

## Solid state reactions of coordination compounds by gas chromatography

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**Abstract** - Here we report a review of the results of our studies in recent years on reactions of coordination compounds in solid state at ordinary and medium temperatures. The studies have been made mainly by means of gas chromatography coupled with various spectroscopic methods. The results are described with respect to the following aspects:

1. Thermal decomposition of coordination compounds,
2. Regulativity of thermal decomposition,
3. Kinetics of thermal decomposition,
4. Supported surface complexes,
5. Finding of efficient catalysts,
6. Activation of small molecules,
7. Synthesis of coordination compounds,
8. Solid state reactions of coordination compounds,
9. Reduction processes of compounds,
10. Other studies.

### INTRODUCTION

Gas chromatography (GC) in modern chemistry lab is usually used in separation and analysis of volatile compounds. However, quite a few of the topics other than analysis have been discussed in several reviews and books (ref. 1&2). In addition, GC has also been applied to the study on thermal decomposition of coordination compounds (ref. 3-6).

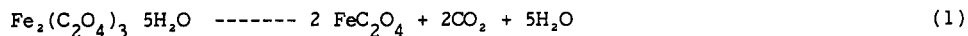
On the other hand, solid state reaction is an important field in inorganic chemistry and the reactions always occur at high temperature. As is well known, almost all coordination compounds would break up at high temperatures, thus their reactions should only be investigated at ordinary and medium temperature. The changes such as volatilization and cracking of the ligands, oxidation and reduction in chosen atmospheres afford possibility of studying the reactions at medium or ambient temperature. A number of papers about solid state reactions of coordination compounds have been published. Owing to coordination unsaturation by escape of ligands, the reactions would sometimes take place in their own accord.

In recent years we have studied the reactions of coordination compounds in solid state by means of GC coupled with various spectroscopic methods. The results are described with respect to the following aspects.

### 1. THERMAL DECOMPOSITION OF COORDINATION COMPOUNDS

(ref. 7-11)

Thermal stability is a basic property of compounds. The most thermal analytical data of coordination compounds are obtained by DTA, DSC and TG, but rarely by GC as chief means of determination. In addition to the results of DTA and TG, GC has the advantage of providing more chemical information. This is illustrated by the thermal decomposition of Fe(III) oxalate as shown in Fig. 1. TG, DTA curves show only the change of weight and heat effect of the compound. Study on thermal decomposition by GC possesses the following advantages: 1. Giving components of gaseous products, 2. Giving ratios of components of effluent gases. According to the amounts of CO<sub>2</sub> and CO, it is, therefore, inferred that the decomposition reaction must proceed according to the following equations:



3. Facilitating the study of the reaction in different atmospheres. 4. Supplying information as to the reaction mechanism by the position and form of the decomposition peaks. 5. Coping with parallel reactions. When a thermodecomposition proceeds by two different reactions simultaneously, the percentage of either reaction can be obtained from the relative amounts of the gaseous components. Thermodecomposition of Ni(HCO<sub>2</sub>)<sub>2</sub> in He (Fig. 2) may take place in two simultaneous reactions:



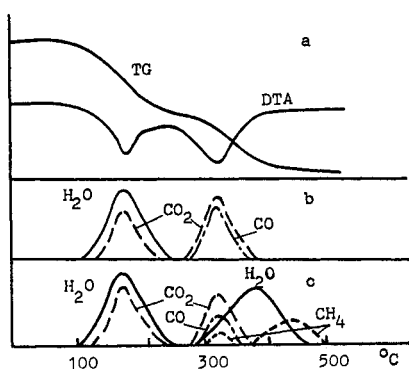


Fig. 1 Thermal decomposition of iron(III) oxalate. (a) DTA, TG. (b) EG curve in He. (c) EG curve in  $H_2$ .

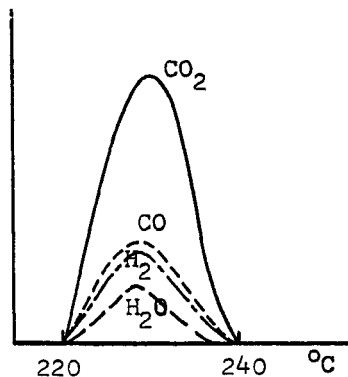


Fig. 2 Thermal decomposition of nickel formate in He.

