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A THERMOANALYTICAL STUDY OF DIPICOLINIC ACID ACTING AS A TERDENTATE LIGAND IN COORDINATION COMPOUNDS OF DIVALENT METAL IONS

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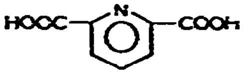
ABSTRACT

The coordination compounds obtained by reaction of hot solutions of dipicolinic acid with the carbonates of the divalent metal ions manganese(II), iron(II), cobalt(II), nickel(II), copper(II) and zinc(II) are studied using TG, DSC and HTRS techniques. For the thermal stability a sequence Mn > Fe > Zn > Co > Ni > Cu may be observed. This series is compared with the similar series obtained with isocinchomeronic acid. The thermal stability is, for each metal of the series, isocinchomeronic > dipicolinic. Thermal stability is discussed in terms of the intermolecular bonds, of the structures and of the stability constants of the complexes examined.

INTRODUCTION

We have previously studied several compounds obtained by reaction between metal ions and heterocyclic ligands[1–10]. Our interest is now centered on the complexes of dipicolinic acid (pyridine-2,6-dicarboxylic acid) 2,6-H_2PC with manganese(II), iron(II), cobalt(II), nickel(II), copper(II) and zinc(II).



The study has been carried out by thermal analysis and high temperature reflectance spectroscopy (HTRS).

EXPERIMENTAL

Instrumentation

The TG and DSC curves of the solid complexes were obtained by using a Du Pont Model 990 DSC cell and console and a Model 951 thermobalance. The heating rate used was 10°C min^{-1} on a sample whose mass ranged from 1 to 10 mg. The furnace atmosphere consisted of either dry nitrogen or air at flow rates of 50–100

TABLE 1

COMPLEXOMETRIC DETERMINATION OF METAL CONTENT IN THE COMPOUNDS

Compound	*Metal %*	
	Found	*Calc.*
$Mn(2,6\text{-}HPC)_2$	14.1	14.18
$Fe(2,6\text{-}HPC)_2 \cdot 2H_2O$	13.4	13.23
$Co(2,6\text{-}HPC)_2 \cdot 3H_2O$	13.3	13.30
$Ni(2,6\text{-}HPC)_2 \cdot 3H_2O$	13.1	13.25
$Cu(2,6\text{-}HPC)_2$	16.1	16.06
$Zn(2,6\text{-}HPC)_2 \cdot 2H_2O$	15.1	15.15

ml min^{-1}. All temperatures were corrected for thermocouple non-linearity. The HTRS curves were obtained using a Beckman DK-2A spectroreflectometer equipped with a heated sample holder previously described[11]. White glass fiber cloth covered with a tin cover glass was used as a reflectance standard. The sample holder atmosphere consisted of dry nitrogen.

Preparation of compounds

Dipicolinic acid Fluka AG purum was used. Other chemicals employed were of reagent grade.

The compounds were prepared by dissolving the metal carbonate in a hot aqueous solution of $2,6\text{-}H_2PC$ while ensuring that the metal to ligand ratio was 1:2. After two days the crystals obtained were separated, recrystallized slowly from aqueous ethanol and dried in vacuo for 48 h at room temperature. Thermogravimetry was used to determine the water content and the residual metal oxide: the metal content was also established by compleximetric titration of the compounds (Table 1).

RESULTS AND DISCUSSION

Manganese(II)-pyridine-2,6-dicarboxylate

A pale pink compound is obtained. The simplest formula is $Mn(2,6\text{-}HPC)_2$ in agreement with the metal determination (Table 1) and with the thermogravimetric data. The compound is anhydrous and it is stable up to 430°C. In air and nitrogen atmosphere (Fig. 1) the decomposition occurs in two steps; in air the oxide Mn_3O_4 (found 19.6%; calc. 19.70%) is formed.

The DSC curve in nitrogen atmosphere shows (Fig. 2) that the decomposition occurs through two partially overlapped endothermic peaks.

