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Synthesis and Characterisation of Metal Hydrazine Nitrate, Azide and Perchlorate Complexes

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SYNTHESIS AND CHARACTERISATION OF METAL HYDRAZINE NITRATE,
AZIDE AND PERCHLORATE COMPLEXES

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ABSTRACT

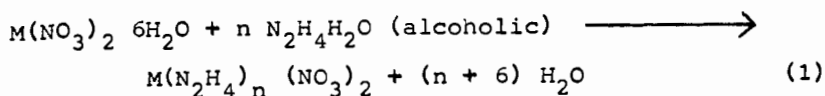
Metal hydrazine nitrate complexes of the type $M(N_2H_4)_n(NO_3)_2$ where $M = Mg$, $n = 2$; $M = Mn, Fe, Co, Ni, Zn$ and Cd and $n = 3$; metal dihydrazine azide complexes of the type $M(N_2H_4)_2(N_3)_2$ where $M = Mg, Co, Ni$ and Zn ; and $Mg(N_2H_4)_2(ClO_4)_2$ have been prepared by dissolving the respective metal powders in the solution of corresponding ammonium salts (NO_3 , N_3 and ClO_4) in hydrazine hydrate. These hydrazine complexes were also prepared by the conventional method involving the addition of alcoholic hydrazine hydrate to the aqueous solution of metal salts. The hydrazine complexes have been characterised by chemical analysis, infrared spectra and differential thermal analysis (DTA). Impact sensitivities of hydrazine complexes were determined by the drop weight method. The reactivity of these hydrazine complexes does not change with the method of preparation.

INTRODUCTION

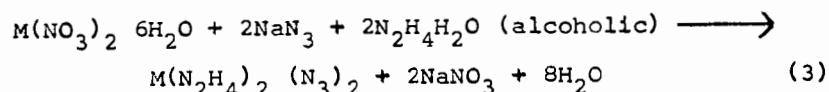
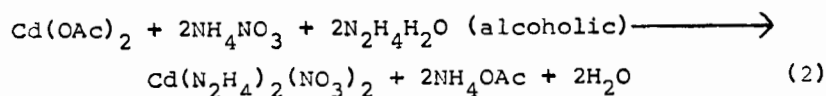
Transition metal hydrazine chlorate and perchlorate complexes are shown to be explosives and have been investigated for their application as initiators¹. Their explosivity is reported to lie between those of primary and secondary explosives. Nickel dihydrazine perchlorate is reported² to have exploded, even in suspension, with the touch of a glass rod. On the other hand, not much appears to be known about the transition metal hydrazine nitrate and azide complexes. The preparation of metal hydrazine nitrate³ and azide⁴ complexes has been described in the literature. The conventional method consists of the addition of alcoholic hydrazine hydrate to an aqueous solution of the corresponding metal salt. However, this method cannot be employed to prepare hydrazine complexes of iron (II) nitrate or magnesium azide which hydrolyze easily. So we have used a novel method of preparing those hydrazine complexes by dissolving the respective metal powders in the solution of the corresponding ammonium salts (nitrate, azide and perchlorate) in hydrazine hydrate. Earlier, the conventional as well as the novel method using metal powder has been used for the preparation of $(N_2H_5)_2 Mg(SO_4)_2$ ⁵. Presently, we report the synthesis and characterisation of some metal hydrazine nitrate, azide and perchlorate complexes. The products have been characterised by chemical analysis, i.r.spectra and DTA.

