

# ACYL HYDRAZINE COMPLEXES OF SOME FIRST ROW TRANSITION METAL (II) PICRATES

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(Received 26 June 1975; revised 22 December 1975)

Cationic complexes of the types  $[M(BH)_2(H_2O)_2](Picrate)_2$  [ $M = Mn(II), Fe(II), Co(II), Ni(II)$  or  $Zn(II)$  and  $BH =$  benzoyl hydrazine],  $[M'(BH)_3](Picrate)_2 \cdot H_2O$  [ $M = Mn(II), Co(II), Ni(II)$  or  $Zn(II)$ ],  $[M''(SH)_2(H_2O)_2](Picrate)_2$  [ $M = Mn(II), Fe(II)$  or  $Co(II)$  and  $SH =$  salicylyl hydrazine],  $[M''(SH)_3](Picrate)_2$  [ $M'' = Ni(II)$  or  $Zn(II)$ ],  $[Cu(BH)_2](Picrate)_2$  and  $[Cu(SH)_2](Picrate)_2$  have been prepared and characterized. Molar conductances of the complexes show that they are 1 : 2 electrolytes. Magnetic and electronic spectral studies indicate that  $Cu(II)$  complexes are square planar, whereas those of  $Mn(II), Fe(II), Co(II)$  and  $Ni(II)$  are spin-free octahedral. Compositions and infrared spectra of the complexes suggest that acyl hydrazines act as a neutral bidentate ligands coordinating via carbonyl oxygen and primary amine nitrogen. Where possible spectral parameters such as  $10 Dq, B, \beta, B^{\circ}$  and  $\lambda'$  have been evaluated from the magnetic and electronic spectral data. The values of  $10 Dq$  and  $B$  suggest a place between water and ammonia for the ligands in the spectrochemical series and the above parameters also indicate that  $SH$  exerts a stronger ligand field than  $BH$ .

Acyl hydrazines as ligands have attracted the attention of several investigators<sup>1-4</sup>. Dutta Ahmad & Chaudhari have shown that acetyl and benzoyl hydrazines act as monodentate ligands towards transition metal ions and coordinate in the 'imidol' form via the nitrogen of the  $-NH$  group<sup>5</sup>. But more recently Alooek *et al.*<sup>6</sup> and Iskandar & coworkers<sup>7</sup> have suggested that these and some other acyl hydrazines enter into bonding in the 'keto' form and function as bidentate ligands coordinating through carbonyl oxygen and terminal nitrogen. In view of the controversy in the literature regarding the mode of bonding of the monoacyl hydrazines in their transition metal complexes it was thought of interest to investigate the mode of bonding and stereochemistry of benzoyl and salicylyl hydrazines complexes of some first row transition metal (II) picrates and the results obtained are described in the present communication. The complexes are of interest to Defence as explosives and detonators.

## EXPERIMENTAL

All the chemicals used were of  $BDH$  or equivalent quality. Solvents were purified and made anhydrous employing the standard procedures. Metal picrates were prepared as described earlier<sup>8</sup>. Benzoyl hydrazine ( $BH$ ) and salicylyl hydrazine ( $SH$ ) were prepared by following the literature procedures<sup>9, 10</sup>.

### Preparation and analysis of the complexes

$[M(BH)_2(H_2O)_2](Picrate)_2$ ,  $[Mn(BH)_3](Picrate)_2 \cdot 2H_2O$  and  $[Cu(BH)_2](Picrate)_2$  were prepared by mixing the aqueous solutions of metal picrates and  $BH$  in  $\sim 1:3$  molar ratio. All the complexes were precipitated immediately. They were filtered, washed with water and dried in vacuo.

$[Co(BH)_3](Picrate)_2 \cdot H_2O$ ,  $[Ni(BH)_3](Picrate)_2 \cdot H_2O$ ,  $[Ni(SH)_3](Picrate)_2$ ,  $[Co(SH)_2(H_2O)_2](Picrate)_2$  and  $[Fe(SH)_2(H_2O)_2](Picrate)_2$  were prepared by reacting an ethanolic solution of the metal picrates and the ligands in  $\sim 1:3$  molar ratio. The complexes were precipitated by concentrating the reaction mixtures and then treating them with water. They were filtered, washed with water and dried in vacuo.