Iron(II)-pyridine-2,6-dicarboxylate

A pale green precipitate is obtained. The simplest formula is $Fe(2,6\text{-}HPC)_2 \cdot 2H_2O$ which agrees with the metal determination (Table 1) and with the thermo-

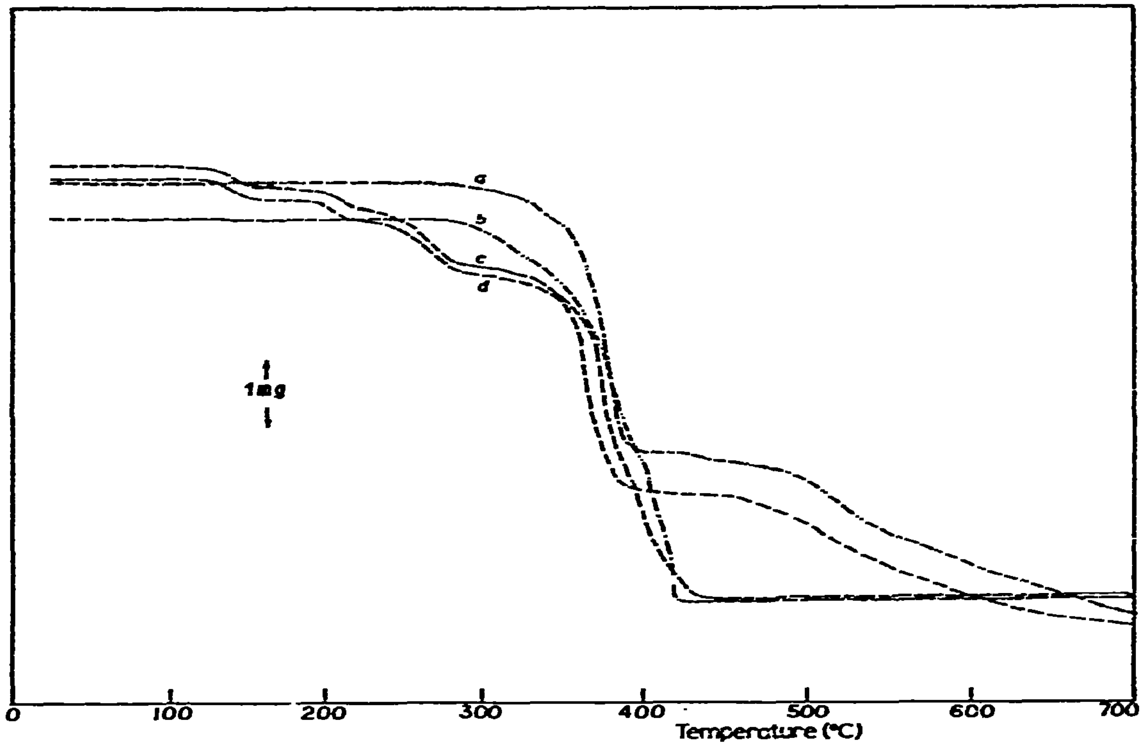


Fig. 1. TG curves of manganese(II) and iron(II) pyridine-2,6-dicarboxylates. Mn, (-..-..-); Fe, (------). Curves *a* and *c* were obtained in air and curves *b* and *d* under nitrogen atmosphere.

