Salicylaldehyde-2-furoic Acid Hydrazide as a Chelating Ligand: Complexes with Nickel(II), Cobalt(II), Copper(II), Zinc(II), Zirconium(IV), Oxomolybdenum(V) & Dioxouranium(VI)†

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A series of new coordination complexes of Ni(II), Co(II), Zn(II), Zr(IV), oxomolybdenum(V) and dioxouranium(VI) with the Schiff base derived from salicylaldehyde and 2-furoic acid hydrazide has been synthesized and characterized by elemental analyses, molecular weight, electrical conductance, oxidimetric titration, electronic and IR spectra and magnetic susceptibility measurements. The Schiff base behaves as a dibasic, tridentate ONO donor ligand and forms the complexes of the types NiL.2H₂O, CoL.2H₂O, CuL, ZnL₂.2H₂O, Zt(OH)₂L.2CH₃OH, Zt(OH)₃L(LH)₂, MoOClL and UO₂L.CH₃OH (where H₂L = Schiff base). The complexes of Ni(II) and Co(II) have normal magnetic moments at room temperature while the Cu(II) and oxomolybdenum(V) complexes exhibit subnormal magnetic moments with antiferromagnetic interaction. The IR spectra of the complexes reveal non-participation of the furan oxygen in coordination. The shifts of the \( \nu(C=O) \) and \( \nu(C-O) \) (phenolic) modes have been followed to find out the coordination sites of the ligand.

The coordination complexes of the Schiff bases have been widely investigated due to their manifestation of novel structural features, unusual magnetic properties and relevance to biological processes. The coordination compounds of arylhydrazones have been reported to act as inhibitors for enzymes. A survey of literature reveals that no work has been carried out on the synthesis of Schiff base (I) and metal complexes of (I) which undergoes keto-enol tautomerism. The Schiff base (I) has five potential donor sites (N₂O₃) with different coordinating abilities which may lead to varied bonding and stereochemical behaviour in complexes with different metal ions. In the present paper we describe the syntheses and characterization of Schiff base (I) and its metal complexes with nickel(II), cobalt(II), copper(II), zinc(II), zirconium(IV), oxomolybdenum(V) and dioxouranium(VI).

Materials and Methods
Nickel(II) acetate tetrahydrate, cobalt(II) acetate tetrahydrate, copper(II) acetate monohydrate, zinc(II) acetate dihydrate and salicylaldehyde were the products of Sarabhai M. Chemical Co. Oxozirconium(IV) dichloride octahydrate was purchased from M/s. Sendez Swijur Chemische Fabrik. Dioxouranium(VI) acetate dihydrate was obtained from BDH (England). 2-Furoic acid hydrazide was obtained from Aldrich Chemical Co. (U.S.A.). Pyridinium oxopentachloromolybdate(V) was prepared according to the published procedure.

Synthesis of the Schiff base
An ethanolic solution of salicylaldehyde (0.61 g, 0.005 mol in 10 cm³) was added to an ethanolic solution of 2-furoic acid hydrazide (0.63 g, 0.005 mol in 10 cm³) and the mixture was refluxed on a water-bath for 0.5 hr. The excess of solvent was partially evaporated under a current of air and the separated white precipitate was filtered under reduced pressure, washed with EtOH and crystallized from EtOH. The compound was dried in vacuo at room temperature over silica gel; yield, 80%. m.p. 171°C [Found: N, 12.21%. Calc. for C₁₂H₁₀N₂O₅: N, 12.17%].

General method of the synthesis of the complexes NiL.3H₂O, CoL.2H₂O, CuL, ZnL₂.2H₂O, Zr(OH)₂L.2CH₃OH, Zr(OH)₃L(H)₂, MoOClL and UO₂L.CH₃OH
Salicylaldehyde (0.49 g, 0.004 mol) and 2-furoic acid hydrazide (0.50 g, 0.004 mol) were dissolved in 20 cm³ MeOH and the mixture was refluxed on a water-bath for 0.5 hr. The clear solution thus obtained was added to a methanolic solution of the appropriate metal salt.