From the effluent curves, it is found that the molecular ratio of  $CO_2:CO$  is about 3:1. It is therefore probable the two reactions proceed at approximately the same rate.

## 2. REGULARITIES OF THERMAL DECOMPOSITION (ref. 12-19)

Owing to the complexity of thermal decomposition of solid coordination compounds and insufficient accumulation of experimental data, not much can be said about solid phase thermal decomposition of coordination compounds. From our studies only a few preliminary conclusions are given as follows: 1. The kind of thermal decomposition products of anionic ligands depends on the nature of the central atoms. Taking thermal decomposition of metal oxalates as example, the reaction may be classified into three categories:



$CoC_2O_4$ ,  $CuC_2O_4$ ,  $HgC_2O_4$ , etc. belong to the first category;  $FeC_2O_4$ ,  $ZnC_2O_4$  and  $MnC_2O_4$  are in the second category;  $CaC_2O_4$ ,  $MgC_2O_4$  etc. fall in the third category.

2. Decomposition peak values of coordination compounds bear a nearly linear relationship with electrode potentials of cations, as shown by the decompositions of oxalates, salicylates and pseudo-prusside.

3. Relationship of thermal stability with symmetry of coordination compounds. by optimization method (ref. 20, 21), the relationship of stability with symmetry has been calculated. It is found that, the higher molecular symmetry, the more stable the molecule. the results of study by Onodera (ref. 3) on the thermal decomposition of a series of  $Co(NH_3)_x(NO_2)_{6-x}$  compounds have confirmed our conclusions.

4. Thermal decomposition temperature depends on the nature of the substituting ligands. Taking the thermal decomposition of a series of  $Na[Fe(CN)_5L] \cdot nH_2O$  compounds as example, it is found that when L is changed, the decomposition temperature changes accordingly as shown by the following list:

L	$CN^-$	$NO_2^-$	$SO_3^-$	$NO^+$	$enH^+$	$N_2H_5^+$	$NH_3$	$H_2O$	Py
T °C	330	320	320	310	220	140	140	120	120

The fact that the order of thermal stabilities of coordination compounds is in concordance with the order of the substituting groups in the spectrochemical series might suggest that coordination of the substituent ligand with the central metal ion plays an important role in thermal stability of the compounds.

## 3. KINETICS OF THERMAL DECOMPOSITION (ref. 8, 22)

Calculated results according to many kinetic equations of thermal decomposition of solids derived from data of TG or DTA curves are satisfactory when the compound decomposes only in one single reaction. but unsatisfactory in two or more simultaneous reactions. The data from GC effluent curves would avoid the defects of TG or DTA.

1. Kinetic equations of thermal decomposition. The following equation is proposed.

$$\frac{d\alpha}{dt} = k_0(1-\alpha)(C_{-1}\alpha^{-1} + 1 + C_1\alpha + C_2\alpha^2)$$

With the above equation, activation energies of 22 coordination compounds have been calculated, the mean deviation between the calculated values and experimental values is only 6.1%.

2. Kinetic equations of supported coordination compounds.

kinetic equations of thermal decomposition reported so far are based on the reaction of pure compounds, however, when a compound is carried on a support, owing to the difference crystal face and interaction with the carrier, a particular surface compound may be considered as formed. Coordination compounds thus absorbed on the surface of different supports must have different activation energies of thermal decomposition. Therefore, we propose that activation energy  $E_a$  of a supported compound is a function of conversion rate  $\alpha$ , i.e.  $E_a = E(\alpha)$ , since the functional form is not known, the equation may be approximately expressed by a quadratic function of  $\alpha$ .

$$E_a = E + C_1\alpha + C_2\alpha^2$$

Considering a compound dispersed on the surface retains original structure only with difference of absorption position on the support surface, the frequency factor may be regarded as unchanged. Therefore, a kinetic equation appropriate for thermal decomposition of solid supported coordination compounds is proposed as follows:

$$d\alpha/dt = Ae^{-(E+C_1\alpha+C_2\alpha^2)/RT}(1-\alpha)^n$$

The errors between values calculated by the above equation and experimental results for thermal decomposition of more than ten compounds are generally below 5%.