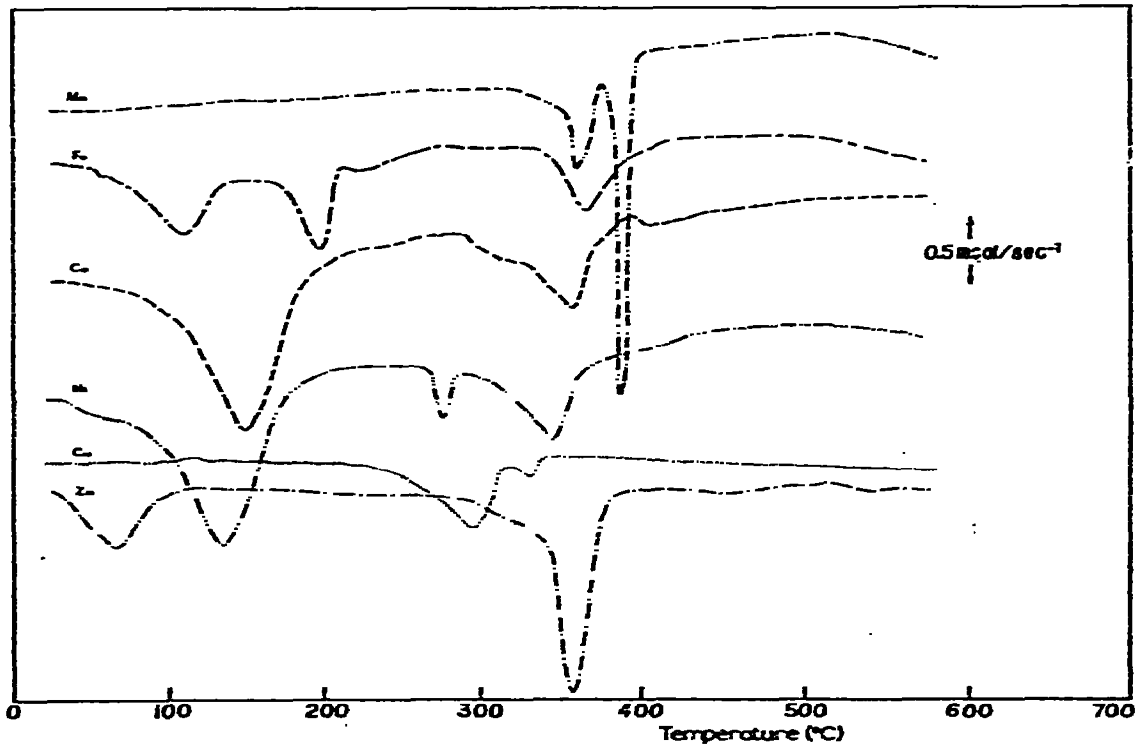


Fig. 2. DSC curves of complexes in nitrogen atmosphere.

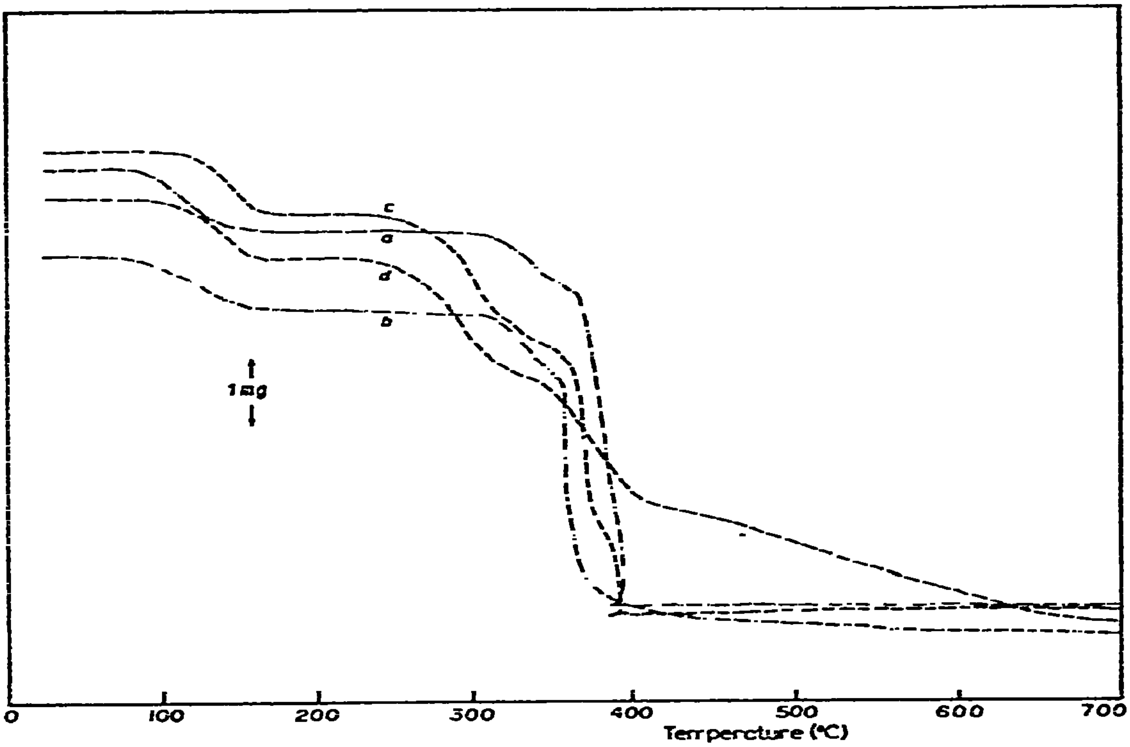


Fig. 3. TG curves of cobalt(II) and nickel(II) pyridine-2,6-dicarboxylates. Co, (-------); Ni, (-------). Curves *a* and *c* were obtained in air and curves *b* and *d* under nitrogen atmosphere.

