

Preparation, characterization and thermal properties of di-N-isothiocyanatodihydrazine metal (II)

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Abstract. Complexes of the type $[M(N_2H_4)_2(NCS)_2]$, where $M = Mn(II), Fe(II), Co(II), Ni(II), Zn(II), Cd(II)$ and $Mg(II)$ have been prepared and characterized by chemical analysis, infrared and Mössbauer spectroscopy and magnetic moments. Hydrazine acts as a bridge between the two metal ions through the N-atom forming a distorted octahedral environment around the metal ion. Thermal decomposition of the complexes was studied in air and nitrogen atmosphere using TG and DTA techniques. The thermal stability of the complexes in nitrogen and the M-N stretching frequencies of M-NCS and M-N₂H₄ obey Irwing-Williams order for the bivalent metal complexes *i.e.* $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} > Zn^{2+} > Cd^{2+}$

Keywords. Hydrazine complexes; infrared spectra; thermal decomposition.

1. Introduction

This work stems from our interest in metal complexes of hydrazine (Patil *et al* 1982, 1982a). Specifically, we deal here with the reactions of N_2H_5SCN with several transition metal ions as well as with Mg and Cd. Complexes of the type $[M(N_2H_4)_2(SCN)_2]$ have been isolated and thoroughly characterized using several physical methods. The thermal decomposition of the complexes is also examined. Several fragmentary studies on such complexes or related species are reported in literature (Srivastava *et al* 1980; Ray and Sarkar 1920; Anangnaostopoulus and Nicholls 1976; Aggarwal and Vallabhaneni 1978; Furlani *et al* 1970; Braibanti *et al* 1968; Ferrari *et al* 1961; Duval 1967). Our work constitutes the first systematic exploration of these complexes.

2. Experimental

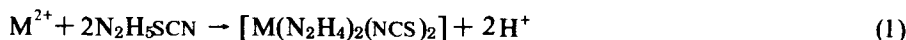
Materials employed: Hydrazine hydrate, $N_2H_4 \cdot H_2O$ was a BDH product (99-100%). Ammonium thiocyanate was GR grade from Sarabhai M. Chemicals, India. The metal salts used were guaranteed pure reagents.

2.1 Preparation of Di N-isothiocyanatodihydrazine metal(II)

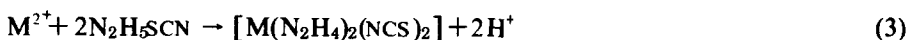
The complexes were prepared by the following two methods: *Method 1:* Stoichiometric quantities of metal(II) salts like chlorides or sulphates of Mn, Fe, Co, Ni, Zn or Cd in alcohol water mixture (1:1 by volume) were added to hydrazinium thiocyanate in 1:2 mole ratio. Alternatively, the metal salt was mixed with ammonium thiocyanate

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and hydrazine hydrate in the mole ratio 1:2:2 in each case, when the complex precipitated. The reaction can be represented as follows:



The precipitated complex was filtered, washed with water followed by alcohol and dried over anhydrous calcium chloride in a desiccator. Yield ~95%. *Method 2:* Metal powders free from the oxide film, were dissolved separately in a solution of N_2H_5SCN as such or metathetically formed by the reaction of $N_2H_4H_2O$ with NH_4SCN . The reaction takes place as follows with the evolution of hydrogen.



All the reactions are exothermic but with different magnitude. Magnesium reacts violently, while the reactions with other metals such as Fe, Ni, Co and Zn are hastened by stirring the solution magnetically and raising the temperature to 40–45° C. The complexes precipitated were separated from the remaining metal powders magnetically and/or by centrifuging and filtered. The complexes were washed with water and alcohol as before and dried over anhydrous calcium chloride. Yield for magnesium complex ~95%; iron complex ~80%; cobalt, nickel and zinc ~30%.

The reaction of N_2H_5SCN with copper salts results in the reduction of Cu(II) to Cu(I) or metallic copper depending on the experimental conditions. The copper complex $[Cu(N_2H_4)_2(NCS)_2]$ could not be prepared as described by Srivastava *et al* (1980). The complex could not be prepared even starting with copper powder.

2.2 Analyses

The metal ions present in all the complexes were estimated using EDTA complexometric titration. The thiocyanate content was estimated gravimetrically as $Cu_2(NCS)_2$ while the hydrazine was estimated volumetrically using KIO_3 solution as a titrant under Andrews conditions after accounting for the thiocyanate interference (Vogel 1951).

