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Synthesis and Structural Studies of Some First Row Transition Metal Complexes of Salicylaldehyde Hydrazone

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A careful survey of literature has shown that no work appears to have been done on the first row transition metal complexes of salicylaldehyde hydrazone except for the preparation of deprotonated complexes of Cu(II) and Ni(II) [1] and the structural studies on the latter complex [2]. Synthesis and structural studies on the title complexes have therefore been undertaken and the results of these investigations are described in the present communication.

Experimental

All chemicals used were of BDH or equivalent quality. Salicylaldehyde hydrazone $C_6H_4(OH)CH=N-NH_2$ (SH) was prepared by the gradual addition of salicylaldehyde to the ethanolic solution of hydrazine hydrate in 1:2 molar ratio. The resulting product was filtered off, washed with ethanol and recrystallised from chloroform, m.p. 96–97 °C (lit. [3] 96–98 °C). Found: N_2H_4 = 23.4%. Calcd. = 23.5% for SH.

Preparation and Analysis of the Complexes

Addition compounds of the compositions $VOSO_4 \cdot 3SH$ and $M(SH)_4Cl_2$ (where M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II)) were prepared by mixing methanolic/ethanolic solutions of SH and the appropriate metal salts in 2:1 molar ratio and stirring the reaction mixture for 5–10 min. The Fe(II) complex was prepared under nitrogen atmosphere to prevent its oxidation. The complexes which precipitated were almost immediately filtered off, washed with alcohol and finally with ether and dried *in vacuo*.

$VO(SH\text{-}H)_2$ was prepared by refluxing the chloroform solutions of $VO(acac)_2$ and SH in ~ 1:2 molar ratio for ~ 30 minutes. Deprotonated complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) were prepared by adding SH dissolved in the minimum amount of NaOH solution to an aqueous solution of the respective metal chloride, keeping the metal–ligand ratio ~1:2. $Fe(SH\text{-}H)_2 \cdot 2H_2O$ was prepared under nitrogen atmosphere by mixing ethanolic solutions of $FeCl_2 \cdot 4H_2O$ and SH in 1:2 molar ratio and raising the pH by the addition of alcoholic KOH. All the deprotonated complexes thus precipitated were suction filtered, washed at first with very dilute acetic acid and then with alcohol (the vanadyl complex was washed only with chloroform) and finally dried in vacuum desiccator over concentrated sulphuric acid.

The complexes were analysed for their metal content employing standard literature procedures after destroying the organic matter at first with a mixture of nitric and hydrochloric acids and then with concentrated sulphuric acid. Sulphate and chloride were estimated as $BaSO_4$ and AgCl, respectively. Nitrogen was determined by microanalysis. Hydrazine was estimated volumetrically using KIO_3 [4] after submitting the complexes to acid hydrolysis for ~2–3 hr. The water content of the hydrated complexes was determined by heating them in the range 80–150 °C and determining the loss in weight.

Physical Measurements

Electrical conductance was measured on a WTW conductivity meter in DMF. The magnetic susceptibility of the complexes was determined by the Faraday method using $Co[Hg(SCN)_4]$ as calibrant and experimental magnetic susceptibilities were corrected for diamagnetism [5]. Analytical data, molar conductances and magnetic moments of the complexes are given in Table I.

The electronic spectra of the complexes and of the ligand were recorded on a Cary-14 spectrophotometer in nujol. The various absorption bands, their assignments and the values of the ligand field parameters such as 10Dq and LFSE calculated as described by Lever [6] are included in Table II.

The infrared spectra of complexes and of the ligand were recorded on a Perkin Elmer spectrophotometer Model 621 in nujol and chloroform, respectively. The important IR bands and assignments thereof are given in Table III.

Results and Discussion

The analytical data given in Table I show that SH forms two types of compounds, *viz.* adducts and deprotonated complexes in neutral and alkaline media, respectively. All the adducts (except $VOSO_4 \cdot 3SH$) and the deprotonated complexes have 1:4 and 1:2 metal to ligand stoichiometries, respectively. The complexes are insoluble in water and organic solvents such as chloroform, ethanol, methanol, tetrahydrofuran, acetone, etc. but soluble in DMF and DMSO. They do not melt but decompose in the temperature range 200–300 °C. The values of the

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TABLE I. Analytical Data and General Behaviour of the SH Complexes.[a]