RESULTS AND DISCUSSION

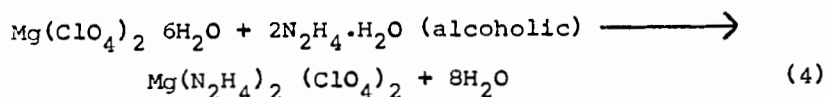
The conventional method of preparing metal hydrazine nitrate, azide and perchlorate complexes involves the reaction of metal salt solutions with alcoholic hydrazine hydrate. These reactions can be represented by equations as follows :



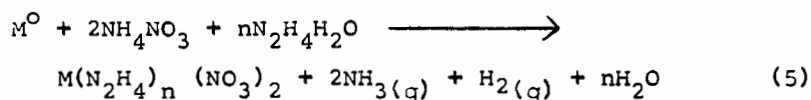
where M = Mg, n = 2; M = Mn, Co, Ni, Zn and Cd and n = 3.



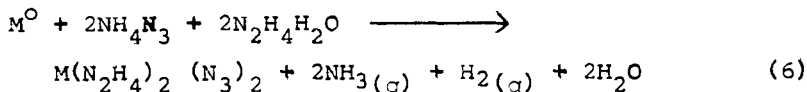
where M = Co, Ni and Zn



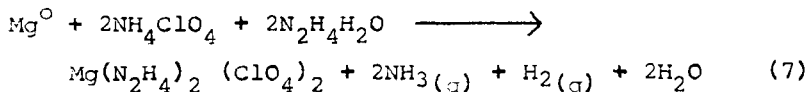
The novel method of preparing those hydrazine complexes, involving the reaction of respective metal powders in the solution of corresponding ammonium salts (NO_3 , N_3 and ClO_4) dissolved in $N_2H_4H_2O$, can be written by equations as follows :



where M = Mg, n = 2; M = Mn, Fe, Co, Ni, Zn and Cd and n = 3.



where M = Mg, Co, Ni and Zn.



The results of chemical analysis of transition metal hydrazine complexes are summarised in Table 1. It can be seen that whereas metal azides form hydrazine complexes of the type $M(N_2H_4)_2 (N_3)_2$, metal nitrates form hydrazine complexes of the type $M(N_2H_4)_3 (NO_3)_2$. The composition of iron hydrazine nitrate complex could not be determined due to its unstable nature. Infrared spectra of the complexes (Tables II and III) show the characteristic absorptions of coordinated hydrazine. The assignment of i.r. frequencies is similar to those reported for $M(N_2H_4)_2 Cl_2$ ⁶. The ν_{N-N} frequency of N_2H_4 is observed in the region $960-980\text{ cm}^{-1}$ indicating the presence of bridged hydrazine as in $M(N_2H_4)_2 Cl_2$. The structure of $M(N_2H_4)_2 (N_3)_2$ could be expected to be similar to the halide complexes, exhibiting the octahedral coordination of the metal ion which is surrounded by 4N atoms of N_2H_4 and 2N atoms of the azide. The observed ν_{M-N} stretching frequencies of $M-N_3$ and $M-N_2H_4$ justify this assignment. However, i.r. spectra of $M(N_2H_4)_3 (NO_3)_2$ complexes show the presence of ionic NO_3 ⁷ (D_{3h} -symmetry) as seen by the characteristic i.r. absorptions at 1390, 1050 and

TABLE I
Thermoanalytical Data of Metal Hydrazine
Nitrate, Azide and Perchlorate complexes

Compound	%Metal		%N ₂ H ₄		DTA ⁺ peak temp °C	Impact sensi- tivity in <u>cms</u>
	Obsd.	Reqd.	Obsd.	Reqd.		
<u>M(N₂H₄)_n (NO₃)₂</u>						
n = 3						
M = Mn	19.90	19.98	34.80	34.91	141(+), 212(+) (150)	11
Fe	-	-	-	-	140(+)	-
Co	21.06	21.13	34.32	34.42	188(+), (210)	8
Ni	21.03	21.13	34.30	34.49	220(+), (215)	9
Zn	22.68	22.91	33.60	33.64	212(+), (310)	13
Cd	33.80	33.81	28.83	28.88	145(+), 243(+) (245)	8.5
Cd, n=2	37.00	37.42	21.00	21.30	241(+)	10.5
<u>M(N₂H₄)₂ (N₃)₂</u>						
M = Co	28.40	28.48	30.83	30.93	223(+)	9
Ni	28.20	28.40	30.90	30.96	196(+)	10
Zn	30.60	30.64	29.90	29.99	212(+)	12
<u>Mg(N₂H₄)₂ X₂</u>						
X = NO ₃	12.11	11.45	30.24	30.14	227(+), 260(+)	
N ₃	14.00	14.11	37.03	37.11	217(+)	
ClO ₄	48.00	48.46	11.11	11.45	267(+)	

