

Adduct of copper(II) bis(nitroacetylacetonate) with γ -picoline

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A green crystalline compound having the composition $[\text{Cu}(\text{NO}_2\text{-acac})_2(\gamma\text{-pic})]$ has been isolated by reaction of copper(II) bis(nitroacetylacetonate) with γ -picoline. This has been characterized as a presumably penta-coordinated mono adduct on the basis of conductance, magnetic susceptibility, infrared, and electronic spectral data.

Bonding of additional ligands along the axis normal to the molecular plane of planar complexes has aroused a considerable interest in recent years. Spectral evidence is available [1] for the coordination of heterocyclic bases to the planar molecule of copper(II) bis(acetylacetonate) and 1:1 adducts of this complex with 4-methyl pyridine and quinoline have been isolated [2, 3]; the base is lost readily. We have been trying for the adduct formation of metal β -diketonates with heterocyclic bases and have isolated [4, 5] a number of penta-coordinated adducts of zinc(II) β -diketonates with heterocyclic amines. It has therefore been thought worthwhile to extend the investigation to the case of copper(II) β -diketonates. Earlier a penta-coordinated quinoline adduct of copper(II) benzoylacetonate has been reported [6]. This communication describes a green crystalline 1:1 γ -picoline adduct of copper(II) bis(nitroacetylacetonate).

Experimental

All the chemicals used were of A.R. grade. Copper(II) bis(nitroacetylacetonate) was prepared by a known method [7] by reaction of acetylacetone in acetic anhydride with solid copper(II) nitrate. A vigorous exothermic reaction took place and the reaction vessel was kept in an ice bath while adding copper(II) nitrate and shaking. On cooling in the ice bath a dirty green crystalline compound separated. It was suction filtered, washed with ethanol and ether, and dried *in vacuo*. Analysis of the compound indicated the composition $\text{Cu}(\text{NO}_2\text{-acac})_2$. The i.r. spectra provided evidence for the formation of nitro chelate.

The chelate was dissolved in γ -picoline by warming till a saturated solution was obtained. The solution was cooled in an ice bath when green crystalline compound separated. Excess of nitrogen base was removed by suction. The compound was filtered under suction, washed quickly with a very small amount of methanol to avoid decomposition and dried *in vacuo*.

Purity of the compound was established by analyzing metal, carbon, hydrogen, and nitrogen.

For $[\text{Cu}(\text{NO}_2\text{-acac})_2(\gamma\text{-pic})]$ calculated: 14.30% Cu, 45.88% C, 9.45% N, 4.28% H; found: 14.14% Cu, 45.52% C, 9.18% N, 3.85% H.

Conductance was measured in 10^{-3} M acetone solution using a Toshniwal conductivity

Table 1

Spectral data of $\text{Cu}(\text{NO}_2\text{-acac})_2$ and $[\text{Cu}(\text{NO}_2\text{-acac})_2(\gamma\text{-pic})]$

	$\text{Cu}(\text{NO}_2\text{-acac})_2$	$[\text{Cu}(\text{NO}_2\text{-acac})_2(\gamma\text{-pic})]$	
<i>Infrared spectra</i> [cm^{-1}]			
$\bar{\nu}(\text{C}=\text{C}) + \bar{\nu}(\text{C}=\text{O})$	1565 v	*1625 vs	1570 s
Asym. NO_2 stretch	1510 s	1520 s	*1450 m
CH_3 deformation	1380 s	1380 s	
Sym. NO_2 stretch	1330 s	1330 s	*1250 s
			*1060 w
			*1030 vs
CH_3 rock	1000 m	1000 m	
C— CH_3 stretch C=O stretch	930 m	940 m	
N—O stretch	825 s	**830 vs	
C—H out of plane	750 w	**745 s	**550 s
M—O stretch	435 s	440 s	
M—N stretch	—	230 s	
<i>Electronic spectra</i>			
λ_{max} [nm]	640	650	
[ϵ]	140	180	

* Bands due to γ -picoline.** Bands due to γ -picoline and nitro chelate.Coordination sensitive bands of γ -picoline: 823 vs, 1015 vs, 1235 s.

bridge. Magnetic susceptibility measurements were made over solid specimens using Gouy method. The i.r. spectra were recorded in Nujol mulls using a Unicam SP-200 spectrophotometer and far-infrared spectra by a Perkin—Elmer spectrophotometer. Electronic spectra were recorded in 10^{-2} M chloroform— γ -picoline solution (in the case of the base adduct and only in chloroform in the case of starting material) using a Unicam SP-500 spectrophotometer. Spectral data are recorded in Table 1.