$[Mn(BH)_2(H_2O)_2](Picrate)_2$ ,  $[Zn(BH)_3](Picrate)_2$ ,  $[Mn(SH)_2(H_2O)_2](Picrate)_2$ ,  $[Cu(SH)_2](Picrate)_2$  and  $[Zn(SH)_3](Picrate)_2$  were prepared by mixing the ethanolic solutions of the metal picrate and the ligand in  $\sim 1:3$  molar ratio. The reaction mixtures were refluxed for  $\sim \frac{1}{2}$  hr. and concentrated on a water bath. The complexes which separated on cooling were filtered, washed with cold ethanol and dried as before. All the soluble complexes were recrystallised from ethanol or acetone.

The complexes were analysed for metal and nitrogen as described earlier<sup>8</sup>. Hydrazine was estimated volumetrically<sup>11</sup> with  $KIO_3$  after submitting the complexes to acid hydrolysis for  $\sim 2$  hr. The water content in the hydrated complexes was estimated by finding out the loss in weight suffered on heating at  $110-150^\circ C$  for  $\sim 3$  hr. The analytical data are given in Table 1.

## Physical Measurements

Equipments and the methods employed for measuring molar conductance, magnetic susceptibility, electronic and infrared spectra were the same as used in our previous studies<sup>8</sup>. The pertinent experimental data are given in Tables 1-3. The values of the spectral parameters  $10 Dq$ ,  $B'$ ,  $\beta$  &  $\beta^\circ$  were calculated as described by Lever<sup>12</sup>.

## DISCUSSION

All the complexes under the present investigation melt in the range 110-210°C and explode when heated at ~ 250°C. They are insoluble in water and organic solvents such as chloroform, benzene, carbon tetrachloride etc., but are soluble in methanol, ethanol and acetone. Molar conductances of the complexes in methanol and molecular weights of the soluble complexes in ethanol show them to be 1 : 2 electrolytes. The loss of water at ~ 150°C from  $[ML_2(H_2O)_2]$  (Picrate)<sub>2</sub> type of complexes (with change in colour) and at ~ 110°C from the other hydrated complexes indicate that the water molecules are coordinated in the former complexes and are held in the lattice in others.

TABLE 1  
ANALYTICAL RESULTS, MOLAR CONDUCTANCES, MOLECULAR WEIGHTS, MELTING POINTS AND MAGNETIC MOMENTS OF THE COMPLEXES