⁺values in paranthesis are from ref.(3).

TABLE II
Infrared Frequencies of Metal Hydrazine Nitrate
Complexes (cm^{-1})

Compound	Hydrazine Frequencies					NO ₃ ⁻ Frequencies				
	NH ₂ asym. stretch- ing	NH ₂ sym. stretch- ing	NH ₂ ⁻ bonding	NH ₂ twist- ing	N-N stretch- ing of H ₂ H ₄	NH ₂ rock- ing	γ_3	γ_1	γ_2	
Mg(N ₂ H ₄) ₂ (NO ₃) ₂	3320	3260, 3180	1620, 1590	1180	965	520	1390	1050	820	
Mn(N ₂ H ₄) ₃ (NO ₃) ₂	3320	3240, 3180	1620, 1590	1180	970	540	1400	1050	820	
Fe(N ₂ H ₄) _n (NO ₃) ₂		3260	1600	1180	950	600, 540	1390	1075	800	
Co(N ₂ H ₄) ₃ (NO ₃) ₂	3330	3260	1620, 1590	1170	970	540	1400	1050	820	
Ni(N ₂ H ₄) ₃ (NO ₃) ₂	3300	3240, 3180	1630	1180	970	550	1400	1050	820	
Zn(N ₂ H ₄) ₃ (NO ₃) ₂	3320	3240, 3180	1620, 1590	1180	970	540	1400	1050	820	
Cd(N ₂ H ₄) ₃ (NO ₃) ₂	3320	3240, 3180	1620, 1590	1150	960	540	1400	1050	820	
Cd(N ₂ H ₄) ₂ (NO ₃) ₂	3320	3260, 3180	1620, 1590	1160	970	520	1390	1050	820	

TABLE III
Infrared Frequencies of Metal Hydrazine Azide Complexes (cm^{-1})

Types of vibrations	$\text{Mg}(\text{N}_2\text{H}_4)_2$ (N_3) ₂	$\text{Co}(\text{N}_2\text{H}_4)_2$ (N_3) ₂	$\text{Ni}(\text{N}_2\text{H}_4)_2$ (N_3) ₂	$\text{Zn}(\text{N}_2\text{H}_4)_2$ (N_3) ₂
NH_2 asym.stretching	3400	3360	3280	3380
NH_2 sym.stretching	3300	3300, 3260	3220, 3170	3310, 3280
N_3^- asym. stretching	2080	2060	2070	2060
NH_2 bending	1600	1620	1610, 1580	1610, 1580
N_3^- sym. stretching	1310	1300	1320	1310
NH_2 twisting	1170, 1080	1180, 1140	1180	1170
N-N stretching of N_2H_4	965	970	970	970
NH_2 rocking	820, 530	560	820, 550	560
N_3^- bending	640	640	640	640
M-N stretching of metal azide	400	370	390	370
M-N stretching of $\text{M-N}_2\text{H}_4$	350	270	280	270

820 cm^{-1} . The metal ion can still have octahedral coordination with all 6N atoms contributed by $3\text{N}_2\text{H}_4$ groups.

