

**Copper(II), Nickel(II) and Dioxouranium Complexes
of New Tetradentate Schiff Base Bis(benzoylacetone)
meso-stilbenediimine**

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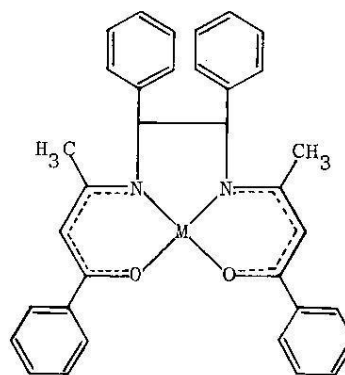
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Summary: The synthesis and properties of copper(II), nickel(II), and dioxouranium complexes with bis(benzoylacetone)meso-stilbenediimine are described. Infrared proton magnetic resonance and thermal stabilities of the complexes are discussed.

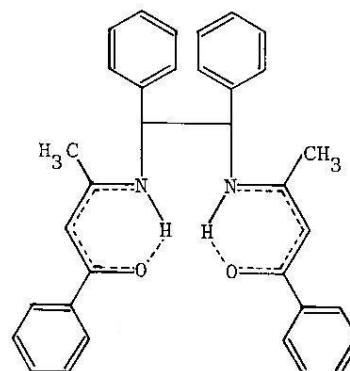
Introduction

Both bidentate and tetradentate ketoamine ligands have been known for a considerable period [1,2,3]. In general the presence of the nitrogen atom in the ligand determines for them a place intermediate between β -diketone and β -thioketone in terms of readily complexed metals. Most of the work has been concentrated on the metal chelates of β -ketoamines derived from β -diketones and salicylaldehyde with ethylenediamine and its derivatives. However only a few papers have appeared on the corresponding use of stilbenediamine (1,2-diphenyl-1,2-diaminoethane). Martell et al. [4] have reported PMR of meso- and -dl bis(acetylacetone)stilbenediamine and its nickel(II)chelate. Pasni and Gullotti [5] have reported oxovanadium complexes of meso- and -dl-bis(acetylacetone)stilbenediimine and bis(salicylaldehyde)stilbenediimine. Recently Kanatomi et al.[6] have characterised the copper(II), nickel(II) and cobalt (II) complexes of meso- and dl- bis(acetylacetone)-stilbenediimine, bis(salicylaldehyde)stilbenediimine and bis (2-hydroxyacetophenone) stilbenediimine. In the present work copper, nickel and uranium complexes have been

prepared to assess them spectrophotometrically and evaluate the volatility and thermal stability of nickel and copper complexes.



M=Cu (II), Ni (II)



Experimental

Preparation of reagent

A mixture of freshly prepared meso-stilbenediamine [7] (2.1g) and benzoylacetone (4.0g) was heated on a water bath for 2 hrs and allowed to stand overnight at room temperature. The precipitates were washed with ether and recrystallised from benzene m.p. 249°C, analysis:calculated for $C_{34}H_{32}N_2O_2$ (%) C=81.6, H=6.4, N=5.6; found (%) C=81.9, H=6.7, N=5.55. PMR showed absorption in ppm at δ 1.78 (CH_3), doublet at δ 4.9 (J=7Hz) (C-H bridge), δ 6.4 (=CH-) δ 7.36 (bridge C_6H_5) and δ 7.83 (COC_6H_5).

Metal chelates

Equimolar quantities of copper (II) acetate, nickel (II) acetate and uranyl nitrate hexahydrate were dissolved in ethanol and added to a solution of bisbenzoylacetone)meso-stilbenediimine in 1,2-dichloroethane. The copper(II) and nickel(II) complexes were refluxed for 1 hr, most of the solvent removed and methanol-water (1:1) added to the residue. The precipitate was filtered off and recrystallised from acetone. The copper(II) complex melted at 278°C, analysis:calculated for $(C_{34}H_{30}N_2O_2)_2Cu$, (%) C=72.64, H=5.38, N=4.98; found (%) C=72.43, H=5.35, N=4.98.

Nickel(II) complex melted at 300°C, analysis calculated for $(C_{34}H_{30}N_2O_2)_2Ni$, (%) C=73.3, H=5.39, N=5.39; found (%) C=72.9, H=5.30, N=4.91 PMR showed absorption in ppm at δ 1.7(CH_3), δ 4.47 (bridge -CH), δ 5.65 (=CH-), δ 7.02 δ 7.34 (bridge C_6H_5) δ 7.73 (Co C_6H_5).

