

TABLE 2 — COLOUR AND ANALYTICAL DATA OF Ni(II) COMPLEXES

Compound	Colour	N (%)	Ni (%)	M (%)
		Calc. (Found)	Calc. (Found)	Calc. (Found)
Ni(H ₂ DAPL)	Yellow	6.56 (6.48)	12.87 (12.02)	— —
Ni(Li ₂ DAPL).4H ₂ O	do	5.48 (5.39)	11.48 (11.26)	2.71 (2.81)
Ni(Na ₂ DAPL).4H ₂ O	Orange	5.16 (5.37)	11.18 (11.66)	8.46 (8.51)
Ni(Mg DAPL).2H ₂ O	Yellow	5.77 (6.48)	12.10 (12.60)	5.01 (4.75)
Ni(Ca DAPL).3H ₂ O	do	5.39 (5.41)	11.31 (11.26)	7.72 (7.10)
Ni(Sr DAPL).3H ₂ O	do	4.94 (5.40)	10.35 (10.62)	15.45 (15.06)
Ni(Ba DAPL).5H ₂ O	do	4.45 (4.89)	9.00 (8.39)	21.07 (21.67)
Ni(H ₂ DAMPL)	do	6.35 (6.32)	26.53 (26.80)	— —
Ni(Na ₂ DAMPL).2.5H ₂ O	Red	5.28 (5.13)	11.08 (11.72)	8.67 (8.01)
Ni(Li ₂ DAMPL).3H ₂ O	do	5.52 (5.89)	11.58 (10.71)	2.74 (2.82)
Ni(Mg DAMPL).6H ₂ O	Yellow	4.90 (4.60)	10.28 (9.36)	4.26 (3.51)
Ni(Ca DAMPL).5H ₂ O	Orange	4.92 (4.76)	10.32 (10.40)	7.04 (6.93)
Ni(Sr DAMPL).4H ₂ O	do	4.67 (4.70)	9.80 (9.82)	14.63 (14.60)
Ni(Ba DAMPL).3H ₂ O	do	4.45 (4.16)	9.32 (9.18)	21.80 (20.98)

violet, were obtained. The grey form was prepared by adding BaCl₂ (1 g) solution to an excess Cu(Na₂DAPL).4H₂O.

Preparation of Ni(Na₂DAPL) and Ni(Na₂DAMPL) — Schiff base (2 g) dissolved in aqueous NaOH 0.6 g dissolved in 75 ml H₂O was heated on a steam-bath and to this Ni(OAc)₂ (~0.05M in 100 ml absolute ethanol) was added slowly with stirring. The solution turned dark-red which on cooling deposited the orange-red silky needles of the disodium derivative of Ni(II) complex. The solution was filtered, washed with ethanol, and dried *in vacuo* for 24 hr over silica gel.

Reaction of Ni(Na₂DAPL) and Ni(Na₂DAMPL) with IA and IIA group elements — The parent complex (0.1M) was dissolved in water (100 ml) and heated on a steam-bath. To this was added a solution of LiCl (0.08M) dil. HCl or a solution (0.04M, 100 ml) of MgSO₄, CaCl₂, Sr(NO₃)₂, or BaCl₂. In most for the cases immediate precipitation occurs. The mixture was heated on a steam-bath for 30 min, cooled and filtered. Finally the precipitate was washed and dried *in vacuo* over silica gel for 2-3 days.

The diffuse electronic (reflectance) spectra were measured on a Zeiss PMQ II spectrophotometer with the sample spread on a filter paper. The room temperature magnetic susceptibilities were measured by the Gouy method.

The author is grateful to the UGC, New Delhi, for the award of a Colombo Plan Fellowship. He is also thankful to Dr D. J. Phillips of the School of Chemistry, University of New South Wales, for suggesting the problem and for helpful suggestions.

References

- HARRIS, C. M. & SINN, L., *Coord. Chem. Rev.*, **4** (1969), 391.
- PODDAR, S. N., *Z. anorg. allg. Chem.*, **322** (1963); 326.
- PHILLIPS, D. J. & CUNNINGHAM, J., unpublished work.
- DUFF, J. & BILLS, E., *J. chem. Soc.*, (1932), 1987.

