

3d-metal complexes of salicylaldehyde ethoxythiocarbonyl hydrazone

N K SINGH, S C SRIVASTVA and R C AGGARWAL*

Department of Chemistry, Banaras Hindu University, Varanasi 221 005, India

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Abstract. Salicylaldehyde ethoxythiocarbonyl hydrazone (H_2L) forms adducts as well as deprotonated complexes having 1 : 1 or/and 1 : 2 metal ligand ratio with the metal ions VO(IV), Ni(II), Co(III), Cu(II), Zn(II), Mn(II) and Fe(II). Based on magnetic, ESR, electronic, infrared and NMR spectral measurements, structures have been assigned to all the compounds. IR spectral studies show neutral bidentate behaviour of the ligand in the adducts and uninegative/binegative tridentate behaviour in the deprotonated complexes, the bonding sites being azomethine nitrogen and thione sulphur in the former type of complexes and phenolate oxygen, azomethine nitrogen and thione/thiolate sulphur in the latter type.

Keywords. 3d metal complexes; IR spectral studies; electronic; nuclear magnetic resonance; electron spin resonance; salicylaldehyde ethoxythiocarbonyl hydrazone.

1. Introduction

Although the transition metal complexes of ONO multidentate Schiff bases derived from salicylaldehyde and acid hydrazides are extensively studied (Sayed and Iskandar 1971; Narang and Aggarwal 1974; Iskandar and Aggan 1975; Biradar and Havinale 1976; Aggarwal *et al* 1981; Dutta and Sarkar 1981) comparatively little work has been done on the complexes of analogous ONS Schiff bases (Ablov and Gerbeleu 1964, 1965; Ali *et al* 1973). Also, no work seems to have been done to date on the complexes of salicylaldehyde ethoxythiocarbonyl hydrazone containing oxygen, nitrogen and sulphur as potential donor sites. The synthesis and structural studies of VO(IV), Mn(II), Fe(II), Co(III), Ni(II), Cu(II), and Zn(II) complexes of the above ligand were therefore undertaken and the results of these investigations are described in the present paper.

2. Experimental

2.1 Materials

All the chemicals used were of BDH or equivalent quality.

2.2 Preparation of ligands

Salicylaldehyde ethoxythiocarbonyl hydrazone, $C_6H_4(OH)CH:N \cdot NHC:S \cdot OC_2H_5(H_2L)$ was prepared by refluxing for ~ 1 hr the ethanolic solutions of ethoxythiocarbonyl hydrazide and salicylaldehyde taken in ~ 1 : 1.2 molar ratio. On cooling a white solid separated out which was filtered, washed with ethanol and

* To whom all correspondence should be addressed.

recrystallised from ethanol, m.p. 163–165°C. Ethoxythiocarbonyl hydrazide required for the purpose was prepared by the reported method (Jensen *et al* 1969). Analysis: C = 53.46, H = 5.5, N = 12.24, S = 13.62, $N_2H_4 = 13.58\%$, $C_{10}H_{12}O_2N_2S$ requires C = 53.58, H = 5.36, N = 12.5, S = 14.28, $N_2H_4 = 14.28\%$.

2.3 Preparation of the complexes

Adducts of Fe(II), Ni(II) and Cu(II) chlorides were prepared by adding ethanolic solutions of the respective metal(II) chloride to the solution of the ligand in the same solvent in $\sim 1:2$ molar ratio. $ZnCl_2(H_2L)$ was, however, prepared by using the ethereal solutions of the ligand and anhydrous $ZnCl_2$.

$VOL \cdot 2H_2O$ and $Co(HL)(L)$ were prepared by mixing the ethanolic solutions of the ligand and the hydrated vanadyl/cobaltous chloride in $\sim 1:2$ molar ratio and stirring the reaction mixture. Few drops of dil HCl were added to the reaction mixture during the synthesis of Co(III) complex.

$MnL \cdot H_2O$ and $ZnL \cdot EtOH$ were obtained by refluxing the ethanolic solutions of the respective metal(II) acetate and the ligand in $\sim 1:2$ molar ratio.