#### 4. SUPPORTED SURFACE COMPLEXES (ref. 23-33)

Coordination compounds are absorbed on various supports by impregnation, owing to the interaction between supports and coordination compounds different types of surface complexes may be formed, whose thermal decomposition reactions are quite different. Effluent curves of GC provide evidence of the presence of these complexes.

1. No significant interaction between coordination compounds and their respective supports. Thermal decomposition of  $K_3[Fe(C_2O_4)_3]$  on support HZSM-5 is such a case.

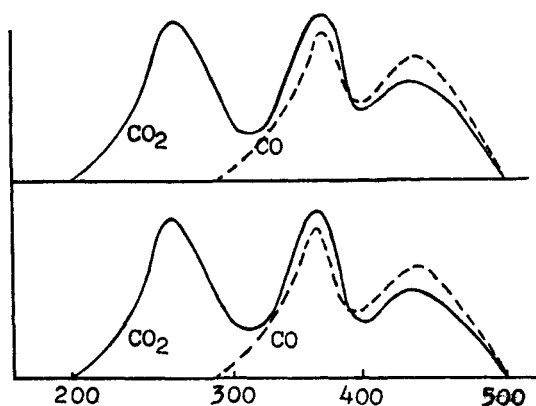


Fig. 3 EG curves of thermal decomposition of (a) unsupported  $K_3[Fe(C_2O_4)_3]$  and (b) supported on HZSM-5.

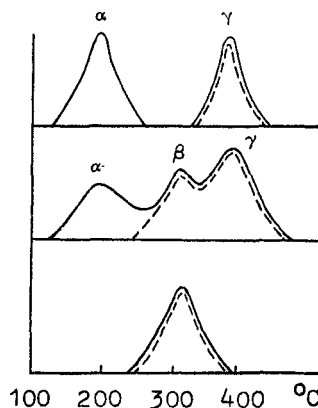


Fig. 4 EG curves of (a)  $Fe_2(C_2O_4)_3$ . (b)  $Fe_2(C_2O_4)_3/HY$ . (c)  $Al_2(C_2O_4)_3$  in He.

Comparison of the effluent curves or Mossbauer parameters of products shows no difference between supported and unsupported complexes. It is, therefore, evident that there is no significant interaction between the coordination compound and the support.

2. Formation of simple surface complexes

Simple surface complexes are formed from ligands set free from coordination compounds with Lewis acid centers on the surface of the support.  $Fe_2(C_2O_4)_3/HY$  system affords an example. In fig. 4b, the new peak  $\beta$  is due to the formation of  $Al_2(C_2O_4)_3$  which is confirmed by IR spectra (Fig. 5). It is concluded that a simple surface complex is formed through coordination of ligand  $C_2O_4^{2-}$  with Lewis acid center  $Al^{+++}$ .

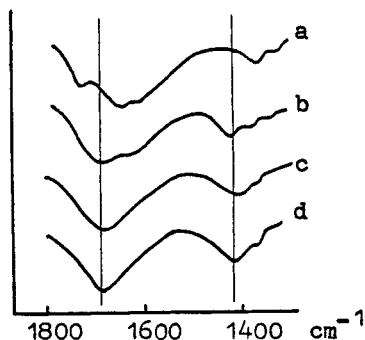


Fig. 5 IR results. (a)  $\text{Fe}_2(\text{C}_2\text{O}_4)_3$ . (b)  $\text{Fe}_2(\text{C}_2\text{O}_4)_3/\text{HY}$ . (c)  $\text{H}_2\text{C}_2\text{O}_4/\text{HY}$ . (d)  $\text{Al}_2(\text{C}_2\text{O}_4)_3$ .

