November, 1986] © *1986 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 59, 3465—3468 (1986)*

Synthesis of Copper(II)-Dithiooxamide Complex in Zirconium Phosphate[1)]

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(Received April 12, 1986)

Copper(II)-dithiooxamide (rubeanic acid) complex was synthesized in the interlayer region of zirconium phosphate. The product, called ZP–CuLra, was chracterized by chemical analysis, thermal analysis, infrared spectroscopy, and X-ray diffractometry. The chemical composition of ZP–CuLra was represented as $ZrCu(H_2NCS)_2(PO_4)_2 \cdot H_2O$ or $ZrCu(HNCS)_2(HPO_4)_2 \cdot H_2O$. The interlayer distance of ZP–CuLra was found to be 9.0 Å. By analogy with Cu(II)-rubeanic acid complex prepared in a solution, a structural model of ZP–CuLra was proposed.

Zirconium phosphates have been studied most extensively as inorganic ionexchangers.[2)] Of these the α-from, $Zr(HPO_4)_2 \cdot H_2O$, is crystalline and its crystal structurc has been determined.[3)] Hence, the interrelation between the ion-exchange reaction and the change in the structure has been investigated for many cations. Also, α-zirconium phosphate behaves as a host when an organic molecule intercalates into the interlayer space.[4)] Recently, the application of α-zirconium phosphate to new materials has been examined.[2)]

Dithiooxamide, $(NH_2CS)_2$, (so-called to rubeanic acid (RA)), has been used in analytical chemistry.[5)] When RA is added to a solution containing Cu(II), a black precipitate (Cu–ra complex) is formed. It has been found that this Cu–ra complex exhibits semiconductivity and antiferromagnetism.[6)] The complex is considered to be a coordination polymer. Since it is amorphous, its physicochemical properties have not been explained theoretically. Abboudi et al. have studied large-angle X-ray scattering of the amorphous compound and proposed a structural model.[7)]

Montmorillonite, a typical clay mineral, has a layered structure similar to α-zirconium phosphate. Many attempts have been made to control tacticity using this clay as a template. Son et al. prepared the Cu–ra complex in an interlayer space of montmorillonite and found that the complex was monomeric and oriented in such a way that the molecular plane of the ligand was parallel to the silicate layer.[8)] They suggested that because the distance between Cu(II) in montmorillonite was too large to bridge with rubeanic acid molucules, only a monomeric compound was formed.[9)] The ion-exchange capacity of the clay used was 0.95 meq g^{-1}. Since α-zirconium phosphate has a larger ion-exchange capacity than montmorillonite, it can be expected that the distance between Cu(II) in the interlayer space will be shorter than that in montmorillonite. Consequently, if Cu(II) can be made to react with rubeanic acid in α-zirconium phosphate layer, a polymeric compound can be formed.

The present study established a preparative method for the Cu–ra complex in α-zirconium phosphate (the product obtained is referred to as ZP–CuLra) and ZP–CuLra was characterized by chemical analysis, infrared spectroscopy, and thermal analysis.

Experimental

Reagents. Rubeanic acid (Tokyo Kasei Co., Ltd.) was recrystallized from ethanol, and then dissolved in acetone. The rubeanic acid was recovered after evaporating the acetone. The other reagents were used without further purification.

Preparation of ZP-CuLra. All ion-exchange reaction was carried out by a batch method. The α-zirconium phosphate was prepared by the direct precipitation method.[10)] It was then converted into the half-exchanged sodium ion form, $ZrNaH(PO_4)_2 \cdot 5H_2O$(ZrNaH).[11)] Copper(II) ion was exchanged by adding ZrNaH to the solution of 0.03 mol dm^{-3} Cu(II) acetate. The mixture was shaken continuously for 48 h at 25 °C in order to prevent the solution from decomposing at elevated temperatures. After the reaction, the solid was centrifuged from the solution, and washed with distilled water. An X-ray diffraction pattern was obtained for the solid, and the sodium ion in the supernatant was determined by atomic absorption spectrometry. The solid was again immersed in Cu(II) acetate solution, and the same procedure repeated. The X-ray diffraction pattern was identical to the copper exchanged form, but the sodium ion was still detected. Since the large amount of the sodium and hydrogen ions in the solid phase was almost exchaned with Cu(II), a solution of 0.03 mol dm^{-3} Cu(II) nitrate was employed and the third ion exchange was carried out. To ensure the exchange, the solid was contacted with 0.01 mol dm^{-3} Cu(II) acetate in the fourth run. The Cu(II) form of the zirconium phosphate (ZP–Cu) was identified by X-ray diffractometry. The ZP–Cu was stored over silica gel in a desiccator.