Ignition temperatures of the complexes have been determined by DTA experiments and are shown in Table I. The observed values are in good agreement with the literature in most cases. However the ignition temperatures of $\text{Co}(\text{N}_2\text{H}_4)_2 (\text{N}_3)_2$ and $\text{Ni}(\text{N}_2\text{H}_4)_2 (\text{N}_3)_2$ show a discrepancy with the reported values. This may probably be due to the difference in the method of determining explosive or ignition temperature by these authors in a melting point apparatus. The method of preparation seems to have no effect on the ignition temperature. All the transition metal hydrazine nitrate and perchlorate complexes on heating decompose violently giving metal oxide. An interesting observation is the decomposition of $\text{Fe}(\text{N}_2\text{H}_4)_n (\text{NO}_3)_2$. The iron complex is quite unstable and ignites itself at room temperature during suction filtering. The product of decomposition is magnetic in nature and was identified by X-ray diffraction to be a mixture of γ - and α - Fe_2O_3 . The results of impact sensitivities are included in Table I. The observed values indicate the complexes to be primary explosives.

As expected, unlike transition metal hydrazine complexes, the magnesium salt (NO_3 , N_3 and ClO_4) hydrazine complexes are non-explosive. The magnesium

hydrazine nitrate and perchlorate complexes decompose exothermically to MgO . On the other hand $\text{Mg}(\text{N}_2\text{H}_4)_2$ (N_3)₂ decomposes exothermically to $\text{Mg}(\text{NH}_2)_2$ initially which decomposes endothermically to MgNH .

EXPERIMENTAL

Preparation of Metal Hydrazine Nitrate Complexes from the Corresponding Metal Nitrate Solutions

Metal hydrazine nitrate complexes of the type $\text{M}(\text{N}_2\text{H}_4)_n (\text{NO}_3)_2$ where $\text{M} = \text{Mg}$, $n = 2$; $\text{M} = \text{Mn}$, Co , Ni , Zn and Cd and $n = 3$ were prepared by the conventional method involving the addition of alcoholic hydrazine hydrate to an aqueous solution of metal nitrate. e.g. $\text{Co}(\text{N}_2\text{H}_4)_3 (\text{NO}_3)_2$ was prepared by the addition of $\text{N}_2\text{H}_4\text{H}_2\text{O}$ (2.58 g ; 0.08 m) in 5 ccs of ethanol to an aqueous solution of cobalt nitrate hexahydrate (5.00 g; 0.017 m) at room temperature. The product (4.60 g; 96%) was precipitated instantaneously.

Preparation of Cadmium Hydrazine Nitrate from Aqueous Solution of Cadmium Acetate

$\text{Cd}(\text{N}_2\text{H}_4)_2 (\text{NO}_3)_2$ (6.55 g; 96%) was prepared by the addition of $\text{N}_2\text{H}_4\text{H}_2\text{O}$ (2.28 g; 0.046 m) in 5 ccs of ethanol to the aqueous mixture of cadmium acetate (5.25 g; 0.023 m) and ammonium nitrate (3.65 g; 0.046 m) at room temperature.

Preparation of Metal Hydrazine Nitrate Complexes from the Corresponding Metal Powders

Metal hydrazine nitrate complexes of the type $\text{M}(\text{N}_2\text{H}_4)_n (\text{NO}_3)_2$ where $\text{M} = \text{Mg}$, $n = 2$; $\text{M} = \text{Mn}$, Fe , Co ,

Ni, Zn and Cd and $n = 3$ were prepared by dissolving the respective metal powders in the solution of ammonium nitrate in hydrazine hydrate e.g. $\text{Ni}(\text{N}_2\text{H}_4)_3(\text{NO}_3)_2$ was prepared as follows.

Stoichiometric amounts of ammonium nitrate (5.05 g; 0.063 m) in hydrazine hydrate (4.73 g; 0.095 m) and nickel powder (1.85 g; 0.032 m) were allowed to react at room temperature. The nickel metal dissolved exothermically completely with the evolution of hydrogen. The solid compound (8.50 g; 97%) was obtained by the addition of alcohol.

