

**Some Investigations of Copper(II), Nickel(II)  
and Dioxouranium (VI) Complexes of  
Bis(salicylaldehyde)meso-stilbenediimine**

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**Summary:** Copper (II), nickel(II) and dioxouranium (VI) complexes of bis(salicylaldehyde) meso-stilbenediimine have been prepared and they are assessed spectrophotometrically. The infra-red, thermal gravimetric analysis and conductivity measurements of the complexes have also been recorded. The conductivity measurements indicates that copper (II) and nickel (II) complexes are non electrolytes, but uranium (VI) complex ionizes appreciably in pyridine and dimethyl sulphoxide. TGA of nickel (II) and copper (II) complexes indicates that the complexes decompose at high temperature and leave some residue behind.

### Introduction

Metal complexes of quadridentate Schiff bases derived from the condensation of salicylaldehyde and ethylenediamine have been widely studied [1,2], but relatively less work has been reported on the corresponding use of bis (salicylaldehyde) stilbenediimine. Pasini et al. [3] reported the preparation of the ligand and metal complexes of oxovanadium (IV) [4], iron (III) [5], Copper (II), nickel (II), cobalt (II) [6,7], palladium (II) and platinum (II) [8] and determined their structures. Pasini et al. have also attempted to develop cobalt (II) and Iron (II) complexes as possible models of biological significance as oxygen carriers [5,7]. Kanatomi et al. [9] have prepared the copper (II), nickel (II) and cobalt (II) complexes of bis (salicylaldehyde) stilbenediimine, and the structure of the reagent and its metal complexes are inferred by means of electronic spectra, and have found to be essentially planar.

Dioxouranium (IV) complex of bis (salicylaldehyde) ethylenediimine was first reported by Pfeiffer et al. [10]

in 1937. Poddar et al. [11] as well as Pasini et al. [12] described the synthesis of hepta coordinated adducts of the type  $UO_2(SB)L$  (Where L is solvent molecule e.g: Pyridine, DMSO, DMF) and suggested that anions of the Schiff base is coordinated to the central metal atom. Bong-IL-Kim [13] and Tandon [14] have prepared the derivatives of the type  $UO_2[H_2SB](NO_3)_2$  where molecule of tetradentate schiff base  $H_2SB$  behaves as the neutral bidentate ligand in the uranyl complexes.

The present work reports the preparation of bis (salicylaldehyde) meso-stilbenediimine dioxouranium (VI) nitrate as  $UO_2[H_2SB](NO_3)_2$  species and explore the potential of the reagent for its possible use as analytical reagent for quantitative determination of copper, nickel and uranium.

### Experimental

The reagent bis-(salicylaldehyde)

meso-stilbenediimine and its nickel (II) and copper (II) complexes were prepared by reported method [9].

*Preparation of Bis-(salicylaldehyde) meso-stilbenediimine dioxouranium nitrate.*

Dissolve bis-(salicylaldehyde)meso-stilbenediimine (1.05g) in dioxane and slowly add the solution of uranyl nitrate hexahydrate (1.25g) in dioxane. The complex readily precipitates out as brown solid. Filter and boil several times with dioxane. Decomp. 300°C. Calculated for  $C_{28}H_{24}N_4O_{10}U$ , % expected C=41.28, H=2.95, N=6.88, % found C=41.17, H=2.97, N=6.69.

Elemental micro-analysis were carried out by Elemental Microanalysis Ltd., U.K., I.R. spectra were recorded on Unicam SP 1025 infra red spectrophotometer using KBr and nujol mull techniques. All absorptometric studies were carried out on Hitachi 220 spectrophotometer. Conductivity measurements were carried out at room temperature (35°C) using WTW, L F-56 conductivity bridge. TGA of nickel (II) and copper (II) complexes were carried out with stanton TG 77 by Elemental Micro Analysis Ltd., at a scan rate of 20°C per minute in flowing nitrogen atmosphere at the rate of 10 cm<sup>3</sup>/min with 10 mg of sample.

