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Solid State Reactions of Coordination Compounds at Low Heating Temperatures

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A review of solid state reactions related to the coordination compounds is presented. Eight types of reaction are listed for the multicomponent systems, and factors influencing the reactions are discussed. © 1993 Academic Press, Inc.

Solid state chemistry is of fundamental importance in material science. Research has long been focused on inorganic oxides at elevated temperatures, but to a much lesser degree on coordination compounds for use at low temperatures or even at room temperature. Several structural differences between inorganic oxides and coordination compounds include: (1) point structure existing in coordination compounds which are not present in the covalent network of an ordinary oxide; (2) low bond energies, where the coordination bonds exist within a molecule, and hydrogen bonds or Van der Waals forces between the molecules, in place of the covalent or ionic bonds in inorganic oxides; (3) many ligands are easily volatilized, or pyrolysized to produce fragment molecules; (4) coordination or crystal water or other solvent molecules can readily escape from the crystal, which increases the defects and improves interfacial contact. Reactions of coordination compounds in the solid state are therefore more easily carried out than those of oxides. Here we present several types of such reactions and discuss possible factors affecting the reactions.

Catalog of Solid State Reactions of Single Component Systems

A large number of solid state reactions of single component systems have been studied. Fujiwara and Bailar (*1*) and Lamay (*2*) have described the reaction types earlier. Combined with our own work, the types include:

1. Thermal Reactions

(*1*) *Dissociation*

$$[Zn(C_5H_5N)_2][Ni(CN)_4] \rightarrow Zn[Ni(CN)_4] + 2C_5H_5N \quad (3)$$

(*2*) *Substitution*

$$[Co(NH_3)_5(H_2O)]Cl_3 \rightarrow [Co(NH_3)_5Cl]Cl_2 + H_2O \quad (4)$$

(*3*) *Redox*

$$12K_3[Fe(CN)_6] \rightarrow 9K_4[Fe(CN)_6] + Fe_2[Fe(CN)_6] + 6\,(CN)_2 \quad (5, 6)$$

(*4*) *Formation of Clusters*

$$2K_2[Ni(CN)_4] \rightarrow K_4[(CN)_3Ni - Ni(CN)_3] + (CN)_2 \quad (7)$$

(*5*) *Polymerization*

$$n\text{NiBr}_2[P(CH_3CH_2CN)_3]_2 \rightarrow \text{polymer} \quad (8)$$

(*6*) *Isomerization*

a. Geometrical isomerization

$$cis\text{-}[Cr(tn)_2Cl_2]Cl \rightarrow trans\text{-}[Cr(tn)_2Cl_2]Cl \quad (9)$$

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b. Optical isomerization

d-[Fe(phen)$_3$] $X_2 \rightarrow$ rac-[Fe(phen)$_3$]X_2 (*10*)

c. Bond isomerization

[Co(NH$_3$)$_5$ONO] $X_2 \rightarrow$ [Co(NH$_3$)$_5$NO$_2$]X_2 (*11*)

d. Transition spin state

$^5T_{2g}$(Oh)-[Fe(bipy)$_2$(NCS)$_2$] $\rightarrow$ $^1A_{1g}$(Oh)[Fe(bipy)$_2$ (NCS)$_2$] (*12*)

(*7*) *Migration of Ligands*

[Cu(en)$_2$][PtCl$_4$] $\rightarrow$ [Pt(en)$_2$][CuCl$_4$] (*13*)

(*8*) *Formation of Chelate Rings*

Na[CoX(HEDTA)] $\rightarrow$ Na[Co(EDTA)] + HX (*14*)

2. Photochemical Reactions (*15*)

(*1*) *Dissociation*

$NH_4[Mn(mal)_2(H_2O)_2] \rightarrow NH_4[Mn(mal)_2] + 2H_2O$

(*2*) *Substitution*

[Cr(en)$_3$](SCN)$_3$ $\rightarrow$ *trans*-[Cr(en)$_2$(SCN)$_2$](SCN) + en

(*3*) *Redox*

$2K_3[Co(C_2O_4)_3] \cdot 3H_2O \rightarrow$
$2K_2[Co(C_2O_4)_2] + K_2C_2O_4 + 2CO_2 + 6H_2O$

(*4*) *Isomerization*

$[Co(NH_3)_5NO_2]Cl_2 \rightarrow [Co(NH_3)_5ONO]Cl_2$

Solid State Reactions of Multicomponent Systems

Only few reports deal with multicomponent systems, especially with those occurring at room temperature.

In the 1960s, Wendlandt and Sveum (*16*) studied the solid state reactions between [Cr(en)$_3$]X_3 and NH$_4$$Y$($X$, Y = F, SCN, Cl, Br, I). It was found that the competitive coordination ability of anions decreased in the order: $F^- > SCN^- > Cl^- > Br^- > I^-$.