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(0.004 mol in 25 cm$^3$) with stirring. The mixture was heated under reflux on a water-bath for 1 hr. The separated precipitates were filtered by suction, washed with MeOH and dried in vacuo over silica gel at room temperature; yields: NiL.3H$_2$O, 60%; CoL.2H$_2$O, 60%; CuL, 80%; ZnL.H$_2$O, 55%; UO$_2$L.CH$_3$OH, 60%.

**Synthesis of Zr(OH)$_3$(LH)$_2$**

Oxozirconium(IV) dichloride octahydrate (0.64 g, 0.002 mol) was dissolved in 15 cm$^3$ MeOH and to this a methanolic solution of anhydrous sodium acetate (0.32 g, 0.004 mol in 10 cm$^3$) was added and stirred for 5 min. The separated sodium chloride was filtered off. Salicylaldehyde (0.49 g, 0.004 mol) and 2-furoic acid hydrazide (0.5 g, 0.004 mol) were mixed with 20 cm$^3$ MeOH and the mixture was refluxed on a water-bath for 0.5 hr. To this solution, the solution containing oxozirconium(IV) diacetate was added and the mixture was refluxed on a water-bath for 2 hr. The partial evaporation of the solvent under a current of air produced an yellow precipitate which was filtered under reduced pressure, washed with MeOH, recrystallized from MeOH and dried in vacuo at room temperature; yield, 50%.

**Synthesis of Zr(OH)$_3$.2CH$_3$OH**

A methanolic solution of the Schiff base (0.004 mol) as prepared above was added to the freshly prepared solution of oxozirconium(IV) diacetate (0.004 mol in 35 cm$^3$) and the mixture was refluxed on a water-bath for 0.5 hr. A methanolic solution of sodium methoxide (0.44 g, 0.008 mol in 20 cm$^3$) was added to the above solution and the mixture was refluxed for further 2 hr. The yellow precipitate formed was filtered, washed with MeOH followed by ether and dried in vacuo at room temperature; yield, 60%.

**Synthesis of MeOCIL**

The Schiff base (0.004 mol, 0.92 g) was dissolved in 20 cm$^3$ of absolute EtOH. To this, solid pyridinium oxopentachloromolybdate(V) (1.8 g, 0.004 mol) was added in one portion with vigorous shaking. The mixture was heated under reflux for 1 hr and the separated brown solid mass was filtered, washed with absolute EtOH and dried in vacuo at room temperature; yield, 50%.

Nickel was estimated gravimetrically as bis(dimethylglyoximato)nickel(II). Copper was determined iodometrically by titration with a solution of Na$_2$S$_2$O$_3$. and cobalt and zinc were determined by complexometric titrations with EDTA after igniting the complexes to their respective metal oxides and dissolving in 6N HCl. Uranium and zirconium contents were determined gravimetrically as U$_3$O$_8$ and ZrO$_2$ respectively after decomposing the complexes with conc. nitric acid and igniting the residue. Molybdenum was determined gravimetrically as bis(8-hydroxyquinolinato)dioxomolybdenum(VI). Nitrogen analyses were done microanalytically. The electrical conductance measurements were carried out in 0.001 M solutions of DMF and DMSO with the help of a Toshiba conductivity bridge (Type CI01-02A) and a dip-type cell calibrated with potassium chloride solutions. IR spectra were recorded in the range 600-4000 cm$^{-1}$ in KBr on a Beckman IR-20 spectrophotometer calibrated with polystyrene. Fourier transform far IR spectra were recorded in the range 100-600 cm$^{-1}$ using a Polytech FIR Fourier far infrared spectrophotometer. Electronic spectra were recorded on a Beckman DU spectrophotometer attached with a reflectance arrangement. Molecular weight measurements were done by the Rast method using biphenyl as the solvent. The magnetic susceptibility measurements were carried out at room temperature by the Gouy method using Hg[Co(NCS)$_4$] as the calibrant. The diamagnetic corrections were taken from a standard source. The susceptibilities were corrected for TIP using a value of 200 x $10^{-6}$ cgs unit for nickel and cobalt, 60 x $10^{-6}$ cgs unit for copper and 55 x $10^{-6}$ cgs unit for molybdenum.