In order to intercalate the Cu–ra complex in α-zirconium phosphate, the ZP–Cu was immersed in an ethanol solution containing rubeanic acid (0.56 g/120 ml) for 7 days with intermittent shaking. The product was separated by centrifugation, and washed with acetone several times. It was then dried in air at room temperature.

Analytical Procedure. The chemical analysis of ZP–CuLra was carried out as follows. A weighed sample was heated in a crucible at about 900 °C, and weight loss was determined. A part of the ignited sample was then weighed and decomposed according to the previous method.[12] The precipitate was separated by filtration and dissolved in hydrochloric acid. Zirconium was separated as mandelate and determined according to the literature.[13] Copper was titrated with a standardized EDTA solution, using 1-(2-pyridylazo)-2-naphthol (PAN) as an indicator. Phosphorus was determined gravimetrically as $Mg_2P_2O_7$.[14] Determinations of carbon, hydrogen, nitrogen, and sulfur were carried out by elemental analysis.

X-Ray powder patterns were measured with a Rigaku Geigerflex RAD-2B. The infrared (IR) spectra were measured on an A-302 infrared spectrophotometer (Japan Spectroscopic Co. Ltd.,). The thermogravimetric (TG) and differential thermal analysis (DTA) curves were obtained with a Shimadzu thermal analyzer at a heating rate of 10 °C min^{-1} in static atomosphere.

Results and Discussion

Chemical Composition of ZP-CuLra. Alluli et al. have reported that ZP-Cu can be prepared by the column method.[15] Since the α-zirconium phosphate used was too fine to apply in a column, a batch method was emploed. The X-ray diffraction pattern of ZP-Cu and the loss on ignition agreed well with values reported.[15]

The chemical composition of ZP-CuLra is shown in Table 1. Thermal analysis showed that ZP-CuLra was monohydrate (see later). When Cu(II) salt (for example, nitrate) reacts with rubeanic acid in an ethanol solution, Cu(II) rubeanate is precipitated and an acid (nitric acid) released. Between the interlayer region of zirconium phosphate the counter ion of Cu(II), namely phosphate, is fixed. It is not likely that Cu(II) can form the salt directly in the region. Consequently, the following two formulae must be considered; $ZrCu(NH_2CS)_2(PO_4)_2\cdot H_2O$(Type I), and $ZrCu(NHCS)_2(HPO_4)_2\cdot H_2O$(Type II). In Type I a molecule of rubeanic acid coordinates to Cu(II). The rubeanate of Cu(II) is sandwiched between zirconium phosphate layer in Type II. In each case the ZP-CuLra has the same elemental composition. The molar ratio of copper to rubeanic acid or rubeanate and to the water of hydration were in agreement with those obtained for the amorphous compound.[7]

Thermal Analysis. Figure 1 shows TG and DTA curves of ZP'-CuLra. Thermal decomposition occurred in three steps. In the first step an endothermic reaction took place in the temperature range of 50—120 °C. Then the second step followed until about 380° C. Though the TG curve indicates that this step consisted of two successive reactions, these reactions can not be separated clearly in the DTA curve. The reactions at this step appears exothermic. It can be considered that the decomposition products are oxidized at the surface of the platinum crucible, and converted to oxides, for example water. At higher temperature (600° C-) the third reaction occurred.

The X-ray diffraction pattern of the solid after heating was identical to that obtained from ZP-Cu. The facts show that the water of hydration and the ligand were removed by heating. The whole process is described as follows:

$$\text{ZP-CuLra} \xrightarrow[\text{step I}]{} \text{anhydrous ZP-CuLra} \xrightarrow[\text{step II}]{} \text{intermediate} \xrightarrow[\text{step III}]{} ZrCu(PO_4)_2.$$

The weight loss at the first step was 4.9% which corresponds to dehydration. The total weight loss of the second and the third step was 23.6%. This is almost equal to the calculated value.

IR Studies. The IR spectra of ZP-CuLra, ZP-Cu, and Cu-ra prepared in a solution are shown in Fig. 2. The spectrum of ZP-CuLra can be considered to be composed of those of ZP-Cu and Cu-ra.

