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Synthesis and Microbial Activity of 5-(2-Methyl-4-N-cyanoethyl-N-benzenesulphonyl aminobenzylidene)rhodanine and its Metal Complexes

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Synthesis of 5-(2-methyl-4-N-cyanoethyl-N-benzenesulphonyl aminobenzylidene)rhodanine (I) by the reaction of 2-methyl-4-N-cyanoethyl-N-benzenesulphonyl aminobenzaldehyde (II) and rhodanine (III) is described. Synthesized rhodanine derivative and its metal complexes were screened for their microbial activities.

Key Words: Synthesis, 5-(2-Methyl-4-N-cyanoethyl-N-benzenesulphonyl aminobenzylidene)rhodanine, Antibacterial activity.

INTRODUCTION

Survey of literature reveals that *p*-dimethyl aminobenzylidene rhodanine is known to be a sensitive reagent for copper, silver and mercury[1, 2]. Along with analytical applications rhodanine derivatives also possess insecticidal and fungicidal properties[3–6]. On the basis of these observations it was thought of interest to prepare 5-substituted rhodanine of synthesized 2-methyl-4-N-cyanoethyl-N-benzenesulphonyl aminobenzaldehyde.

EXPERIMENTAL

Synthesis of 5-(2-methyl-4-N-cyanoethyl-N-benzenesulphonyl aminobenzylidene)rhodanine

All chemicals used were of extra pure grade. Melting points were taken in open capillary and were uncorrected. The products were routinely checked for their purity by TLC on silica gel. Components gave satisfactory C, H, N and S analysis. IR spectra were taken as KBr pellets on Shimadzu 8201 PC FTIR. A mass spectrum was recorded on Jeol D-300 (EI/Cl).

The 2-methyl-4-N-cyanoethyl-N-benzenesulphonyl aminobenzaldehyde required in the synthesis was prepared in three steps. Monocyanoethylation of *m*-toluidine was carried out as reported in the literature[7]. The product 3-(*m*-toluidine) propionitrile was converted into N-cyanoethyl-N-benzenesulphonyl *m*-to-

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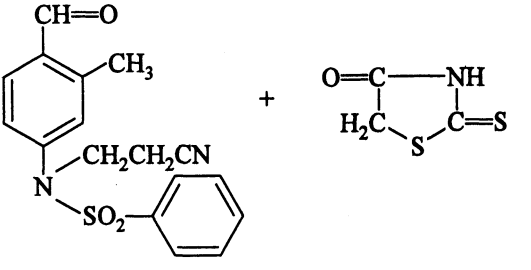
luidine and formylation was carried out in DMF and phosphorous oxychloride. Pradhan[8] reported 42% yield.

The rhodanine needed for the condensation was synthesized according to Julian and Sturgis[9]. Condensation of aldehyde and rhodanine was carried out according to general procedure of Campbell and Mckail[10] and Stephen and Townshend[11].

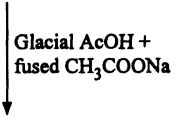
Aldehyde (0.002 mol, 0.656 g) and rhodanine (0.002 mol, 0.266 g) were dissolved in 10 mL of glacial acetic acid and 0.05 g fused sodium acetate and refluxed in an oil bath for 5–6 h. The product was cooled, filtered, washed with little glacial acetic acid and well with water and dried. Brown coloured 5-(2-methyl-4-N-cyanoethyl-N-benzenesulphonyl aminobenzylidene)rhodanine recrystallized with glacial acetic acid; 45% yield, m.p. 135°C.

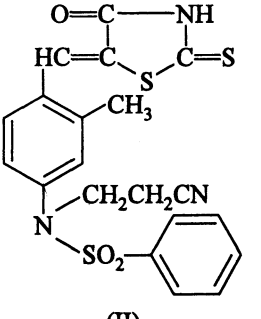
Synthesis of Metal Complexes

Ethanolic solutions of metal acetate (Ni, Co, Cu and Zn) were treated separately with ethanolic solution of 5-(2-methyl-4-N-cyanoethyl-N-benzenesulphonyl aminobenzylidene)rhodanine in 1 : 2 ratio and refluxed on a water bath for 1 h, when the metal chelate separated out. These were filtered, washed with ethanol/acetic acid followed by ether and dried *in vacuo*. Colour of Ni and Cu complex is brown while that of Co and Zn is light pink and white respectively.



(I)





(II)

RESULTS AND DISCUSSION

5-(2-methyl-4-N-cyanoethyl-N-benzenesulphonyl aminobenzylidene)rhodanine is a brown coloured shining crystalline compound with sharp m.p. 135°C.