Zn(II), Cu(II), Ni(II) & Co(II) Complexes of N-(Salicylidene)-N'-[2-(salicylaldehyde)-benzoyl]hydrazine, the Schiff Base Derived from o-Aminobenzoylhydrazine & Salicylaldehyde

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Received 1 July 1975; accepted 16 August 1975

Zn(II), Cu(II), Ni(II) and Co(II) complexes of N-(salicylidene)-N'-[(2-salicylaldehyde)benzoyl]hydrazine, the Schiff base derived from o-aminobenzoylhydrazine and salicylaldehyde, (LH) have been synthesized and characterized on the basis of analytical, electronic and infrared spectral and magnetic moment data.

MONOAMINE oxidase (MAO) enzyme inhibition by acylhydrazines^{1,2} has been suggested to take place via metal-acylhydrazine Schiff base complex³. In view of this and because of very little work reported on the complexes of Schiff bases derived from hydrazine and acylhydrazines, we report in this note the preparation and characterization of Cu(II), Zn(II), Ni(II) and Co(II) complexes with the title ligand (I).

The ligand (I) was prepared by condensing o-aminobenzoylhydrazine⁴ and salicylaldehyde in 1:2 molar ratio and crystallizing the product from ethanol; m.p., 218° (Found: C, 71.01; H, 5.00; N, 12.10 Reqd: C, 70.19; H, 4.74; N, 11.70%)

Cu(II) and Ni(II) complexes (b, c and d; Table 1) were prepared by reacting Cu(II) and Ni(II) chlorides and the ligand in 1:1 and 1:2 (metal: ligand) molar ratios in hot ethanol. The products were filtered and washed with hot ethanol. Complexes a, e and f (Table 1) were prepared by reacting a solution of the ligand in NaOH with excess metal salts and acidifying the resultant mixture with acetic acid. The solids obtained were filtered, washed with dilute acetic acid and hot ethanol and dried at room temperature.

The ligand in the complexes was estimated volumetrically in 10N H₂SO₄ with standard KMnO₄ using a calibration curve. The complexes were

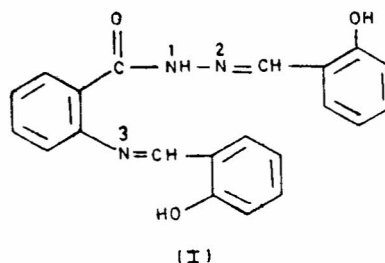


TABLE 1 — ANALYTICAL, ELECTRONIC SPECTRAL AND MAGNETIC DATA OF Zn(II), Cu(II), Ni(II) AND Co(II) COMPLEXES

Complex and colour	m.p. (°C)	Found (Calc.), (%)			$\mu_{\text{eff.}}$ (BM)	λ_{max} (nm)
		Metal	N	Ligand		
(a) ZnL ₂ light yellow	202	7.9 (8.3)	11.5 (10.8)	91.1 (91.6)	Diamagnetic	235, 250, 300, 370
(b) CuL ₂ deep green	155	7.7 (8.5)	10.7 (10.8)	92.5 (91.9)	1.6	240, 285, 387, 430, 687
(c) [CuL]Cl green	170	13.9 (14.4)	10.00 (9.30)	80.0 (79.5)	1.8	305, 362, 437, 600
(d) [NiL]Cl light green	240	13.6 (13.1)	9.7 (9.3)	78.5 (79.1)	3.3	263, 320, 400, 600
(e) NiL ₂ yellow	240	8.1 (7.6)	11.2 (10.8)	93.0 (92.4)	3.1	235, 260, 315, 438
(f) CoL ₂ brown	230	7.2 (7.6)	11.4 (10.8)	92.9 (92.4)	1.9	250, 375

analysed for nitrogen using a Coleman nitrogen analyser, and for the metal by usual procedures.

Infrared and electronic spectra were recorded on a Perkin-Elmer spectrophotometer model 621 and a Cary-14 model spectrophotometer respectively in nujol. Magnetic measurements were carried out on a Faraday balance.

