suspension with constant stirring. The blue $Cu(acac)_2$ changed to violet $[Cu(acac)(OCH_3)]_2$. The violet solid was filtered, washed with methanol and dried in vacuum at 60°C for 4 hours.

Cu(acac) $(salNMe_2)$ was then prepared by adding 1 mmole of $[Cu(acac)(OCH_3)]_2$ to the corresponding above Schiff base. The mixture was heated to reflux for 2 hours. The green solution thus obtained was filtered, concentrated to 15 ml and allowed to cool. Shining green crystals (mp. 185°C) of composition Cu(acac) $(salNMe_2)$ precipitated. Found: Cu, 17.83; C, 54.45; H, 5.97; N, 8.01%. Calcd for $C_{16}H_{21}N_2O_3Cu$: Cu, 17.94; C, 54.39; H, 5.94; N 7.93%.

Cu(acac) $(salNEt_2)$ was prepared in a similar fashion. The green concentrated solution required an addition of small amounts of water before crystals could be separated. Shining green crystals (mp. 96°C) of composition Cu(acac) $(salNEt_2) \cdot CH_3OH$ were isolated. Found: Cu, 15.45; C, 55.32; H, 7.11; N, 7.08%. Calcd for $C_{19}H_{29}O_4N_2Cu$: Cu, 15.38; C, 55.20; H, 7.02; N, 6.97%.

Physical Measurements

Magnetic susceptibilities were determined by the Gouy method using $Hg[Co(NCS)_4]$ as the standard. Electron spin resonance spectra were obtained with a

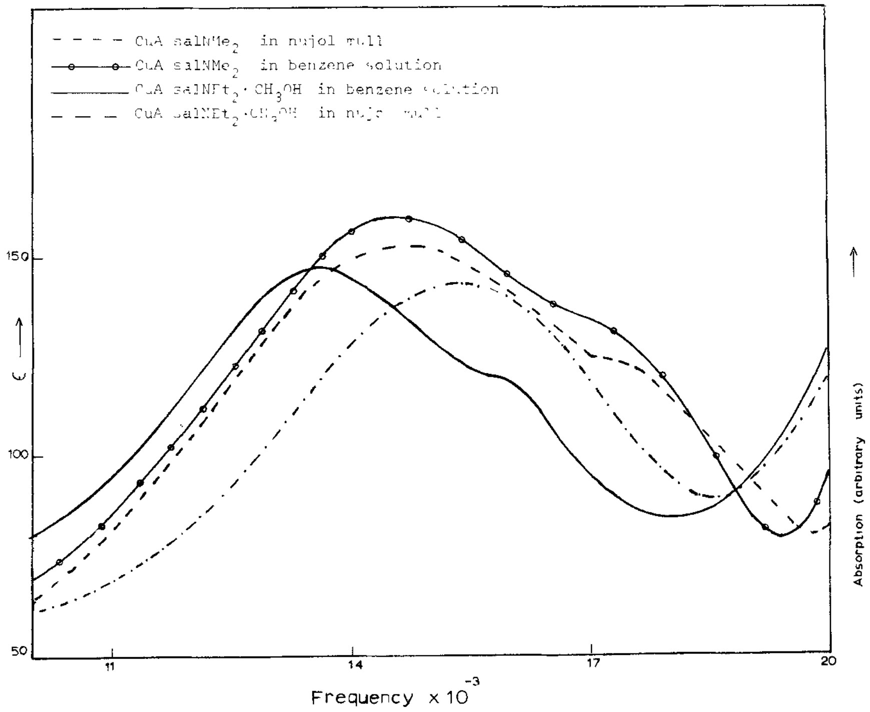


FIGURE. 1 Electronic Spectra

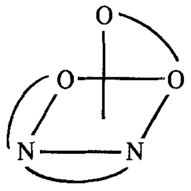
Varian V–4502–12 X–band spectrometer using 100-kc modulation and a 9 inch electromagnet. Cylindrical quartz sample tubes and a cylindrical cavity were employed. DPPH was used as an internal standard. The frequency was monitored with a Hewlett-Packard Model 5340A automatic micro-wave frequency counter. Infrared spectra were obtained on a Perkin-Elmer Model 621 instrument employing a nujol mulling technique. The electronic spectra were recorded using a Cary Model 14 recording spectrophotometer. Solid-state spectra were obtained in nujol mulls and solution spectra were obtained in benzene using 1-cm matched quartz cells. Molecular weight measurements were obtained in benzene with a Mechrolab Model 301A vapor pressure Osmometer calibrated with benzil. Several concentrations were used in the measurements.