$NiL \cdot NH_3$ was obtained as a red crystalline product by adding concentrated ammonia solution dropwise to the ethanolic solutions of $NiCl_2 \cdot 6H_2O$ and the ligand in a 1:1 molar ratio till present in slight excess and concentrating the red solution to incipient crystallization. The resulting compound was filtered, washed with ethanol and dried in air.

$Ni(HL)_2$ and $CuL \cdot H_2O$ were prepared by digesting for ~ 10 – 15 min the solutions of the respective hydrated metal(II) chloride and the ligand in $\sim 1:2$ molar ratio after raising the pH to ~ 5 – 6 with dil NH_4OH . $Fe(HL)_2$ was prepared by mixing and subsequent stirring of the ethanolic solutions of $FeCl_2 \cdot 4H_2O$, ligand and KOH in 1:2:2 molar ratio in hydrogen atmosphere to prevent the oxidation of Fe(II). The complexes thus obtained were suction-filtered and washed with ethanol/ether; however, the deprotonated complexes of Fe(II), Ni(II) and Cu(II) were washed first with water and then with ethanol. The complexes were dried *in vacuo*.

2.4 Analysis

The complexes were analysed for their metal contents 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. Sulphur was estimated as $BaSO_4$ and chloride as $AgCl$. Nitrogen was determined by microanalysis. Hydrazine was estimated volumetrically using KIO_3 (Vogel 1971) after submitting the complexes to acid hydrolysis for ~ 2 – 3 hr. The water or ethanol content of the complexes was determined by heating them in the range 100–140°C and finding out the loss in weight. The analytical data are given in table 1.

2.5 Physical measurements

The equipment and the methods employed for recording molar conductance, magnetic susceptibility, and electronic and infrared spectra were the same as described in our previous studies (Aggarwal *et al* 1981). The values of the various spectral parameters such as 10Dq, B' and LFSE were calculated as described in Lever (1968a).

ESR spectra of $Cu(H_2L)_2Cl_2$ and $CuL \cdot H_2O$ were recorded at room temperature and

Table 1. Analytical data and general behaviour of the complexes.

Compound	Colour	% Metal		% N ₂ H ₄		% Nitrogen		% Cl		% S		μ_{eff} (BM)	m.p. (°C)
		Found	Cal.	Found	Cal.	Found	Cal.	Found	Cal.	Found	Cal.		
Fe(H ₂ L)Cl ₂	Dark brown	16.38	15.92	—	—	7.62	7.98	20.10	20.21	8.89	9.12	4.80	160
Ni(H ₂ L)Cl ₂ ·2H ₂ O	Green	15.22	15.07	8.86	8.21	6.98	7.18	17.90	18.20	8.01	8.21	3.30	> 300
Cu(H ₂ L) ₂ Cl ₂	Dark green	10.40	10.91	11.18	10.99	9.86	9.61	11.82	12.17	10.60	10.99	1.75	145
Zn(H ₂ L)Cl ₂	Light yellow	18.40	18.15	9.05	8.88	7.39	7.77	19.28	19.67	8.34	8.88	dia-	175
Fe(HL) ₂	Dark brown	10.86	11.13	—	—	10.90	11.16	—	—	12.42	12.76	magnetic	205 ^d
Ni(HL) ₂	Yellowish green	11.40	11.63	12.26	12.69	11.48	11.10	—	—	12.98	12.69	3.24	235
Co(HL)(L)	Dark brown	11.42	11.69	13.07	12.70	11.40	11.11	—	—	12.36	12.70	dia-	255 ^d
VOL·2H ₂ O	Light grey	15.16	15.68	10.01	9.84	8.58	8.62	—	—	9.24	9.84	1.70	250 ^d
MnL·H ₂ O	Light yellow	18.61	18.63	10.60	10.85	9.30	9.49	—	—	10.50	10.85	5.82	> 300
NiL·NH ₃	Red	19.25	19.72	11.13	10.75	13.80	14.11	—	—	10.16	10.75	dia-	200 ^d
CuL·H ₂ O	Chocolate	21.05	20.94	10.03	10.54	9.60	9.22	—	—	10.40	10.54	magnetic	258
ZnL·EtOH	White	21.37	21.42	10.73	10.53	9.44	9.17	—	—	10.01	10.53	dia-	> 300