The oxidation state of the molybdenum in the complex was determined as follows:

MoOCl$_2$(sal-fahz) (0.1 g) was dissolved in 25 ml of 2 N H$_2$SO$_4$ and 75 ml of 0.1 N ferric alum solution by stirring in a stoppered iodine flask. The solution was cooled in ice and 5 ml of syrupy phosphoric acid was added to the solution. The solution was then titrated immediately with standard KMnO$_4$ solution. The oxidation state of Mo was found to be +5 (found 4.95).

**Results and Discussion**

The analytical data (Table 1) indicate that the metal:ligand stoichiometry is 1:1 in all the complexes. In the case of Zr(IV), a 1:2 complex, Zr(OH)$_2$(LH)$_2$ (where LH$_2$ = Schiff base, I.) has also been synthesized. The oxomolybdenum(V), dioxouranium(VI) and Zr(IV) (1:2) complexes are soluble in methanol, ethanol, dimethylformamide and dimethyl sulphoxide. All other complexes are insoluble in water and common non-coordinating solvents but are soluble in coordinating solvents like DMF and DMSO. All the complexes show very low $\Lambda_M$ values (-1.0-16.0 ohm$^{-1}$cm$^2$mol$^{-1}$) in DMF/DMSO indicating their non-electrolytic nature.

The magnetic moment values of the Ni(II) and Co(II) complexes are 3.09 and 4.83 B.M. respectively at room temperature and show that the complexes are of high-spin type with pseudo-octahedral environment.
around the metal ion. The absorption spectrum of the Ni(II) complex shows bands at 10800, 17200 and 26300 cm<sup>-1</sup> due to the transitions respectively in an octahedral field. The ν<sub>2</sub> : ν<sub>1</sub> ratio is 1.6 which occurs in the usual range (1.6-1.82) expected for octahedral Ni(II) complexes. The spectral parameters of the Ni(II) complexes as calculated according to the method of Lever are as follows: D<sub>q</sub> = 1080 cm<sup>-1</sup>, B′ = 707 cm<sup>-1</sup>, α = -189 cm<sup>-1</sup>. The reduction of the Racah parameter from the free ion value of 1056 cm<sup>-1</sup> and the (β value of 32.96%) testify to the presence of strong M-L covalent bonding in the complexes. We were interested to prepare complexes of the type NiL and CoL which might show the presence of magnetic exchange similar to that in CuL. Although in the synthesis of the complexes a 1:1 metal-ligand ratio was maintained, the complexes of the type [Ni(H<sub>2</sub>O)<sub>3</sub>]L and [Co(H<sub>2</sub>O)<sub>3</sub>]L were obtained in contrast to the expected ML type complexes. The magnetic moments of [Ni(H<sub>2</sub>O)<sub>3</sub>]L and [Co(H<sub>2</sub>O)<sub>3</sub>]L are within the range observed for magnetically dilute octahedral complexes indicating the absence of magnetic exchange at room temperature. Such behaviour has been previously noticed in the cases of the Ni(II) and Co(II) complexes of similar Schiff bases. The Co(II) complex, CoL<sub>2</sub>H<sub>2</sub>O, is apparently five-coordinated but the magnetic and electronic spectral data of the complex indicate an octahedral structure. Thus, we suggest a μ-bis(schiff base) (tetra-aquo)cobalt(II), [Co(OH)<sub>2</sub>(schiff base)]<sub>2</sub> structure with two aquo molecules in the trans positions of the two Co(I) atoms in O<sub>h</sub> symmetry. Such structures have been suggested for Co(II) complexes of other Schiff bases. The bridge in the above complex may arise from the involvement of either the enolic oxygen atom or the phenolic oxygen atom of the ligand. The shift of the ν(C=O) (phenolic) to higher energy by ~10 cm<sup>-1</sup> is usually taken as an evidence of the formation of a phenolic oxygen bridge. As the present Co(II) complex shows a shift of 5 cm<sup>-1</sup> in the ν(C=O) (phenolic) mode it seems plausible to rule out the involvement of the phenolic oxygen atom in the bridge formation and to suggest the other alternative, i.e., the bridge formation by the enolic oxygen atom. The Cu(II) and oxomolybdenum(V) complexes are of the types CuL and MoOCIL and exhibit magnetic moments of 1.32 and 1.00 B.M. respectively at room
temperature. The magnetic moment values are significantly less than the expected values [1.8-2.2 B.M. for magnetically dilute Cu(II) complexes, 1.68-1.78 B.M. for magnetically dilute oxomolybdenum(V) complexes]. This is indicative of the presence of an antiferromagnetic exchange interaction with S=0 ground state. The values of exchange integral, J, of the complexes calculated from the Bleaney Bowers equation\(^\text{13}\) are negative and are in the range 314-474 cm\(^{-1}\). The Cu(II) complex exhibits an asymmetric electronic spectral band at 15400 cm\(^{-1}\) characteristic of the CuNO\(_3\) coordination sphere\(^\text{14}\). The Mo(V) complex shows bands at 11760, 16660 and 23250 cm\(^{-1}\) due to the \(^2B_2\rightarrow^2E\), \(^2B_2\rightarrow^2B_1\) and \(^2B_2\rightarrow^1A_1\) transitions respectively\(^\text{15}\).