2.3 Physico-chemical studies

Magnetic susceptibility was measured by the standard Gouy method at room temperature (23° C) using powdered samples of the complexes. The infrared spectra of the complexes in Nujol mull were recorded on a Perkin-Elmer spectrometer (model no. 597) in the region 200–4000 cm^{-1} . The Mössbauer spectrum of the complex $[Fe(N_2H_4)_2(NCS)_2]$ was recorded at room temperature (25° C) on an ECIL spectrometer (model MBS-35) with multichannel analyzer. The radioactive source (γ -ray emitter) was ^{57}Co in palladium matrix and the drive velocity was 0.06 $mm\ sec^{-1}$. The isomer shift was reported with reference to steel.

The DTA experiments were carried out by a DTA unit constructed for controlled atmosphere as described by Savant and Patel (1968), fitted with a two-pen strip chart recorder. About 100 mg of the powdered samples were used with close packing. The TG experiments were carried out using a Stanton Redcroft 750/770 thermobalance. The sample weight taken was about 7 mg. Both TG and DTA experiments were done in

air and nitrogen atmospheres with a flow rate of 25 ml min⁻¹ with a heating rate of 10° C min⁻¹.

3. Results and discussion

Results of chemical analysis and the magnetic moment data are in table 1. All the complexes are insoluble in water except the magnesium complex. The complexes

Table 1. Chemical analyses and magnetic moments of $[M(N_2H_4)_2(NCS)_2]$.

$[M(N_2H_4)_2(NCS)_2]$ M(II)=	Colour	μ_{eff} (BM) 23° C		%Metal		%N ₂ H ₄		%NCS	
		Found	Calc. for spin only formula	Found	Calc.	Found	Calc.	Found	Calc.
Mn	White	5.87	5.91	23.24	23.38	26.98	27.25	49.84	49.37
Fe	White	4.91	4.89	23.33	23.68	27.73	27.14	48.25	49.18
Co	Pink	4.70	3.87	24.62	24.66	27.25	26.79	47.96	48.55
Ni	Blue	2.82	2.82	25.14	24.59	26.73	26.81	48.11	48.60
Zn	White	-	-	26.70	26.64	25.65	26.09	48.33	47.27
Cd	White	-	-	38.21	38.44	22.20	21.89	40.40	39.67
Mg	White	-	-	11.86	11.90	31.33	31.32	57.08	56.78

Table 2. Infrared spectra and the probable assignments for $[M(N_2H_4)_2(NCS)_2]$.

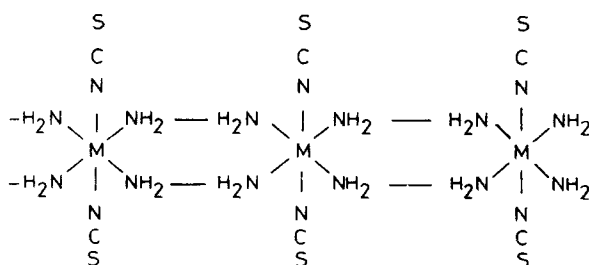
Mn	Fe	Co	Ni	Zn	Cd	Mg	Assignments
3222 s	3315	3308	3320	3328	3323	3332	
3300 s	3295	3290	3308	3304	3300	3312	
3215 s	3200	3200	3220	3212	3238	3224	N-H stretchings
3150 w	3135	3140	3142	3138	3155	3165	
2088 s	2070	2068	2092	2075	2070	2084	C-N stretchings
2024 sh	2010	2020	2024	2025	2020	2030	
1605 sh	1603	1600	1607	-	1588	1607	
1593 s	1590	1586	1593	1597	1587	1593	NH ₂ bending
1580 s	1572	1568	1573	1578	1578	1573	
1558 sh	1558	-	1560	-	-	1560	
1409 sh	-	1418	1410	-	-	1410	
1364 sh	1368	-	1368	1368	1368	1350	
1339 m	1340	1338	1342	1342	1342	1313	NH ₂ wagging
1296 m	1300	1302	1310	1306	1294	1310	
1174 m	1183	1191	1206	1189	1164	1195	
1140 s	1150	1152	1164	1153	1140	1156	NH ₂ twisting
960 sh	-	-	-	-	-	974	
951 s	960	965	975	958	960	963	N-N stretching
941 sh	-	945	-	-	936	-	
793 m	796	794	795	792	788	802	C-S stretching
569 s	582	595	619	600	580	586	NH ₂ asym rocking
494 s	515	539	575	536	502	523	NH ₂ sym rocking
479 s	480	480	478	482	477	489	NCS bending
471 s	473	472	468	468	468	482	
460 sh	-	435	-	-	-	-	
330 m	354	367	395	354	335	383	M-N (of N ₂ H ₄) stretching
312 sh	331	342	362	315	300	343	M-N (of NCS) stretching