In 1972, Thabet et al. (*17*) synthesized the ML_2 or MCl_2L_2 type complexes at room temperature by the reaction of some transition metal chlorides MCl_2 (M = Co, Ni, Cu) with organic compounds (L), such as Ph$_3$P, Ph$_3$PO, Ph$_3$AsO and dimethylglyoxime in the solid state.

In 1984, Oki and Yasuda (*18*) and Oki (*19*) investigated the reaction between [Cr(NH$_3$)$_6$](NO$_3$)$_3$ and alanine, and synthesized [Cr(Ala)$_3$].

Since 1986, Bassi and co-workers (*20–24*) have reported in succession the solid state reactions of some anhydrous transition metal acetates(CuAc$_2$, CoAc$_2$, ZnAc$_2$, and UO$_2$Ac$_2$) with organic compounds such as aminobenzoic acid, aniline hydrobromides, 8-hydroxyquinoline etc. at about 100°C. The capillary technique and mass loss method were used to investigate the kinetics of the reactions.

Beg *et al.* (*25*) also investigated the reaction of 8-hydroxyquinoline(oxin) with ZnCO$_3$ and CdCO$_3$, which produced MCO$_3$ · 2oxin; the kinetics was investigated as well.

Rao and co-workers (*26–28*) have published several papers on the solid state reactions of metal oxides with NH$_4$HF$_4$ or NH$_4$F at room temperature.

It is evident that almost all the previous work was carried out at about 100°C except that of Thabet et al. and of Rao and coworkers which was done at room temperature; these were limited to the substitution and addition reactions.

Over the years we have investigated many solid state transformations of coordination compounds at low heating temperatures. These are listed as follows:

1. Example

We take the reaction of anhydrous nickel acetate with salicylaldoxime (HSAO) as an example (*29*).

A weighed amount of anhydrous nickel acetate (180–200 mesh) and salicylaldoxime were placed in a 1 : 2 molar ratio and mixed. We ground the mixture gently for 3 min to obtain the best possible homogeneity, and then transferred the material to a thermostat with the temperature kept at 30 ± 0.1°C.

The weight loss increased linearly with time, and reached a constant value in 4 hr. The total weight loss percentage was 26.4%, which was very close to the theoretical value of 26.6% calculated for the loss of two moles of acetic acid. The final dark green product was analyzed as $Ni(SAO)_2$(Found: C, 51.03; H, 3.80; N, 8.84; Ni, 17.3. theoretical: C, 50.73; H, 3.62; N, 8.46; Ni, 17.7%), with a yield of 99%. The IR spectra and XRD patterns further established that the product was trans-$[Ni(SAO)_2]$. The process is therefore believed to occur as follows:

$$NiAc_2 + 2HSAO \rightarrow \textit{trans}\text{-}[Ni(SAO)_2] + 2HAc. \quad (1)$$

The variation of conductivity with time is shown in Fig. 1. The conductivity value of the reactants ($NiAc_2$ and HSAO) and of the product ($[Ni(SAO)_2)$ are all of the order of 10^{-6} S while the value achieved in the course of the reaction reaches 10^{-5} S as a result of the formation of acetic acid in accord with Eq. 1. Let

$$\alpha = \frac{\sigma_t - \sigma_o}{\sigma_m - \sigma_o},$$

where σ_o, σ_t, σ_m are the initial, time, and maximum conductivity value of the reaction separately. Then the data can be fitted by the following relation:

$$[-\ln(1-\alpha)]^{1/4} = kt + a$$

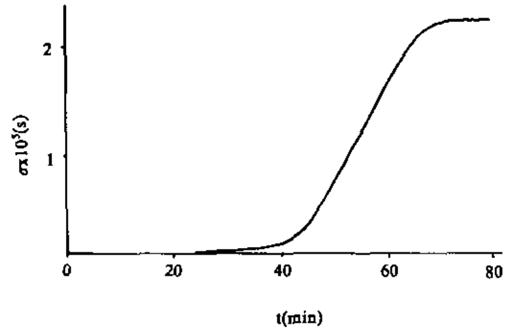


FIG. 1. The relation of conductivity with time for $NiAc_2$–HSAO (1 : 2) system at 30°C.

The activation energy is calculated to be 40.2 kJ · mol^{-1}.