Complex	Colour	Metal (%)	N, H <sub>4</sub> (%)	H <sub>2</sub> O (%)	m.p. (°C)	Molar conductance at 10 <sup>-3</sup> M in MeOH (Cm <sup>2</sup> mhos/mole)	$\mu$ eff (B.M.)	Mol. weight in EtOH
$[Mn(BH)_2(H_2O)_2]$ (Picrate) <sub>2</sub>	Yellow	7.37 (6.71)	7.70 (7.81)	4.70 (4.39)	120	196	6.12	—
$[Fe(BH)_2(H_2O)_2]$ (Picrate) <sub>2</sub>	Yellowish green	7.70 (6.82)	7.72 (7.80)	4.52 (4.39)	115	212	5.08	268.0 (273.3)
$[Co(BH)_2(H_2O)_2]$ (Picrate) <sub>2</sub>	Yellow	7.71 (7.17)	7.40 (7.70)	4.12 (4.37)	145	218	5.18	—
$[Ni(BH)_2(H_2O)_2]$ (Picrate) <sub>2</sub>	Yellowish green	7.09 (7.17)	8.10 (7.70)	5.00 (4.37)	175	218	3.13	—
$[Cu(BH)_2]$ (Picrate) <sub>2</sub>	Green	7.86 (8.03)	17.83* (17.68)	—	146	174	1.86	—
$[Zn(BH)_2(H_2O)_2]$ (Picrate) <sub>2</sub>	Yellow	7.40 (7.84)	7.60 (7.72)	4.30 (4.34)	190	210	Diamag.	281.8 (276.3)
$[Mn(BH)_2]$ (Picrate) <sub>2</sub> · 2H <sub>2</sub> O	Yellow	5.85 (5.76)	9.73 (10.05)	3.50 (3.77)	115	220	6.17	—
$[Co(BH)_2]$ (Picrate) <sub>2</sub> · H <sub>2</sub> O	Dull-red	6.43 (6.27)	10.60 (10.20)	2.00 (1.92)	155	198	4.65	320.5 (312.3)
$[Ni(BH)_2]$ (Picrate) <sub>2</sub> · H <sub>2</sub> O	Yellowish green	6.06 (6.23)	9.80 (10.22)	9.97 (9.92)	215	193	3.07	—
$[Zn(BH)_2]$ (Picrate) <sub>2</sub> · H <sub>2</sub> O	Yellow	6.80 (6.90)	9.43 (10.14)	2.03 (1.90)	145	198	Diamag.	—
$[Mn(SH)_2(H_2O)_2]$ (Picrate) <sub>2</sub>	Yellow	6.33 (6.46)	7.51 (7.52)	4.40 (4.23)	135-40	216	6.13	—
$[Fe(SH)_2(H_2O)_2]$ (Picrate) <sub>2</sub>	Brown	6.95 (6.55)	7.05 (7.27)	4.15 (4.23)	130-32	204	5.50	279.4 (284.0)
$[Co(SH)_2(H_2O)_2]$ (Picrate) <sub>2</sub>	Yellow	6.83 (6.90)	7.57 (7.48)	4.10 (4.21)	170-75	199	4.75	—
$[Ni(SH)_2]$ (Picrate) <sub>2</sub>	Yellowish green	5.68 (6.04)	9.37 (9.88)	—	180	203	3.05	—
$[Cu(SH)_2]$ (Picrate) <sub>2</sub>	Green	7.57 (7.71)	7.65 (7.76)	—	145	192	1.88	—
$[Zn(SH)_2]$ (Picrate) <sub>2</sub>	Yellow	5.81 (6.65)	9.44 (9.82)	—	140-45	200	Diamag.	—

Calculated values are given in parentheses.

Mol. wt. given in parentheses are apparent values expected for 1 : 2 electrolytes.

\*Represents nitrogen analysis.