Results and discussion

Analysis of the green crystalline compound corresponds to the composition $[\text{Cu}(\text{NO}_2\text{-acac})_2(\gamma\text{-pic})]$. The low conductance value (8.5 mhos) in acetone is indicative of the non-electrolytic nature of the complex. Magnetic measurements show the complex to be paramagnetic ($\mu_{\text{eff}} = 82$ and 1.78 B.M. for the nitro chelate) in the presence of one unpaired electron.

Infrared spectra of $\text{Cu}(\text{NO}_2\text{-acac})_2$ are given in Table 1 along with the assignments. As seen from the study of the spectra of $[\text{Cu}(\text{NO}_2\text{-acac})_2(\gamma\text{-pic})]$, the bands due to $\text{Cu}(\text{NO}_2\text{-acac})_2$ and the nitrogen donor ligand (γ -picoline) are shifted, indicating bonding of the nitrogen donor ligand to the metal ion. The spectra are very complicated for assignment, the only information regarding the bonding of γ -picoline can be obtained from the finger-printing technique. This evidence is substantiated by the Cu—N and Cu—O stretching frequencies in the far-infrared region (Table 1). Hence, the compound is probably penta-coordinated. The complex loses the nitrogen base after exposure to air for a few days. It is observed that the base adduct of nitro chelate is more stable than the adduct of simple chelate in the air. Substitution of the hydrogen atom at the

central carbon atom by electron-withdrawing group (nitro group) results in an electron drawn from the ring system, by which the residual positive charge on the metal ion increases and it forms more stable adducts with σ -bonding heterocyclic base. Graddon and Watton [8] prepared mono adducts of $\text{Cu}(\text{acac})_2$ and $\text{Cu}(\text{bzac})_2$ with pyridine and γ -picoline. All of them were dark green or bright green in colour and were unstable, decomposing on exposure with loss of base leaving a residue of β -diketone complex.

A single broad absorption band was observed for $[\text{Cu}(\text{NO}_2\text{-acac})_2(\gamma\text{-pic})]$ at 650 nm having a molar extinction coefficient (ϵ) of 180 whereas in the case of $\text{Cu}(\text{NO}_2\text{-acac})_2$ the band was observed at 640 nm with ϵ 140. Though the band does not shift much on coordination with the nitrogen donor ligand, there is an increase in the extinction coefficient. Gillard and Wilkinson [3] studied the absorption spectra of $\text{Cu}(\text{acac})_2$ and $\text{Cu}(\text{acac})_2 \cdot \text{Q}$ in dichloromethane and reported bands at 658 nm (ϵ 41) for the former and 650 nm (ϵ 71) for the latter compound. Shigmatsu *et al.* [9] observed λ_{max} for $[\text{Cu}(\text{acac})_2 \cdot \text{py}]$ at 660 nm in benzene, acetone, and chloroform solutions. More recently Fackler and co-workers [10] prepared mono adducts of copper(II) bis(dipavoloyl methanate) with nitrogen bases, *e.g.*, pyridine, γ -picoline, piperidine, *etc.*, and reported λ_{max} in the $15\,800\text{ cm}^{-1}$ region. Graddon also observed an increase in the extinction coefficient of the mono adducts of copper(II) β -diketonates without much shift in the position of absorption maxima.

So the compound under report is presumably penta-coordinated. Nothing is known exactly about the geometry of the molecule. Ooi and Fernando [11] determined the X-ray crystal structure of $[\text{Cu}(\text{acac})_2 \cdot \text{Q}]$ and showed a square pyramidal structure for the compound. Hence $[\text{Cu}(\text{NO}_2\text{-acac})_2(\gamma\text{-pic})]$ is expected to have the same configuration.

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