Preparation of Metal Hydrazine Azide Complexes from Aqueous Solution

Metal hydrazine azide complexes of the type $\text{M}(\text{N}_2\text{H}_4)_2(\text{N}_3)_2$ where M = Co, Ni and Zn were prepared by the conventional method involving the addition of alcoholic hydrazine hydrate to the aqueous mixture of metal nitrate and sodium azide e.g. $\text{Zn}(\text{N}_2\text{H}_4)_2(\text{N}_3)_2$ (2.8 g; 97%) was prepared by the addition of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ (1.36 g; 0.027 m) in 5 ccs of ethanol to the aqueous mixture of zinc nitrate hexahydrate (4.05 g; 0.014 m) and sodium azide (1.63 g; 0.025 m) at room temperature.

Preparation of Metal Hydrazine Azide Complexes from the Corresponding Metal Powders

Metal hydrazine azide complexes of the type $\text{M}(\text{N}_2\text{H}_4)_2(\text{N}_3)_2$ where M = Mg, Co, Ni and Zn were prepared by dissolving the corresponding metal powders in the solution of ammonium azide in hydrazine hydrate. e.g.

$\text{Ni}(\text{N}_2\text{H}_4)_2 (\text{N}_3)_2$ was prepared by the stoichiometric reaction of nickel powder (2.03 g; 0.035 m) with ammonium azide (4.15 g; 0.07 m) dissolved in $\text{N}_2\text{H}_4\text{H}_2\text{O}$ (3.46 g; 0.07 m) at room temperature. The nickel metal dissolved exothermically completely with the evolution of hydrogen. The solid compound (6.80 g; 95%) was obtained by the addition of alcohol.

Preparation of $\text{Mg}(\text{N}_2\text{H}_4)_2 (\text{ClO}_4)_2$

$\text{Mg}(\text{N}_2\text{H}_4)_2 (\text{ClO}_4)_2$ (3.95 g; 90%) was prepared by the addition of excess of $\text{N}_2\text{H}_4\text{H}_2\text{O}$ (3.05 g; 0.061 m) in 5 ccs of ethanol to an aqueous solution of magnesium perchlorate hexahydrate (5.05 g; 0.015 m) at room temperature.

$\text{Mg}(\text{N}_2\text{H}_4)_2 (\text{ClO}_4)_2$ can also be prepared by the reaction of magnesium powder (0.54 g; 0.022 m) with ammonium perchlorate (5.25 g; 0.045 m) dissolved in $\text{N}_2\text{H}_4\text{H}_2\text{O}$ (2.23 g; 0.045 m) at room temperature. The magnesium metal dissolved exothermically completely with the evolution of hydrogen. The solid compound (6.15 g; 96%) was obtained by the addition of alcohol.

All the above mentioned complexes were washed with ethanol and ether and then dried in a suction filter. These complexes were characterised by chemical analysis, infrared spectra and differential thermal analysis (DTA). The hydrazine content was determined by titration with 0.025 M KIO_3 solution under Andrew's condition⁸. The metal content was determined by EDTA

titration⁹. The i.r. spectra were recorded using Carl-Zeiss UR-10 and Perkin-Elmer spectrophotometers. The samples were prepared as Nujol mulls and KBr pellets. Differential thermal analysis (DTA) was carried out using a DTA-02 Universal Instrument. All DTA runs were made in air. The heating rate employed was 10°C/min. Pt cups were used as sample holders; 10 mg samples were used for DTA experiments. Impact sensitivities of the complexes were determined by ball and drop method using a steel ball (weight = 500 gms) for 50% explosion.

Although transition metal hydrazine nitrate, azide and perchlorate complexes are explosive in nature as indicated by DTA experiments as well as impact sensitivity tests, no special precautions were taken during the synthesis and characterisation of these materials upto 10 grams of quantity. Special mention however should be made of azide complexes which were highly friction sensitive especially in the dry state.

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