TABLE 2  
 ELECTRONIC SPECTRAL BANDS AND THEIR ASSIGNMENTS

Compound	Medium	Bands (cm <sup>-1</sup> )	Assignments
Benzoyl hydrazine	Ethanol	44400 (8136)	$\pi \rightarrow \pi^*$
Salicylyl hydrazine	Ethanol	33000 (5000), 41320 (7800)	$\pi \rightarrow \pi^*$
	Nujol	31750, 41320	$\pi \rightarrow \pi^*$
[Fe(BH) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](Picrate) <sub>2</sub>	Ethanol	14600 (85), 25000 (16000), 27780 (28500), 43000 (36500)	${}^5T_{2g} \rightarrow {}^3E_g$ (D) L
[Fe(SH) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](Picrate) <sub>2</sub>	Ethanol	25000 (13500), 27930 (23200), 32250 (16000), 42550 (35200)	L
[Co(BH) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](Picrate) <sub>2</sub>	Ethanol	8930 (6.25) 25000 (16500), 27780 (24000) 42800 (40500)	${}^4T_{1g} \rightarrow {}^4T_{2g}$ (F) L
[Co(SH) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](Picrate) <sub>2</sub>	Ethanol	9000 (6.25), 19400 (31) 25000 (13500), 27780 (19600), 32260 (17000), 42550 (37000)	${}^4T_{1g} \rightarrow {}^4T_{2g}$ (F), ${}^4T_{1g}$ (P) L
[Ni(BH) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](Picrate) <sub>2</sub>	Acetone Ethanol	9400 (11.75), 15400 (13.25) 25000 (20000), 27780 (30000) 42550 (44000)	${}^3A_{2g} \rightarrow {}^3T_{2g}$ (F), ${}^3T_{1g}$ (F) L
[Ni(BH) <sub>2</sub> ](Picrate) 1. H <sub>2</sub> O	Acetone Ethanol	9760 (9.0), 16000 (9.0) 25000 (21800), 27780 (31000) 42900 (46500)	${}^3A_{2g} \rightarrow {}^3T_{2g}$ (F), ${}^3T_{1g}$ (F) L
[Ni(SH) <sub>2</sub> ](Picrate) <sub>2</sub>	Nujol	10350 16800 22730 35715, 40050	${}^3A_{2g} \rightarrow {}^3T_{2g}$ (F), ${}^3T_{1g}$ (F) L
[Cu(BH) <sub>2</sub> ](Picrate) <sub>2</sub>	Nujol	16950 24100 27780, 42550	${}^2B_{1g} \rightarrow {}^2A_{1g}$ & ${}^2B_{1g} \rightarrow {}^2E_g$ L
[Cu(SH) <sub>2</sub> ](Picrate) <sub>2</sub>	Nujol	18350 22470 37310, 39680	${}^2B_{1g} \rightarrow {}^2A_{1g}$ & ${}^2B_{1g} \rightarrow {}^2E_g$ L

<sup>max</sup> values are given in parentheses.

L = intraligand transitions.

