

HYDRAZINE COMPLEXES OF SOME FIRST ROW TRANSITION METAL (II) PICRATES AND PICRAMATES

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Hydrazine complexes of the compositions $M(N_2H_4)_2$ (Picrate)₂ H_2O (where $M = Mn$ (II), Ni (II), Cu (II) or Zn (II), Co (N_2H_4) (Picrate)₂, Ni (N_2H_4)₃ (Picrate)₂, $Zn(N_2H_4)_4$ (Picrate)₂, and M' (N_2H_4)₂ (Picramate)₂ (where $M' = Mn$ (II), Fe (II), Co (II), Ni (II), Cu (II) or Zn (II)) have been prepared and characterized by analysis, molar conductance, magnetic susceptibility, electronic and infrared spectral data. Molar conductances of the soluble complexes indicate that they are non-electrolytes in THF. Magnetic susceptibility and electronic spectral data suggest that all the complexes are spin-free octahedral except $Co(N_2H_4)$ (Picrate)₂ which is tetrahedral. Infrared spectral studies show that hydrazine behaves as a monodentate ligand in its complexes with metal picramates and as a bidentate bridging ligand in all complexes with metal (II) picrates, except $Zn(N_2H_4)_4$ (Picrate)₂ where it is monodentate.

A large number of complexes of hydrazine with transition and non-transition metal ions have been prepared in which it has been found to act as a monodentate^{1,2} or bidentate bridging ligand^{3,4}. Since, there is no previous work on the complexes of hydrazine with transition metal picrates and picramates, it was thought of interest to undertake such a study and the results of these investigations are described in the present communication.

EXPERIMENTAL PROCEDURE

All the chemicals used were of BDH or equivalent quality. Metal picrates and picramates were prepared as described earlier^{5,6}.

Preparation and analysis of the complexes

$M(N_2H_4)_2$ (picrate)₂ H_2O and $Co(N_2H_4)$ (Picrate)₂ were prepared by mixing ~5% ethanolic solutions of hydrazine hydrate and metal picrates. The yellow precipitate formed in each case was magnetically stirred for ~ $\frac{1}{2}$ hr., filtered, washed with ethanol and dried in air.

$Zn(N_2H_4)_4$ (Picrate)₂ and $Ni(N_2H_4)_3$ (Picrate)₂ were prepared by adding ~50% ethanolic solution of hydrazine hydrate to about 10% solution of metal picrates in the same solvent. The yellow coloured complexes precipitating from the solutions were filtered, washed with ethanol and dried as before.

$M'(N_2H_4)_2$ (Picramate)₂ were prepared by adding ~10% ethanolic solution of hydrazine hydrate to an ethanolic suspension of metal (II) picramate and magnetic stirring for ~6 hr. The resulting solid product in each case was filtered, washed several times with ethanol and dried at ~80°C.

The hydrazine complexes prepared as described above were analysed for metal, nitrogen and/or hydrazine as described earlier^{6,7}. The analytical data are given in Table 1.

TABLE 1

ANALYTICAL DATA, COLOUR, MOLAR CONDUCTANCES, MAGNETIC MOMENTS AND MELTING POINTS OF HYDRAZINE COMPLEXES OF TRANSITION METAL PICRATES AND PICRAMATES

Complexes	Colour	Metal (%)	N_2H_4 (%)	Nitrogen (%)	Molar conductance at 10^{-3} M in THF	μ eff. (B.M.)	M. P./exp. temperature
$Mn(N_2H_4)_2$ (Picrate) ₂ H_2O	Yellow	9.50 (9.27)	11.00 (10.79)		33.00	5.92	210
$Ni(N_2H_4)_2$ (Picrate) ₂ H_2O	Dirty-yellow	9.50 (9.81)	10.65 (10.72)	23.69 (23.45)	33.75	3.00	175(exp.)
$Cu(N_2H_4)_2$ (Picrate) ₂ H_2O	Yellow	11.02 (10.56)	10.14 (10.63)	..		1.99	>250