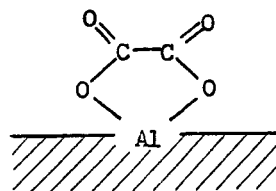


Fig. 6 Simple surface coordination Compound.

### 3. Surface mixed complexes

Oxygen atoms in the support surface bind with central metal atoms of coordination compounds forming mixed surface complexes. When  $\text{Ni}(\text{HCO}_2)_2$  is supported on  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{NaY}$ ,  $13\text{X}$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{MgO}$  or any other oxide, it is found that different oxide supports all give  $\beta$  peak, and all  $\beta$  peak temperatures fall on  $240 \pm 2^\circ\text{C}$ , the decomposition products and the mole ratio of  $\text{CO}_2/\text{CO}$  is all the same. All the above findings are easily explained by the formation of mixed surface complex.

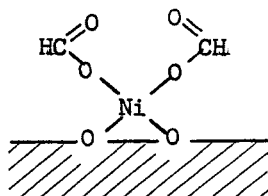


Fig. 7 Mixed surface coordination compound.

### 4. Surface hydrolytic complex

If the support oxide is quite basic so as to make the coordination compound on its surface hydrolyse, a hydroxo compound would be formed.  $\text{Ni}(\text{HCO}_2)_2$  supported on  $\text{MgO}$  is such an example.

## 5. FINDING OF EFFICIENT CATALYSTS (ref. 23, 24, 34-36)

Catalysts have been searched mainly by experience. The study on thermal decomposition by GC affords another path to search for new efficient catalysts. If a poly atomic ligand breaks off intact from the central metal ion, the latter would not be considered to have catalytic effect on such a class of ligands, conversely, if the leaving poly atomic ligand of the complex can form new coordination compounds by decomposition and/or addition, the central metal might serve as a catalyst and thus worth further investigation. In the following the discovery of an efficient methanation catalyst is described.

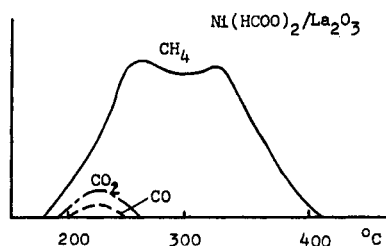


Fig. 8 EG curve of the thermal decomposition of nickel formate supported on  $\text{La}_2\text{O}_3$ .

Nickel formate supported on  $\text{La}_2\text{O}_3$ , gives effluent curves which are quite different from the other supports, the main products of thermal decomposition being  $\text{CH}_4$  and thus this system may be an excellent catalyst for methantion (Fig. 8)

Test of catalytic property.

After completion of the decomposition of the  $\text{Ni}(\text{HCO}_2)_2/\text{La}_2\text{O}_3$  system, pass in  $\text{CO}_2$  and  $\text{H}_2$  (1:10) at a rate of 8000/hr g. Observe the conversion rate and compare with commercial catalyst. The following results were obtained.

Sample	Temperature °C			
	250		300	
	Turnover	Selectivity	Turnover	Selectivity
$\text{Ni}(\text{HCOO})_2/\text{SiO}_2$	12.7	73.4	41.2	86.5
$\text{Ni}(\text{HCOO})_2/\text{Al}_2\text{O}_3$	24.7	90.3	41.2	86.5
$\text{Ni}(\text{HCOO})_2/\text{La}_2\text{O}_3$	64.0	97.5	100.0	100.0
Commercial catalyst	30.0	100.0	89.8	100.0

## 6. ACTIVATION OF SMALL MOLECULES (ref. 16, 17, 37)

Activation of small molecules is at present an active domain of research. With regard to multi-bond activation, many models have been suggested. here presents an experimental study on the activation of the triple bond of  $\text{CN}^-$ .

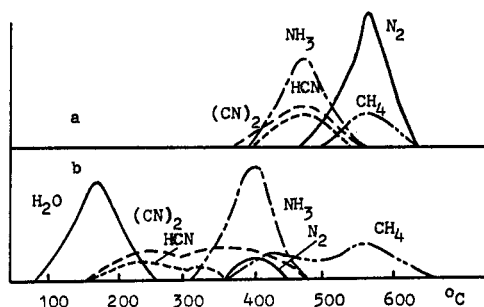


Fig. 9 EG curves of (a)  $\text{K}_4\text{Fe}(\text{CN})_6$   
(b)  $\text{KFe}[\text{Fe}(\text{CN})_6]$  in  $\text{H}_2$ .

