

Preparation and characterization of hydrazine derivatives. Part-II : Reaction of transition metal ammonium double sulphates with hydrazine hydrate

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Abstract. Transition metal ammonium double sulphates $(\text{NH}_4)_2\text{M}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, where $\text{M} = \text{Fe}, \text{Co}$ and Ni react with hydrazine hydrate in air giving crystalline compounds of the general formula $\text{N}_2\text{H}_5 [\text{M}(\text{N}_2\text{H}_3\text{COO})_3] \text{H}_2\text{O}$. The reaction proceeds through $(\text{N}_2\text{H}_5)_2 \text{M}(\text{SO}_4)_2 \cdot 3\text{N}_2\text{H}_4$, $(\text{N}_2\text{H}_5)_2 [\text{M}(\text{OH})_4 \cdot (\text{N}_2\text{H}_4)_2]$, $\text{M}(\text{N}_2\text{H}_3\text{COO})_2 \cdot (\text{N}_2\text{H}_4)_2$ and $\text{N}_2\text{H}_5 [\text{M}(\text{N}_2\text{H}_3\text{COO})_3]$ intermediates. The reaction sequence is followed by chemical analysis and infrared spectra. A possible reaction mechanism has been suggested.

Keywords. Hydrazine derivatives; hydrazido carbonates.

1. Introduction

The reaction of simple ammonium salts as well as transition metal ammonium double sulphates with hydrazine hydrate in stoichiometric quantities yield corresponding hydrazinium salts or hydrazinium metal double sulphates (Patil *et al* 1978). However, the reaction of the double sulphates with excess hydrazine hydrate (more than the stoichiometry) yield variety of products whose composition change with time. The presence of atmospheric carbon dioxide appears to play an important role in these heterogeneous reactions. Presently, we have attempted to isolate the various intermediates and characterise them by chemical analysis and infrared spectra. A possible reaction mechanism for the observed reaction sequence has been suggested.

2. Experimental

Analytical grade metal (iron, cobalt and nickel) ammonium double sulphates of the general formula $(\text{NH}_4)_2 \text{M}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ where $\text{M} = \text{Fe}, \text{Co}$ and Ni were used in this study. Hydrazine hydrate (99-100%) was commercially available and was used as such. The following set of experiments were carried out. The results are summarised in table 1.

Table 1. Analytical data of hydrazine derivatives.

Compound	Colour	% Hydrazine		% Metal		% Carbon dioxide	
		Obs.	Theor.	Obs.	Theor.	Obs.	Theor.
$(\text{N}_2\text{H}_5)_2 \text{Fe} (\text{SO}_4)_2 \cdot 3\text{N}_2\text{H}_4$	Bluish white	38·63	39·04	13·60	13·63
$(\text{N}_2\text{H}_5)_2 [\text{Fe} (\text{OH})_4 (\text{N}_2\text{H}_4)_2]$	White	50·43	50·42	22·00	21·99
$\text{Fe} (\text{N}_2\text{H}_3\text{COO})_2 \cdot (\text{N}_2\text{H}_4)_2$	Bluish green	47·32	46·67	20·95	20·74	32·50	32·59
$(\text{N}_2\text{H}_5) [\text{Fe} (\text{N}_2\text{H}_3\text{COO})_3]$	Bottle green	40·44	40·44	17·73	17·80	41·75	42·05
$\text{N}_2\text{H}_5 [\text{Fe} (\text{N}_2\text{H}_3\text{COO})_3] \cdot \text{H}_2\text{O}$	Pale bottle green	38·61	38·57	17·00	16·82	39·69	39·77
$(\text{N}_2\text{H}_5)_2 \text{CO} (\text{SO}_4)_2 \cdot 3\text{N}_2\text{H}_4$	Pale orange	38·92	37·74	14·25	14·28
$(\text{N}_2\text{H}_5)_2 [\text{CO} (\text{OH})_4 (\text{N}_2\text{H}_4)_2]$	Orange white	49·79	49·81	22·92	22·94
$\text{CO} (\text{N}_2\text{H}_3\text{COO})_2 \cdot (\text{N}_2\text{H}_4)_2$	Bright orange	46·00	46·18	21·32	21·59	32·70	32·23
$\text{N}_2\text{H}_5 [\text{CO} (\text{N}_2\text{H}_3\text{COO})_3]$	Dark red	40·50	40·37	18·70	18·61	41·41	41·64
$\text{N}_2\text{H}_5 [\text{CO} (\text{N}_2\text{H}_3\text{COO})_3] \cdot \text{H}_2\text{O}$	Dark red	38·27	38·22	17·54	17·59	39·40	39·41
$(\text{N}_2\text{H}_5)_2 \text{Ni} (\text{SO}_4)_2 \cdot 3\text{N}_2\text{H}_4$	Pink	38·78	38·79	14·25	14·28
$(\text{N}_2\text{H}_5)_2 [\text{Ni} (\text{OH})_4 (\text{N}_2\text{H}_4)_2]$	Pink violet	49·86	49·86	22·89	22·87
$\text{Ni} (\text{N}_2\text{H}_3\text{COO})_2 \cdot (\text{N}_2\text{H}_4)_2$	Violet	46·20	46·21	21·38	21·53	32·76	32·70
$\text{N}_2\text{H}_5 [\text{Ni} (\text{N}_2\text{H}_3\text{COO})_3]$	Dark blue	40·66	40·37	18·57	18·61	41·16	41·64
$\text{N}_2\text{H}_5 [\text{Ni} (\text{N}_2\text{H}_3\text{COO})_3] \cdot \text{H}_2\text{O}$	Dark blue	38·27	38·24	17·53	17·54	39·51	39·43