2. Reaction types:

(1) Addition

As proposed by Beg *et al.* (*25*), the mixture of $ZnCO_3$ and 8—Oxin undergoes an addition reaction as follows:

$$ZnCO_3 + 2(8\text{—Oxin}) \rightarrow ZnCO_3 \cdot 2(8\text{—Oxin}).$$

(2) Ion exchange

$$K_4[Fe(CN)_6] \cdot 3H_2O + 2CuCl_2 \cdot 2H_2O \xrightarrow{RT} Cu_2[Fe(CN)_6] \cdot nH_2O + 4KCl + (7-n)H_2O \ (30)$$

The reaction is instantaneous and goes to completion immediately, on mixing at room temperature, to produce a red brown product, namely $Cu_2[Fe(CN)_6] \cdot nH_2O$.

Several hours are required for sodium nitroprusside to react with $CuCl_2 \cdot 2H_2O$ (1 : 1) at room temperature, giving a green ion-exchanged product of $Cu[Fe(CN)_5NO] \cdot nH_2O$ (*31*).

(3) Acid-base reaction

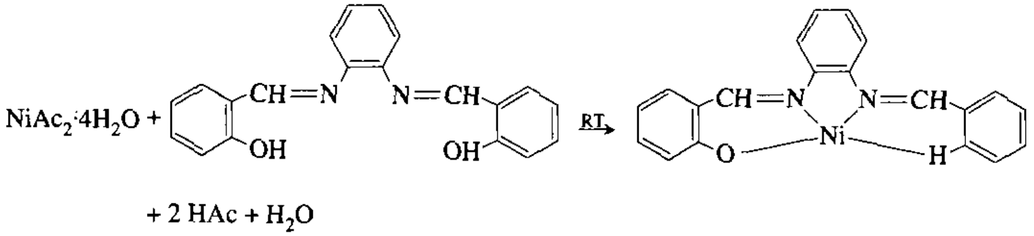
Cis-$[Cu(Gly)_2] \cdot H_2O$ could be obtained by the solid state reaction of glycine with freshly prepared $Cu(OH)_2$(*32*):

$$Cu(OH)_2 + 2HGly \xrightarrow{RT} \text{cis-}[Cu(gly)_2] \cdot H_2O + H_2O$$

(4) Substitution

The substitution reactions between the transition metal acetates such as $CoAc_2 \cdot 4H_2O$, $NiAc_2 \cdot 4H_2O$, $CuAc_2 \cdot H_2O$, $ZnAc_2 \cdot 2H_2O$, or anhydrous $CuAc_2$, $NiAc_2$, etc. and organic compounds such as amino acids (*32*), Schiff bases (*33*), 8-hydroxyquinoline (*32*), salicylaldoxime (*34*) etc. have been investigated at or close to room temperature. For example:

$$CuAc_2 \cdot H_2O + 2dl - Ala \xrightarrow{RT} \text{trans—}[Cu(dl\text{-}Ala)_2] + 2\,HAc + H_2O$$



$$MAc_2 + HSAO \xrightarrow{RT} trans\text{-}[M(SAO)_2] + 2\ HAc\ (M = Cu, Ni)$$

By maintaining the mixture of $K_3[Fe(CN)_6]$ and $H_2C_2O_4 \cdot 2H_2O$ at room temperature for two weeks, a green product is obtained which is characterized as $K_3[Fe(CN)_4(C_2O_4)]$ (*35*):

$$K_3[Fe(CN)_6] + H_2C_2O_4 \cdot 2H_2O \xrightarrow{RT} K_3[Fe(CN)_4(C_2O_4)] + 2HCN + 2H_2O$$

Mössbauer spectra (Fig. 2) show that a new pair of peaks appears with a larger quadripolar splitting ($\delta = 0.07\ mm \cdot s^{-1}$, $\Delta E_Q = 1.29\ mm \cdot s^{-1}$), is compared with the original two peaks of the unreacted $K_3[Fe(CN)_6]$($\delta = -0.08\ mm \cdot s^{-1}$, $\Delta E_Q = 0.28\ mm \cdot s^{-1}$).

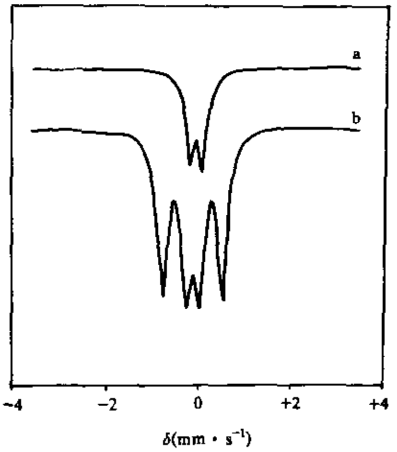


FIG. 2. Mössbauer spectra of (a) $K_3[Fe(CN)_6]$, (b) $K_3[Fe(CN)_6] + H_2C_2O_4 \cdot 2H_2O$ (1 : 1).

