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Salicylaldehyde Salicylhydrazone Complexes of Some Transition Metal Ions

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Salicylaldehyde Salicylhydrazone (SSH) complexes M(SSH–H)$_2$, M = Cu(II), Co(II), Mn(II), VO(IV), TiO(IV); M'(SSH–2H), M' = Cu(II), Ni(II), Co(II), and Cu^{I}(SSH–H) have been synthesised and characterised by analysis, infrared and electronic spectra and magnetic measurements. They are insoluble in common solvents and decompose above 250° C without melting. Subnormal magnetic moments have been observed in some of them. Comparison of electronic absorption bands of SSH and metal complexes show the presence of ligand–metal charge transfer bands. Cu(II) complexes are square planar while Ni(II) and Co(II) complexes have octahedral stereochemistry. In M' (SSH–2H) complexes, infrared spectra indicate the involvement of –OH, >CO and >C=N groups. In others, only –OH and >C=N appear bonded. Metal–metal interactions via oxo-bridge structures have been discussed in the light of magnetic, electronic and infrared data.

Introduction

Mono acyl hydrazines have been reported to coordinate through >CO and NH$_2$ groups.[1–5] When the terminal NH$_2$ group is condensed with aldehydes and ketones, the proton of –NH– group becomes more labile and the acyl hydrazones react with metal ions in enol form.[6] Although phenolic –OH group is reactive in bases obtained from salicylaldehyde,[7–10] but in salicyl hydrazine and isopropylidene salicyl hydrazone, the –OH group has not been shown to take part in bonding with metal ions.[11] Since the reactions of salicylhydrazones as ligands are still open to investigation, salicylaldehyde salicylhydrazone HOC$_6$H$_4$CONHN: CHC$_6$H$_4$OH (SSH) has been taken up for the present study. SSH is an interesting ligand having two phenolic –OH groups in addition to >C=O and N–N groups. The presence of several bonding sites is likely to give stability to complexes and SSH may prove to be a versatile chelating ligand. The complexes of SSH with some bivalent transition metal ions including some oxo cations of first short series have been prepared and their probable structures discussed in the present communication.

Experimental

Metal salts of BDH LR grade were used. SSH was prepared by condensing salicylaldehyde with salicylhydrazine, HOC$_6$H$_4$CONHNH$_2$, as described by Curtius[12] and recrystallised from hot ethanol. M.p. 275° C (Lit. 277° C). Found: C = 65.62, H = 4.65, N = 11.02. Calculated for SSH: C = 65.72,H = 4.63, N = 11.49%.

Metal complexes of SSH were prepared by mixing aqueous solutions of metal salts (metal excess) and alkaline solution of SSH, made neutral by acetic acid. The resulting products were filtered, washed successively with dilute acetic acid, water and finally with hot ethanol to remove the unreacted ligand. Copper(II), Nickel(II) and Cobalt(II) complexes were also prepared by refluxing ethanolic solution of SSH and excess metal chloride for 5–6 hr. The complexes were filtered, washed with ethanol and dried at ~110° C. Metals were analysed by following standard literature procedures,[13] after destroying the organic moiety by HCl/HNO$_3$ mixture, followed by evaporation of HNO$_3$ with concentrated H$_2$SO$_4$. Nitrogen was analysed by microanalysis.

Infrared and electronic spectra were recorded on Perkin Elmer model 621 and Cary model 14 in nujol phase. In some cases, visible spectra in nujol were not properly resolved, so reflectance spectra were obtained on Hilger and Watts model No. H 700.308/61637 and ultra violet spectra in ethanol solutions. The magnetic measurements were made on Faraday balance using Hg[Co(NCS)$_4$] as calibrant.

The analytical data and some general characteristics of the complexes have been summarized in Table I.