### Results and Discussion

The preparation of dioxouranium (VI) complex did not encounter much difficulty. Its infra-red spectrum also agrees with its structure particularly the bands at 1540, 1270 cm<sup>-1</sup> and 930, 870 cm<sup>-1</sup> for NO<sub>3</sub> and UO<sub>2</sub> groups respectively as expected. The coloured copper (II), nickel (II) and uranium (VI) complexes prompted us to explore their potentials for the quantitative determinations of metal ions. The

absorptometric data is summarized in table-1. The results indicate that copper (II) complex is less sensitive, but nickel (II) complex shows reasonable sensitivity and obeys the Beer's law between 1-7 g/ml of nickel at 418 nm. Uranium (VI) complex is only slightly soluble in ethanol, methanol, chloroform, but readily dissolves in pyridine and dimethylsulphoxide to form coloured solution. The complex indicates molar absorptivity of  $3.6 \times 10^3$  l.mole<sup>-1</sup> cm<sup>-1</sup> pyridine at 390 nm. A calibration curve (Fig.1) is fairly linear, but it fails to obey Beer's law. This could be explained due to appreciable dissociation of loosely bonded nitrate group in pyridine. This is further supported by measurement of the conductivity of its solution in pyridine and DMSO. The values of molar conductance  $M_2$  are in the range of 14 and 15 mho cm<sup>2</sup> mole<sup>-1</sup> in pyridine and DMSO respectively as compared to the value of 0.2 mho cm<sup>2</sup> mole<sup>-1</sup> for copper (II) and nickel (II) complexes in dioxane.

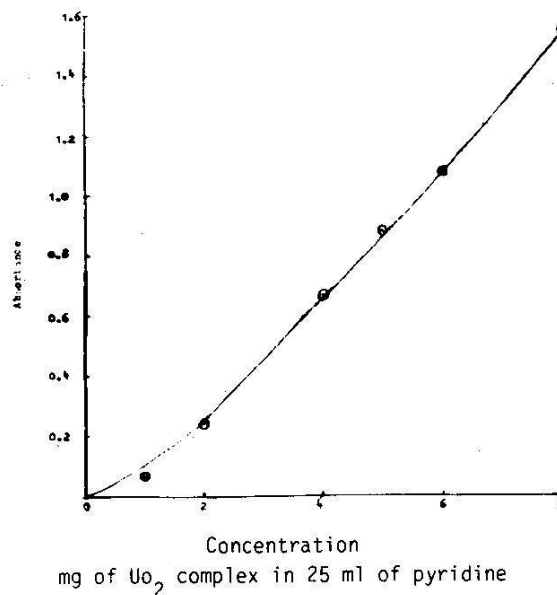


Fig.1: Calibration curve of Bis(salicylaldehyde)meso-stilbenediimine dioxouranium nitrate.

Table 1: Quantitative absorptiometric data of copper (II), nickel (II) and uranium (VI) complexes of bis-(salicylaldehydes) meso-stilbenediimine.

Metal ion	Solvent	Colour of complex	$\lambda$ max nm	$\epsilon$ (mole <sup>-1</sup> cm <sup>-1</sup> )	Calibration range
Nickel(II)	Chloroform	Yellow	550 418	185 7773	Obeys the Beer's law in the range of 8-56 g/ml of complex corresponding to 0.98-6.9 $\mu$ g/ml of nickel at 418 nm in chloroform
Copper(II)	Dioxane chloroform	Blue Purple	575 558	366 377	Obeys the Beer's law in the range of 0.198-1.88 mg/ml of complex corresponding to 26.1-248 $\mu$ g/ml of copper at 58 nm in chloroform.
Uranium (VI)	Pyridine	Golden Yellow	460 390	777 3618	
	DMSO	Yellow	460 380	209 932	

Volatility and thermal stability of the nonelectrolyte and planner nickel (II) and copper (II) complexes were also checked by recording their TGA curve. The results indicate that the copper(II) complex loses weight mostly at 340°C, leaving about 35% residue, which continues to lose weight upto 650°C. Similarly nickel (II) complex indicates maximum loss in weight at about 360°C leaving 14% residue. This leads us to suggest that the complexes are not sufficiently volatile and thermally stable and some decomposition occurs at high temperature.

### Conclusion

The reagent Bis (salicylaldehyde)

meso-stilbenediimine and its copper (II) and nickel(II) complex were prepared by reported method but is dioxouranium complex seems to have been reported for the first time. Spectrophotometric studies show that the copper complex is relatively less sensitive, but its nickel (II) complex shows reasonable sensitivity at 418 nm with molar absorptivity of  $7.7 \times 10^3$  l.mole<sup>-1</sup> cm<sup>-1</sup>. The dioxouranium complex also indicates the molar absorptivity of  $3.6 \times 10^3$  l.mole<sup>-1</sup> cm<sup>-1</sup>, at 390 nm, but the change in absorbance versus concentration deviates from Beer's law, due to the appreciable dissociation of nitrate groups. The conductivity measurements indicate that copper (II) and nickel

(II) complexes are nonelectrolytes, but uranium (VI) complex partially ionizes and conducts certain electricity. Finally the copper and nickel complexes decompose at higher temperature and leave certain residue behind.

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