(*5*) *Isomerization*

$$[Co(en)_2CO_3]Cl + 2\ NH_4SCN \xrightarrow{100°C} cis\text{-}[Co(en)_2(SCN)_2]Cl + 2NH_3 + H_2O + CO_2$$

$$cis\text{-}[Co(en)_2(SCN)_2]Cl \xrightarrow{100°C} trans\text{-}[Co(en)_2(SCN)_2]Cl\ (36)$$

The existence of *cis*-$[Co(en)_2(SCN)_2]Cl$ as an intermediate was examined by NMR spectra (Fig. 3).

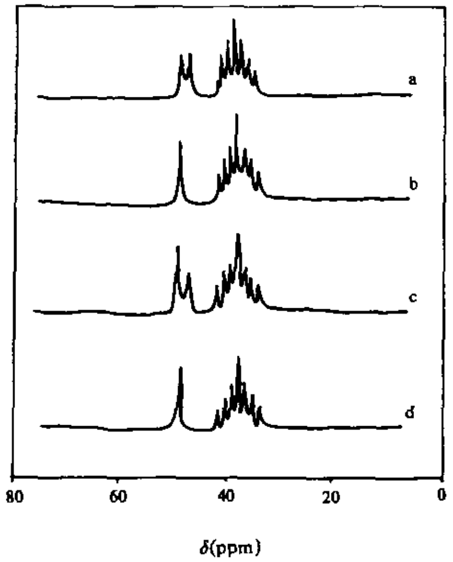


FIG. 3. NMR spectra of (a) *cis*-$[Co(en)_2(NCS)_2]Cl$; (b) *trans*-$[Co(en)_2(NCS)_2]Cl$; (c) $[Co(en)_2CO_3]Cl$ + NH_4SCN heating at 100°C for 30 min; (d) $[Co(en)_2CO_3]Cl$ + NH_4SCN heating at 100°C for 60 min.

(*6*) *Redox*

$$2K_3[Fe(CN)_6] + 2KI \xrightarrow{RT} 2K_4[Fe(CN)_6] + I_2 \quad (37)$$

$$[Fe(phen)_3](ClO_4)_3 + K_4[Fe(CN)_6] \xrightarrow{RT} [Fe(phen)_3](ClO_4)_2 + K_3[Fe(CN)_6] + KClO_4 \quad (38)$$

As a solid, the oxidization capabilities of $[Fe(phen)_3](ClO_4)_3$ and $[Fe(bipy)_3](ClO_4)_3$ are found to be greater than that of $K_3[Fe(CN)_6]$.

(*7*) *Formation of Clusters*

More than forty new cluster compounds have been synthesized by the solid state reactions at about 80°C, of which $[n\text{-}Bu_4N]_4[Cu_{12}Mo_8S_{32}]$ (*39*) is one of the largest sulfur containing clusters reported so far.

$$(NH_4)_2MoS_4 + CuCN + n\text{-}Bu_4NBr \xrightarrow{80°C} [n\text{-}Bu_4N]_4[Cu_{12}Mo_8S_{32}]$$

(*8*) *Thermal Decomposition: The Effects of Anions or Cations*

Figure 4 shows the evolved gas analysis (EGA) curves of hexaamminecobalt(III) chloride in a hydrogen atmosphere, both for the salt and with an anion added. It is clear that the peak temperature decreases by the addition of anions. The deammine activation energies have been calculated by employing the Coats–Redfern method, which increases in the order: $OH < SCN < I < Br, Cl, CN$. The properties of added anions salts such as the coordination ability, redox property, phase transition, and strong H-bond interaction are possible factors that contribute to a decrease in the stability of complex (*40*).

The effects of anions on the thermal decomposition of $[Cr(NH_3)_5(H_2O)](NO_3)_3$ and some other cobalt (III)-ammine complexes were explored (*40a*). The presence of some transition metal (Mn, Co, Ni, Cu) chlorides decreased the thermal stability of sodium nitroprusside as well (*31*).

Factors Affecting the Solid State Reactions

1. Structure of the Reactants

The reactions of the transition metal acetates such as $CoAc_2 \cdot 4H_2O$, $NiAc_2 \cdot 4H_2O$, $CuAc_2 \cdot H_2O$, and $ZnAc_2 \cdot 2H_2O$ with 8-hydroxyquinoline have been shown to be related to the structure of reactants (*32*). The XRD result establishes that $CuAc_2 \cdot H_2O$ reacts with 8-oxin immediately on mixing at room temperature (20 ± 2°C) and goes to completion within one hour. It requires 5 hr for $ZnAc_2 \cdot 2H_2O$ to complete the reaction under the same conditions, while for $CoAc_2 \cdot 4H_2O$ and $NiAc_2 \cdot 4H_2O$, there is no reaction. The reaction rate follows the sequence: $CuAc_2 \cdot H_2O > ZnAc_2 \cdot 2H_2O \gg CoAc_2 \cdot 4H_2O \sim NiAc_2 \cdot 4H_2O$.

