

Metal-hydrazine complexes as precursors to oxide materials

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Abstract. Metal-hydrazine complexes, $[M(N_2H_4)_n]^{2+}$ ($M = Mn, Fe, Co, Ni, Zn$ and Cd , $n = 2$ or 3) with different anions like sulphate, sulphite, acetate, formate, oxalate, hydrazino-carboxylate, nitrate and perchlorate have been investigated as precursors to oxide materials. The thermal reactivity of these complexes changes dramatically with the anion, e.g. sulphate, sulphite, acetate and formate complexes - decompose; oxalate and hydrazinocarboxylates - deflagrate and nitrate and perchlorate complexes - detonate. The deflagrating nature of the metal-hydrazine oxalates and hydrazinocarboxylates has been employed in the combustion synthesis of fine particle γ - Fe_2O_3 , Fe_3O_4 , ferrites and cobaltites at low temperature.

Keywords. Metal-hydrazine complexes; precursors to oxide materials.

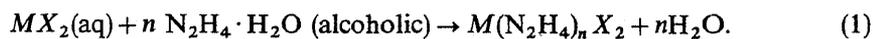
1. Introduction

The chemistry of hydrazine is of interest since it has a potent N-N bond, two free electron pairs and four substitutable H-atoms. The coordination of hydrazine to the metal ion can either be as a unidentate or bridged bidentate ligand. Hydrazine has positive heat of formation ($\Delta H_f^\circ = \sim 12 \text{ kcal mol}^{-1}$) and therefore is thermodynamically unstable. Practically, however, it is quite stable and can be handled safely. Hydrazine is susceptible to catalysis and can explode even at room temperature in presence of rust (Fe_2O_3). Thermal reactivity of metal-hydrazine complexes is of interest since the stability of the complexes changes dramatically, depending upon the anion as well as the cation. In this paper, an attempt is made to correlate the reactivity of metal-hydrazine complexes, $[M(N_2H_4)_n]^{2+}$ ($M = Mn, Fe, Co, Ni, Zn$ and Cd , $n = 2$ or 3) as a function of anions like sulphate, sulphite, acetate, formate, oxalate, hydrazino-carboxylate, nitrate and perchlorate.

2. Experimental

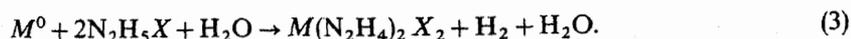
2.1 Preparation of metal-hydrazine complexes, $M(N_2H_4)_nX_2$

The general method of the preparation of metal hydrazine complexes, $M(N_2H_4)_nX_2$ ($M = Mn, Fe^*, Co, Ni, Zn$ and Cd , $n = 2$ or 3), and $X =$ acetate, oxalate, formate nitrate or sulphate) involves the reaction of an aqueous solution of the corresponding metal salt with alcoholic hydrazine hydrate.

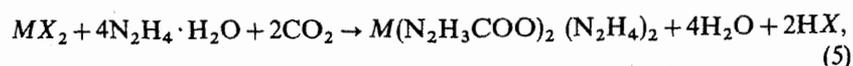
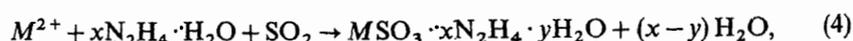


* Fe complexes are unstable and spontaneously ignite during suction drying.

The complexes can also be prepared by dissolving the metal powders in a solution of ammonium (NH_4^+) or hydrazinium (N_2H_5^+) salts in hydrazine hydrate or water,



Metal sulphite and metal hydrazinocarboxylate hydrazine complexes were prepared by the reaction of aqueous metal ions with hydrazine hydrate saturated with SO_2 and CO_2 , respectively,



2.2 Analysis

The metal content in the complexes was determined by EDTA complexometric titrations. Hydrazine content was estimated volumetrically using 0.025 M KIO_3 solution under Andrews conditions (Vogel 1961).

2.3 Physicochemical studies

Infrared spectra of the complexes were recorded as nujol mulls or KBr discs using a Perkin-Elmer 781 spectrophotometer. Simultaneous TG-DTG-DTA of the complexes were recorded using a TGD-5000 RH thermobalance of ULVAC Sinku Riko, Japan. Thermal analysis curves were recorded in air using 4–5 mg samples. The heating rate employed was $10^\circ\text{C}/\text{min}$. Platinum cups were used as sample holders.