Uranium (VI) complex precipitated out readily. The orange precipitate was filtered and boiled several times with ethanol. The product was filtered and dried in vacuum desiccator, decomposed at 290°C, calculated for $(C_{34}H_{32}N_2O_2UO_2)(NO_3)_2 \cdot 3H_2O$, % C=43.00, H=4.00, N=5.90, found % C=42.85, H=3.53, N=5.86.

Physical Measurements

Infra red spectra were recorded on Unicam SP 1025 infra red spectrophotometer in the range of 3600-650 cm^{-1} using KBr and Nujol mull techniques. Proton magnetic resonance spectra were recorded on Jeol PMX-60 NMR spectrometer at HEJ Research Institute of Chemistry, University of Karachi in the range of 0-10 ppm in $CDCl_3$ containing tetramethylsilane as internal standard.

The solutions of copper(II) and nickel(II) chelates in spectroscopic grade acetone and uranium (VI) complex in pyridine and dimethylsulphoxide (DMSO) were used for conductivity measurements with WTW, LF-56 conductivity bridge at room temperature (30°C).

TGA and DTA were recorded with Stanton TG 770 from Elemental Micro Analysis Ltd., U.K. at the scan rate of 20°C min^{-1} in flowing nitrogen atmosphere at 6 $cm^3 min^{-1}$ between room temperature and 500°C with samples of 10 mg nickel and 2.5 mg copper complex.

Elemental analyses were performed at the chemistry department, University of Birmingham and Elemental Micro-Analysis Ltd. U.K.

The dried chelate was sublimed at reduced pressure immersed in an oil bath and the sublimate collected on a cold finger.

Results and Discussion

The preparation of the dibasic complexing reagent and its nickel (II), copper (II) and uranium (VI) complexes did not present difficulties. The infra-red spectra of the compounds are quite complex, but the weak intensity absorption at 3200 cm^{-1} observed in spectrum of the ligand is assigned to the chelated N-H group. However the band disappeared in copper (II) and nickel (II) chelates on complexation.

Secondly, in the region from $1610\text{--}1460\text{ cm}^{-1}$, there are a number of strong bands, but there is no indication for the free keto group. The assignments of these bands must be considered as tentative, since C=O , C=C , C=N and phenyl ring vibrations all may be expected in the lower 1600 cm^{-1} region. In fact both C-O and C-N bonding would be expected to have partial double bond character, assuming a pseudo-aromatic ring.

The band at the highest wavelength observed in the spectrum of the reagent is assigned to the hydrogen bonded conjugated C=O group as it disappears in copper (II), nickel (II) and uranium chelates upon complexation. This is in perfect agreement with what is reported by other authors for similar Schiff bases [8,9,19]. The next absorption bands assigned for C=C and C=N/NH bands in the reagent slightly shifts towards higher frequency and become more intense in copper and nickel chelates.

Little work has been reported on the uranyl complexes of tetradentate Schiff bases. Pasini et al. [12] isolated UO_2LS complex, where L is a Schiff base and S is a solvent molecule. Bong-IL-Kim [9] have prepared the uranyl complexes of bis (acetylacetone)ethylenediimine and its derivatives and have reported the forma-

tion $\text{UO}_2(\text{H}_2\text{L})(\text{NO}_3)_2$ complexes where H_2L ligand acts as a bidentate neutral molecule with two oxygen atoms involved in the complexation. The present work also reports similar uranyl complex and supports Bong-IL-Kims [9] work. The I.R. spectrum of the dioxouranium (VI) complex indicates a weak band at 3300 cm^{-1} , and is assigned to OH and NH groups of the water and reagent molecules. The bands at 1545 and 1275 cm^{-1} for NO_3 and at 912 cm^{-1} for UO_2 are in good agreement as expected. The NMR of the base shows a doublet at 4.6 ppm corresponding to two protons probably for the bridged-CH-, due to the presence of NH tautomeric form, which changes into a singlet at 4.7 ppm in the nickel chelate.

Electrical conductivity measurement on acetone solution of copper and nickel complexes give Λ_M values of 0.36 and $0.42\text{ mho cm}^2\text{ mole}^{-1}$ respectively and confirm that these are non-electrolytes. However the values of molar conductance of uranyl complex in pyridine and dimethylsulphoxide are in the range of 26.0 and $73.3\text{ mho cm}^2\text{ mole}^{-1}$ respectively. This leads us to suggest that the solvent, particularly DMSO, is able to displace weakly coordinate two nitrate groups with considerable increase in the conductivity as reported earlier also [11].