Table I gives the bond lengths and angles in the structures of these acetates (*41*). It is obvious that the structures of these salts vary considerably. The oxygen octahedron about Cu^{2+} in the structure of the copper acetate monohydrate dimer is strongly distorted: four oxygen atoms from the bridging acetate ions are located at the corners of a square and are the closest neighbors of Cu^{2+}. A water molecule and a second copper atom are located normal to the plane of four oxygen atoms. The longest bond in the octahedron (Cu–Cu = 2.616 Å) and the shortest bond (Cu–O = 1.945 Å) differ considerably ($\Delta = 0.671$ Å).

In the structure of zinc acetate dihydrate the Zn–O bond lengths are equal; the O–Zn–O bond angles deviate strongly from 90°, which produces a considerable distortion of the octahedron. For cobalt and nickle acetate tetrahydrates; however, the approximately equal M–O bond lengths and the O–M–O angles (close to 90°) give rise to a comparatively regular octahedral arrangement about the metal ions. The reactivities of acetates are therefore affected in terms of their different structures. Those of $CuAc_2 \cdot H_2O$ and $ZnAc_2 \cdot 2H_2O$ with distorted octahedron are more active than $CoAc_2 \cdot 4H_2O$ and $NiAc_2 \cdot 4H_2O$ with a regular octa-

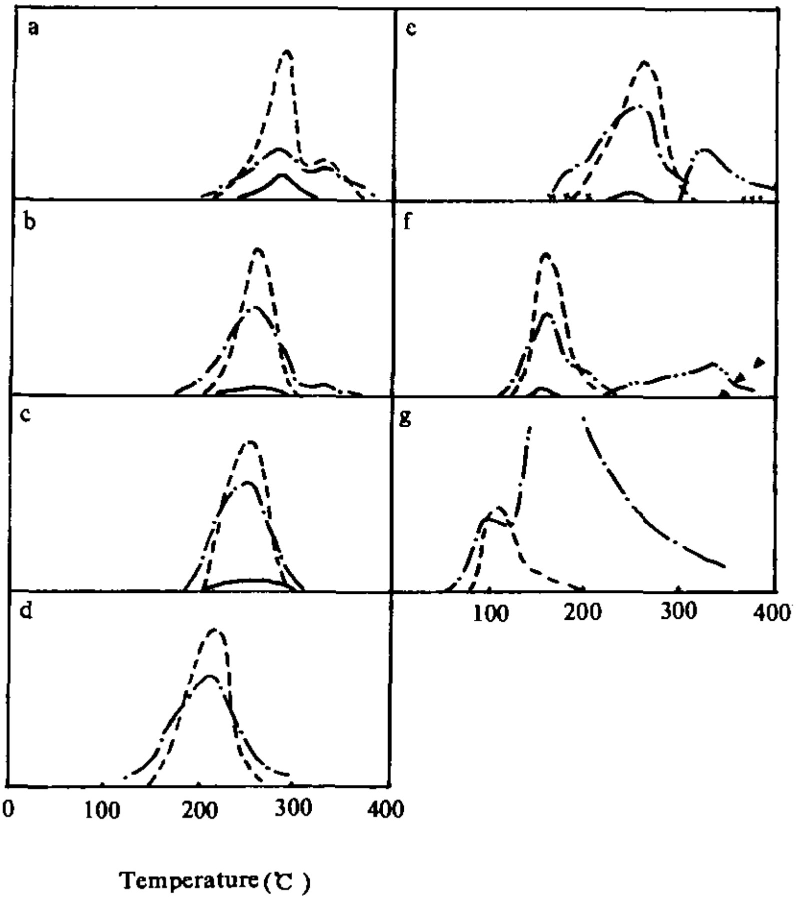


FIG. 4. EGA curves of $[Co(NH_3)_6]Cl_3$–KY in a hydrogen atmosphere (a) $[Co(NH_3)_6]Cl_3$; (b) $[CoNH_3)_6]Cl_3$ + KCl; (c) $[Co(NH_3)_6]Cl_3$ + KBr; (d) $[Co(NH_3)_6]Cl_3$ + KI; (e) $[Co(NH_3)_6]Cl_3$ + KCN; (f) $[Co(NH_3)_6]Cl_3$ + KSCN; (g) $[Co(NH_3)_6]Cl_3$ + KOH. – – – NH_3;—N_2; x x x $(CN)_2$; · · · · CH_4; – ▲ – H_2S; – · · – HCN; – · – HCl (a, b, e, f), HCl + HBr (c), HI (d), H_2O (g).

hedron, which is in accordance with the experimental results. The high activity of $CuAc_2 \cdot H_2O$ may be linked to its stronger distortion.