The decomposition/combustion residues of the complexes were characterized by x-ray powder diffraction patterns recorded on a Philips pw 1050/70 diffractometer using Cu K_α and Co K_α radiation.

Temperature profile measurements to determine the surface temperatures in the combustion of $\text{FeC}_2\text{O}_4 \cdot 2\text{N}_2\text{H}_4$ and $\text{Fe}(\text{N}_2\text{H}_3\text{COO})_2(\text{N}_2\text{H}_4)_2$ were carried out using chromel-alumel thermocouple embedded in 1 cm^3 pellets. A time-temperature plot was obtained by feeding the output to a strip-chart recorder.

BET surface area of Fe_3O_4 , $\gamma\text{-Fe}_2\text{O}_3$, ferrites and cobaltites were measured by nitrogen adsorption using Micromeritics Accusorb 2100 E instrument. Mossbauer spectra of Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ were recorded at room temperature employing a ECIL MBS 35 spectrophotometer with a multichannel analyser. Coercivity of $\gamma\text{-Fe}_2\text{O}_3$ was measured using EG & G vibrating sample magnetometer fitted with bipolar power supply.

3. Results and discussion

Preparation, infrared spectra and thermal analysis of metal-hydrazine complexes $[\text{M}(\text{N}_2\text{H}_4)_n]^{2+}$ ($M = \text{Mn, Fe, Co, Ni, Zn}$ and Cd) with anions like nitrate, perchlorate and azide (Patil *et al* 1982b), oxalate (Patil *et al* 1982a), formate (Ravindranathan and Patil 1983), hydrazinocarboxylate (Ravindranathan and Patil 1985), sulphate (Patil *et*

al 1981; Govindarajan *et al* 1985), acetate (Mahesh and Patil 1985) and sulphite (Budkuley 1984) have been investigated.

The hydrazine molecule is coordinated to the metal as a bridged bidentate ligand in all these complexes except in the case of hydrazinocarboxylates in which it is coordinated to the metal atom as a unidentate ligand. Infrared spectra serve as a fingerprint technique and the presence of unidentate N_2H_4 in $M(N_2H_3COO)_2(N_2H_4)_2$ is indicated by the characteristic N-N stretching frequency of $N_2H_4 \sim 930\text{ cm}^{-1}$ (Nicholls and Swindells 1968). The x-ray crystal structure of $Zn(N_2H_3COO)_2(N_2H_4)_2$ has been determined and the structures of Mn, Fe, Co & Ni complexes are reported to be isomorphous (Ferrari *et al* 1966). This study supports the presence of unidentate N_2H_4 in these complexes.

The presence of bridged bidentate hydrazine in sulphate, sulphite, formate, acetate, nitrate and oxalate complexes has been indicated by the presence of ν_{N-N} of N_2H_4 in the region $960\text{--}980\text{ cm}^{-1}$ (Patil *et al* 1981, 1982a, b; Braibanti *et al* 1968) and x-ray crystal structure studies (Ferrari *et al* 1965).

Thermal reactivity of metal-hydrazine complexes has been investigated by TG-DTA studies. Table 1 summarizes the results of the thermal decomposition of metal sulphate, sulphite, formate and acetate hydrazine complexes. All these complexes initially lose hydrazine exothermically leaving behind the respective metal salts which decompose to the corresponding metal oxides at higher temperatures. The oxide formation temperatures are lower compared to those reported for hydrated metal salts. The metal salts formed by the dehydrazination of the complexes are reactive and decompose at lower temperatures.

Table 2 summarizes the results of TG-DTA studies of metal nitrate, oxalate and hydrazinocarboxylate hydrazine complexes. All these complexes show single step decomposition in TG giving corresponding metal oxides. The decomposition of nitrate complexes is violent. The oxalate and hydrazinocarboxylate complexes exhibit autocatalytic combustion behaviour, i.e., combustion is self-sustained once initiated.

Table 1. Thermogravimetric (temperature range °C) and differential thermal analysis* (peak temperature °C) data of metal hydrazine complexes $M(N_2H_4)_2X_2$.