 TABLE 3  
 IMPORTANT INFRARED SPECTRAL BANDS (cm<sup>-1</sup>) AND THEIR ASSIGNMENTS

Compound	$\nu(\text{OH})$	$\nu(\text{NH})$ & $\nu(\text{NH})_2$	$\delta(\text{HOH})$	$\nu(\text{C}=\text{O})$	$\beta(\text{NH}_2)$	$\nu(\text{N}-\text{N})$	$\rho_r(\text{H}_2\text{O})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$
BH(KBr)	—	3285, 3170	—	1664	1612	885	—	—	—
BH(CH <sub>2</sub> CN)	—	3350	—	1672	1634	—	—	—	—
[Mn(BH) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](Picrate) <sub>2</sub>	3600 <sub>m</sub> , 3500 <sub>m</sub> 3365 <sub>m</sub> , 3350 <sub>m</sub> 3200	3320 <sub>s</sub> , 3250 <sub>m</sub> 3200	1653 <sub>m</sub>	1640 <sub>s</sub>	1610	912	—	490	340
[Fe(BH) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](Picrate) <sub>2</sub>	3350 <sub>s</sub> , 3325 <sub>s</sub>	3285, 3090	1650 <sub>w</sub>	1633 <sub>s</sub>	1608	910	758	432	325
[Co(BH) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](Picrate) <sub>2</sub>	3365 <sub>s</sub> , 3330 <sub>s</sub>	3285, 3085	1654 <sub>m</sub>	1632 <sub>s</sub>	1605	910	—	468, 430	350
[Ni(BH) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](Picrate) <sub>2</sub>	3368 <sub>s</sub> , 3330 <sub>s</sub>	3265 <sub>m</sub> , 3200 <sub>m</sub>	1642 <sub>m</sub>	1630 <sub>s</sub>	1600	908	792	425	340
[Cu(BH) <sub>2</sub> ](Picrate) <sub>2</sub>	—	3140 <sub>s</sub> , 3085 <sub>m</sub>	—	1625 <sub>s</sub>	1608	912	—	464	366
[Zn(BH) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](Picrate) <sub>2</sub>	3365 <sub>s</sub> , 3332 <sub>s</sub>	3265 <sub>s</sub> , 3085 <sub>m</sub>	1654 <sub>m</sub>	1632 <sub>s</sub>	1600	906	—	446	350
[Mn(BH) <sub>2</sub> ](Picrate) <sub>2</sub> · 2H <sub>2</sub> O	3600 <sub>m</sub> , 3500 <sub>m</sub> , 3350 <sub>s</sub> , 3325 <sub>s</sub>	3250 <sub>s</sub> , 3200 <sub>s</sub>	1655 <sub>m</sub>	1642 <sub>s</sub>	1610	912	—	434	358
[Co(BH) <sub>2</sub> ](Picrate) <sub>2</sub> · H <sub>2</sub> O	3525 <sub>m</sub>	3275 <sub>s</sub> , 3170 <sub>s</sub>	1648 <sub>m</sub>	1625 <sub>s</sub>	1608	918	—	466, 432	350
[Ni(BH) <sub>2</sub> ](Picrate) <sub>2</sub> · H <sub>2</sub> O	3650 <sub>m</sub> , 3485 <sub>m</sub>	3290 <sub>s</sub> , 3215 <sub>s</sub>	1650 <sub>m</sub>	1625 <sub>s</sub>	1600	904	—	458	340
[Zn(BH) <sub>2</sub> ](Picrate) <sub>2</sub> · H <sub>2</sub> O	3545 <sub>m</sub> , 3400 <sub>m</sub>	3330 <sub>m</sub> , 3210 <sub>s</sub> 3085 <sub>m</sub>	1646 <sub>m</sub>	1632 <sub>s</sub>	1604	912	—	458	350
SH(Nujol)	—	3330, 3275	—	1640	1630	880	—	—	—
SH(CH <sub>2</sub> CN)	3620—3540	3330, 3230	—	1650	—	880	—	—	—
[Mn(SH) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](Picrate) <sub>2</sub>	3600 <sub>m</sub> , 3530 <sub>m</sub>	3320, 3290, 3200	1638	1620	1607	912	—	475	340
[Fe(SH) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](Picrate) <sub>2</sub>	3516, 3340 <sub>s</sub>	3315, 3245	1629	1616	1604	914	—	425	330
[Co(SH) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](Picrate) <sub>2</sub>	3465, 3385 <sub>s</sub>	3310, 3255	1635	1625	1608	914	756	454	312
[Ni(SH) <sub>2</sub> ](Picrate) <sub>2</sub>	3550 <sub>m</sub>	3300, 3260	—	1620	1600	912	—	492	340
[Cu(SH) <sub>2</sub> ](Picrate) <sub>2</sub>	3550 <sub>m</sub>	3220 <sub>s</sub>	—	1620	1612	916	—	458	344
[Zn(SH) <sub>2</sub> ](Picrate) <sub>2</sub>	3600 <sub>m</sub>	3285 <sub>s</sub> , 3205 <sub>s</sub>	—	1628	1605	908	—	490	354

S=Strong, m=Medium, w=Weak.

*Magnetic Susceptibility Studies*

Magnetic data of Table 1 show that *Zn(II)* complexes are diamagnetic as expected for a  $d^{10}$  electron configuration of the metal ion. The corrected magnetic moments of *Mn(II)*, *Fe(II)*, *Co(II)* and *Ni(II)* complexes suggest an octahedral arrangement of the ligands around the central metal ions<sup>13</sup>. The magnetic moments of  $[Cu(BH)_2](Picrate)_2$  and  $[Cu(SH)_2](Picrate)_2$  are close to those of *Cu(II)* square planar complexes<sup>14</sup>.

*Electronic Spectral Studies*

The u.v. spectrum of *BH* in ethanol gives a band at  $44400\text{ cm}^{-1}$  ( $\epsilon_{\max}=8136$ ) while that of *SH* in the same solvent yields two bands at  $33000$  and  $41320\text{ cm}^{-1}$  with  $\epsilon_{\max}$  values of  $5000$  and  $7800$  respectively. The nujol spectrum of *SH* also yields two bands at  $31750$  and  $41300\text{ cm}^{-1}$ . The  $44400$  and  $41300\text{ cm}^{-1}$  bands of *BH* and *SH* respectively appear to be due to  $\pi \rightarrow \pi^*$  transition of  $>C=O$  group in resonance with benzene ring while the  $33000\text{ cm}^{-1}$  band of *SH* may be attributed to the phenolic group<sup>15</sup>. It may be pointed out that the  $n \rightarrow \pi^*$  transitions expected for these compounds have not been observed presumably because of their occurrence in the same region as the more intense  $\pi \rightarrow \pi^*$  bands<sup>16</sup>.