Comparison of the effluent curves of these two compounds: it is clear that the decomposition products of Prussian blue all are correspondingly lower than those of  $\text{K}_4[\text{Fe}(\text{CN})_6]$  by 100 - 200 °C. Evidently this is due to the difference in coordination of  $\text{CN}^-$ . Bonding at both ends with iron atoms greatly intensifies the weakening of the triple bond  $\text{CN}^-$ . As a result  $\text{CN}^-$  in Prussian blue breaks and adds on hydrogen much more easily than that in  $\text{K}_4[\text{Fe}(\text{CN})_6]$ .

## 7. SYNTHESIS OF COORDINATION COMPOUNDS (ref. 4, 10, 38)

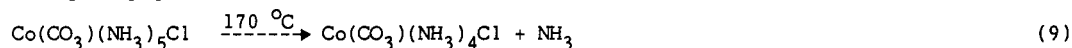
Through of the GC effluent curves often indicate existence of some stable decomposition or reaction products and thus may give clue to preparation of new coordination compounds. In the following, a part of such work is described.

1. Reductive Syntheses. A simple example is the thermal decomposition of  $\text{Fe}_2(\text{C}_2\text{O}_4)_3 \cdot 5\text{H}_2\text{O}$  in  $\text{H}_2$ . At 240°C, the end of the first decomposition peak,  $\text{Fe}_2(\text{C}_2\text{O}_4)_3$  is converted to  $\alpha\text{-FeC}_2\text{O}_4$ . Similarly  $\text{K}_4[\text{Fe}(\text{CN})_6]$  could be obtained by heating  $\text{K}_3[\text{Fe}(\text{CN})_6]$  at 370°C in  $\text{H}_2$ .

2. Substitutive Syntheses. In the process of thermal decomposition, volatile ligand in the innersphere escapes and that in the outersphere enters to take its place, thus forming a new coordination compound. Thermodecomposition of  $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$  and coordination number of Ni is changed from 6 to 4, the reaction is as follows:

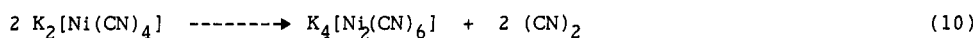


3. Innersphere Substitutive Syntheses. During the thermal decomposition of  $\text{Co}(\text{CO}_3)(\text{NH}_3)_5\text{Cl}$  in He, the first effluent  $\text{NH}_3$  ligand liberation from the inner sphere and formation of  $\text{Co}(\text{CO}_3)(\text{NH}_3)_4\text{Cl}$ .



The ligand  $\text{CO}_3^-$  is changed from a monodentate ligand to a bidentate. IR spectra also confirms the result.

4. Syntheses of Cluster Compounds. The thermal decomposition effluent curves of  $K_2[Ni(CN)_4]$  in  $H_2$  show that  $K_2Ni(CN)_4$  is converted to a brick red nickel cluster  $K_4[Ni_2(CN)_6]$  at  $390^\circ C$  with the evolution of  $(CN)_2$ .



## 8. SOLID STATE REACTIONS OF COORDINATION COMPOUNDS (ref. 39, 40)

Solid state reactions have not been investigated so widely as liquid state reactions. Most of solid state reactions studied occurred at high temperatures in such fields as ceramics, metallurgy, silicates and glass manufacture. Because of the unstability of coordination compounds at such high temperatures, the study of their solid state reactions have to be carried out at medium or low temperatures.

The study of solid state reactions by gas chromatography is based on the changes of composition of the effluent gas and peak temperatures, from which the reaction process may be inferred. The solid redox reaction of  $Fe_2(C_2O_4)_3$  with  $NaNO_3$  in  $H_2$  may be taken for illustration.