^d - decomposes

77 K in DMF and chloroform, respectively on a Varian X-band spectrometer, Model E-4, using DPPH as a g marker. The ESR magnetic parameters g_{av} , g_{\parallel} , g_{\perp} , A_{iso} , A_{\parallel} , and A_{\perp} deduced from the analysis of the spectra are discussed.

The ^1H NMR spectra of the ligand and 1:1 deprotonated complexes of Zn(II) were recorded on a Varian A-60D spectrophotometer in CDCl_3 and $\text{DMSO}(d_6)$, respectively.

3. Results and discussion

The analytical data given in table 1 show the formation of 1:1 adducts with Fe(II), Ni(II) and Zn(II) chlorides, 1:2 adduct with Cu(II) chloride, and deprotonated complexes of the types $\text{M}(\text{HL})_2$ [$\text{M}=\text{Fe}(\text{II})$ and $\text{Ni}(\text{II})$] and $\text{M}'\text{L}\cdot n\text{Y}$ [$\text{Y}=\text{H}_2\text{O}$ for VO(IV), Mn(II), Cu(II); NH_3 for Ni(II) and EtOH for Zn(II); $n = 2$ for VO(IV) and one for others]. The loss of weight between 120–140°C for $\text{ZnL}\cdot\text{EtOH}$, $\text{VOL}\cdot 2\text{H}_2\text{O}$, $\text{MnL}\cdot\text{H}_2\text{O}$ and $\text{CuL}\cdot\text{H}_2\text{O}$ suggests the coordinated nature of the solvent molecule(s) which is further supported by ^1H NMR or IR spectral studies discussed later. The complexes are insoluble in water and non-polar organic solvents such as chloroform, benzene etc., (Ali and Livingstone 1974) but with a few exceptions they are soluble in ethanol, DMF and DMSO. The molar conductance values of the soluble complexes in DMF show them to be non-ionic in nature (Geary 1971).

3.1 Magnetic moments

The magnetic moment data given in table 1 show that $\text{NiL}\cdot\text{NH}_3$ and $\text{Co}(\text{HL})(\text{L})$ are diamagnetic indicating that the former complex is square planar while the latter is a low-spin octahedral Co(III) complex. The magnetic moments of other Ni(II) complexes are consistent with spin-free octahedral geometry around Ni(II) and those of Mn(II) and Fe(II) complexes indicate them to be spin-free in nature (Ali and Livingstone 1974). μ_{eff} values of oxovanadium(IV) and copper(II) complexes are normal but give no specific information about the stereochemistry.

3.2 Electronic spectra

The electronic spectrum of the ligand in ethanol shows four bands at 30000, 32570, 42740 and 33900 cm^{-1} with ϵ_{max} values of 18400, 20000, 18400 and 16800, respectively. The first three bands may be attributed to $\pi \rightarrow \pi^*$ transition arising from the salicylaldimine part (Sacconi *et al* 1957) while the fourth to the $>\text{C}=\text{S}$ chromophore (Walter and Reubke 1970) present in the ligand.

$\text{VOL}\cdot 2\text{H}_2\text{O}$ shows two bands at 10000 and 18180 cm^{-1} assigned to $d_{xy} \rightarrow d_{yz}$, d_{xz} and $d_{x^2-y^2}$ transitions, respectively on the basis of octahedral geometry of the complex (Lever 1968b). 10Dq and LFSE have been calculated to be 18180 cm^{-1} and 89 kJ mol^{-1} respectively.

The spectra of $\text{Fe}(\text{H}_2\text{L})\text{Cl}_2$ and $\text{Fe}(\text{HL})_2$ yield one band at 17390 and 16670 cm^{-1} respectively which may be attributed to charge transfer transition (Lever 1968b).