gravimetric data. The water molecules are lost in two separate steps in air or in nitrogen (Fig. 1). The weight losses are respectively 4.3% (calc. 4.27%) and 4.3% (calc. 4.27%) for the first and second step. Both the reactions are endothermic (Fig. 2). The decomposition of the anhydrous compound occurs in two steps in air or in nitrogen (Fig. 1). In air the second step gives a constant weight corresponding to the oxide Fe_2O_3 (found 19.1%; calc. 18.91%).

On the DSC curve in nitrogen atmosphere (Fig. 2) endothermic peaks only appear for the decomposition reaction.

Cobalt(II)-pyridine-2,6-dicarboxylate

A purple compound is obtained, whose simplest formula is Co(2,6-HPC) · $3H_2O$ in agreement with the metal determination (Table 1) and with the thermogravimetric data. The TG curves in air or in nitrogen (Fig. 3) show only one step for the water loss (found 12.2%; calc. 12.19%). The anhydrous compound decomposes through two steps giving, in the air atmosphere, the oxide Co_3O_4 (found 18.1%; calc. 18.11%).

The DSC curve in nitrogen (Fig. 2) shows only one peak for the dehydration while the decomposition occurs through two endothermic peaks.

Nickel(II)-pyridine-2,6-dicarboxylate

A green compound is obtained, corresponding to the simplest formula Ni(2,6-HPC)$_2$ · 3H_2O according with the metal determination (Table 1) and with the thermogravimetric data. The three water molecules are lost in only one step in air or in nitrogen atmosphere (Fig. 3) (found 12.1%; calc. 12.20%) then the anhydrous compound decomposes in two steps, partially overlapped, giving in the air the oxide NiO (found 16.7%; calc. 16.86%).

The DSC curve in nitrogen atmosphere (Fig. 2) gives for the dehydration an initial small endothermic peak overlapped by a very large one.

The decomposition of the residue in nitrogen gives a small endothermic peak immediately followed by another, much larger peak.

Copper(II)-pyridine-2,6-dicarboxylate

According to the TG curve the blue copper complex is anhydrous and its simplest formula, in agreement with the metal determination (Table 1), is Cu(2,6-HPC)$_2$. The anhydrous compound decomposes very rapidly in air atmosphere (Fig. 4) to give the oxide CuO (found 20.7%; calc. 20.10%) while in nitrogen atmosphere the decomposition is not very fast and does not reach a constant weight. The DSC curve in nitrogen atmosphere shows that the decomposition occurs only through endothermic peaks.