It is interesting to note that some authors have assigned a band at \(\sim 19000\) cm\(^{-1}\) to the Mo–O–Mo or Mo–O–Mo bridges\(^\text{16}\). But the appearance of this band in many non-metallic complexes\(^\text{15}\) such as MoOCl\(_2\)(CH\(_3\))\(_2\), MoOCl\(_2\) (tetrahydrofuran), etc., casts doubt on these assignments. It is worthwhile to mention that no band characteristic of M–N bond\(^\text{21}\) for the majority of Mo(V) complexes does not contain the Zr=O bond in the present Zr(IV) complexes. The \(\nu(C-O)\) (phenolic) shifts to higher energy by 5 cm\(^{-1}\) indicating the absence of phenolic oxygen bridges in these complexes\(^\text{12}\). Hence the other alternative, i.e., the enolic oxygen bridge is present in Cu(II) and Mo(V) complexes. The \(\nu(Mo=O)\) in the oxomolybdenum(V) complex appears at 960 cm\(^{-1}\) and this occurs in the usual range (900-1007 cm\(^{-1}\)) observed for the majority of Mo(V) complexes\(^\text{19}\). The observation of the \(\nu(M=O)\) in the above range precludes the presence of a...Mo=O...Mo=O... chain structure which would lead to the lowering of \(\nu(Mo=O)\) to < 850 cm\(^{-1}\). We recorded the far IR spectra of the ligand and the Mo(V) complex in order to find out the nature of the chlorine atoms which may be acting as either terminal or bridging atoms in the complex. In Mo(V) complexes the terminal Mo–Cl stretching frequency \(\nu_M(Mo-Cl)\) usually occurs\(^\text{20-21}\) at higher energy in the region \(\sim 310-345\) cm\(^{-1}\) than the bridging metal-chlorine stretching frequency \(\nu_M(Mo-Cl)\) which occurs in the region \(\sim 190-295\) cm\(^{-1}\) due to the delocalisation of electrons in the chelate ring in the latter case. The ratio \(\nu_M(M-Cl)/\nu_M(M-CI)\) is about 0.60-0.85. In the present Mo(V) complex, the presence of a non-ligand band at 345 cm\(^{-1}\) and the absence of a new band in the region 190-295 cm\(^{-1}\) identifies the Mo–Cl stretch as \(\nu_M(Mo-Cl)\). Non-ligand bands occurring at 585 (broad) and 450 (sharp) cm\(^{-1}\) have been assigned to \(\nu(Mo-O)\) and \(\nu(Mo-N)\)\(^\text{22-23}\) respectively since \(\nu(M-O)\) usually occurs\(^\text{20}\) at higher energy than \(\nu(M-N)\). Further, \(\nu(M-O)\) band is usually broad and strong while the \(\nu(M-N)\) is usually sharp and strong as a larger dipole moment change is involved in the vibration of M–O bond in comparison with that in the M–N bond\(^\text{21}\).