The u.v. spectra of benzoyl hydrazine complexes in ethanol show two bands in  $27780$ - $28170$  and  $42550$ - $44050\text{ cm}^{-1}$  regions and a shoulder around  $25000\text{ cm}^{-1}$  with  $\epsilon_{\max}$  values in the ranges  $27000$ - $31000$ ,  $35000$ - $46500$  and  $16000$ - $21800$  respectively. The position and intensity of these bands suggest that they may be assigned to  $\pi \rightarrow \pi^*$  transition and intramolecular charge-transfer transition of the bonding  $\pi$ -electrons of the phenolic group to a vacant energy level of the nitrogroups<sup>17</sup>. The  $42550$ - $44050\text{ cm}^{-1}$  band in the complexes is presumably due to the coupling of  $41320$ - $41665\text{ cm}^{-1}$  band of the metal picrate<sup>3</sup> and  $44400\text{ cm}^{-1}$  band of *BH*. As expected the intensity of this band increases on complex formation.

Of the salicylyl hydrazine complexes studied in the present investigation, only *Co(II)* and *Fe(II)* complexes are sufficiently soluble in common organic solvents to permit the recording of their solution spectra. The ethanolic solution spectra of *Fe(II)* and *Co(II)*-*SH* complexes in u.v. region yield three bands in  $27780$ - $27930$ ,  $32260$ - $32250$  and  $42550\text{ cm}^{-1}$  regions and a shoulder at  $25000\text{ cm}^{-1}$  with  $\epsilon_{\max}$  values in the ranges  $19650$ - $23200$ ,  $16000$ - $17000$ ,  $35200$ - $37000$  and  $13500$  respectively. As discussed above these bands may be assigned to intraligand transitions.

The visible region spectrum of  $[Fe(BH)_2(H_2O)_2](Picrate)_2$  in ethanol shows one band at  $14600\text{ cm}^{-1}$  ( $\epsilon_{\max}=85$ ) which may be assigned to  ${}^5T_{2g} \rightarrow {}^5E_g$  (D) transition in octahedral environment of the metal ion<sup>18</sup>. Thus the  $10 Dq$  and LFSE values are  $14600\text{ cm}^{-1}$  and  $16.64\text{ kcal/mole}$  respectively. The  $d-d$  transition band of  $[Fe(SH)_2(H_2O)_2](Picrate)_2$  appears to have submerged under the high intensity intraligand band.

The spectra of  $[Co(BH)_2(H_2O)_2](Picrate)_2$  and  $[Co(SH)_2(H_2O)_2](Picrate)_2$  show a broad band at  $8930$  and  $9000\text{ cm}^{-1}$  respectively with the same  $\epsilon_{\max}$  value,  $6.25$ . *Co(II)*-*SH* complex shows an additional band at  $19400\text{ cm}^{-1}$  ( $\epsilon_{\max}=31$ ). The band found around  $9000\text{ cm}^{-1}$  is characteristic of octahedral cobalt (II) complexes and may be assigned to  ${}^4T_{1g} \rightarrow {}^4T_{2g}$  (F) transition. The broadening of this band suggests some tetragonal distortion in the above complexes<sup>7</sup>. Assignment of the second band in *Co(II)*-*SH* complex to  ${}^4T_{1g} \rightarrow {}^4T_{2g}$  (P) transition leads to  $10 Dq$  and  $B'$  values of  $10120$  and  $770\text{ cm}^{-1}$  respectively. The other ligand field parameters for the complex are:  $\beta=0.792$ ,  $\beta^0=20.78\%$ , LFSE— $20.78\text{ kcal/mole}$  and  $\lambda'=114\text{ cm}^{-1}$ .