(i) Stoichiometric quantities of the double sulphates and hydrazine hydrate were mixed and allowed to react. The reaction was instantaneous with colour change and evolution of ammonia giving corresponding hydrazinium metal double sulphate hydrazinates as found by analysis— $(\text{N}_2\text{H}_5)_2 \text{M} (\text{SO}_4)_2 \cdot 3\text{N}_2\text{H}_4$ —I.

(ii) The double sulphates were treated with large excess of hydrazine hydrate almost twice the amount required for stoichiometric reaction (i) so as to cover the solid with hydrazine hydrate. Reaction similar to (i) took place with further change in colour and composition of the solid product. The mother liquor answered tests for SO_4^{2-} ions indicating substitution of SO_4^{2-} ions from the double sulphates with OH^- groups. The amount of SO_4^{2-} was determined by the addition of BaCl_2 solution. The amorphous solid had the composition $(\text{N}_2\text{H}_5)_2 [\text{M} (\text{OH})_4 (\text{N}_2\text{H}_4)_2]$ —II.

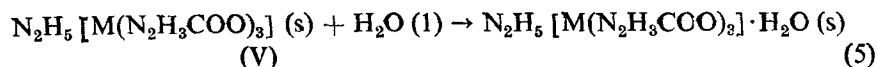
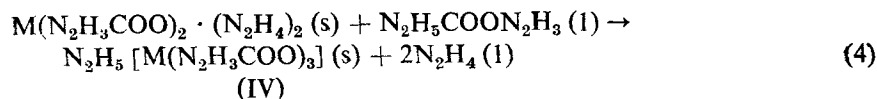
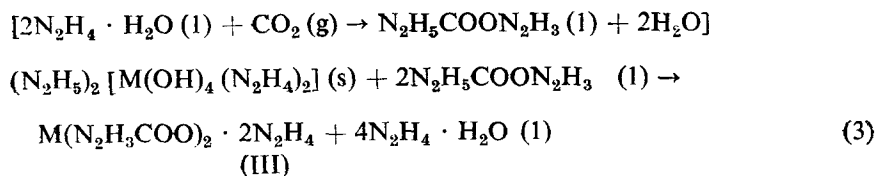
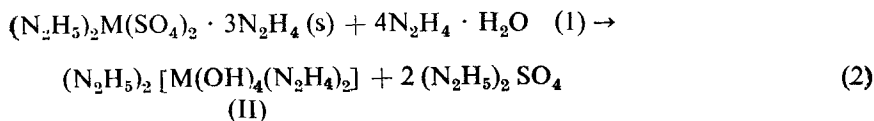
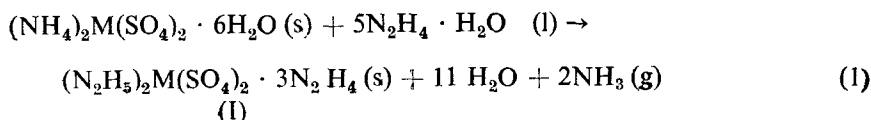
(iii) The reaction mixture (ii) was allowed to crystallise and the container was kept open to atmosphere. The amorphous solid slowly (few days) became crystalline with further change in the composition. The products were found to have the general formula $\text{M} (\text{N}_2\text{H}_3\text{COO})_2 \cdot (\text{N}_2\text{H}_4)_2$ —III.