Metal (M)	Anion (X)				Reaction
	Sulphate	Sulphite	Formate	Acetate	
Mn	175-245 (180)	202-295 (233)	110-178 (170-endo)	130-205 (150, 190)	Dehydrazination
Fe	100-250 (160)†	130-142 (135)†	—	—	Dehydrazination and Decomposition
Co	185-385 (200, 325)	150-160 (157)	100-204 (167-endo)	160-220 (180, 220)	Dehydrazination
Ni	230-485 (280, 455)	104-215 (182)	116-233 (217)†	190-245† (205, 230)	Dehydrazination
Zn	100-425 (110, 245, 350)	200-235 (215)	100-324 (168-endo)	150-195 (130)	Dehydrazination
Cd	155-385 (175, 330)	—	100-285 (187-endo)	115-215 (175, 200)	Dehydrazination

* All DTA peaks are exothermic unless indicated otherwise (endo = endothermic).

† Dehydrazination is accompanied by decomposition.

Table 2. Thermogravimetric (temperature range °C) and differential thermal analysis* (peak temperature °C) data of metal-hydrazine complexes, $M(N_2H_4)_nX_2$.

Metal <i>M</i>	Nitrate†	Oxalate	Anion (<i>X</i>)		Product
			Hydrazinocarboxylate		
Mn	(141)	204–225 (217)	130–290 (174, 195)		MnO
Fe	(140)	180–310 (202)	130–205 (135, 175)		Fe ₂ O ₃
Co	(188)	204–358 (209, 262)	210–269 (190, 200)		Co ₃ O ₄
Ni	(220)	226–419 (219, 244, 290)	187–200 (195, 228)		NiO
Zn	(212)	120–466 (216, 301, 406)	155–325 (200, 310)		ZnO
Cd	(145)	169–456 (182, 291, 353)	—		CdO

* All DTA peaks are exothermic; † $M(N_2H_4)_3(NO_3)_2$.

The decomposition/combustion of these complexes is accompanied by the evolution of large amounts of gases like NH₃, H₂O, CO₂ and N₂. The combustion residues thus left behind are fine and porous metal oxides.

Based on the thermal decomposition studies of metal-hydrazine complexes they can be classified into three distinct groups:

- 1) Complexes which decompose, i.e., lose hydrazine leaving behind corresponding metal salts. e.g. $M(N_2H_4)_2X_2$, where *X* = sulphate, sulphite, formate and acetate.
- 2) Complexes which deflagrate, i.e., exhibit self-sustained (controlled) combustion, e.g. $M(N_2H_4)_2C_2O_4$ and $M(N_2H_3COO)_2(N_2H_4)_2$.
- 3) Complexes which detonate, e.g. $M(N_2H_4)_3(NO_3)_2$ and $M(N_2H_4)_2(ClO_4)_2$.

This dramatic change in the reactivity of the metal-hydrazine complexes can thus be attributed to the nature of the anion i.e. inert, reducing or oxidising. The sulphate and acetate anions are quite inert and do not exhibit any deflagration or detonation. Whereas formate and sulphite complexes although lose hydrazine during decomposition, exhibit self-sustained combustion like oxalate and hydrazinocarboxylate complexes. The explosive nature of nitrate and perchlorate complexes can be attributed to the redox reactions of oxidizer-fuel groups in the complexes.

The role of cation (metal) is also quite important since the explosive nature of transition metal perchlorate hydrazine complexes (Friedrich and Vervoorst 1926; Maissen and Schwarzenbach 1951) changes to deflagration in the case of magnesium and aluminium perchlorate complexes (Patil *et al* 1982b). Thus, the highly unstable and explosive nature of N₂H₄ can be controlled by suitably complexing it with selective metal ions and anions.

4. Combustion synthesis

The deflagrating nature of metal oxalate and hydrazinocarboxylate hydrazine complexes has been employed in the combustion synthesis of fine particle Fe₃O₄, γ-Fe₂O₃, ferrites and cobaltites.

4.1 Synthesis of Fe_3O_4

The decomposition/combustion of $Fe(N_2H_3COO)_2(N_2H_4)_2$ in vacuum at $\approx 250^\circ C$ yields finely divided Fe_3O_4 . Formation of Fe_3O_4 was confirmed by x-ray powder diffraction pattern of the residue ($a = 8.46 \text{ \AA}$). The crystallite sizes of Fe_3O_4 calculated from x-ray line broadening are in the range of 170–250 \AA . The surface area of Fe_3O_4 is $50 \text{ m}^2/\text{g}$. The Mossbauer spectrum of Fe_3O_4 shows the expected hyperfine spectra with the central doublet indicating super paramagnetic nature of the particles. The DTA of this fine particle Fe_3O_4 shows two exotherms at $200^\circ C$ and $630^\circ C$ corresponding to the oxidation of $Fe_3O_4 \rightarrow \gamma-Fe_2O_3$ and $\alpha-Fe_2O_3$ respectively.

