

Fig. 1 — Determination of copolymer composition and  $r_1$  values [(1) = AM-AA; (2) = AM-MAA]

It is known<sup>5</sup> that the composition of the copolymer containing AM and AA can be controlled by varying pH. The  $r_1$  value increases from  $0.48 \pm 0.06$  to  $1.32 \pm 0.12$  when the pH is varied from 2.17 to 6.25. At low pH values AM is present in its protonated form which causes the reactivity to be low whereas at high pH values the reactivity of AA is decreased when it dissociates to form the acrylate anion. In these extreme cases the system is a binary copolymerization of AA and protonated AM or AM and acrylate anion respectively. In the present case, the pH of the medium is initially high (above 5.5 with the maximum acid concentration used) and as the system undergoes electrolysis, the pH value goes further to the alkaline side (above 7) within a very short period. The experimental  $r_1$  value (1.54) thus obtained is practically for alkaline conditions and is in tune with the earlier work<sup>5</sup>.

The value of  $r_1$  in AM-MA system is found to be lower than that in AM-AA system. Similar observation was made by Palit *et al.*<sup>6</sup>. It is known that the order of monomer reactivities corresponds to the order of increased resonance stabilization by the particular substituents of the radical formed from the monomer. Thus the methyl substituent in MAA would be expected to show a higher reactivity than AA in copolymerization reaction and correspondingly a lower value of  $r_1$  is expected in our present system.

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## Binuclear Cu(II) & Ni(II) Chelates of Tetradentate Schiff Bases Derived from 3-Formylsalicylic Acid & 1,2-Diaminopropane & 1,2-Diamino-2-Methylpropane

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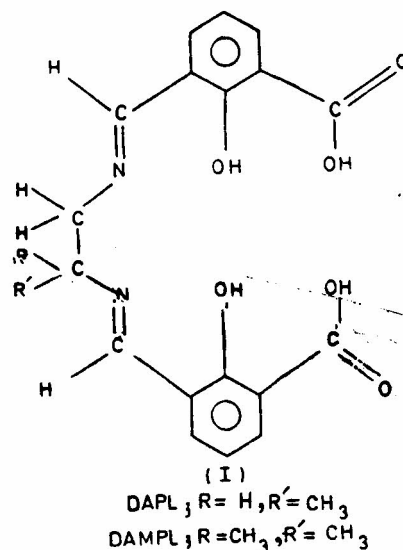
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Solid binuclear Cu(II) and Ni(II) chelates of tetradentate Schiff bases derived from 3-formylsalicylic acid (3FSA) and 1,2-diaminopropane (DAP) and 1,2-diamino-2-methylpropane (DAMP) have been prepared. These react further with alkali and alkaline earth metal ions to give the corresponding alkali or alkaline earth derivatives. Only the Li and Na complexes are ionic in nature. The binuclear Cu(II) or Ni(II) chelates of Mg(II) are soluble in methyl alcohol but the remaining binuclear chelates are insoluble in most of the common solvents. While the Ni(II) chelates are diamagnetic, Cu(II) chelates have magnetic moments around 2.0 BM.

COPPER (II), Ni(II) or Zn(II) complexes of tetradentate Schiff bases (TSB) derived from salicylaldehyde or *o*-hydroxyacetophenone readily react further<sup>1</sup> with metal halides,  $M'X$  [ $M' = \text{Cu(II)}$  or  $\text{Zn(II)}$ ] or metal perchlorates  $M'(\text{ClO}_4)_n$  [ $M' = \text{Cu(II)}$ ,  $\text{Ni(II)}$ ,  $\text{Co(II)}$ ,  $\text{Fe(II)}$ ,  $\text{Al(III)}$ ,  $\text{Mg(II)}$ ,  $\text{Ca(II)}$ ,  $\text{Sr(II)}$ ,  $\text{Na(I)}$ ,  $\text{Zn(II)}$  or  $\text{Ag(I)}$ ] to form the bi- or tri-nuclear complexes of the types  $[(\text{MTSB})M'X_2]$  or  $[M'(\text{MTSB})_2(\text{ClO}_4)_n]$ .

Some binuclear complexes of TSB derived from 3-formylsalicylic acid and some amines have been synthesized by Poddar<sup>2</sup>, and Phillips and Cunningham<sup>3</sup>.