Complex	Colour	Metal (%)	N_2H_4 (%)	Nitrogen (%)	Cl(SO_4) H_2O (%)	μ_{eff} (B.M.)	M.p.(dec. temp.) (°C)
$VOSO_4 \cdot 3SH$	Green	9.20 (8.92)	16.53 (16.82)	14.71 (14.70)	16.70 (16.84)	1.73	>250
$MnCl_2 \cdot 4SH$	Light yellow	7.65 (8.21)	19.05 (19.11)	17.04 (16.72)	10.35 (10.59)	6.08	210
$FeCl_2 \cdot 4SH$	Light brown	9.02 (8.72)	18.87 (19.08)	16.50 (16.69)	10.40 (10.57)	4.92	215
$CoCl_2 \cdot 4SH$	Dark red	8.46 (8.75)	18.95 (19.00)	16.17 (16.63)	10.36 (10.52)	4.75	225
$NiCl_2 \cdot 4SH$	Green	8.98 (8.71)	18.76 (19.01)	16.33 (16.63)	10.80 (10.53)	3.20	220
$CuCl_2 \cdot 4SH$	Green	9.67 (9.37)	–	16.53 (16.51)	10.75 (10.45)	1.89	210
$ZnCl_2 \cdot 4SH$	Light yellow	10.13 (9.61)	18.70 (18.81)	16.49 (16.46)	10.28 (10.42)	Diamag.	208
$VO(SH\text{-}H)_2$	Green	14.40 (14.35)	19.00 (19.00)	15.38 (15.77)	–	1.76	210
$Mn(SH\text{-}H)_2 \cdot 2H_2O$	Orange yellow	15.50 (15.21)	17.40 (17.70)	15.15 (15.52)	9.80 (9.97)	6.10	Above 250
$Fe(SH\text{-}H)_2 \cdot 2H_2O$	Brown	15.10 (15.42)	17.75 (17.68)	15.52 (15.47)	10.25 (9.95)	5.05	
$Co(SH\text{-}H)_2 \cdot 2H_2O$	Reddish yellow	16.25 (16.14)	17.32 (17.54)	15.18 (15.34)	10.10 (9.86)	4.88	
$Ni(SH\text{-}H)_2 \cdot 2H_2O$	Dirty yellow	16.02 (16.10)	17.40 (17.55)	15.27 (15.36)	9.45 (9.87)	3.16	
$Cu(SH\text{-}H)_2$	Dirty yellow	18.57 (19.06)	–	17.34 (16.80)	–	1.87	
$Zn(SH\text{-}H)_2 \cdot 2H_2O$	Yellow	18.10 (17.56)	17.30 (17.23)	15.17 (15.08)	9.85 (9.68)	Diamag.	

[a] Calculated values are given in parentheses.

TABLE II. Electronic Spectral Data and Ligand-field Parameters of the SH Complexes.

Complex	Band maxima (cm^{-1})[a]	Assignments	10Dq (cm^{-1})	LFSE (kJ/mol)
$VOSO_4 \cdot 3SH$	12740, 15750	$d_{xy} \rightarrow d_{yz}, d_{xz}; d_{x^2-y^2}$	15750	75.10
$VO(SH\text{-}H)_2$	12500, 15300, 19610	$d_{xy} \rightarrow d_{yz}; d_{xz}; d_{x^2-y^2}$	15300	72.83
$FeCl_2 \cdot 4SH$	8400, 10990	$^5T_{2g} \rightarrow {}^5E_g(D)$	10990	52.41
$Fe(SH\text{-}H)_2 \cdot 2H_2O$	8500, 11110	$^5T_{2g} \rightarrow {}^5E_g(D)$	11110	52.97
$CoCl_2 \cdot 4SH$	9660, 20000	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F); {}^4T_{1g}(P)$	10910	104.00
$Co(SH\text{-}H)_2 \cdot 2H_2O$	10000	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	–	–
$NiCl_2 \cdot 4SH$	9000, 12000, 14810, 17200	$^3B_{1g} \rightarrow {}^3E_g{}^a; {}^3B_{2g}; {}^3A_{2g}{}^a; {}^3E_g{}^b$	–	–
$Ni(SH\text{-}H)_2 \cdot 2H_2O$	9500, 15400	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F); {}^3T_{1g}(F)$	9500	136.0
$CuCl_2 \cdot 4SH$	13350, 11800 (sh)	$^2B_{1g} \rightarrow {}^2E_g, {}^2B_{2g}; {}^2A_{1g}$	13350	95.50
$Cu(SH\text{-}H)_2$	15000	Envelope of $^2B_{1g} \rightarrow {}^2A_{1g}, {}^2B_{2g}, {}^2E_g$ (17)	15000	107.30

[a] All the complexes, in addition to the d–d transition(s) listed above, yield two bands at ~28000 and ~34400 cm^{-1} due to intra-ligand transitions.

molar conductance in DMF lying in the range 5–15 cm^2 mhos mol^{-1} show the non-electrolytic nature of both types of complexes [7].