Cu(II) forms both 1:1 and 1:2 (metal-ligand) complexes (Table 1) depending on the metal-ligand ratio used but Ni(II) forms only 1:1 complex even when Ni(II) salt and the ligand are reacted in 1:2 molar ratio. The chloride ions are partially replaced in the complexes (c and d Table 1) prepared from ethanolic medium. Under similar conditions, Co(II) complex fails to precipitate. The alkaline solution of the ligand, however, reacts with Zn(II), Ni(II) and Co(II) salts forming neutral complexes. The complexes are coloured, insoluble in water and common organic solvents but dissolve slightly in tetrahydrofuran and nitrobenzene unlike the amine schiff base complexes. The ligand loses one proton in both 1:1 and 1:2 complexes. It has three labile protons, viz. those of one -NH and two -OH groups out of which the -OH protons are more labile. Since, the -OH groups are hydrogen bonded as in Schiff bases, the one which is strongly hydrogen bonded may be strongly ionized and hence more labile. The

electrons on ³N being in conjugation with two benzene rings (I), are less available for hydrogen bonding than those of ²N which is in resonance with only one benzene ring. Although both the -OH protons should be reactive in alkaline medium, the 1:2 compositions of Zn(II), Ni(II) and Co(II) complexes (a, e and f, Table 1) indicate that one of the -OH group is re-formed when the reaction mixture is acidified with acetic acid. From these observations and previous experience^{5,6}, it can be said that OH group of salicylidene moiety on ²N takes part in coordination.

The visible spectrum of the ligand shows bands at 245 and 337 nm. In the metal complexes these bands are shifted considerably (Table 1). Cu(II) complexes (b and c) show one band in the red region (~600 nm) due to the transition ²T_{2g} ← ²E_g

corresponding to planar structure⁷. Octahedral, Ni(II) complexes show two bands corresponding to the transitions ³A_{2g} → ³T_{1g}(F) and ³A_{2g} → ³T_{1g}(P) respectively⁸. In the present Ni(II) complexes (d and e) the band corresponding to the transition ³A_{2g} → ³T_{2g}(P) is masked by a charge-transfer band but a band around 600 nm is present in complex (d).

Infrared spectra (band positions in cm⁻¹) of the ligand and its metal complexes show a band around 3400 indicating the presence of -OH group. A broad band (ν N-H) centred at 3200 in the ligand is shifted to 3340 in metal complexes. This increase in ν N-H frequency is analogous to a similar increase in ν N-H in the complexes of secondary amides when > C=O group coordinates⁹. The ν C=O band observed at 1640 in the ligand shifts to lower frequency side ($\Delta\nu = 20$) in metal complexes, confirming the involvement of > C=O group in coordination.

The Cu(II) complexes (b and c) show $\mu_{\text{eff.}}$ values which are slightly less than those expected for one unpaired electron. As the visible spectral band in the case of complex (c) is shifted more towards the blue region, it indicates the greater planarity of the complex. Due to this increased planarity, some M-M interactions may have caused the lowering of magnetic moment.

One of the authors (R.A.L.) is thankful to the CSIR New Delhi, for the award of a junior research fellowship.

References

- ZELLER, E. A., BARSKY, J., FOUTS (Jr), KIRCHHEIMER, W. F. & VAN-ORDEN, L. S., *Experientia*, **8** (1952), 349.
- YONEDA, M., KOTA, N. & OKAJIMA, *Nature*, **170** (1952), 803.
- WEIGAND, R. C., *J. Am. chem. Soc.*, **78** (1956), 5307.
- PRAGER, B., JACOBSON, P., SCHIMDT, P. & STERN, D., *Belstein hand buch der organischen Chemie*, **14** (1931), 323.
- NARANG, K. K. & AGGARWAL, A., *Indian J. Chem.*, **13** (1975), 1972.
- NARANG, K. K. & AGGARWAL, A., *Inorg. chim. Acta*, **9** (1974), 137.
- SACCONI, L. & CIAMPOLINI, M., *J. chem. Soc.*, (1964), 276.
- BALLHAUSEN, C. J., *Introduction to ligand field theory* (McGraw-Hill, New York), 1962, 256.
- PAUL, R. C. & CHADHA, S. L., *J. inorg. nucl. Chem.*, **31** (1969), 2753.