### 1. Solid State Redox Reaction of Iron Oxalate.

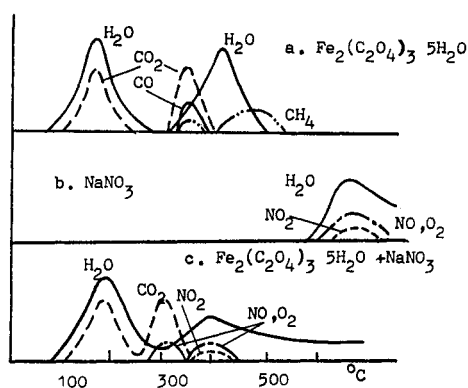
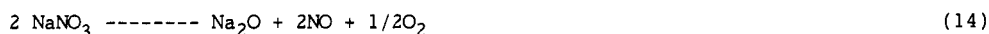
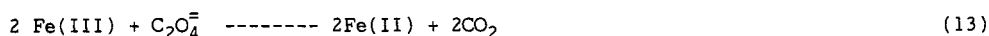
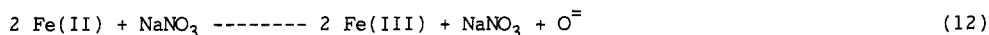
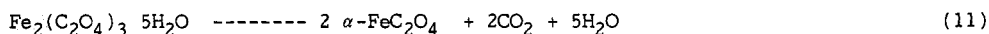


Fig. 10 EG curves of  $Fe_2(C_2O_4)_3 \cdot 5H_2O$  and  $NaNO_3$  in  $H_2$ . (a)  $Fe_2(C_2O_4)_3 \cdot 5H_2O$ . (b)  $NaNO_3$ . (c) 1:5 mole of  $Fe_2(C_2O_4)_3 \cdot 5H_2O$  and  $NaNO_3$ .

Comparing Fig. 10a, b and c, the gas chromatographic effluent curves of pure  $Fe_2(C_2O_4)_3$ , pure  $NaNO_3$  and  $Fe_2(C_2O_4)_3$  mixed with  $NaNO_3$  respectively, it is clear that they are quite different. If there were no solid state reaction between  $Fe_2(C_2O_4)_3$  and  $NaNO_3$ , Fig. 10c should be a simple superposition of Fig. 10a and Fig. 10b. The characteristic curves of Fig. 10c indicate that there is a solid state reaction taking place between the two solids. Below  $240^\circ C$ , fig. 10c is same as Fig. 10a, indicating that the decomposition of  $Fe_2(C_2O_4)_3$  is not affected by the presence of  $NaNO_3$ , between  $240-300^\circ C$ , a new peak appears and the gaseous products being  $CO_2$  and a little amount of  $NO, O_2$ , the lack of  $CO$  excluding the possibility of the thermal decomposition of  $\alpha-FeC_2O_4$ , the following mechanism is revealed and which is supported by Mossbauer spectra (ref. 39).



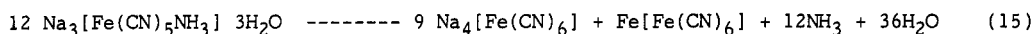
The catalytic effects of iron compounds on the thermal decomposition of  $NaNO_3$  and  $NaNO_2$  can also be observed in Fig. 10, the presence of iron(III) compounds shifts the thermal decomposition peak of  $NaNO_3$  from  $650^\circ C$  to  $380^\circ C$  in  $H_2$  atmosphere.

### 2. Solid State Displacement Reaction.

The thermal decomposition of a series of  $Na_n[Fe(CN)_5L] \cdot mH_2O$  has been studied and the temperature of releasing L ligand is as follows:

L	$NH_3$	$N_2H_5^+$	Py	$enH^+$
T $^\circ C$	80	100	80	135

The thermal decomposition equation is as follows (Taking  $L = \text{NH}_3$  as an example):



Mossbauer spectra reveals that there are two kinds of Fe(II) in the solid products of thermal decomposition, one is a high spin Fe(II), the other is a low spin Fe(II), which is illustrated in Fig. 11.