TABLE 1

Complexes	Colour	Metal (%)	N_2H_4 (%)	Nitrogen (%)	Molar conductance at 10^{-3} M in THF	μ eff. (B.M.)	M.P./exp. temperature
$Zn(N_2H_4)_2(Picrate)_2 \cdot H_2O$	Yellow	11.00 (10.77)	10.74 (10.61)		36.50	diamag.	190
$Co(N_2H_4)(Picrate)_2$	Dark-brown	11.53 (10.78)	5.98 (5.83)	20.02 (20.47)		4.40	
$Ni(N_2H_4)_3(Picrate)_2$	Yellow	10.30 (10.46)	15.88 (15.71)			3.01	
$Zn(N_2H_4)_4(Picrate)_2$	Yellow	10.20 (10.10)	19.87 (17.40)	20.72 (29.20)		diamag.	165(exp.)
$Mn(N_2H_4)_2(Picramate)_2$	Orange	10.82 (10.68)	11.80 (12.40)	26.86 (27.18)		6.14	
$Fe(N_2H_4)_2(Picramate)_2$	Dark-brown	11.03 (10.82)	11.82 (12.36)			5.04	
$Co(N_2H_4)_2(Picramate)_2$	Brown	11.60 (11.38)	11.43 (12.33)	26.55 (26.70)		5.06	>250
$Ni(N_2H_4)_2(Picramate)_2$	Light red	10.56 (11.30)	12.76 (12.33)	26.96 (26.90)		3.18	>250
$Cu(N_2H_4)_2(Picramate)_2$	Chocolate brown	11.47 (12.13)	13.00 (12.20)			1.91	>250
$Zn(N_2H_4)_2(Picramate)_2$	Reddish-yellow	13.08 (12.38)	12.50 (12.20)	26.45 (26.66)		diamag.	

Calculated values are given in parentheses

Physical measurements

Equipments and the methods employed for the measurements of molar conductance, magnetic susceptibility, electronic and infrared spectra were the same as used in our previous studies^{5,6}. The pertinent experimental data are given in Tables 1, 2 & 3.

DISCUSSION

Hydrazine forms 1:2 (Metal : Ligand) complexes with $Mn(II)$, $Ni(II)$, $Cu(II)$ and $Zn(II)$ picrates as well as with $Mn(II)$, $Fe(II)$, $Co(II)$, $Ni(II)$, $Cu(II)$ and $Zn(II)$ picramates whereas it yields 1:1 complex with $Co(II)$ picrate. It also gives 1:3 and 1:4 complexes with $Ni(II)$ and $Zn(II)$ picrates respectively (Table 1). $Mn(N_2H_4)_2(Picrate)_2 \cdot H_2O$ and $Zn(N_2H_4)_2(Picrate)_2 \cdot H_2O$ melt with decomposition at 210° and 190°C, respectively while the other complexes explode when heated above 250°C, except $Ni(N_2H_4)_2(Picrate)_2 \cdot H_2O$ and $Zn(N_2H_4)_4(Picrate)_2$, which explode at 175° and 165°C respectively. $Mn(N_2H_4)_2(Picrate)_2 \cdot H_2O$ and $Mn(N_2H_4)_2(Picramate)_2$ also explode violently on addition of concentrated sulphuric acid. All the complexes are insoluble in benzene, chloroform, carbon tetrachloride, ethanol, methanol etc. while complexes of the type $M(N_2H_4)_2(Picrate)_2 \cdot H_2O$ are slightly soluble in THF and the values of the molar conductance of these compounds in the above solvent show that they are non-electrolyte. All hydrazine complexes of metal picrates are slightly soluble in DMF giving intense yellow colour.

Magnetic susceptibility studies

The magnetic data of Table 1 show that $Zn(II)$ complexes are diamagnetic as expected for d^{10} electronic configuration of the metal ion. The magnetic moment of $Ni(N_2H_4)_3(Picrate)_2$ and $M'(N_2H_4)_2(Picrate)_2 \cdot H_2O$ and $M'(N_2H_4)_2(Picramate)_2$ types of complexes are well within the range reported for high-spin octahedral complexes of these metal ions⁸. The magnetic moment of $Co(N_2H_4)(Picrate)_2$ is close to the tetrahedral complexes⁹ of $Co(II)$.

Electronic-spectral studies

The nujol spectra of all the hydrazine complexes of metal picrates and picramates generally yield three to four bands in the u.v. region (Table 2) which correspond to the bands of parent metal picrates and picramates and are therefore assigned to intraligand transitions ^{5,6}.