The elemental analysis is in complete agreement with the molecular formula, *i.e.*, $C_{20}H_{17}N_3S_3O_3$ and found to contain C = 54.3%; H = 3.7%; N = 9.3% and S = 21.5%. Calcd. C = 54.1%; H = 3.8%; N = 9.1% and S = 21.2%.

The IR spectrum has typical absorbance at 3065 cm^{-1}, 1710 cm^{-1} and 1085 cm^{-1} for rhodanine derivatives[12]. Absorption band at 3064 cm^{-1} corresponds to ν(N—H), 2923 cm^{-1} is attributed to C—H stretching of $\nu_{asym}(CH_3)$[13], 2856 cm^{-1} is due to $\nu_{sym}(CH_2)$, characteristic weak band at 2262 cm^{-1} is attributed to alkyl nitrile, 1710 cm^{-1} is attributed to C=O stretching, 1452 cm^{-1} δ CH_2 vibrations. Absorption band at 1377 cm^{-1} is for sulphonamide stretch and a typical C—N stretch for aromatic tertiary amine[14] at 1315 cm^{-1}, stretching vibrations due to SO_2 appear at 1164 cm^{-1}, ν(C=S) represent at 1085 cm^{-1} typical thioamide band (—N—C=S), δ CH_2 appears at 721 cm^{-1}. The SO_2 bands appear as doublet at 562 cm^{-1}. A medium band at 447 cm^{-1} is for C=N torsion.

A bar graph of mass spectrum shows a mole peak at 444 M/e. Elemental data however reveal molecular weight 443. It is believed that fragmentation occurs and the fragment 389 M/e stabilizes by delocalization of lone pair[13] and form the base peak. Other fragment ion, *viz.*, $SO_2C_6H_5$ 141 M/e etc. also formed.

Microbial Activity

Antimicrobial activity of rhodanine and its metal complexes in dimethyl formamide was studied by serial tube dilution technique. The solution was added to N-Broth to get 200, 100, 50, 25, 12.5, 6.25, 3.12 and 1.56 μg/mL concentration. MIC values for the rhodanine and its metal complexes were found to be as follows:

S.No.	Compound	*E. coli*	*S. aureus*	*B. sublitis*	*P. aruginosa*
1.	Rhodanine	+	++	+	++
2.	Nickel complex	+	+	+	+
3.	Cobalt complex	+	+	+	+
4.	Copper complex	+	++	+	+
5.	Zinc complex	+	+	+	+

MIC values: ++ > 200 μg/mL, + <200 μg/mL.

5-(2-methyl-4-N-cyanoethyl-N-benzenesulphonyl aminobenzylidene)rhodanine is found to be active against *S. aureus* and *P. aruginosa*. Minimum inhibitory concentration value is found to be 200 μg which is important from clinical viewpoint. The compound is less active against *B. subtilis* and *E. coli* and MIC values are found to be above 200 μg. Metal complexes of 5-(2-methyl-4-N-cyanoethyl-N-benzenesulphonyl aminobenzylidene)rhodanine are found to be less active than parent compound and MIC was above 200 μg except Cu.

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REFERENCES

1. F.J. Welcher, Organic Analytical Reagents, D. Van Nostrand Co. Inc., p. 417 (1956).
2. J.A. Ryan and C.W. Culshaw, *Analyst*, **60**, 370 (1944).
3. S.P. Gupta and P. Dureja, *J. Indian Chem. Soc.*, **51**, 936 (1974).
4. S.P. Gupta and S. Rani, *J. Indian Chem. Soc.*, **55**, 483 (1978).
5. B. Dash and P.K. Mohapatra, *J. Indian Chem. Soc.*, **61**, 271 (1984).
6. K. Das, D. Panda and B. Das, *J. Indian Chem. Soc.*, **67**, 58 (1990).
7. S. Allen Heininger, *J. Org. Chem.*, **22**, 12 (1957).
8. A. Pradhan, Ph.D. Thesis, Jiwaji University, Gwalior (1992).
9. P.L. Julion and B.M. Sturgis, *J. Am. Chem. Soc.*, **57**, 1126 (1935).
10. N. Campbell and J.E. Mckail, *J. Chem. Soc.*, 1251 (1948).
11. W.I. Stephen and A. Town Shend, *J. Chem. Soc.*, 5127 (1965).
12. ———, *J. Chem. Soc.*, 3738 (1965).
13. R.M. Silverstein and G.E. Bassler, Spectrophotometric Identification of Organic Compounds, Wiley, New York (1981).
14. J.R. Dyer, Application of Absorption Spectroscopy of Organic Compounds, Prentice-Hall, New Delhi (1994).

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