The freshly prepared methanolic solution of Zr(IV) acetate reacts with (I) in 1:2 ratio and gives the bis complex, Zr(OH)\(_2\)(LH)\(_2\). On the other hand, the freshly prepared Zr(IV) acetate reacts with (I) in 1:1 molar ratio in presence of NaOCH\(_3\) in methanol and gives the mono complex Zr(OH)L\(_2\)CH\(_3\)OH. The mono complex does not lose methanol on heating at 110°C and this indicates the presence of coordinated methanol. The \(\nu(C-O)\) (alcoholic)\(^\text{24}\) band which occurs in methanol at 1034 cm\(^{-1}\), is observed at 1020 cm\(^{-1}\) in the complex indicating the oxygen coordination of methanol. Zr(OH)L\(_2\)(LH)\(_2\) also does not show any mass loss on heating at 110°C for one hr. The molecular weight data of Zr(OH)L\(_2\)(LH)\(_2\) [Found: 595, calc. 583] indicate monomeric nature of the structure and rule out a bridged Zr–O–Zr type structure. Zr(OH)L\(_2\)CH\(_3\)OH is not soluble in a suitable solvent for molecular weight measurements. The absence of a new band in the region 850-950 cm\(^{-1}\) due to the \(\nu(Zr=O)\) and the presence of a new band at 1145 cm\(^{-1}\) due to the \(\delta(Zr-OH)\) favour\(^\text{25}\) the formulation of Zr(IV) complexes as Zr(OH)L\(_2\)CH\(_3\)OH and not as ZrO(LH)LH\(_2\)H\(_2\)O/ZrOL(H\(_2\)O)\(_2\)CH\(_3\)OH. We wish to mention that zirconyl chloride octahydrate which is commonly used as the starting material for the preparation of Zr(IV) complexes does not have Zr=O bond and has the structure [Zr\(_4\)(OH)\(_6\)(H\(_2\)O)\(_6\)\(_2\)Cl\(_8\)] as indicated by single crystal X-ray work\(^\text{26}\). Since the starting material for the synthesis of the present Zr(IV) complexes does not contain the Zr=O bond, the presence of Zr=O bond in the complexes is precluded.

Oxo-zirconium(IV) complexes are known to react with 3M HCl to protonate the oxo group. We have done non-aqueous titration of the Zr(IV) complexes in order to prove the absence of Zr=O bond. The Zr(IV) complexes were dissolved in excess of 3M HCl in methanol (0.1 g in 50 cm\(^3\)) and the titration of the mixture with standard NaOH solution in methanol indicated that there was no reaction of the complexes with 3M HCl. This conclusively proves the absence of Zr=O bond in the present Zr(IV) complexes. The dioxo uranium(VI) complex is of the type UO\(_2\)L\(_2\)CH\(_3\)OH. The presence of coordinated methanol is indicated by the lowering of the \(\nu(C-O)\)
The Schiff base (I) exhibits three electronic spectral bands in DMF at $v_{max}$: 3000(17800), 31300(18600) and 34250(16800) cm$^{-1}$ due to the $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, and hydrogen bonding and association respectively. In the dioxouranium(VI) complex, the $n \rightarrow \pi^*$ transition shifts to lower energy at 28170 ($\epsilon = 14470$) cm$^{-1}$, and the band due to the hydrogen bonding and association is absent as expected. The band due to $\pi \rightarrow \pi^*$ transition moves to lower energy at 31250 cm$^{-1}$ ($\epsilon = 3250$). These shifts or disappearance of the bands are indicative of coordination of the Schiff base to UO$_2^{2+}$.

The dioxouranium(VI) complexes exhibits a new band at 23800 cm$^{-1}$ ($\epsilon = 5400$) which is assigned to the $\Sigma_g^+ \rightarrow \pi_u$ transition typical of OOU symmetric stretching frequency for the first excited state. The $v_{as}(OUO)$ and $v_v(OUO)$ modes of the complex occur at 885 and 790 cm$^{-1}$ respectively and these are in the usual range ($v_{as} = 870-950; v_v = 780-885$ cm$^{-1}$) as reported for the majority of dioxouranium(VI) complexes. The frequency for the first excited state ($\epsilon = 14470$) cm$^{-1}$, and $v_{as}(OUO)$ and $v_v(OUO)$ modes of the complex occur at 885 and 790 cm$^{-1}$ respectively and these are in the usual range ($v_{as} = 870-950; v_v = 780-885$ cm$^{-1}$) as reported for the majority of dioxouranium(VI) complexes.

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References

18. Ref. 6, p. 158.