The value of the Racah parameter  $B'$  for the complex show a considerable amount of covalency in the metal-ligand bond which is also supported by the value of the effective spin-orbit coupling constant,  $\lambda'$  ( $=63.3\%$  of the free metal ion value).

The two weak intensity bands occurring in the ranges  $9400$ - $10350$  and  $15400$ - $16800\text{ cm}^{-1}$  in the spectra of nickel (II) complexes may be assigned to  ${}^3A_{2g} \rightarrow {}^3T_{2g}$  (F),  $\nu_1$  and  ${}^3T_{1g}$  (F),  $\nu_2$  transitions respectively in  $O_h$  symmetry<sup>19</sup>. The ratio of  $\nu_2$  and  $\nu_1$  for the complexes lie in the range  $1.62$ - $1.64$ , usually accepted for octahedral nickel (II) complexes<sup>20</sup>. The splitting of  $\nu_1$  band in  $[Ni(BH)_2(H_2O)_2](Picrate)_2$  indicates a trans-octahedral geometry for the complex<sup>21</sup>. The values of the ligand field parameters calculated from  $\nu_1$  and  $\nu_2$  values are given in Table 4.

TABLE 4

LIGAND FIELD PARAMETERS FOR BH AND SH COMPLEXES OF NICKEL (II) PICRATE

Complex	$10 Dq$ ( $\text{cm}^{-1}$ )	$B'$ ( $\text{cm}^{-1}$ )	$\beta$	$\beta^\circ$ (%)	$\nu_2/\nu_1$	$\lambda'$ ( $\text{cm}^{-1}$ )	LFSE (kcal/ mole)
$[\text{Ni}(\text{BH})_2(\text{H}_2\text{O})_2](\text{Picrate})_2$	9400	900	0.852	14.77	1.63	195	32.00
$[\text{Ni}(\text{BH})_2](\text{Picrate})_2 \cdot \text{H}_2\text{O}$	9760	934	0.884	11.55	1.64	152	33.37
$[\text{Ni}(\text{SH})_2](\text{Picrate})_2$	10350	912	0.863	13.63	1.62	143	36.00

According to the average environment rule, the  $Dq$  value of  $[\text{Ni}(\text{BH})_2(\text{H}_2\text{O})_2](\text{Picrate})_2$  should be  $934 \text{ cm}^{-1}$  which is in excellent agreement with the observed value of  $940 \text{ cm}^{-1}$ . The value of  $Dq$  and  $B'$  (Table 4) suggest a place between water and ammonia for the ligands with the following order of the spectrochemical series :



The electronic spectra of  $[\text{Cu}(\text{BH})_2](\text{Picrate})_2$  and  $[\text{Cu}(\text{SH})_2](\text{Picrate})_2$  show one band at  $16950$  and  $18350 \text{ cm}^{-1}$  respectively which may be assigned to the envelope of  ${}^2B_{1g} \rightarrow {}^2A_{1g}$  and  ${}^2B_{1g} \rightarrow {}^2E_g$  transitions as reported for a number of square planar complexes<sup>19</sup> of copper (II).