Quantitative absorptiometric data is summarized in Table 1. The blue colour of copper complex shows the absorption bands at 630 nm and 562 nm with molar absorptivities of 239 and $278\text{ l. mole}^{-1}\text{ cm}^{-1}$. The yellow colour of nickel (II) complex indicates reasonable sensitivity at 405 nm with molar absorptivity of 1×10^4

Table-1: Quantitative Absorptiometric Data Cu (II), Ni(II) and U(VI) complexes of bis(benzoylacetone) meso-stilbenediimines

Metal Ion	Solvent	λ_{max} nm	ϵ mole ⁻¹ cm ⁻¹	Stability
Ni(II)	Acetone	570	418	> week
		405	10020	
Cu(II)	1,2-dichloroethane	630	239	> week
		562	278	
U(VI)	DMSO	442	31	> week
		430	36	
		410	34	
	Pyridine	444	54	> week
		432	77	
		410	104	

1.mole⁻¹ cm⁻¹. The nickel (II) complex obeys the Beer's law at 405 nm in acetone in the range of 8-48 µg/ml complex, corresponding to 0.8-5 µg/ml of nickel.

The orange dioxouranium complex is insoluble in ethanol, acetone, benzene, chloroform and methyl-isobutylketone (MIBK). However the complex is soluble in pyridine and DMSO to form a yellow solution of low intensity. The lower values of molar absorptivities particularly in DMSO coordinates with the increase in molar conductivity which could be due to the ionization of loosely bonded nitrate ions.

Copper(II), nickel(II) and uranium (VI) chelates show remarkable solution stability and the absorbance of the solution did not change within a week. The complexes in solid state when placed at room temperature (30-35°C) for four months did not indicate any deterioration.

Traces of TGA and DTG of nickel and copper chelate in Fig.1 indicate that the copper complex starts to loose in weight at 270°C and loss in weight is about 82% by 440°C, leaving behind a residue. Similarly nickel (II) chelate loses weight at 350°C and decrease in weight is about 79% at 480°C with a brown residue. Thus they are not sufficiently volatile and probably some decomposition also occurs at high temperature. This is supported by the analysis of the sublimate of the copper and nickel complexes collected at 210°C at 2mm pressure. Analysis for copper complex found (%) C=73.88, H,5.35, N=4.79 and nickel chelate showed (%) C=69.29, H=4.92, N=4.90.

Conclusion

The ligand bis (benzoylacetone) meso-stilbenediimine easily reacts with copper(II), nickel(II) and uranium (VI) to form coloured com-

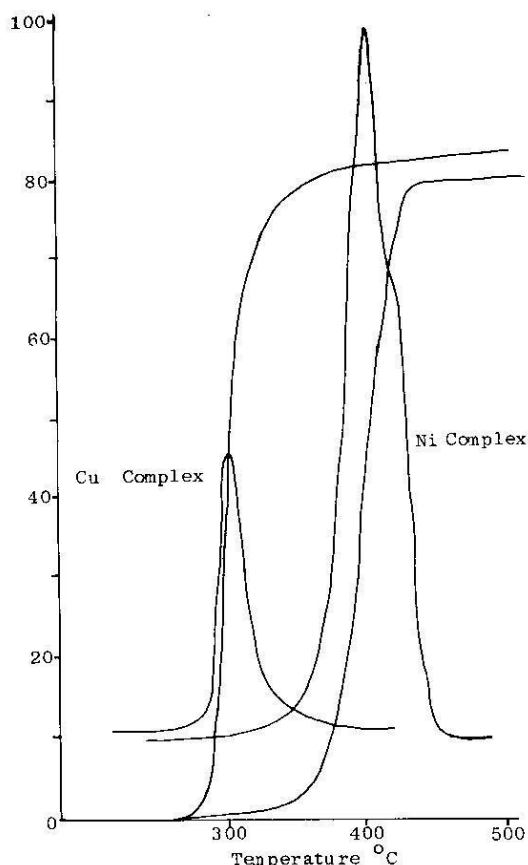


Fig.1: Thermograms of Cu(II) and Ni(II) complexes of Bis(benzoylacetone) meso-stil-benediamine.

plexes. Nickel (II) and copper(II) are nonelectrolytes but uranium(VI) complex ionizes appreciably, particularly in DMSO, with decrease in colour intensity. Copper and uranium complexes are weakly coloured but nickel complex shows reasonable sensitivity with molar absorptivity of $1 \times 10^4 \text{ l.mole}^{-1} \text{ cm}^{-1}$ at 405 nm. The nickel(II) and copper (II) complexes are somewhat volatile but decomposition occurs at high temperature.

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