(iv) When the reaction mixture (ii) was allowed to stay for longer time, even after the formation of $M(N_2H_3COO)_2 \cdot (N_2H_4)_2$ crystals, further reaction took place resulting in the dissolution of the crystals in the mother liquor, imparting their colour to the solution. On prolonged stay a new crop of crystals appeared with altogether different colours from (iii) leaving behind colourless solution. The composition of these crystals was found to be $N_2H_5 [(M(N_2H_3COO)_2)]$ —IV by chemical analysis.

(v) On prolonged stay (iv) gave hydrated salts of the formula $N_2H_5 [M(N_2H_3COO)_3] \cdot H_2O$ —V. Hydrazine and metal analysis was carried out as reported earlier (Patil *et al* 1978). Carbon dioxide was estimated gasometrically. Infrared spectra of compounds I, III, IV and V were recorded as nujol mulls and that of II was recorded as KBr pellet using Carl Zeiss UR-10 spectrophotometer.

3. Results and discussion

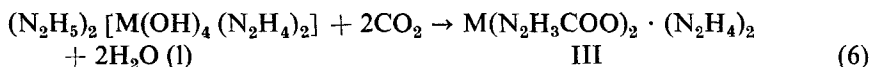
The results of experiments from (i) to (v) forming products I to V indicate the probable reaction sequence to be as follows :



where M = Fe, Co and Ni.

The results of chemical analysis (table 1) are in good agreement with the proposed formulae of the products (I) to (V). The evidence for the formation of I has already been reported (Patil *et al* 1978) and included here for better understanding. Formation of hydroxo complex (II) was confirmed by chemical analysis of the amorphous solids as well as by the analysis of the supernatant liquid for sulphate. The analysis indicated quantitative substitution of the SO_4^{2-} ions by hydroxo groups.

It is well known (Audreith and Ogg 1951) that hydrazine hydrate reacts with atmospheric CO_2 to give hydrazinium hydrazido carbonate $\text{N}_2\text{H}_5\text{COON}_2\text{H}_3$. So one can write equation (3) for the reaction of hydroxo complex with hydrazine exposed to the atmosphere. A close examination of equation (3) reveals that $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ is not actually taking part in the reaction. Therefore reaction (3) should be possible with CO_2 gas also. To check this idea the reaction was carried out in a vacuum desiccator with solid CO_2 and the hydroxo complex-(II) and the same product(III) was obtained.



The CO_2 (gas)-hydroxo complex-II (s) heterogeneous reaction [equation (6)] appears to be faster than the corresponding $\text{N}_2\text{H}_5\text{COON}_2\text{H}_3$ (l)-hydroxo complex-II (s) [equation (3)] since the product-III could be obtained within 24 hr by the former process.

Further, Macek *et al* (1976) have reported the formation of type III compounds in the case of Co, Ni but not with Fe. This was probably not possible because they have prepared these by the reaction of the simple metal salts with hydrazine