Note: s-strong, w-weak, sh-shoulder and m-medium

prepared by both the methods are identical. The transition metal complexes are of high spin type, showing that hydrazine and thiocyanate are weak ligands. These values are in good agreement with those reported earlier. (Anagnaostopoulus and Nicholls 1976; Aggarwal and Vallabhaneni 1978).

3.1 Bonding and structure of the complexes

The infrared spectra of all the metal complexes are closely similar (table 2). The probable assignments of the frequencies are made on the basis of the comparison with earlier studies on hydrazine (Braibanti *et al* 1968; Sacconi and Sabatini 1963) as well as thiocyanate (Norbury 1975; Burmeister 1972) complexes. The thiocyanate is bonded to the metal through N-atom, as evidenced from the characteristic ν_{CN} , $\nu_{\text{C-S}}$ and δ_{NCS} around 2075, 790 and 480 cm^{-1} respectively. The N-N stretching frequency is observed around 960 cm^{-1} indicating the presence of hydrazine bridging between the two metal ions (Braibanti *et al* 1968). The metal-nitrogen stretching frequencies, $\nu_{\text{M-N}}$ of hydrazine and $\nu_{\text{M-N}}$ of thiocyanate are observed around 400 and 350 cm^{-1} respectively. The $\nu_{\text{M-N}}$ of hydrazine is almost of double intensity as that of $\nu_{\text{M-N}}$ of NCS, supporting the assignments since the $\text{NH}_2:\text{NCS}$ ratio is 2:1 in these complexes. Further, since the two $\nu_{\text{M-N}}$ frequencies are observed, it shows that the bond strength of M-N of NCS is slightly lower than that of M-N of N_2H_4 , suggesting that the molecular symmetry around the metal ion is not perfect octahedral, but a distorted one and the molecule is axially compressed. The molecular symmetry around the metal ion is therefore, D_{4h} . The IR assignments are in good agreement with the proposed polymeric structure (Ferrari *et al* 1961) as given below:



The Mössbauer spectrum of $[\text{Fe}(\text{N}_2\text{H}_4)_2(\text{NCS})_2]$ shows a two-finger pattern with the isomer shift (IS) value of 1.03 mm sec^{-1} and the quadrupole splitting (QS) value of 1.54 mm sec^{-1} . The observed values indicate the presence of high spin Fe^{2+} in distorted octahedral environment (Bancroft and Platt 1972) and are comparable with those of $[\text{Fe}(\text{IQ})_4(\text{NCS})_2]$, where IQ = isoquinoline (C.S. = 1.37 mm sec^{-1} and QS = 1.50 mm sec^{-1}) and $[\text{Fe}(\text{Py})_4(\text{NCS})_2]$ (C.S., = 1.35 mm sec^{-1} and QS = 1.54 mm sec^{-1}).

3.2 Thermal decomposition of $[\text{M}(\text{N}_2\text{H}_4)_2(\text{NCS})_2]$

The results of TG and DTA studies both in air and nitrogen atmospheres are summarized in tables 3 and 4 respectively. Both Mn(II) and Zn(II) complexes decompose to the corresponding metal isothiocyanates in the temperature range of 190–250°C with the loss of two molecules of hydrazine, producing nitrogen and ammonia which were identified by mass spectra. The solid intermediates were found to be metal isothiocyanates from the observed weight loss, qualitative tests and the IR spectra (ν_{CN} of NCS,

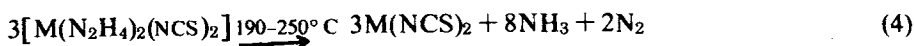
Table 3. Thermal decomposition of $[M(N_2H_4)_2(NCS)_2]$ in nitrogen.