2. Temperature

The reaction of 8-hydroxyquinoline with $CoAc_2 \cdot 4H_2O$ or $NiAc_2 \cdot 4H_2O$ does not occur at room temperature for 20 hr, but goes to completion on heating at 40°C for only 10 min. Several other systems have been investigated with similar results. This suggests that there exists a nucleation temperature under some circumstances, above which a reaction sets in.

3. Acid–Base Effects

The effects of solid acids or bases on the reactions can be summarized as follows:

(1) To Provide Acidity or Basicity

$K_2[Ni(CN)_4] \cdot H_2O$ reacts with $H_2C_2O_4 \cdot 2H_2O$ to produce $Ni(CN)_2 \cdot xH_2O$ at room temperature (*42*). The proton-providing ability is considered as the main mechanism for initiating the reaction. With other organic acids such as malonic, fumaric, succinic, adipic acid in place of oxalic acid, the results have been obtained with the decreasing acidity in the order: oxalic > malonic >

TABLE I

M–O BOND LENGTHS AND O–M–O ANGLES IN THE STRUCTURE OF SOME ACETATES

$Zn(OCOCH_3)_2 \cdot 2H_2O$		$Cu(OCOCH_3)_2 \cdot H_2O$		$Ni(OCOCH_3)_2 \cdot 4H_2O$		$Co(OCOCH_3)_2 \cdot 4H_2O$	
$Zn–2O_1$	2.18	$Cu_1–O'_1$	1.986	$Ni–2O_1$	2.068	$Co–2O_1$	2.12
$Zn–2O_2$	2.17	$Cu_1–O_2$	1.994	$Ni–2O_{w1}$	2.081	$Co–2O_{w1}$	2.11
$Zn–2O_{w1}$	2.14	$Cu_1–O'_3$	1.945	$Ni–2O_{w2}$	2.048	$Co–2O_{w2}$	2.06
$Zn–O_m$	2.16	$Cu_1–O_4$	1.950	$Ni–O_m$	2.065	$Co–O_m$	2.09
		$Cu_1–O_4$	2.156				
$O_1–Zn–O_2$	61°	$Cu_1–Cu'_1$	2.616	$O_1–Ni–O_{w1}$	89.8°	$O_2–Co–O_{w1}$	90° 44′
$O_1–Zn–H_2O$	103°	$Cu–O_m(Ac)$	1.969	$O_1–Ni–O_{w2}$	90.8°	$O_1–Co–O_{w2}$	90° 33′
$O_1–Zn–O'_1$	158°			$O_{w1}–Ni–O_{w2}$	91.6°		
$O_1–Zn–O'_2$	104°	$O_5–Cu_1–O'_1$	98.4°				
$O_2–Zn–H_2O$	96°	$O_5–Cu_1–O_2$	93.0°				
$H_2O–Zn–H_2O$	94°	$O_5–Cu_1–O'_3$	97.7°				
$O_2–Zn–O'_2$	85°	$O_5–Cu_1–O_4$	93.3°				
$H_2O–Zn–O'_1$	92°	$O'_1–Cu_1–O_2$	168.6°				
$H_2O–Zn–O'_2$	152°	$O'_1–Cu–O'_3$	87.5°				
		$O'_1–Cu_1–O_4$	91.1°				
		$O_2–Cu_1–O'_3$	90.1°				
		$O_2–Cu_1–O_4$	89.1°				
		$O'_3–Cu_1–O_4$	168.9°				

fumaric > succinic > adipic acid (see Fig. 5), which is identical to what occurs in solution.

$K_3[Fe(CN)_6]$ cannot react with $NaBH_4$ at room temperature, or even on heating to 300°C, although $NaBH_4$ is one of the rather strong reducing reagents in solution. The addition of solid NaOH brings the reaction to completion (Fig. 6).