4.2 Synthesis of $\gamma-Fe_2O_3$

The decomposition/combustion of $FeC_2O_4(N_2H_4)_2$ in air at $\approx 200^\circ C$ yields a mixture of γ and $\alpha-Fe_2O_3$ as evidenced by the x-ray powder diffraction of the combustion residue. However, the decomposition/combustion of $Fe(N_2H_3COO)_2(N_2H_4)_2$ in air at $\approx 200^\circ C$ gave $\gamma-Fe_2O_3$ only as indicated by the xrd pattern of the combustion residue ($a = 8.37 \text{ \AA}$). The crystallite sizes of $\gamma-Fe_2O_3$ are in the range of 170–250 \AA and the surface area is $40 \text{ m}^2/\text{g}$. Mossbauer spectra of $\gamma-Fe_2O_3$ showed the expected hyperfine split pattern. The hyperfine field calculated from the fitting of the spectrum is 490 kOe and the isomer shift is 0.3435 mm/sec with respect to stainless steel. The coercivity force observed from the B-H curve of $\gamma-Fe_2O_3$ is 170 oersteds. The DTA of $\gamma-Fe_2O_3$ showed an exotherm at $\approx 630^\circ C$ corresponding to the conversion of $\gamma \rightarrow \alpha-Fe_2O_3$.

Temperature profile measurement of $FeC_2O_4(N_2H_4)_2$ (Kishore *et al* 1986) showed that the maximum temperature attained during the combustion is $\approx 600^\circ C$ although ignition occurs at $\sim 200^\circ C$. On the other hand, in the case of $Fe(N_2H_3COO)_2(N_2H_4)_2$ combustion the maximum temperature attained was only $425^\circ C$. This difference in the exothermicity of the combustion of $FeC_2O_4(N_2H_4)_2$ and $Fe(N_2H_3COO)_2(N_2H_4)_2$ is probably responsible for the formation of a mixture of γ , $\alpha-Fe_2O_3$ in the former and exclusively $\gamma-Fe_2O_3$ in the latter. It is well known that $\gamma-Fe_2O_3$ is converted to $\alpha-Fe_2O_3$ at $\approx 600^\circ C$.

4.3 Synthesis of ferrites

The preparation of spinel ferrites by the decomposition/combustion of mixed metal oxalate hydrazinates, $MFe_2(C_2O_4)_3(N_2H_4)_6$ where $M = Mn, Fe, Co, Ni$ and Zn at low temperatures has been reported (Gajapathy and Patil 1983).

Ultrafine ferrite powders have been prepared by the decomposition/combustion of solid solution precursors of the type $M_{1/3}Fe_{2/3}(N_2H_3COO)_2(N_2H_4)_2$, where $M = Mg, Mn, Co, Ni$ and Zn . These precursors decompose at lower temperatures ($125\text{--}150^\circ C$) with the evolution of large amounts of gases like NH_3, H_2O, CO_2 and N_2 to yield corresponding ferrites. Formation of ferrites was confirmed by their characteristic xrd patterns. The crystallite sizes of the ferrites calculated from the x-ray line broadening are in the range of 130–250 \AA . The surface area of the ferrites range from $75\text{--}120 \text{ m}^2/\text{g}$.

4.4 Synthesis of cobaltites

The preparation of $MgCo_2O_4$ and $NiCo_2O_4$ by the decomposition/combustion of

$\text{MgCo}_2(\text{C}_2\text{O}_4)_3 \cdot 5\text{N}_2\text{H}_4$ and $\text{NiCo}_2(\text{C}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$ has been reported (Patil *et al* 1983). The decomposition/combustion of solid solution precursors of the type, $\text{M}_{1/3}\text{Co}_{2/3}(\text{N}_2\text{H}_3\text{COO})_2(\text{N}_2\text{H}_4)_2$, where $M = \text{Mg, Mn, Fe, Ni}$ and Zn yield fine particle cobaltites, MCo_2O_4 at low temperatures (200–400°C). Further work is in progress on the characterization of these cobaltites.

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