The 18000 and 25000 cm^{-1} bands in the spectrum of $\text{Co}(\text{HL})(\text{L})$ may be assigned to $^1A_{1g} \rightarrow ^1T_{1g}$ and $^1T_{2g}$ transitions, respectively in octahedral geometry of Co(III) (Lever 1968b), the calculated value of B comes out to be 437 cm^{-1} . The spectrum of $\text{NiL}\cdot\text{NH}_3$ shows three $d-d$ bands at 16670, 20000 and 24000 cm^{-1} which may be assigned to

$^1A_{1g} \rightarrow ^1A_{2g}$, $^1B_{1g}$ and $^1E_{1g}$ transitions respectively in square planar geometry. The single electron parameters Δ_1 , Δ_2 and Δ_3 have been calculated as suggested by Gray and Ballhausen (1963) assuming after Shupack *et al* (1964) that $F_2 = 10F_4 = 800 \text{ cm}^{-1}$ and the calculated values are 19470, 4930 and 3600 cm^{-1} respectively.

$\text{Ni}(\text{HL})_2$ and $\text{Ni}(\text{H}_2\text{L})\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ show two $d-d$ transition bands at 11430, 16950 and 11430, 17390 cm^{-1} , respectively. These two bands in each case may be assigned to $^3A_{2g} \rightarrow ^3T_{2g}(F)$ and $^3T_{1g}(F)$ transitions, respectively in octahedral environment of Ni(II) (Sacconi 1968). The values of $10Dq$ (cm^{-1}), B (cm^{-1}) and LFSE (kJ mole^{-1}) have been calculated for each of the complexes and they are 11430; 680, 602; and 164.2 respectively.

$\text{Cu}(\text{H}_2\text{L})_2\text{Cl}_2$ and $\text{CuL} \cdot \text{H}_2\text{O}$ show a broad band at 14290 and 18180 cm^{-1} , respectively. The positions of these bands suggest octahedral geometry for the former complex which may be assigned to the envelope of $^2B_{1g} \rightarrow ^2Eg$; $^2B_{2g}$ and $^2A_{1g}$ transitions and square planar geometry for the latter may be assigned to the envelope of $^2B_{1g} \rightarrow ^2A_{1g}$; $^2B_{2g}$ and 2Eg transitions, respectively (Sacconi and Ciampolini 1964; Procter *et al* 1968; Patel and Goldberg 1972). The $10Dq$ (cm^{-1}) and LFSE (kJ mole^{-1}) values of the complexes are calculated to be 14290, 18180 and 102.7, 130.6 respectively.

3.3 ESR spectra

$\text{Cu}(\text{H}_2\text{L})_2\text{Cl}_2$ and $\text{CuL} \cdot \text{H}_2\text{O}$ show isotropic ESR spectra at room temperature and are axially symmetric at 77 K. The values of the various ESR magnetic parameters calculated from the spectra of $\text{Cu}(\text{H}_2\text{L})_2\text{Cl}_2$ are: $g_{av} = 2.0962$; $g_{||} = 2.2006$; $g_{\perp} = 2.0441$; $A_{iso}(\text{Cu}) = 85 \text{ G}$; $A_{||}(\text{Cu}) = 170 \text{ G}$; $A_{\perp}(\text{Cu}) = 43.3 \text{ G}$ and $A_{iso}(^{14}\text{N}) = 15 \text{ G}$ and for $\text{CuL} \cdot \text{H}_2\text{O}$ the various values are: $g_{av} = 2.0790$; $g_{||} = 2.1567$; $g_{\perp} = 2.0401$; $A_{iso}(\text{Cu}) = 87 \text{ G}$; $A_{||}(\text{Cu}) = 183 \text{ G}$ and $A_{\perp}(\text{Cu}) = 35.83 \text{ G}$.