Analyses

Copper analyses were determined on a Sergent-Welch electrolytic analyzer by plating copper onto a platinum electrode. Carbon, hydrogen and nitrogen analyses were obtained from Galbraith Laboratories, Knoxville, Tennessee.

RESULTS AND DISCUSSION

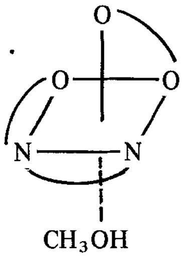
CuAB complexes were obtained by refluxing 2 mmoles of HB with 1 mmole of methoxo-bridged[6] $Cu_2A_2(OCH_3)_2$ in methanol. These complexes give rise to characteristic infrared spectra. Both complexes show a strong band in the region 1620-1640 cm^{-1} assigned to $\nu_{C=N}$ of the Schiff base moiety. There are two strong bands in the range 1585-1600 cm^{-1} and 1510-1520 cm^{-1} which are probably due to the combination of $\nu_{C \cdots C}$ and $\nu_{C \cdots O}$ stretches of the A moiety[7] with additional contributions from aromatic vibrations of Schiff base. The complex CuA salNEt$_2$ · CH$_3$OH shows an additional broad band at ~3450 due to ν_{O-H}. CuA salNMe$_2$ is non-conducting in benzene and has a normal magnetic moment (μ_{eff} = 1.85 and 1.86 BM at 295 and 78°K respectively) in the solid state. The molecular weight in benzene (determined osmometrically) was found to be 360 ± 15 which agrees well with the calculated molecular weight of 354. The electronic spectrum in nujol mull shows a band at ~ 14,400 cm^{-1} and a shoulder at ~17,400 cm^{-1}. The spectrum in benzene solution is very similar to that in the solid state (Fig. 1). These two closely-spaced low energy bands suggest a pentacoordinate geometry.[8,9] The ~14,000 cm^{-1} band can be assigned to d_{xy}, $d_{z^2} \rightarrow d_{x^2-y^2}$ and ~17,000 cm^{-1} band to $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ in idealized C_{4v} symmetry. The spectrum is very similar to the spectrum of Cu(sal) ($salNMe_2$) which has been found[10] to have square pyramidal structure. These evidences lead us to believe that the most probable structure of CuA $salNMe_2$ is *C*.



C

Further evidence in favor of the proposed geometry is provided by the powder esr spectrum. The complex CuA $salNMe_2$ gives rise to an axial esr spectrum with the parameters $g_\perp \sim 2.07$ and $g_\parallel \sim 2.25$ and the quantity G which is equal to $(g_\parallel - 2)/(g_\perp - 2)$ is ~ 3.5 for this complex. The value of G should be 4 for the gross square pyramidal C_{4v} geometry.[9,11] Our complex can not have strict axial symmetry due to the lack of symmetry intrinsic in the ligand molecules. However, if the atoms directly involved in the immediate coordination sphere primarily decide the nature of the ligand field, then the powder esr can provide information about the geometry of the coordination sphere.

The complex CuA $salNEt_2 \cdot CH_3OH$ has a normal magnetic moment (~ 1.84 BM, 295°K). The molecular weight in benzene solution was found to be 200 ± 10. This is in good agreement with the calcd 386/2, provided the molecules dissociate completely into two species. The electronic spectrum in nujol mull of CuA $salNEt_2 \cdot CH_3OH$ exhibits a band ~15,600 cm^{-1} which can be assigned to the $t_{2g} \rightarrow e_g$ transition in an octahedral environment. In benzene solution the spectrum changes considerably from the solid state spectrum. The solution spectrum is similar to that of pentacoordinated CuA $salNMe_2$ (Fig. 1) except that the energies are slightly lower. All these results indicate that the structure of the complex under discussion is *C* in solution phase and *D* in solid state



D

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