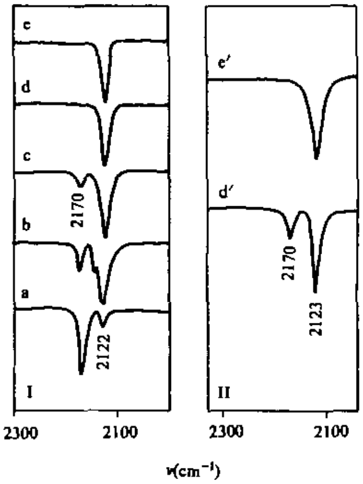


FIG. 5. Infared spectra of $K_2[Ni(CN)_4] \cdot H_2O$-organic acid systems I. standing at room temperature for one day. (a) oxalic; (b) malonic; (c) fumaric; (d) succinic; (e) adipic acid. II. heating at 100°C for 2 hr (d′) succinic; (e′) adipic acid.

$$8K_3[Fe(CN)_6] + NaBH_4 + 8NaOH \xrightarrow{RT} 8NaK_3[Fe(CN)_6] + NaBO_2 \cdot xH_2O + (6 - x)\,H_2O \quad (35)$$

It is proposed that B(III) of $NaBH_4$ captures oxygen from NaOH to form thermodynamically stable $NaBO_2$, which promotes the reaction.

(2) *Catalysis Effects*

When $CuAc_2 \cdot H_2O$ is ground to mix with glycine (1 : 2) at room temperature, sky-blue *trans*-$[Cu(Gly)_2] \cdot H_2O$ obtained after standing for 3 hr. With NaOH present at less than 5% *cis*-$[Cu(Gly)_2] \cdot H_2O$ is produced. If anhydrous sodium carbonate is added the reaction is suppressed (*43*).

$$CuAc_2 \cdot H_2O + 2\,HGly \xrightarrow{RT} trans\text{-}Cu(Gly)_2 \cdot H_2O + 2HAc$$

$$CuAc_2 \cdot H_2O + 2\,HGly \xrightarrow{5\%NaOH} cis\text{-}Cu(Gly)_2 \cdot H_2O + 2HAc$$

$$CuAc_2 \cdot H_2O + 2\,HGly \xrightarrow{Na_2CO_3} \text{no reaction}$$

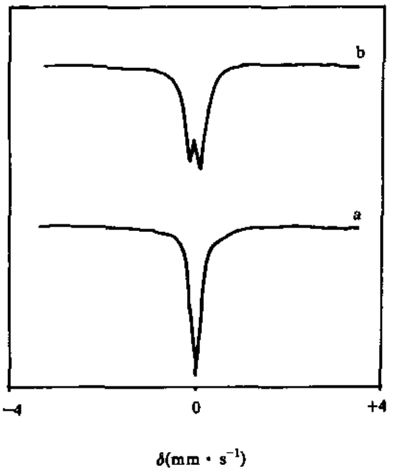


FIG. 6. Mössbauer spectra. (a) $K_3[Fe(CN)_6]$ + $NaBH_4$(1 : 6) at RT. (b) $K_3[Fe(CN)_6]$ + $NaBH_4$ + NaOH(1 : 4 : 2) at RT.

4. Crystal Water

(*1*) *Liquid Bridge*

Vaporized crystal water forms a liquid bridge on the interface which accelerates the reaction. As mentioned above, $CuAc_2 \cdot H_2O$ does not react with glycine at the presence of $NaCO_3$ but goes to completion if $NaCO_3$ is replaced by $NaCO_3 \cdot 10H_2O$. The absorption of crystal water by anhydrous $NaCO_3$ is suggested as the mechanism that stops the reaction. The difference between liquid bridge and solution is that the former corresponds to a solid state reaction with solvent molecules flowing within the interface of solids, while the latter corresponds to a solution reaction with solute dispersing in the solvent.

(*2*) *Defect*

In the course of reaction, part of the crystal water may evolve from the system, which produces a large point defect concentration in the crystal lattice and facilitates the reaction.

In a real system, both of the above two actions affect the solid state reactions. We have investigated the reactions of $NiAc_2 \cdot 4H_2O$, $CuAc_2 \cdot H_2O$, and their corresponding anhydrous salts with other compounds. It is evident that the presence of crystal water accelerates the reaction and decreases the reaction temperature and activation energy.

Applications to Synthesis

1. Synthesis of Cluster Compounds

As mentioned above, solid state reactions at low temperatures have been used to synthesize cluster compounds. More than forty obtained by this method are new, most of them being sulfur containing clusters. They include:

(1) huge cluster, e.g., $[(C_4H_9)_4N]_4[Cu_{12}Mo_8S_{32}]$

(2) heptanuclear polymeric cluster, e.g. $[MoS_4Cu_6Br_4Py_4]_n$

(3) neutral cubane-like cluster, e.g. $[Cu_3WS_4Cl(PPh_3)_3]$

(4) anionic cubane-like cluster, e.g. $[(n\text{-}Bu)_4N]_3[Ag_3MoS_4I_3Br]$

(5) miscellaneous, e.g., $[Cu_4Br_8]^{4-}$ (linear), $[MoOS_3Cu_3(NCS)_3]^{3-}$(Nido)

2. Synthesis of Compounds by One Step Method

It is possible to apply some reactions in the solid state to achieve a one-step synthesis of compounds, with a simpler procedure and a higher yield. Table II provides some examples.