Magnetic Moments

The corrected magnetic moment data (Table I) indicate spin-free octahedral geometry for all Fe(II),

TABLE III. Important Infrared Spectral Bands (cm^{-1}) and Their Assignments.

Compound	ν(O–H)	ν(N–H)	ν(C=N)	ν(C–O(H))	ν(N–N)	$\rho_r H_2O$ [21]	ν(M ← N) [25, 26]	ν(M–Cl) [24]
$C_6H_4(OH)CH{:}N{\cdot}NH_2$	3450, 3400w	3300s	1625s	1270s	940	–	–	–
$C_6H_4(OH)(CH{\cdot}Cl_3)$	3695, 3410w	3300s	1625s	1270s	940	–	–	–
$VOSO_4{\cdot}3SH$	3500–3400w,b	3310s	1610s	1272s	965	–	384	–
$MnCl_2{\cdot}4SH$	3535–3410w,b	3310s	1612s	1270s	960	–	310	235
$FeCl_2{\cdot}4SH$	3550–3390w,b	3300s	1615s	1275s	962	–	312	235
$CoCl_2{\cdot}4SH$	3550–3410w,b	3300s	1615s	1275s	968	–	337	240
$NiCl_2{\cdot}4SH$	3600–3450w,b	3300s	1608s	1270s	968	–	340	240
$CuCl_2{\cdot}4SH$	3575–3400b	3300s	1615s	1275s	970	–	344	245
$ZnCl_2{\cdot}4SH$	3500–3400b	3300s	1615s	1270s	968	–	340	230
				ν(C–O)				ν(M–O) [27, 28]
$VO(SH\text{-}H)_2$	–	3295s	1590s	1535s	960	–	380	470
$Mn(SH\text{-}H)_2{\cdot}2H_2O$	3460b	3290s	1595s	1530s	960	820	335	275
$Fe(SH\text{-}H)_2{\cdot}2H_2O$	3400w,b	3300s	1600s	1530s	965	820	340	280
$Co(SH\text{-}H)_2{\cdot}2H_2O$	3460b	3290s	1595s	1530s	965	760	340	300
$Ni(SH\text{-}H)_2{\cdot}2H_2O$	3460b	3290s	1595s	1532s	975	835	350	315
$Cu(SH\text{-}H)_2$	–	3290s	1590s	1530s	960	–	355	320
$Zn(SH\text{-}H)_2{\cdot}2H_2O$	3500w,b	3290s	1600s	1532s	975	825	350	265

CO(II) and Ni(II) complexes [5] and spin-free tetrahedral or octahedral geometry for Mn(II) complexes. The magnetic moments of oxovanadium(IV) and Cu(II) complexes are normal, indicating the absence of metal–metal interaction but giving no definite information about their geometry.

Electronic Spectra

The nujol spectrum of $VO(SH\text{-}H)_2$ shows three bands at 12500, 15300 and 19610 cm^{-1} which may be assigned to the transitions $d_{xy} \rightarrow d_{yz}$, d_{xz} and $d_{x^2-y^2}$ respectively in the square pyramidal geometry with C_{2v} symmetry of the above complex [8]. The spectrum of $VOSO_4{\cdot}3SH$, however, shows only two bands at 12740 and 15750 cm^{-1} assigned to $d_{xy} \rightarrow d_{yz}$, d_{xz} and $d_{xy} \rightarrow d_{x^2-y^2}$ transitions on the basis of octahedral geometry for the above complex.

The spectra of $Fe(SH)_4Cl_2$ and $Fe(SH\text{-}H)_2{\cdot}2H_2O$ give two peaks in the regions 8400–8500 and 10990–11110 cm^{-1}. This doublet is attributed to Jahn–Teller distortion of the excited E state [10] and hence a distorted octahedral geometry may be proposed for these complexes.

The spectrum of $Co(SH)_4Cl_2$ shows a broad band centered at 9660 cm^{-1} and a strong band at 20000 cm^{-1} which may be assigned to the transitions ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}$ (ν_1) and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) respectively in octahedral environment of cobalt (II). Using the above values of ν_1 and ν_3, Dq, B′ and ν_2 work out as 1091, 767 and 20490 cm^{-1} respectively. Further the ν_2/ν_1 ratio is found to be 2.12 which lies well within the limit reported for slightly distorted octahedral Co(II) complexes [11].

The spectrum of diaquo cobalt(II) complex yields a broad band with its centre at ~ 10000 cm^{-1}. The position and shape of the above band is characteristic of octahedral cobalt(II) complexes and may therefore be assigned to the transition ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}$ (ν_1) [12]. The ν_3 band is probably masked by strong absorption of the salicylaldehydato ion in its neighbourhood.