The trend $g_{||} > g_{\perp} > g_e$ (2.0023; free spin value) observed for the complexes under study indicates that the unpaired electron is most likely in the $d_{x^2-y^2}$ orbital of Cu(II). Further the ratio $(g_{||}-2)/(g_{\perp}-2) \approx 4$ is also an evidence that $d_{x^2-y^2}$ ground state is present in these complexes (Procter *et al* 1968). The ESR spectrum of $\text{Cu}(\text{H}_2\text{L})_2\text{Cl}_2$ at 77 K displays a well resolved super hyperfine splitting (*ca* 15G) arising from the interaction of the unpaired electron density of ^{63}Cu with ^{14}N atoms of the ligand (Kokoszka *et al* 1967; Danopoulos and Paraskewas 1981).

3.4 Infrared spectra

The IR spectrum of the ligand in CHCl_3 shows two bands at 3340 and 3160 cm^{-1} which may be assigned to $\nu(\text{OH})$ and $\nu(\text{NH})$ modes respectively. The positions of these bands remain practically unchanged or show some positive shifts in the spectra of the adducts indicating the non-involvement of imino nitrogen and phenolic oxygen in bonding.

The bands occurring at 1620, 965, 1480, 1310 and 800 cm^{-1} in the CHCl_3 solution spectrum of the ligand are assigned to $\nu(\text{C}=\text{N})$, $\nu(\text{N}-\text{N})$ (Braibanti *et al* 1968), thioamide bands: $\beta\text{NH} + \nu\text{CN}$ (mainly βNH), $\nu\text{CN} + \beta\text{NH}$ (high νCN) and $\nu(\text{C}=\text{S})$, respectively (Burns 1968). The corresponding bands in the spectra of all the adducts are observed in 1590–1600, 985–1000, 1500, 1320–1350 and 770–790 cm^{-1} regions respectively. Negative shifts in $\nu(\text{C}=\text{N})$ (20–30 cm^{-1}) and $\nu(\text{C}=\text{S})$ (10–30 cm^{-1}) (Burns 1968) indicate coordination through azomethine nitrogen and thione sulphur. The bonding through these atoms are further supported by positive shifts in $\beta\text{NH} + \nu\text{CN}$ (20 cm^{-1}), $\nu\text{CN} + \beta\text{NH}$ (10–40 cm^{-1}) and $\nu(\text{N}-\text{N})$ (20–35 cm^{-1}) modes (Braibanti *et al* 1968).

The $\nu(\text{C-O})$ (phenolic) band observed in the ligand at 1270 cm^{-1} remains practically unchanged showing non-involvement of phenolic oxygen in bonding (Yamada 1959). In the spectra of $\text{Fe}(\text{HL})_2$ and $\text{Ni}(\text{HL})_2$ the disappearance of the above band and appearance of a new band due to $\nu_{\text{asym}}(\text{C-O-M})$ at $\sim 1530 \text{ cm}^{-1}$ indicate bonding through phenolic oxygen with the metal ions and monodentate behaviour of C-O group (Sinn and Harris 1969). The spectral features in $\nu(\text{N-H})$, $\nu(\text{C=N})$, $\nu(\text{N-N})$ and thioamide frequency regions in the spectra of 1 : 2 deprotonated complexes are the same as for the adducts discussed above. The IR spectral studies thus show mononegative tridentate behaviour of H_2L in 1 : 2 deprotonated complexes; the bonding sites being phenolate oxygen, azomethine nitrogen and thione sulphur as reported for salicylaldehyde thiosemicarbazone complexes (Ablov and Gerbelevu 1964, 1965). The tridentate behaviour of H_2L is consistent with the octahedral geometry of the above complexes inferred from magnetic and electronic spectral studies discussed earlier.

The disappearance of $\nu(\text{OH})$, $\nu(\text{N-H})$, and $\nu(\text{C=S})$ bands in the spectra of anhydrous 1 : 1 deprotonated complexes and appearance of new bands due to $\nu_{\text{asym}}(\text{C-O-M})$ and $\nu(\text{C-S})$ (Geetharani and Sathyanarayana 1977) modes in $1520\text{--}1540$ and $715\text{--}730 \text{ cm}^{-1}$ regions, respectively indicate removal of the phenolic as well as thioenolic protons as a result of chelation. A negative shift in $\nu(\text{C=N})$ ($\sim 25 \text{ cm}^{-1}$) and a positive shift in $\nu(\text{N-N})$ ($45\text{--}55 \text{ cm}^{-1}$) in the spectra of these complexes suggest coordination through azomethine nitrogen. The IR spectral studies thus indicate dinegative tridentate behaviour of the ligand in 1 : 1 deprotonated complexes.