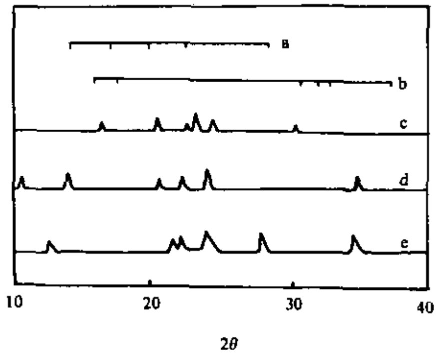


FIG. 7. XRD patterns of $Ni(phen)_xCl_2$. (a) phen · H_2O; (b) $NiCl_2 \cdot 6H_2O$; (c) $Ni(phen)_3Cl_2$; (d) $Ni(phen)_2Cl_2$; (e) $Ni(phen)Cl_2$.

TABLE II

THE ELEMENTAL ANALYSIS RESULTS OF PRODUCTS BY SOLID STATE REACTIONS OF SOME TRANSITION METAL ACETATES WITH ORGANIC COMPOUNDS

Solid sample	Found (requires) % C	H	N	*M*	Yield %
$Co(oxin)_2 \cdot 2H_2O$	56.49	3.93	7.69	15.88	82
	(56.36)	(4.17)	(7.31)	(16.13)	
$Ni(oxin)_2 \cdot 2H_2O$	56.12	3.90	7.35	15.11	81
	(56.39)	(4.18)	(7.31)	(15.32)	
$Cu(oxin)_2$	61.68	3.38	8.20	17.98	85
	(61.44)	(3.44)	(7.96)	(18.06)	
$Zn(oxin)_2 \cdot H_2O$	58.00	4.10	8.13	17.04	77
	(58.17)	(3.80)	(7.53)	(17.11)	
trans-$Cu(Gly)_2 \cdot H_2O$	20.98	4.30	12.32	27.44	90
	(20.91)	(4.39)	(12.20)	(27.62)	
cis-$Cu(Gly)_2 \cdot H_2O$	21.11	4.44	12.03	27.14	92
	(20.91)	(4.39)	(12.20)	(27.62)	
trans-$Cu(DL\text{-}Ala)_2 \cdot H_2O$	28.60	5.79	10.97	24.13	90
	(27.95)	(5.47)	(10.86)	(24.67)	
trans-$Cu(DL\text{-}Val)_2$	40.41	6.71	8.93	21.53	89
	(40.57)	(6.13)	(9.47)	(21.49)	
trans-$Cu(DL\text{-}Leu)_2$	44.14	7.56	8.42	19.60	86
	(44.50)	(7.47)	(8.64)	(19.62)	

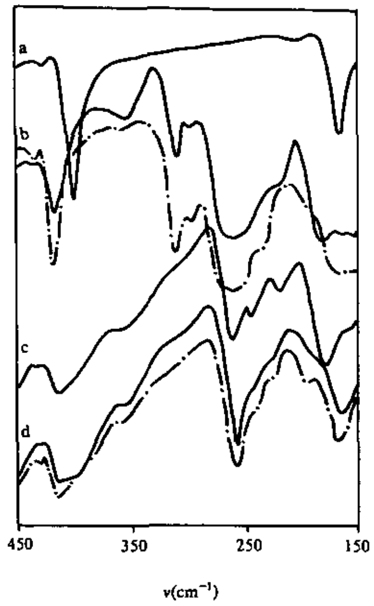


FIG. 8. Far infrared spectra of $Co(bipy)_xCl_2$. — solid product; – · – solution product. (a) bipy; (b) Co $(bipy)Cl_2$; (c) $Co(bipy)_2Cl_2$; (d) $Co(bipy)_3Cl_2$.

3. Synthesis of Intermediate Compounds

By the method of solid state reactions, we have obtained intermediate products such as $ML_xCl_2 \cdot nH_2O$ (M = Fe(II), Co(II), Ni(II), Cu(II); L = phen, 2,2′-bipy; x = 1, 2), which could not be synthesized easily from solution.

Figure 7 shows the XRD patterns of $Ni(phen)_xCl_2 (x = 1, 2, 3)$ synthesized in the solid state. It is clear that peaks of reactants disappear completely. The far infrared spectra (Fig. 8) indicate that every vibration absorption of $Co(bipy)_xCl_2$ synthesized from solid state is identical with that obtained in solution (*44*). The preparation of Co $(bipy)_2Cl_2$, however, has not been realized by solution methods so far.

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