$[M(N_2H_4)_2(NCS)_2]$	DTA peak temp. °C	TG Temp. region °C	% wt loss		Proposed reaction products
			Obsd.	Calcd.	
$[Mn(N_2H_4)_2(NCS)_2]$	197(+)	190-250	27.20	27.25	$Mn(NCS)_2$
	-	530-620	62.50	63.00	MnS
$[Fe(N_2H_4)_2(NCS)_2]$	218(+)	200-230	39.00	40.72	$Fe(NCS)_2^*$ $Fe(CN)_2$ or $Fe(NCS)(CN)$
	-	440-550	62.50	62.76	FeS
$[Co(N_2H_4)_2(NCS)_2]$	222(+)	215-260	39.21	40.19	$Co(NCS)_2 +$ $Co(CN)_2$ or $Co(NCS)(CN)$
	334(+)	370-500	62.90	62.00	CoS
$[Ni(N_2H_4)_2(NCS)_2]$	240(+)	230-280	41.80	40.24	$Ni(NCS)_2 +$ $Ni(CN)_2$ or $Ni(NCS)(CN)$
	-	-	-	62.02	NiS^*
$[Zn(N_2H_4)_2(NCS)_2]$	198(-)				
	204(+)	195-240	25.00	26.08	$Zn(NCS)_2$
	-	450-600	58.70	60.33	ZnS
$[Cd(N_2H_4)_2(NCS)_2]$	207(+)	190-270	29.30	32.85	$Cd(NCS)_2 +$ $Cd(CN)_2$ or $Cd(NCS)(CN)$
	-	450-650	50.00	50.63	CdS
$[Mg(N_2H_4)_2(NCS)_2]$	264(+)	230-360	47.00	47.00	$Mg(NCS)_2 +$ $Mg(CN)_2$ or $Mg(NCS)(CN)$
	-	360-480	72.50	72.44	MgS

*The final product was identified to be NiS by qualitative analysis.

(+) exotherm and (-) endotherm

2060 and 2070 cm^{-1} respectively for Mn(II) and Zn(II) complexes). The thermal decomposition can, therefore, be represented as follows:



The decomposition is more or less, similar to that of $[M(Py)_4(NCS)_2]$ (Liptay *et al* 1969a,b).

The metal(II) isothiocyanate formed as an intermediate further decomposes to the corresponding metal sulphide in the temperature range of 450-620° C according to the equation (Bell and Morcom 1979).



The observed weight loss corresponds to the formation of the corresponding metal sulphide (table 3). In air, the metal sulphides were oxidized forming the sulfate or oxide or their mixture depending on the metal ions (table 4). For example, $Zn(NCS)_2$ is oxidised directly to zinc oxide whereas $Mn(NCS)_2$ decomposes to $Mn(NCS)(CN)$ at

Table 4. Thermal decomposition of $[M(N_2H_4)_2(NCS)_2]$ in Air

$[M(N_2H_4)_2(NCS)_2]$	DTA peak	TG temp.	% wt loss Obsd.	Calcd.	Proposed
$[Mn(N_2H_4)_2(NCS)_2]$	197(+)	180-250	27.26	27.25	$Mn(NCS)_2$
	503(+)	400-550	40.20	40.88	$Mn(SCN)(CN)$
	-	560-640	48.85	48.89	$2MnSO_4 \cdot Mn_2O_3$
$[Fe(N_2H_4)_2(NCS)_2]$	173(+)	150-180	39.30	40.72	$Fe(NCS)(CN)$
	450(+)	350-500	-	66.18	$Fe_2O_3^*$
$[Co(N_2H_4)_2(NCS)_2]$	190(+)	180-220	40.60	40.20	$Co(NCS)(CN)$
	443(+)	380-530	50.0	55.29	$CoSO_4 \cdot Co_2O_3$
$[Ni(N_2H_4)_2(NCS)_2]$	226(+)	220-280	39.20	40.29	$Ni(NCS)(CN)$
	485(+)	410-550	54.82	55.00	$NiO + NiSO_4$
$[Zn(N_2H_4)_2(NCS)_2]$	189(-)				
	198(+)	190-260	25.00	26.08	$Zn(NCS)_2$
	503(+)	550-900	67.30	66.87	ZnO
$[Cd(N_2H_4)_2(NCS)_2]$	203(+)	190-270	29.30	32.85	$Cd(NCS)(CN)$
	485(+)	450-650	49.00	50.60	CdS
$[Mg(N_2H_4)_2(NCS)_2]$	261(+)	230-360	47.00	47.00	$Mg(NCS)(CN)$
	-	360-500	72.50	72.44	MgS
		500-650	79.50	80.39	MgO

*The final residue was found to be Fe_2O_3 by qualitative analysis.