The infrared spectral features of $\text{Co}(\text{HL})(\text{L})$ are similar to those of 1 : 1 and 1 : 2 deprotonated complexes discussed above in the $\nu(\text{OH})$, $\nu(\text{C-O-M})$, $\nu(\text{C=N})$ and $\nu(\text{N-N})$ frequency regions indicating bonding through phenolate oxygen and azomethine nitrogen. But unlike the 1 : 1 and 1 : 2 deprotonated complexes which give only one band at ~ 720 and $\sim 770 \text{ cm}^{-1}$, respectively, $\text{Co}(\text{HL})(\text{L})$ yields two bands in $700\text{--}800 \text{ cm}^{-1}$ region due to $\nu(\text{C-S})$ and $\nu(\text{C=S})$ modes. The above observation shows uni- and binegative tridentate behaviour of the two ligands attached to $\text{Co}(\text{III})$. The bands observed at $3320\text{--}3400$ and $740\text{--}760 \text{ cm}^{-1}$ regions in the spectra of the hydrated complexes but absent in the anhydrous complexes may be assigned to $\nu(\text{OH})$ and $\rho_r(\text{H}_2\text{O})$ modes of the coordinated water molecule (Nakagawa and Shimanouchi 1964). The non-ligand bands occurring at $330\text{--}350$, $280\text{--}370$, $300\text{--}420$ and $280\text{--}400 \text{ cm}^{-1}$ regions may be tentatively assigned to $\nu(\text{M-Cl})$ (Specia *et al* 1976), $\nu(\text{M-N})$ (Beeroff *et al* 1974; Lever and Mantovani 1971), $\nu(\text{M-O})$ (Sathyanarayana and Patel 1968; Ohkaku and Nakamoto 1971) and $\nu(\text{M-S})$ (Geetharani and Sathyanarayana 1977) modes, respectively.

3.5 ^1H NMR spectra

The ^1H NMR spectrum (CDCl_3) of salicylaldehyde ethoxythiocarbonyl hydrazone shows signals at δ 1.47 (*t*, $J = 8 \text{ Hz}$, 3H, $-\text{OCH}_2\text{CH}_3$), 4.70 (*q*, $J = 8 \text{ Hz}$, 2H, $-\text{OCH}_2\text{CH}_3$), 6.60–7.60 (*m*, 4H, aromatic), 8–10 (*s*, 1H, $-\text{CH}=\text{N}-$), 10.47 (*br*, $-\text{NH}-$) and 11.20 (*s*, $-\text{OH}$). The signals due to $-\text{NH}-$ and $-\text{OH}$ groups disappear on D_2O exchange. The ^1H NMR spectrum of 1 : 1 deprotonated complex of $\text{Zn}(\text{II})$ shows signals at δ 1.25 (*t*, $J = 8 \text{ Hz}$, 3H, $-\text{OCH}_2\text{CH}_3$), 4.28 (*q*, $J = 8 \text{ Hz}$, 2H, $-\text{OCH}_2\text{CH}_3$), 6.60–7.60 (*m*, 4H, aromatic) and 8.88 (*s*, 1H, $-\text{CH}=\text{N}-$). Additional signals observed at δ 1.07 (*t*, $J = 7 \text{ Hz}$, 3H, $-\text{CH}_2\text{CH}_3$), 3.43 (*q*, $J = 7 \text{ Hz}$, 2H, $-\text{CH}_2\text{CH}_3$) and 3.33 (*s*, $-\text{OH}$) may be attributed to the presence of coordinated ethanol. The absorption at

δ 3.33 disappears in the Zn(II) complex under investigation on deuteration as expected for the proton of the –OH group in ethanol.

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