Results and Discussion

The composition of complexes varies with the mode of preparation and the metal ion. In ethanolic medium Copper(II) and Cobalt(II) form 1:2 metal:SSH complexes but Nickel(II) forms 1:1 complex. In alkaline medium, however, 1:1 metal:SSH composition is obtained in case of Copper(II) and Nickel(II) but 1:2 metal: SSH with other metal ions. The absence of

TABLE I. Analytical, Electronic and Magnetic Data of Transition Metal–SSH Complexes.[a]

Complex	Colour	% of Metal	% of Nitrogen	Electronic spectra λ_{max}, mμ	Magnetic moment μ_{eff}, BM
Cu(SSH–H)	Green	19.6 (19.9)	8.82 (8.79)	227 258 315 330 390	Diamagnetic
Cu(SSH–2H)	Dirty Green	19.8 (20.0)	9.02 (8.81)	240 285 330 410 670	1.6
Ni(SSH–2H)·H_2O	Green	17.5 (17.8)	8.40 (8.46)	300 395 430 600 940	2.3
Ni(SSH–2H)·$2H_2O$	Greenish–yellow	16.7 (16.9)	8.21 (8.02)	237 285 330 390 590 950	1.4
Co(SSH–2H)·$2H_2O$	Orange	16.6 (16.9)	8.62 (8.02)	208 290 300 327 410 540 620	4.7
Cu$(SSH–H)_2$	Green	10.8 (11.1)	10.01 (9.78)	237 275 325 375 687	1.5
Co$(SSH–H)_2$	Yellowish–brown	10.0 (10.3)	9.89 (9.84)	237 265 325 420	4.1
Mn$(SSH–H)_2$	Yellow	10.1 (9.7)	9.80 (9.91)	240 310 390 413	7.7
Fe$(SSH–H)_2$	Brown	10.1 (9.9)	10.09 (9.89)	287 300 330 390 460 585	5.8
VO$(SSH–H)_2$	Green	8.6 (8.8)	9.90 (9.70)	265 330 400 420 600 660	1.6
TiO$(SSH–H)_2$	Orange	8.6 (8.3)	9.70 (9.73)	238 285 330	Diamagnetic

[a] Figures in parentheses are calculated values.

TABLE II. *Some Important Infrared Bands of SSH and its Metal Complexes (Frequencies in cm^{-1}).*

Complex	νC=O νC=N	Amide II νC–O (Φ)	Amide III	νC–O	νN–N	νM–O (phenyl)	νM–O (C=O)	νM–N
SSH	1645 1610	1550	1370	1225	1015	–	–	–
Cu^{I}(SSH–H)	1625 1595	1548	1380	1250	1045	585	485	–
Cu(SSH–2H)	1620 1600	1565	1370 1390	1250	1040	570	470	345
Ni(SSH–2H)·H_2O	1600 broad	1560	1370	–	–	598	–	330
Ni(SSH–2H)·$2H_2O$	1630 1600	1560	1380	1240	1035	–	480	–
Co(SSH–2H)·$2H_2O$	1600	1545	1380	1240	1040	590	500	325
Cu$(SSH–H)_2$	1620 1600	1570	1372	1240	1035	–	495	330
Co$(SSH–H)_2$	1595	1560	1375	1260	1035	580	495	–
Mn$(SSH–H)_2$	1610 1590	1545	1375	1250	1030	590	510	–
Fe$(SSH–H)_2$	1610	1540	1380	1250	–	–	–	320
VO$(SSH–H)_2$	1610 1600	1565	1375	1240	1030	–	510	–
TiO$(SSH–H)_2$	1600	1548	1375	1250	–	575	–	–

anion of original metal salt in the resulting complexes indicates liberation of protons of –OH group and /or ≡C–OH group formed from enolization of >C=O group at high pH. The 1:1 Nickel(II) complex prepared from alkaline medium carries two water molecules, which are not removed by drying the complex at ~110° C. The water molecules may be coordinated to metal ion.

All the complexes decompose above 250° C without melting. They are insoluble in water and non polar organic solvents but are very slightly soluble in polar organic solvents like ethanol, nitrobenzene, tetrahydrofuran and dimethyl sulfoxide. The solutions in these solvents show very small conductance indicating that the complexes are not dissociated in the above solvents. The solubility and high decomposition temperature indicate the ionic or polymeric nature of complexes in solid state.

Electronic Spectra

The ultraviolet spectra of SSH show bands at 288, 298 and 330 mμ. Since SSH has >C=O and >C=N chromophores substituted in two benzene rings besides the –OH groups, it appears that the primary and secondary bands of benzene at 204 and 256 mμ are considerably red shifted as in salicylaldehyde[14] and salicylic acid.[15] The 330 mμ band is characteristic of free salicylaldehyde.[14] In metal complexes the more common bands appear around 240, 285, 330 and 380–410 mμ. The chelation may cause splitting of the submerged bands and also the appearance of newer bands. The bands around 240 and 380 mμ are analogous to those observed for phenolate ion[16] and salicylaldehydato ion[14], respectively.