TABLE 2

ELECTRONIC SPECTRAL BANDS (IN NUJOL) OF THE HYDRAZINE COMPLEXES OF TRANSITION METAL PICRATES AND PICRAMATES

Complex	Bands (cm ⁻¹)	Assignments	Stereochemistry
<i>Mn</i> (N ₂ H ₄) ₂ (Picrate) ₂ . H ₂ O	23800, 27780, 30300sh, 37735 42550	L	Octahedral
<i>Co</i> (N ₂ H ₄) ₂ (Picrate) ₂	5800, 6900 23000, 27030, 37850	⁴ A ₂ → ⁴ T ₁ (F) : ν ₂ L	Tetrahedral
<i>Ni</i> (N ₂ H ₄) ₂ (Picrate) ₂ .H ₂ O	10500 23000, 27400, 37700	³ A _{2g} → ³ T _{2g} (F) L	Octahedral
<i>Ni</i> (N ₂ H ₄) ₃ (Picrate) ₂	10800 23000, 27200, 37700, 42000	³ A _{2g} → ³ T _{2g} (F) L	
<i>Cu</i> (N ₂ H ₄) ₂ (Picrate) ₂ .H ₂ O	13400 23530, 27780, 38500	² E _g → ² T _{2g} L	
<i>Zn</i> (N ₂ H ₄) ₂ (Picrate) ₂	23000, 27400, 39200	L	—
<i>Mn</i> (N ₂ H ₄) ₂ (Picramate) ₂	25000, 27400, 40000	L	Octahedral
<i>Co</i> (N ₂ H ₄) ₂ (Picramate) ₂	10250 24400, 35100, 4000	⁴ T _{1g} → ⁴ T _{2g} (F) L	
<i>Ni</i> (N ₂ H ₄) ₂ (Picramate) ₂	10300, 17200	³ A _{2g} → ³ T _{2g} (F), ³ T _{1g} (F) L	
<i>Cu</i> (N ₂ H ₄) ₂ (Picramate) ₂		³ E _g → ² T _{2g} L	

L=Intraligand transitions

The position and the number of electronic spectral bands and the assignments thereof as given in Table 2 indicate that *Co*(N₂H₄)₂ (Picrate)₂ is tetrahedral^{10,11} while *Ni* (N₂H₄)₂ (Picrate)₂. H₂ O, *Ni* (N₂H₄)₃ (Picrate)₂, *Ni* (N₂H₄)₂ (Picramate)₂, *Cu* (N₂H₄)₂ (Picrate)₂ and *Cu* (N₂H₄)₂ (Picramate)₂ are octahedral^{12,13,14}. The 10D_q and LFSE for these complexes calculated from the first transition are given in Table 3.

TABLE 3

 10 D_q AND LFSE OF HYDRAZINE COMPLEXES OF FIRST TRANSITION METAL PICRATES AND PICRAMATES

Complex	10 D _q cm ⁻¹	LFSE (kcal/mole)
<i>Ni</i> (N ₂ H ₄) ₂ (Picrate) ₂ . H ₂ O	10500	36.0
<i>Ni</i> (N ₂ H ₄) ₃ (Picrate) ₂	10800	37.02
<i>Ni</i> (N ₂ H ₄) ₂ (Picramate) ₂	10300	35.51

Infrared spectral studies

The infrared spectral bands of hydrazine and their assignments are described in the literature^{15,16}. These assignments have been used for interpreting the I.R. spectra of hydrazine complexes under the present study (Table 4).

TABLE 4
IMPORTANT INFRARED SPECTRAL BANDS (CM^{-1}) AND THEIR ASSIGNMENTS FOR THE HYDRAZINE COMPLEXES OF TRANSITION METAL (II) PICRATES AND PICRAMATES

Compound	$\nu(\text{OH})$	$\nu(\text{N}-\text{H})$	$\frac{\delta(\text{NH}_2)}{\delta(\text{HOH})}$	$\nu(\text{N}-\text{N})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$
<i>Mn</i> (N_2H_4) ₂ (Picrate) ₂ · H ₂ O	3450m, 3360m	3285s, 3230m	1628m 1604m	962m	392	243
<i>Co</i> (N_2H_4) (Picrate) ₂		3275s, 3230m	1627m 1607m	975w	416	370
<i>Ni</i> (N_2H_4) ₂ (Picrate) ₂ · H ₂ O	3500	3260s, 3160m	1627s 1608s	975w	454	392
<i>Zn</i> (N_2H_4) ₂ (Picrate) ₂ · H ₂ O	3532, 3415m	3360s, 3340 3168m	1628s 1608s	967m	425	384
<i>Cu</i> (N_2H_4) ₂ (Picrate) ₂ · H ₂ O	3550w, 3366	3324, 3232, 3100	1632s 1608m	986m	462	392
<i>Zn</i> (N_2H_4) ₄ (Picrate) ₂		3400, 3360, 3310, 3260, 3150	1622s, 1606m	933w		350
<i>Ni</i> (N_2H_4) ₃ (Picrate) ₂		3285, 3150	1625s, 1608	975w		400
<i>Mn</i> (N_2H_4) ₂ (Picramate) ₂		3470, 3385, 3315, 3270, 3190, 3110	1625m, 1618 1615	915	430	330
<i>Fe</i> (N_2H_4) ₂ (Picramate) ₂		3473; 3370, 3310, 3268, 3185	1625, 1610	920	440	335
<i>Co</i> (N_2H_4) ₂ (Picramate) ₂		3430, 3360, 3310, 3270, 3180.	1620, 1610	915	460	350
<i>Ni</i> (N_2H_4) ₂ (Picramate) ₂		3500, 3385, 3310, 3265, 3240, 3190, 3146	1645m, 1615m	932	468	370
<i>Cu</i> (N_2H_4) ₂ (Picramate) ₂		3530, 3435, 3285, 3240, 3184, 3100	1620m, 1604	935	490	384
<i>Zn</i> (N_2H_4) ₂ (Picramate) ₂		3445m, 3354s, 3325s 3260s, 3160m, 3100	1624m, 1610m	920	430	390