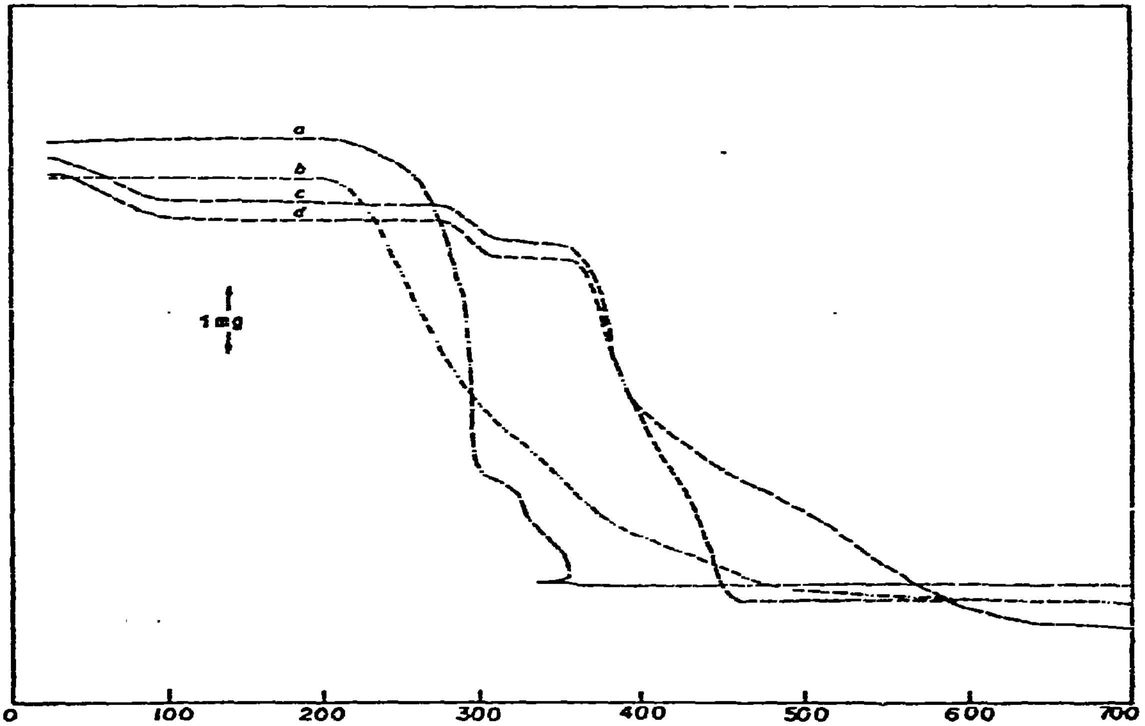


Fig. 4. TG curves of copper(II) and zinc(II) pyridine-2,6-dicarboxylates. Cu, (········); Zn, (------). Curves *a* and *c* were obtained in air and curves *b* and *d* under nitrogen atmosphere.

Zinc(II)-pyridine-2,6-dicarboxylate

This white compound precipitates as the dihydrate $Zn(2,6\text{-}HPC)_2 \cdot 2H_2O$ in accordance with the TG data and the metal determination (Table 1). The water molecules are lost only in one step in air or in nitrogen atmosphere (found 8.5%; calc. 8.41%) (Fig. 4). The decomposition of the anhydrous compound occurs in two steps in air or in nitrogen (Fig. 4). In air the second step gives the oxide ZnO (found 18.8%; calc. 18.85%) while in nitrogen it does not reach a constant weight.

The DSC shows only one endothermic peak in nitrogen atmosphere (Fig. 2) for the dehydration, while for the decomposition of the anhydrous compound it gives only endothermic peaks.

DISCUSSION

The thermal stability order, for the divalent metal ions examined, shown by the experimental data is

Mn(II) > Fe(II) > Zn(II) > Co(II) > Ni(II) > Cu(II)

The temperature sequence thus determined is in agreement with that previously found for quinolinic ($2,3\text{-}H_2PC$), lutidinic ($2,4\text{-}H_2PC$) and isocinchomeronic ($2,5\text{-}H_2PC$) acids. This sequence is in inverse order to the sequence reported by Anderegg[12] for the stability constants of those complexes in solution, which is

	Cu(II) >	Ni(II) >	Co(II) >	Zn(II) >	Fe(II) >	Mn(II)
$\log \beta_2$	16.52	13.50	12.75	11.88	10.36	8.49

in agreement with the general sequence proposed by Irving and Williams[13].

A hypothesis to justify this behaviour has been previously reported[5]. The thermal stability order is also the reverse, except for zinc, of the ion "electronegativity density" estimated from the second and third ionization potential and from the ionic radii[14], as previously proposed[10], while it is the reverse of the enthalpies of formation of gaseous ions in their valence states, as found by George and McClure[15].

The reaction of the metal(II) carbonates with aqueous solutions of pyridine-2,6-dicarboxilic acid affords all complexes of the type $M(2,6\text{-}HPC)_2 \cdot nH_2O$ where M is the divalent metal ion and $0 \leq n \leq 3$, while it was impossible to obtain, by any means, the complete series with the 1:1 ligand-metal molar ratio.