### Infrared Spectral Studies

The bands occurring in the ranges  $3650$ - $3350$  and  $3530$ - $3465 \text{ cm}^{-1}$  in the spectra of the hydrated complexes of  $\text{BH}$  and  $\text{SH}$  respectively which are absent in the anhydrous complexes may be assigned to  $\nu(\text{OH})$  of the water molecules. The  $\nu(\text{OH})$  occurring at  $3620$ - $3540 \text{ cm}^{-1}$  in  $\text{SH}$  in the acetonitrile solution is shifted to  $3600$ - $3550 \text{ cm}^{-1}$  in the spectra of its anhydrous metal complexes indicating that this group is not involved in bonding. The small negative shift appears to be due to intermolecular hydrogen bonding between phenolic group of the ligand and the nitro group of the picrate ion and this seems to be the reason for  $-\text{OH}$  group not involving in coordination. The spectra of benzoyl hydrazine in  $\text{KBr}$  and acetonitrile solution have been discussed by Mashima<sup>22</sup>.  $\text{BH}$  shows only one band at  $3350 \text{ cm}^{-1}$  while  $\text{SH}$  shows two bands at  $3330\text{s}$  and  $3230\text{w} \text{ cm}^{-1}$  in the acetonitrile solution spectra assigned to  $\nu(\text{NH})$  and these bands shift to  $3320$ - $3140$  and  $3310$ - $3060 \text{ cm}^{-1}$  in their respective complexes. A negative shift in  $\nu(\text{NH})$  of  $30$ - $210 \text{ cm}^{-1}$  in the  $\text{BH}$  complexes and  $10$ - $110 \text{ cm}^{-1}$  in the  $\text{SH}$  complexes indicate that  $-\text{NH}-$  and/or  $-\text{NH}_2$  groups are involved in coordination. The spectrum of  $\text{BH}$  shows a band at  $1672 \text{ cm}^{-1}$  assigned<sup>22</sup> to  $\nu(\text{C}=\text{O})$ . Salicylyl hydrazine shows two bands at  $1642$  and  $1630 \text{ cm}^{-1}$  in solid state while in solution it gives only one band at  $1650 \text{ cm}^{-1}$ . The bands at  $1642$  and  $1630 \text{ cm}^{-1}$  may be assigned to  $\nu(\text{C}=\text{O})$  and  $\beta(\text{NH}_2)$  respectively. Because of the breakdown of the hydrogen bonding in solution,  $\beta(\text{NH}_2)$  and  $\nu(\text{C}=\text{O})$  are expected to occur at higher frequency than in the solid state. The existence of broad band at  $1650 \text{ cm}^{-1}$  in the solution spectrum of  $\text{SH}$  may be due to the coupling of  $\nu(\text{C}=\text{O})$  and  $\beta(\text{NH}_2)$  modes. A strong band occurring at  $1642$ - $1625$  and  $1628$ - $1616 \text{ cm}^{-1}$  in the spectra of the metal complexes of  $\text{BH}$  and  $\text{SH}$  respectively may be assigned to  $\nu(\text{C}=\text{O})$ . A negative shift of  $30$ - $47$  and  $20$ - $32 \text{ cm}^{-1}$  in  $\nu(\text{C}=\text{O})$  indicates coordination through the carbonyl oxygen. The bands occurring in the ranges  $1600$ - $1610$  and  $1600$ - $1612 \text{ cm}^{-1}$  in the  $\text{BH}$  and  $\text{SH}$  complexes respectively may be assigned to  $\beta(\text{NH}_2)$ . A negative shift of  $24$ - $34$  and  $38$ - $50 \text{ cm}^{-1}$  in this mode indicates coordination taking place through the primary amine nitrogen of the ligand. The  $\nu(\text{N}-\text{N})$  band occurring at  $885$  and  $880 \text{ cm}^{-1}$  in  $\text{BH}$  and  $\text{SH}$  are shifted in  $910$ - $918$  and  $908$ - $916 \text{ cm}^{-1}$  ranges respectively in their complexes. Thus the  $\nu(\text{N}-\text{N})$  falls in the range reported for the complexes in which only one of the nitrogens of acyl hydrazines is involved in bonding<sup>23,24</sup>. The bands observed in the range  $792$ - $756 \text{ cm}^{-1}$  in  $[\text{ML}_2(\text{H}_2\text{O})_2](\text{Picrate})_2$  type of complexes which are absent in the anhydrous complexes may be assigned to  $\rho_r(\text{H}_2\text{O})$  mode of the coordinated water molecule<sup>25</sup>. The non-ligand bands occurring in the ranges  $492$ - $425$  and  $366$ - $312 \text{ cm}^{-1}$  regions may be assigned to  $(\text{M} \leftarrow \text{O})$  and  $(\text{M} \leftarrow \text{N})$  vibrations respectively<sup>26</sup>.

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