Visible spectra of Copper(I) complex consists of ligand bands together with a new band around 390 mμ. Since Copper(I) has d^{10} electrons, no d–d transition band is expected. The band around 390 mμ may either be due to ligand–metal charge transfer transition or it may arise from salicylaldehydato ion. The 1:1 Copper(II) complex, in addition to a band around 410 mμ, shows a band at 670 mμ. The band around 800 mμ, due to $^2T_{2g} \leftarrow {}^2E_g$ transition, is observed in octahedral Copper(II) complexes[17] but Jahn–Teller distortions lead, in extreme case, to square planar structures. The broad band is considerably blue shifted as has been reported in some olive green square planar Copper(II) chelates[18] with which Cu(II)–SSH complexes bear colour similarity as well. The appearance of a high energy band around 400 mμ, in some Copper(II) complexes, has been a subject matter of considerable discussion and it has been related to the presence of binuclear structures of Copper(II) complexes.[19,20] Keeping the above facts and observed low magnetic moments in view, it is plausible to assign oxo-bridge structures for the Copper(II)–SSH complex. It is quite likely that ligand–metal charge transfer band and the high energy band reported to arise from binuclear structures may have overlapped in the blue region. In 1:2 Copper(II) complex, prepared in ethanol, the band appearing around 680 mμ shows distorted square planar stereochemistry around the metal atom.

In Nickel(II)–SSH complexes, three absorption bands around 940, 600 and 400 mμ corresponding to the transitions $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ have been observed. Even if absorption due to the $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transition is neglected for it, probably, being mixed with charge transfer transition or a band arising out of salicylaldehydato ion, the other two bands are characteristic of octahedral Nickel(II) complexes.[17] The visible spectral bands of Cobalt(II)–SSH complexes can also be related to those observed for octahedral Cobalt(II) complexes but those of Manganese(II), Iron(II) and oxo Vanadium(IV) complexes cannot be unambiguously related to octahedral or tetrahedral stereochemistry. As expected for d^0 system the oxo Titanium(IV) complex shows no absorption band in visible region.

Magnetic Measurements

Subnormal magnetic moments have been observed in SSH complexes of Copper(II), Nickel (II) and Cobalt(II). Copper(II) usually shows magnetic moment values corresponding to one electron but several workers have observed abnormal magnetic behaviour of Copper(II) carboxylato complexes.[19,21–24] It is believed that antiferromagnetic coupling phenomenon occurs in polymetallic Copper(II) systems by virtue of a super exchange mechanism, as there is little opportunity for a direct interaction to take place.[25,26] The low magnetic moment of Copper(II)–SSH complexes may also be explained on the above basis.

Nickel(II) shows magnetic moment values of two unpaired electrons in octahedral and tetrahedral complexes while its square planar complexes are diamagnetic.[27] The magnetic moment values observed in the present study are much less than the expected values for spin free octahedral or tetrahedral complexes. Although mixed stereochemistries in solid state due to molecular association have been reported and the reduction in magnetic moment has been explained on the basis of absorption spectra[28–30] but the absorption bands of Nickel(II)–SSH complexes correspond to those observed for octahedral Nickel(II) complexes. Further, Aggarwal and Narang have observed in transition metal complexes of diacetylhydrazine[31] and acetyl benzoyl hydrazine[32] that hydrazine bridges do not cause lowering of magnetic moments. It is, therefore, reasonable to believe that the lowering of magnetic moments is due to the presence of oxo-bridges. In view of various interpretations given for subnormal magnetic moments,[33] bimetallic structures similar to those discussed by Sinn and Harris[10] and others[34,35] for Schiff base complexes seem appropriate for metal–SSH complexes. However, polymetallic structures cannot be ruled out. The anomalously high magnetic moment of Manganese(II)–SSH complex may be due to the presence of ferromagnetic impurities as has been reported by Robinson *et al.*[36] for dimeric Copper(II) complexes.

Infrared Spectra

Infrared spectra of SSH shows a broad weak band in the region 3500–3300 cm^{-1} similar to that observed in salicylaldehyde and O-hydroxyacetophenone[37] indicating the presence of strong intramolecular hydrogen bonding between phenolic hydrogen atoms and the >C=O and >C=N groups. The 1640, 1625 and 1610 cm^{-1} bands in SSH, due to H-bonded >C=O and >C=N similar to those observed for aromatic Schiff bases,[38,39] appear around 1620 and 1600 cm^{-1} in metal–SSH complexes. The negative shifts of bands may be attributed to the coordination of oxygen of >C=O and /or nitrogen of >C=N groups.