(+) exotherm and (-) endotherm

400-550° C and finally to a mixture of $MnSO_4$ and Mn_2O_3 in the temperature range of 560-640° C.

The iron(II), cobalt(II), nickel(II), cadmium(II) and magnesium(II) complexes decompose in a different way from those of Zn(II) and Mn(II) complexes. The weight loss does not correspond to the formation of metal isothiocyanate alone (table 3). But the intermediate residues contain thiocyanate as evidenced by qualitative tests and IR spectra. The intermediate solid product does not show the presence of sulphide, but the gaseous products of thermal decomposition contained H_2S . The intermediate formed at 230-360° C by the thermal decomposition of magnesium complex showed bands at 2200 and 2080 cm^{-1} corresponding to M-CN and M-NC of NCS respectively. Similarly, cadmium complex intermediate also shows bands at 2320 and 2035 cm^{-1} . On the basis of these observations, the intermediate of thermal decomposition of iron, cobalt, nickel, cadmium and magnesium complexes could be given as $M(NCS)(CN)$ which subsequently decomposes slowly at higher temperature (~350 to 650° C) to the respective metal sulphides.

In air, the intermediate $Fe(NCS)(CN)$ is oxidized to Fe_2O_3 while $Mg(NCS)(CN)$ and $Cd(NCS)(CN)$ decompose to the corresponding metal sulphides. Magnesium sulphide is further oxidized to magnesium oxide in air. The nickel and cobalt intermediates are oxidized to a mixture of the corresponding sulfate and oxide (table 4).

3.3 Stability of the complexes

The stability of the co-ordination compounds is usually determined from the strength of the metal ligand bonds. The NH_2 twisting, symmetric and asymmetric rocking, N-N stretching of N_2H_4 , and M-N stretching of both M-NCS and M- N_2H_4 of the complexes (table 2) follow the Irving-Williams order of stability of the bivalent metal complexes

i.e. $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} > Zn^{2+} > Cd^{2+}$. A similar order was reported by Sacconi and Sabatini (1960; 1963) for $[M(N_2H_4)_2Cl_2]$.

The DTA peak temperature or the TG inception temperature of decomposition, in general, can be taken as a measure of the thermal stability of the metal complexes. The data in table 3 indicate the thermal stability order of $[M(N_2H_4)_2(SCN)_2]$ as $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} > Zn^{2+} > Cd^{2+}$. Thus, there appears to be a correlation between thermal stability and M-N of N_2H_4 or NCS bond strength.

References

- Anagnaostopoulus A and Nicholls D 1976 *J. Inorg. Nucl. Chem.* **38** 615
Aggarwal R C and Vallabhaneni C S 1978 *Trans. Met. Chem.* **3** 309
Bancroft G M and Platt R H 1972 *Adv. Inorg. Radiochem.* **15** 59
Bell C F and Morcom R E 1979 *J. Therm. Anal.* **17** 7
Braibanti A I, Dallavalle F, Phellinghelli H A and Leporati E 1968 *Inorg. Chem.* **7** 1430
Burmeister J 1972 *Coordn. Chem. Rev.* **6** 407
Duval C 1967 *Inorganic thermogravimetric analysis* (New York: Elsevier) 2nd ed p. 336
Ferrari A, Braibanti A and Lanfredi A M 1961 *Gazz. Chim. Ita.* **4** 189
Liptay G, Papp-Molnar E and Burger K 1969a *J. Inorg. Nucl. Chem.* **31** 247
Liptay G, Burger K, Papp-Molnar E, Szobeni S and Ruff F 1969b *J. Inorg. Nucl. Chem.* **32** 2359
Norbury A H 1975 *Adv. Inorg. Radiochem.* **17** 232
Patil K C, Gajapathy D and Kishore K 1982a *Thermochim. Acta* **52** 113
Patil K C, Nesamani C and Pai Verneker V R 1982 *Synth. React. Inorg. Met. Org. Chem.* **12** 383
Ray P and Sarkar P V 1920 *J. Chem. Soc.* **117** 321
Sacconi L and Sabatini A 1960 *Nature (London)* **186** 549
Sacconi L and Sabatini A 1963 *J. Inorg. Nucl. Chem.* **25** 1389
Savant V V and Patel C C 1968 *Indian J. Technol.* **6** 231
Srivastava A K, Varshney A L and Jain P C 1980 *J. Inorg. Nucl. Chem.* **42** 47
Vogel A I 1951 *A text-book of quantitative inorganic analysis* (London: Longmans Green) p. 365