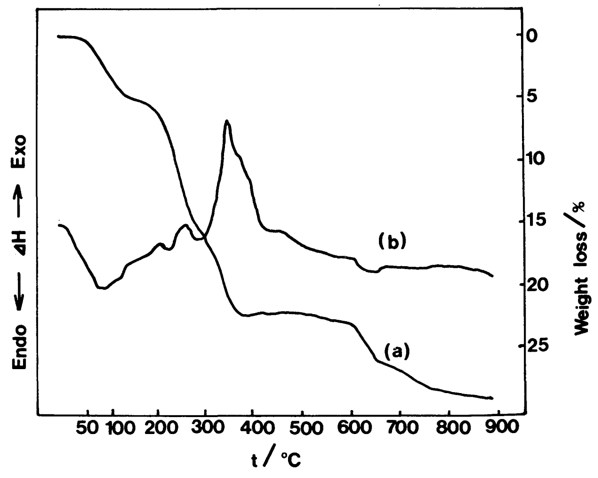

Fig. 1. TG(a) and DTA curve (b) of ZP-CuLra.

Table 1. Chemical Composition of ZP-CuLra/%

	Zr	Cu	PO_4	H	C	N	S
Found	18.11	13.72	37.60	1.27	4.75	5.50	11.14
	(1.00)	(1.08)	(1.99)	(6.35)	(1.99)	(1.98)	(1.75)
Calcd	18.89	13.16	39.33	0.83	4.97	5.80	13.28
	(1.00)	(1.00)	(2.00)	(6.00)	(2.00)	(2.00)	(2.00)

The values in parentheses are the molar ratios of each element to zirconium.

In order to determine Type I or II, it is important to examine the spectra in the region of 3500—3000 cm^{-1}, because the N-H bond gives an absorption band in this region. However, the O-H bond can also be assigned in the same region. According to Horsly et al., the absorption band at 3280 cm^{-1} was assigned to OH in P-OH, and bands at about 3500 and 1620 cm^{-1} to OH in the hydrated water in α-zirconium phosphate.[16] The absorption bands around 3460 and 1620 cm^{-1} disappeared in the IR spectrum after ZP-CuLra was heated in an air-bath at 150 °C. This fact suggests that these bands can be assigned to the hydrated water, and that the water was present in a similar manner as in α-zirconium phosphate.

On the other hand, the absorption bands at 3230 and 1520 cm^{-1} were still present after heating. Taking account of the above observation and the assignment of the spectrum for ZP-CuLra,[17] these bands can be assigned to -NH in $^{\mathrm{H}}_{\mathrm{Cu}}{>}\mathrm{N}-$.

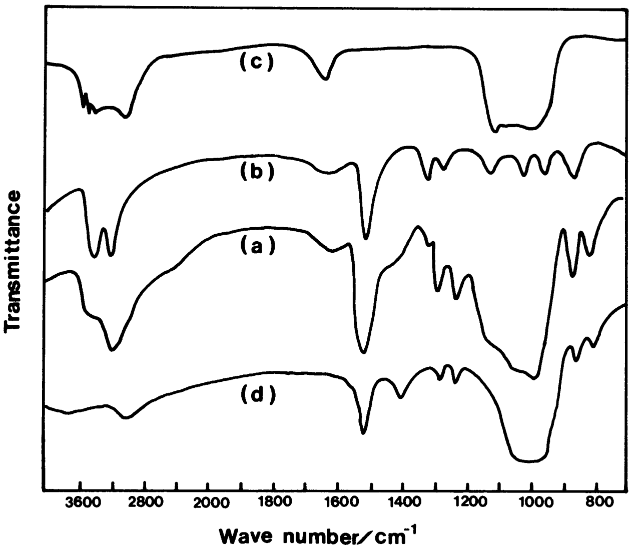

Fig. 2. IR spectrum of (a)ZP-CuLra, (b)Cura, and (c) ZP-Cu. The curve (d) is the spectrum of the sample obtained by heating of ZP-CuLra.

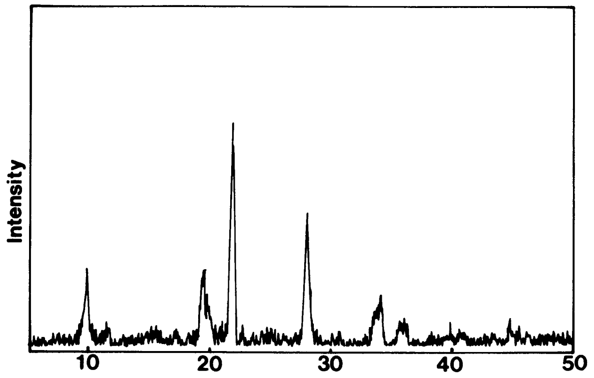

Fig. 3. X-Ray powder pattern of ZP-CuLra.