A few mono- and binuclear complexes of Cu(II) and Ni(II) with the tetradentate Schiff bases (I) derived from 3-formylsalicylic acid (3-FSA) and 1,2-diaminopropane (DAP) and 1,2-diamino-2-methylpropane (DAMP) have now been prepared.



\*The work reported in this note was carried out at the School of Chemistry, University of New South Wales, Sydney, Australia.

Schiff bases were prepared following Poddar's method<sup>2</sup> for the preparation of ethylenediamine Schiff base. The complexes  $\text{Cu}(\text{Na}_2\text{DAPL})\cdot 4\text{H}_2\text{O}$ ,  $\text{Cu}(\text{Na}_2\text{DAMPL})\cdot 5\text{H}_2\text{O}$ ,  $\text{Ni}(\text{Na}_2\text{DAPL})\cdot 4\text{H}_2\text{O}$  and  $\text{Ni}(\text{Na}_2\text{DAMPL})\cdot 2\cdot 5\text{H}_2\text{O}$  are the basic compounds from which all other complexes of Cu(II) and Ni(II) have been prepared by the replacement of either one or two sodium atoms by cations of groups I A and II A. The complexes obtained (Tables 1 and 2) are quite stable in air and beautifully coloured. Only the complexes of Li and Na are ionic in nature. Attempts to prepare the potassium derivatives of Cu(II) and Ni(II) chelates failed.

The bisodium derivatives of the Cu(II) and Ni(II) complexes react with strong acids to give the corresponding parent complexes.

All the copper complexes have magnetic moments of about 2.0 BM. The Ni(II) complexes are diamagnetic. The diamagnetism of the Ni(II) complexes indicates a square-planar configuration. The molar conductivities of Na complexes were found to be about  $150\text{ ohm}^{-1}\text{ cm}^2\text{ mole}^{-1}$  and those of Li complexes about  $75\text{ ohm}^{-1}\text{ cm}^2\text{ mole}^{-1}$  in  $10^{-3}\text{ M}$ , aqueous solution at  $25^\circ$ . These results indicate that unlike the Na complexes the Li complexes behave as uni-univalent electrolytes in solution. The lithium and sodium complexes of both the transition metals are soluble in water. Mg(II) derivatives are soluble in methyl alcohol but the remaining binuclear complexes are insoluble in water, acetone, ethanol, chloroform, carbon tetrachloride, ether, benzene, pyridine and dimethyl sulphoxide.

The diffuse electronic (reflectance) spectra of the Cu(II) complexes show absorption in the range

18000-19000  $\text{cm}^{-1}$  and those of the Ni(II) complexes at 19000  $\text{cm}^{-1}$ .

Cu was determined gravimetrically as  $(\text{Cu en}_2)(\text{HgI}_4)$  after destroying the ligand by treatment with sulphuric acid and nitric acid. Ni(II) was determined gravimetrically as its dimethylglyoxime complex. Mg(II) was determined gravimetrically as magnesium ammonium phosphate in the solution after removal of copper and nickel as mentioned above. Ba(II) and Sr(II) were determined gravimetrically as their respective sulphates. Ca(II) Na and Li were determined using a flame photometer.

3-Formylsalicylic acid was prepared from salicylic acid and hexamine following the method of Duff and Bills<sup>4</sup>.

*Preparation of Cu (Na<sub>2</sub>DAPL) and Cu(Na<sub>2</sub>DAMPL) — Schiff base (2g) dissolved in aq. NaOH (0.6 g, dissolved in 75 ml H<sub>2</sub>O) was heated on a steam bath and Cu(OAc)<sub>2</sub> (0.5M in 100 ml absolute ethanol) added slowly with stirring. The solution turned dark violet (or dark red) which on cooling deposited the violet coloured silky needles of the sodium salt of the copper complex. The solution was filtered and the solid complex washed with ethanol and dried in vacuo over silica gel for 2-3 days.*

*Reaction of Cu(Na<sub>2</sub>DAPL) and Cu(Na<sub>2</sub>DAMPL) 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 (0.7 g, 0.08M), dil. HCl, or a solution (0.04M, 100 ml) of MgSO<sub>4</sub>, CaCl<sub>2</sub>, Sr(NO<sub>3</sub>)<sub>2</sub> or BaCl<sub>2</sub>. The mixture was further heated on a steam-bath for 30 min, cooled and filtered. With Ba(II) two types of complexes, viz. grey and*