When  $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3] \cdot 3\text{H}_2\text{O}$  is mixed with KCN at  $90^\circ\text{C}$  for 1hr, the solid state replacement reaction takes place,  $\text{CN}^-$  ligand enters the inner coordination sphere of  $\text{Na}_3[\text{Fe}(\text{CN})_5\text{L}]$ , and the L ligand is replaced, and this process is proved by Mossbauer spectra (Fig. 12) which shows that there is only one kind of Fe(II) in low spin state in existence in the solid state replacement reaction of  $\text{Na}_3[\text{Fe}(\text{CN})_5\text{L}]$  and KCN.

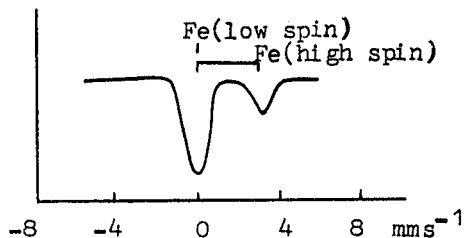


Fig. 11 Mossbauer spectra of decomposition products of  $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3] \cdot 3\text{H}_2\text{O}$  at  $200^\circ\text{C}$ .

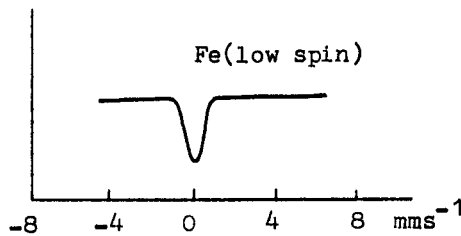
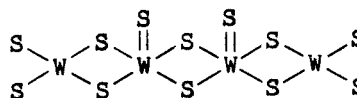
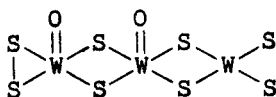


Fig. 12 Mossbauer spectra of the solid products of  $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3] \cdot 3\text{H}_2\text{O}$  mixed with KCN at  $90^\circ\text{C}$ , 1hr.

From Fig. 12, it can also be inferred that the solid state replacement reaction is complete.

### 3. Cluster Formation Reaction

Various Mo-S, W-S Clusters were generally synthesised in solutions,  $(\text{NH}_4)_2\text{MoS}_4$  and  $(\text{NH}_4)_2\text{WS}_4$  are the best starting materials. But they can also be synthesised in solid state and different clusters might be obtained at different temperatures. For example, keep the mixture of  $(\text{NH}_4)_2\text{MoS}_4$  and  $[(n\text{-Bu})_4\text{N}]\text{Br}$  at  $120^\circ\text{C}$ ,  $[\text{Mo}_2\text{OS}_7]^-$  can be produced while at  $130^\circ\text{C}$  for 2hr,  $[\text{Mo}_3\text{OS}_8]^-$  can be obtained. By the similar method, we have synthesised many new Mo-S, W-S clusters, and many reported clusters also synthesised in this way. Following clusters are the representative clusters synthesised.



The rate of the formation clusters was also studied. Heteronuclear linear clusters were also synthesised.

## 9. REDUCTION PROCESSES OF COMPOUNDS (ref. 18, 19, 41)

Heteropoly acids and their salts are a group of efficient oxidation catalysts. To study their reduced state in  $\text{H}_2$  has some significance in elucidating their catalytic reaction mechanism. Four  $\text{H}_2\text{O}$  peaks generally appear in all effluent curves of the heteropoly acid and its salts of various metals. The first peak is assigned to the expelling of crystal water, the following peaks are reduced water peaks. three stages have been identified in this process.

## 10. OTHER STUDIES

Gas chromatographic effluent curves have been studied in the following subjects:

1. Thermal stabilities of drugs (ref. 42), such as antimony potassium tartrate, ferrous gluconate, vitamin C etc.
2. Catalytic decomposition (ref. 39). Many inorganic and organic compounds would undergo catalytic decomposition in the presence of a transition metal ion.
3. Photochemical decomposition (ref. 43)
4. Explosives (ref. 44)
5. Rare-earth compounds (ref. 45)

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