s = strong; M = medium; w = weak

All the compounds of metal picrates with hydrazine, except $\text{Zn}(\text{N}_2\text{H}_4)_4$ (Picrate)₂ have strong broad bands in the $\text{N}-\text{H}$ stretching frequency region which occur at a lower frequency compared to the location of these bands in hydrazine. The negative shifts observed in $\nu(\text{N}-\text{H})$ in the above complexes are analogous to those reported for $\text{MCl}_2(\text{N}_2\text{H}_4)_2$ complexes³ where hydrazine has been shown to function as bidentate bridging ligand.

Metal picramates give two bands⁶ at ~ 3310 and $3270-3240 \text{ cm}^{-1}$ in NH stretching frequency region and their position remains practically unchanged in their hydrazine complexes indicating that $-\text{NH}_2$ group of metal picramates remains coordinated to the metal ions. The spectra of the hydrazine complexes in addition to these two bands show generally four other bands in $\nu(\text{NH})$ region. Two of them occur on the higher frequency side and the other two on the lower frequency side of the two bands of the $-\text{NH}_2$ group of metal picramates. The latter bands suffer a negative shift and the former bands a positive shift in the hydrazine complexes as compared with the vapour phase spectrum of hydrazine⁽¹⁵⁾. From these observations it may be concluded that hydrazine acts as a monodentate ligand in the metal picramate-hydrazine complexes. This conclusion is in accord with the position of the NH stretching bands of hydrazine observed in $\text{BH}_3\text{N}_2\text{H}_4$, SiF_4 , $2\text{N}_2\text{H}_4$, GeF_4 , $2\text{N}_2\text{H}_4$ and $(\text{CH}_3)_3\text{B}\cdot\text{N}_2\text{H}_4$ where hydrazine is known to act as a monodentate ligand^{2, 16 & 17}.

N-N Stretching bands

$\nu(N-N)$ in the vapour phase spectrum of hydrazine is reported to occur² at $\sim 873 \text{ cm}^{-1}$ and is shifted to higher frequency on complex formation¹⁸. It is reported to occur in 936-931 and 980-948 cm^{-1} regions for unidentate and bidentate coordination of hydrazine respectively¹⁹. The occurrence of $\nu(N-N)$ in the hydrazine complexes of metal picramates and $Zn(N_2H_4)_4(\text{Picrate})_2$ and all other complexes in 938-932 and 975-962 cm^{-1} regions respectively shows that the hydrazine behaves as a monodentate ligand in the first case and as a bidentate bridging ligand in the second case.

Metal-oxygen (M-O) and metal-nitrogen (M-N) stretching bands

The non-ligand bands occurring in 490-392 and 400-342 cm^{-1} regions may be tentatively assigned to $\nu(M-O)$ ^{20,22} and $\nu(M \leftarrow N)$ ^{3,23} vibrations respectively.

The I.R. data taken from Table 3 on the variation of *N-H*, *N-N* and *M-N* stretching modes indicate the stability sequence $Mn < Fe < Co < Ni < Cu > Zn$ for the hydrazine complexes under the present study. This order is the same as the well known Irving-William order for the stability of the complexes²⁴ of *Mn* (II) to *Zn* (II).

Importance in Defence

Since all the hydrazine complexes of metal picrates and picramates prepared in the present investigation decompose with explosive violence when heated, and some of them viz. $Mn(N_2H_4)_2(\text{Picrate})_2 \cdot H_2O$ and $Mn(N_2H_4)_2(\text{Picramate})_2$ also explode violently on addition of concentrated sulphuric acid, they are considered to be of great importance in Defence Science as Explosives and Detonators.

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