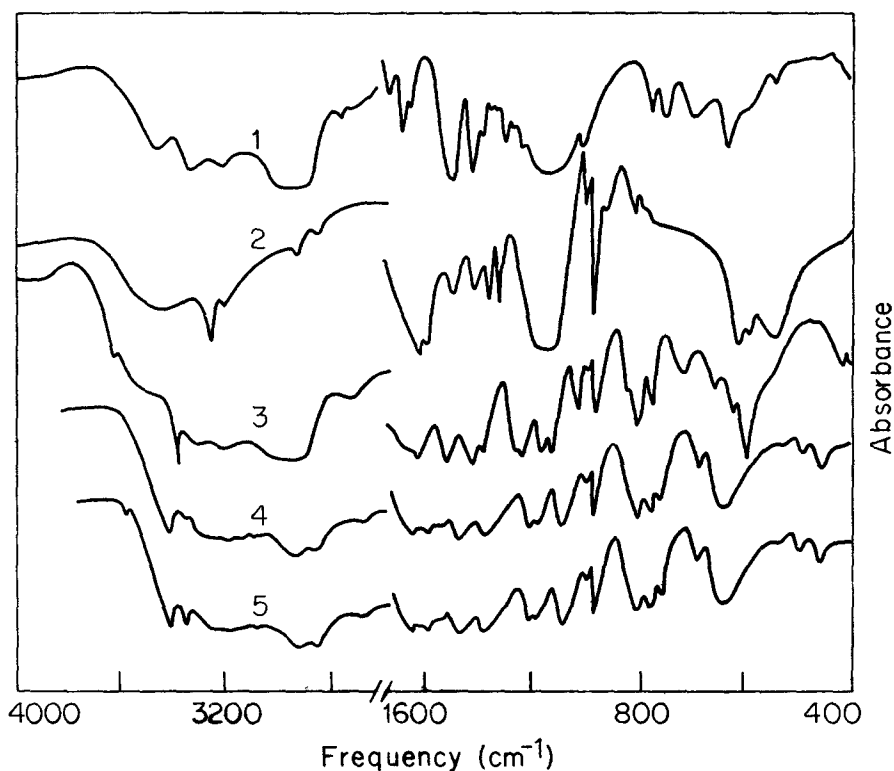
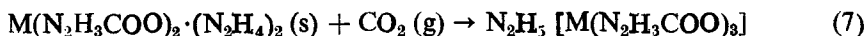


Figure 1. Infrared absorption spectra of (1) $(\text{N}_2\text{H}_5)_2 \text{Fe}(\text{SO}_4)_2 \cdot 3\text{N}_2\text{H}_4$. (2) $(\text{N}_2\text{H}_5)_2 [\text{Fe}(\text{OH})_4 (\text{N}_2\text{H}_4)_2]$. (3) $\text{Fe}(\text{N}_2\text{H}_3\text{COO})_2 \cdot (\text{N}_2\text{H}_4)_2$. (4) $\text{N}_2\text{H}_5 [\text{Fe}(\text{N}_2\text{H}_3\text{COO})_2]$. (5) $\text{N}_2\text{H}_5 [\text{Fe}(\text{N}_2\text{H}_3\text{COO})_3] \cdot \text{H}_2\text{O}$.

hydrate saturated with carbon dioxide. This reaction with simple iron salt always yielded iron(II) hydroxide which was oxidised by atmospheric oxygen. However, the reaction of ferrous ammonium sulfate with hydrazine hydrate stabilizes Fe(II) probably because of the presence of $(\text{N}_2\text{H}_5)_2\text{SO}_4$ in reaction-2.

The reaction from III to IV takes longer time (weeks). Once again a CO_2 gas-solid (III) reaction was possible giving IV from III as shown below :—



The gas-solid reaction was faster than liquid-solid reaction as the former took place within 2–3 days compared to the latter which normally took weeks.

Macek *et al* (1976) have obtained hydrate salts of type V, where as we could obtain both IV and V salts. Hydrated salts-V are the normal products but by the gas-solid reaction between III and CO_2 , only anhydrous salts-(IV) are formed.

More evidence for the observed reaction sequence comes from infrared studies. The infrared spectra of iron complexes have been given as representative of the series (figure 1). Important infrared frequencies are tabulated in table 2. The assignment of the observed frequencies of compounds I to V are made on the basis of earlier studies on similar compounds by earlier workers. The infrared spectra of the products I to V clearly exhibit the changes in the anion frequencies as the reaction proceeds. The characteristic absorption of SO_4^{2-} (Nieupoort and Reedijk 1973; Nicholls *et al* 1968) OH^- (Nakamoto 1969) to $\text{N}_2\text{H}_5\text{COO}^-$ (Braibanti *et al* 1968; Nicholls *et al* 1968) anions are seen in I, II and III–V respectively. The $\nu\text{N-N}$ frequency characteristic of the co-ordinated hydrazine has been observed in the region $940\text{--}990\text{ cm}^{-1}$ indicating the presence of monodentate or bridged hydrazine groups. The $\nu\text{N-N}$ frequency of N_2H_5^+ cation in these complexes is observed at $980\text{--}1010\text{ cm}^{-1}$ as reported by earlier workers. The $\nu\text{N-N}$ of $\text{N}_2\text{H}_3\text{COO}^-$ (which is present as a bidentate ligand) also appears at $990\text{--}1013\text{ cm}^{-1}$ as reported earlier. All the type-III compounds exhibit a sharp absorption frequency at 3345 cm^{-1} . This has been assigned to the H-bonded $\text{N-H}\cdots\text{O}$ between the monodentate hydrazine proton and oxygen atoms of the hydrazido carbonate. This frequency (3345 cm^{-1}) is characteristic of H-bonded NH group with a neighbouring carbonyl group (Rao 1963). However, no such absorption has been observed in the case of type-IV complexes. This is understandable since the two monodentate hydrazine molecules in $\text{M}(\text{N}_2\text{H}_5\text{COO})_2 \cdot (\text{N}_2\text{H}_4)_2$ are now replaced by a bidentate ligand-like $\text{N}_2\text{H}_3\text{COO}^-$ and no H-bonding is possible.