X-Ray Studies. It is well known that α-zirconium phosphate and its salt forms have a layered structure, and that the interlayer spacing is dependent on the cations present.[2] Hence, the change in an interlayer distance can be estimated from the lowest angle reflection in an X-ray diffractogram.

The X-ray powder pattern of ZP-CuLra is shown in Fig. 3. The interlayer distance of the exchanger phases was changed as follows.

α-$Zr(HPO_4)_2\cdot H_2O$ 7.6 Å, $ZrNaH(PO_4)_2\cdot 5H_2O$ 12.1 Å,
$ZrCu(PO_4)_2\cdot 4H_2O$ 9.7 Å, ZP-CuLra 9.0 Å.

It is noteworthy that the interlayer spacing of ZP-CuLra was smaller than that of ZP-Cu. The molecular structure of rubeanic acid was known to be a planar form and the molecular dimensions were given.[18] The bond angle of HNH and CNH and the bond length of NH were not reported in the literature.[18] The molecular structure of rubeanic acid can be posturated by assuming that these are almost equal to those in thioformamid, $HSCNH_2$, that is, the angle HNH 122°, CNH 118—120°, and the length 1.01 Å.[19] The molecular size of rubeanic acid is estimated as shown in Fig. 4. The width of molecular plane is equal to be 3.60 Å.

The copper complex can be arranged between the layers of zirconium phosphate in three manners, namely, parallel, perpendicular and inclined to the layers. If the plane of the rubeanic acid is parallel to

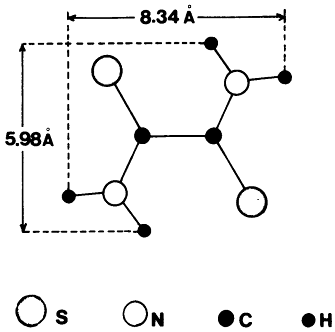

Fig. 4. Molecular size of rubeanic acid.

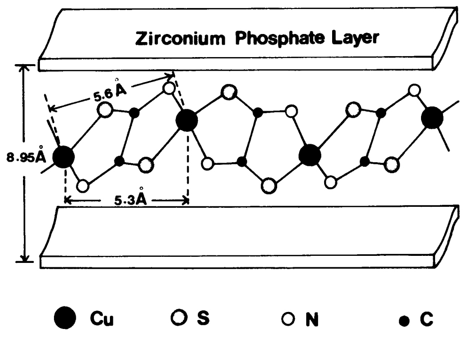

Fig. 5. Proposed model of CuLra complex between the zirconium phosphate layers.

that of the zirconium phosphate, the interlayer distance of ZP–CuLra will be shorter than that observed. When the plane of the acid is perpendicular to that of the exchanger, the distance will be longer. In the third case, the distance is dependent on the slant of the complex plane to the zirconium phosphate layer.

According to Alberti and Costantino,[4] the arrangement of the fixed charge in α-zirconium phosphate is an hexagonal array and the distance between them is equal to be 5.3 Å. It is possible to consider that the projective distance between Cu(II) in the copper form is 5.3 Å. On the other hand, the distance between Cu(II) in Cu–ra prepared in a solution is 5.6 Å according to the structural model proposed by Abboudi et al.[7]

The crystal structure of the salt form of zirconium phosphate has not been analyzed except for the ammonium form. Since the ammonium form has essentially a similar structure to α-zirconium phosphate,[20] it is possible to infer that the crystal structure of ZP–CuLra also is similar to α-zirconium phosphate.

Though the position of the hydrated water molecule was not determined, it is thought that the water molecule is involved in hydrogen bonding with hydrogen atoms over the oxygen atoms in phosphates (see IR Studies).

Assuming that the molecular structure of Cu–ra is persistent in the exchanger phase, the following model is proposed (Fig. 5). The ligand is coordinated to Cu(II) through the nitrogen and sulfur atoms. Between the zirconium phosphate layers the complex forms a polymeric zigzag chain composed of $Cu(NHCS)_2 \cdot H_2O$ as an unit, and the plane of the complex is slightly twisted to the layers of the exchanger.

The authors wish to express their thanks to Prof. Isao Tomita, Tokyo University of Fisheries, for the measurement of thermal analysis.

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