Thus examining the 2,*n*-pyridinecarboxylic acid complexes previously studied, the only possible comparison is with the isocinchomeronic complexes having the same 2:1 ligand-metal molar ratio, while the lutidinic and quinolinic acids give 1:1 ligand-metal molar ratio complexes. The thermal stability of each series of the pyridine carboxylic acid complexes for each metal ion is

$M(2,5\text{-}HPC)_2$ > $M(2,6\text{-}HPC)_2$
isocinchomeronic > dipicolinic

Now considering the hypothesis that the strength of the intermolecular bonds plays a notable part in the thermal stability of the solid compounds, the proposed thermal stability scale can be explained by the fact that the bond strength between the ligand and the central ion is greater for the dipicolinic acid complexes than for isocinchomeronic acid complexes. This agrees with the constant stability scale of the copper complexes proposed by Petitfaux and Fournaise[16]. The higher stability

	$Cu(2,6\text{-}HPC)_2$ >	$Cu(2,5\text{-}HPC)_2$
$\log \beta_2$	16.4	14.3

constant of the 2,6-pyridine-dicarboxylic acid complexes can be justified by the fact that this acid acts as a terdentate ligand[17] involving coordination from two equivalent

TABLE 2

DIFFUSE REFLECTANCE SPECTRA OF COMPLEXES OF PYRIDINE-2,6-DICARBOXYLIC ACID

Complex	*Absorption maxima (nm)*
$Mn(2,6\text{-}HPC)_2$	510 (very weak band)
$Fe(2,6\text{-}HPC)_2 \cdot 2H_2O$	485
$Co(2,6\text{-}HPC)_2 \cdot 3H_2O$	480 (sh), 520 (sh), 595
$Ni(2,6\text{-}HPC)_2 \cdot 3H_2O$	630
$Cu(2,6\text{-}HPC)_2$	755
$Zn(2,6\text{-}HPC)_2 \cdot 2H_2O$	no maxima

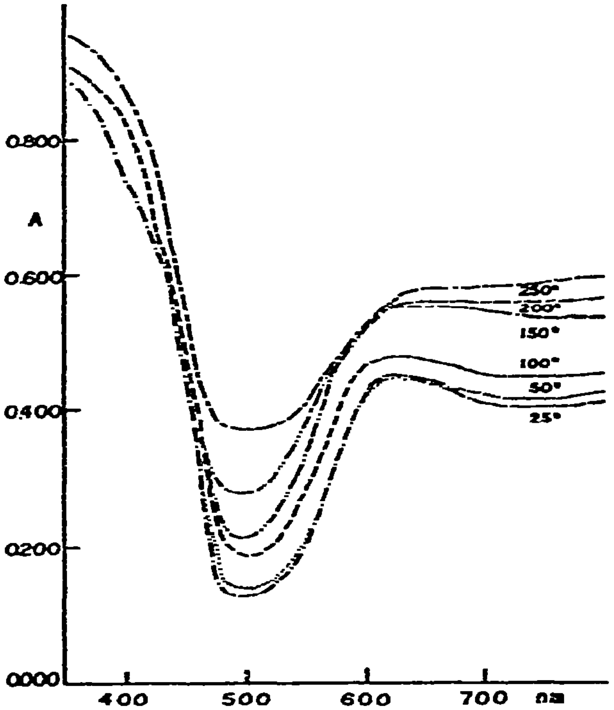


Fig. 5. High temperature reflectance curves of nickel-pyridine-2,6-dicarboxylate.

terdentate monoanionic 2,6-HPC ligand molecules giving, as confirmed by the reflectance spectra (Table 2), octahedral structure through two chelated five membered rings that strongly stabilize the complex.

In all cases the reflectance spectra of the anhydrous compound are similar to those of the complexes from which they were obtained, e.g. the nickel compound (Fig. 5), suggesting that the water molecules are not present in the coordination sphere in accordance with the thermal data.

Another possible explanation lies in the different charge densities and charge distribution in the pyridine ring. Any back coordinated charge from the metal to the pyridine ring will be localized mainly on the 2-, 4- and 6-positions, the electron withdrawing groups such as –COOH in positions 2-, 4- and 6- cause the electron density in the ring to be lowered so that the σ-bonding is lowered and the π-bond increases but the increase in π bond strength is insufficient to offset the reduction in σ-bonding.

In the dipicolinic complexes there is also the interaction of the 6-carboxyl groups with the metal ion that brings about symmetrical charge distribution through the two carboxyl groups, the aza-group and the metal ion giving a system with a higher stability constant and lower thermal stability compared with the isocinchomeronic complexes where the charge distribution is not symmetrical, giving a non-uniform charge density, unlike the case of the dipicolinic complexes. This accounts for the higher stability of the solid lattice of isocinchomeronic acid complexes compared with those of dipicolinic acid.

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