4. Conclusions

Transition metal ammonium sulfates $(\text{NH}_4)_2\text{M}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ when treated with large excess of hydrazine hydrate give $\text{N}_2\text{H}_5 [\text{M}(\text{N}_2\text{H}_3\text{COO})_3] \cdot \text{H}_2\text{O}$ —V through $(\text{N}_2\text{H}_5)_2\text{M}(\text{SO}_4)_2 \cdot 3\text{N}_2\text{H}_4$ —I, $(\text{N}_2\text{H}_5)_2 [\text{M}(\text{OH})_4 \cdot (\text{N}_2\text{H}_4)_2]$ —II, $\text{M}(\text{N}_2\text{H}_3\text{COO})_2 \cdot (\text{N}_2\text{H}_4)_2$ —III and $\text{N}_2\text{H}_5 [\text{M}(\text{N}_2\text{H}_3\text{COO})_3]$ —IV. Hydroxo complexes (II) react with $\text{CO}_2 (\text{g})$ to give hydrazido carbonate derivatives III and IV. Solid-gas reactions are much faster than the solid-liquid reactions.

Table 2. Some important infra-red absorption frequencies of iron compounds.

I	II	III	IV
3410 } ν N-H weak 3300 } H-bond 3180 }	3280 } Bonded OH 3220 } cis	3345 (γ N-H...O)	3420 (free NH)
	2920 } Bonded OH 2860 } trans	3250 } γ N-H weak 3170 } H-bond	1650 (δ -NH) 1590
2730 (γ N-H strong H bond)	1610 } δ OH 1580 }	1680 } δ N-H 1640 }	1470 (—) 1390 (γ_s COO ⁻)
1690 } 1640 } δ N-H 1610 }	1480 (bridged 1400 O-H)	1580 (δ N ₂ H ₅ ⁺) 1380 (N-H bond) 1220 (ρ N ₂ H ₅)	1210 (ρ_r N ₂ H ₅) 1180 } γ C-N 1090 }
1350 } 1310 } N-H bond 1250 } 1230 }	1350 } 1310 } N-H bond	1200 (N-H wagging)	1000 (γ N-N of N ₂ H ₅ COO ⁻)
1200 (N-H wagging) 1120 (γ S-O-sym) 1100 (γ_3 - SO ₄ ²⁻) 1008 (γ N-N of N ₂ H ₅ ⁺) 995 (γ N-N of N ₂ H ₄)	990 (γ N-N of N ₂ H ₅ ⁺) 975 (γ N-N of co-ord N ₂ H ₄) 815 (ρ NH ₂) 620 ($\rho\gamma$ NH ₂ or COO ⁻)	1120 } γ C-N 1090 } 990 (γ N-N of N ₂ H ₅ COO ⁻) 940 (γ N-N of N ₂ H ₄)	980 (γ N-N of N ₂ H ₅ ⁺) 810 (ρ NH ₂ or γ O-C-O)
645 625 (γ_4 - SO ₄ ²⁻)	600 ($\rho\gamma$ NH ₂ or COO ⁻)	780 } 760 } ρ_ω NH ₂	770 (ρ_ω NH ₂)
610 (N-H deform) 575 (NH ₃ rock) 480 (γ_2 - SO ₄ ²⁻)	550 (γ M-N)	700 $\rho\gamma$ NH ₂ 650 (ρ COO ⁻) 590 (δ COO ⁻)	

- I. (N₂H₅)₂Fe(SO₄)₃ · 3N₂H₄
 II. (N₂H₅)₂ [Fe(OH)₄(N₂H₄)₂]
 III. Fe(N₂H₅COO)₂ · (N₂H₄)₂
 IV. N₂H₅ [Fe(N₂H₅COO)₃]

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