The nujol spectrum of $Ni(SH\text{-}H)_2{\cdot}2H_2O$ shows two bands at 9500 and 15400 cm^{-1} assigned to ${}^3A_{2g} \rightarrow {}^3T_{2g}$ (ν_1) and ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (ν_2) transitions respectively, characteristic of octahedral geometry [13]. The 10Dq value (9500 cm^{-1}) is close to reported values for high-spin octahedral complexes of Ni(II) in the coordination environment of two nitrogen and four oxygen atoms [14].

The electronic spectrum of $Ni(SH)_4Cl_2$ is markedly different from that of $Ni(SH\text{-}H)_2{\cdot}2H_2O$ since it shows two additional weak bands at 12000 and 14810 cm^{-1} between ν_1 and ν_2 bands of octahedral complexes. These additional bands probably arise from the splitting of ν_1 and ν_2 bands because of the lowering in symmetry of the ligand field from O_h to D_{4h} [6b]. Assuming a tetragonal model (D_{4h}) the observed bands may be assigned to the transitions: 9000 ${}^3B_{1g} \rightarrow {}^3E_g{}^a$; 12000 ${}^3B_{1g} \rightarrow {}^3B_{2g}$; 14810 ${}^3B_{1g} \rightarrow {}^3A_{2g}{}^a$; 17200 ${}^3B_{1g} \rightarrow {}^3E_g{}^b$ [6b]. After applying correction to Dt [15], the values of the various ligand-field parameters for $Ni(SH)_4Cl_2$, *viz.* DqL, Dqz, Dt_{corr}, D_s and B work out as 1200, 663, 307, 462 and 386

cm^{-1} respectively and these values are very close to those reported for tetragonal nickel(II) complexes in weak field [6b].

$Cu(SH)_4Cl_2$ and $Cu(SH\text{-}H)_2$ yield one broad band at 13350 and 15000 cm^{-1}, respectively. The former complex gives an additional well defined shoulder at 11800 cm^{-1} on the low energy side. These spectral features together with the composition of the complexes indicate distorted octahedral geometry for the former complexes [11] and square planar geometry for the latter [16].

Infrared Spectra

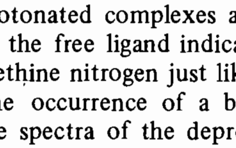
The positions of the bands due to $\nu(OH)$, $\nu(NH)$ and $\nu(C–O)$ [18] modes of SH remain practically unchanged in the spectra of the addition complexes indicating that phenolic oxygen and terminal nitrogen atoms are not involved in bonding. However, a negative shift of 10–17 cm^{-1} in $\nu(C{=}N)$ and a positive shift of 20–30 cm^{-1} in $\nu(N–N)$ [19] taken together in the spectra of the addition complexes as compared to the spectrum of the ligand indicate that only one of the nitrogens, *viz.* the azomethine nitrogen, is involved in coordination.

A negative shift of 25–35 cm^{-1} in $\nu(C{=}N)$, a positive shift of 20–35 cm^{-1} in $\nu(N–N)$ and practically no shift in $\nu(NH)$ bands in the spectra of the deprotonated complexes as compared to the spectrum of the free ligand indicate bonding through the azomethine nitrogen just like in the addition complexes. The occurrence of a band at 1530–1535 cm^{-1} in the spectra of the deprotonated complexes assigned to $\nu(C–O)$ suggests bonding through the phenolic oxygen and the monodentate nature of the C–O group [20].

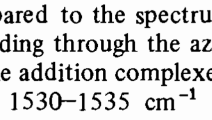
The presence of three bands at 1205, 1140 and 1030 cm^{-1} in the ν_3 region of $VOSO_4 \cdot 3SH$ indicates that the sulphato group is chelating [22, 23].

The infrared spectral studies thus indicate that SH behaves as a neutral monodentate ligand in the addition compounds and as a uninegative bidentate ligand in the deprotonated complexes, the bonding sites being the azomethine nitrogen in the former complex and the azomethine nitrogen and phenolic oxygen in the latter.

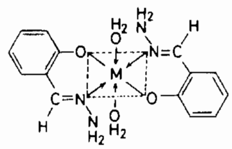
Based on analytical data, general behaviour and physico-chemical studies, the following structures may be proposed for the adducts and deprotonated complexes:



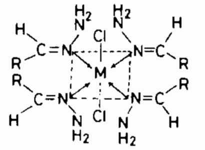
VO(SH-H)$_2$



VO SO$_4$·3 SH
R = C$_6$H$_4$(OH)



M(SH-H)$_2$·2H$_2$O
M = Mn, Fe, Co, Ni, Zn



MCl$_2$·4SH
M = Mn, Fe, Co, Ni, Cu, Zn

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