Amide II band in isopropylidene salicylhydrazone appears around 1550 cm^{-1}. It seems, a band observed at 1550 cm^{-1} in SSH splits up and shows positive as well as negative shift in metal complexes. The decrease in frequency of Amide II band may be related to coordination of >C=O groups as in metal complexes of amides[40,41] and acid hydrazides.[2–4] The band appearing around 1560 cm^{-1} may indicate the presence of bridging C–O (phenolic) group.[10,42] Amide III band at 1370 cm^{-1} in SSH shifts to higher frequencies by 5–10 cm^{-1}. Of some significant interest are the marked changes in νC–O which occur between 1300–1100 cm^{-1} [43] and depend on the electron affinity of metal ions.[44] A band appearing at 1225 cm^{-1} in SSH may be due to νC–O. This band shifts to higher frequencies in metal complexes, the maximum shift being in Copper(II) complexes.

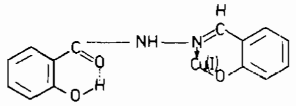
N–N stretching frequency increases from 885 cm^{-1} in N_2H_4[45] to 973 in $N_2H_5^+$[46] or to 980 in $N_2H_5[ThF_5]$ and $ThF_4N_2H_4$[47] and to 1024 in $N_2H_6^{2+}$.[48] Further it appears between 986–1014 cm^{-1} in metal complexes of monosubstituted hydrazines of the type $NH_2NH–Y$.[49] But in metal complexes of NN′-diacyl hydrazines[32,50] νN–N has been observed between 970–1040 cm^{-1}. By carefully examining the spectra of SSH and its complexes, a band at 1015 cm^{-1} in SSH may be assigned to νN–N, shifts to higher frequencies by 10–20 cm^{-1} in metal complexes.

The νM–O and νM–N bands are expected below 600 cm^{-1} because of the relatively heavy mass of metal and low bond order.[51] Due to the presence of aromatic rings and other chromophores in SSH, the region below 600 cm^{-1} contains several bands. From the infrared spectra discussed above, it is evident that SSH bonds to metals through phenolic oxygen, carbonyl oxygen and hydrazidic nitrogen. The νM–O (phenolic) may be expected at higher frequencies than νM–O (carbonyl) for difference in bond order. The νM–N may appear near the latter νM–O. On examining the spectra of SSH and its complexes below 600 cm^{-1}, the new bands appearing in the ranges 590–580, 500–490 and 330–310 cm^{-1} are tentatively assigned to νM–O (phenolic), νM–O (carbonyl), and νM–N respectively.

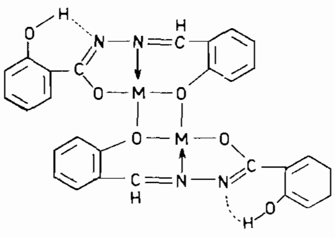
The following structures are proposed for some of the complexes on the basis of observations discussed above:

(I) for Cu(SSH–H); (II) for Cu(SSH–2H), Ni(SSH–2H)·2H_2O, Co(SSH–2H)·2H_2O; (III) for Ni(SSH–2H)·H_2O, Ni(SSH–2H)·2H_2O (alternative to that in II) and Co(SSH–2H)·2H_2O (alternative to that in II); and (IV) for $Cu(SSH–H)_2$, $Co(SSH–H)_2$, $Mn(SSH–H)_2$, $Fe(SSH–H)_2$, $VO(SSH–H)_2$, and TiO$(SSH–H)_2$.

I

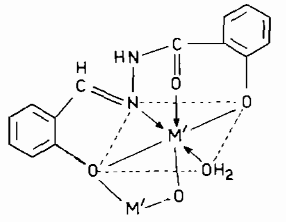


II



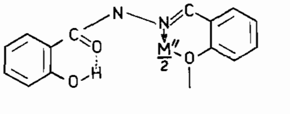
M = Cu(II), Ni(II)(H_2O)$_2$, Co(II)(H_2O)$_2$

III



M′= Ni(II), Ni(II)(H_2O), Co(II)(H_2O)

IV



M″= Cu(II), Co(II), Mn(II), Fe(II)
OV(IV), OTi(IV)

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