TABLE 1 — COLOUR, MAGNETIC MOMENT AND ANALYTICAL DATA OF Cu(II) COMPLEXES

Compound	Colour	$\mu_{\text{eff.}}$ (BM)	N (%) Calc. (Found)	Cu (%) Calc. (Found)	M (%) Calc. (Found)
$\text{Cu}(\text{H}_2\text{DAPL})$	Purple	2.02	6.49 (6.73)	14.89 (14.49)	—
$\text{Cu}(\text{Li}_2\text{DAPL})\cdot 2\text{H}_2\text{O}$	Red	2.06	5.83 (6.36)	13.24 (12.84)	2.89 (2.93)
$\text{Cu}(\text{Na}_2\text{DAPL})\cdot 4\text{H}_2\text{O}$	Violet	1.91	5.11 (5.16)	11.59 (11.20)	8.39 (8.41)
$\text{Cu}(\text{MgDAPL})\cdot \text{H}_2\text{O}$	Pink	2.01	5.93 (6.08)	13.46 (13.30)	5.15 (4.84)
$\text{Cu}(\text{CaDAPL})\cdot 5\text{H}_2\text{O}$	Violet	1.82	5.00 (5.20)	11.35 (11.36)	7.16 (6.38)
$\text{Cu}(\text{SrDAPL})\cdot 3\text{H}_2\text{O}$	do	1.85	4.90 (5.20)	11.11 (10.75)	15.32 (15.22)
$\text{Cu}(\text{BaDAPL})\cdot 2\text{H}_2\text{O}$	Grey	1.83	4.64 (4.30)	10.54 (10.40)	22.78 (22.34)
$\text{Cu}(\text{H}_2\text{DAMPL})$	Blue	1.92	6.28 (6.64)	14.25 (14.26)	—
$\text{Cu}(\text{Li}_2\text{DAMPL})\cdot 1\cdot 5\text{H}_2\text{O}$	Red	1.81	5.77 (5.95)	13.10 (13.60)	2.86 (2.89)
$\text{Cu}(\text{Na}_2\text{DAMPL})\cdot 5\text{H}_2\text{O}$	Violet	1.78	4.83 (4.59)	10.96 (11.00)	7.93 (8.01)
$\text{Cu}(\text{LiNaDAMPL})\cdot 4\text{H}_2\text{O}$	Brick-red	1.80	4.81 (4.61)	10.92 (10.11)	Li Na 1.93 3.99 (2.00) (3.72)
$\text{Cu}(\text{MgDAMPL})\cdot 4\text{H}_2\text{O}$	Violet	1.78	5.19 (5.75)	11.77 (11.58)	4.50 (4.62)
$\text{Cu}(\text{CaDAMPL})\cdot 2\cdot 5\text{H}_2\text{O}$	do	1.78	5.29 (4.81)	12.01 (12.00)	7.58 (7.47)
$\text{Cu}(\text{SrDAMPL})\cdot 4\text{H}_2\text{O}$	do	1.78	4.64 (4.35)	10.53 (10.76)	14.52 (14.30)
$\text{Cu}(\text{BaDAMPL})\cdot 2\text{H}_2\text{O}$	do	1.78	4.54 (4.54)	10.30 (10.15)	22.26 (22.21)

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

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

violet, were obtained. The grey form was prepared by adding BaCl<sub>2</sub> (1 g) solution to an excess Cu(Na<sub>2</sub>DAPL).4H<sub>2</sub>O.

**Preparation of Ni(Na<sub>2</sub>DAPL) and Ni(Na<sub>2</sub>DAMPL)** — Schiff base (2 g) dissolved in aqueous NaOH 0.6 g dissolved in 75 ml H<sub>2</sub>O was heated on a steam-bath and to this Ni(OAc)<sub>2</sub> (~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(Na<sub>2</sub>DAPL) and Ni(Na<sub>2</sub>DAMPL) 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 MgSO<sub>4</sub>, CaCl<sub>2</sub>, Sr(NO<sub>3</sub>)<sub>2</sub>, or BaCl<sub>2</sub>. 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.

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

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Zn(II), Cu(II), Ni(II) and Co(II) complexes of N-(salicylidene)-N'-[(2-salicylaldimine)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<sup>1,2</sup> has been suggested to take place via metal-acylhydrazine Schiff base complex<sup>3</sup>. 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-aminobenzoylhydrazine<sup>4</sup> 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 H<sub>2</sub>SO<sub>4</sub> with standard KMnO<sub>4</sub> using a calibration curve. The complexes were

