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Growth of Bis-Dimethylglyoximate Co (III) Single Crystals

Single crystals of bis-dimethylglyoximate Co(III) up to 8 × 6 × 2 mm. in size have been grown by the first time, using diffusion method at room temperature. Optimum size and quality were obtained at *p*H = 6. These crystals are orange in colour and an X-ray study shows it to be monoclinic, space group P $2_1/n$, with $a = 8.432(4)$, $b = 14.147(3)$, $c = 13.746(6)$ and $\beta = 103.78(3)°$. The effects of different experimental devices on the growth features are discussed.

Han sido crecidos por primera vez monocristales de bis-dimetilglioamato Co(III) de hasta 8 × 6 × 2 mm. de tamaño mediante la técnica de difusion a temperatura ambiente. El tamaño y calidad óptima fueron obtenidos a *p*H = 6. Estos cristales son de color naranja y un estudio de rayos X muestra que pertenecen al sistema monoclínico, grupo espacial P $2_1/n$, con $a = 8.432(4)$, $b = 14.147(3)$, $c = 13.746(6)$ y $\beta = 103.78(3)°$. Se discuten en este artículo el efecto de diferentes diseños experimentales sobre las características de crecimiento.

1. Introduction

Recently a large number of paper dealing with the trans-bis-(dimethylglyoximate) cobalt (III) derivatives have appeared in the literature. The synthesis and study of these compounds have a great interest because of its similarity to the cobalamine (one of the B_{12} vitamine components) (SASAKI, MATSUNAGA; HOHOKABE, YAMAZAKI; SCHAUZER) and furthermore some of them present catalitic activities against different substrates (NEMETH et al.; SZEVERENYL et al.). In addition it is interesting to remark that distortions of the bis-(dimethylglioximate)-moiety have been found in the last works on the crystal structure of cobaloximes.

It was thought to isolate the double complex salt $[Co(DMGH)_2(NH_3)_2]$ $[Co(DMGH)_2(CN)_2]$ — where $DMGH^-$ stands for dimethylglioximate ion which was prepared by one of the authors (C. LOPEZ MARTINEZ). Attempts to growth crystals of that compound from solutions generally gave poor results in terms of crystal quality and size. This has been traced to the low aqueous solubility of these salts. After a set of homogeneous crystallization experiences which also failed, we tried to use diffusion techniques through gels. The aim of this paper is to present the feasibility of growing $[Co(DMGH)_2(NH_3)_2]$ $[Co(DMGH)_2(CN)_2]$ single crystals in gels and to describe the growth features and morphology of the as-grown crystals.

2. Experimental

Bis-dimethylglyoximate Co(III) — here in after (CN) in short — has been obtained by a double decomposition reaction between the two soluble salts $K[Co(DMGH)_2(CN)_2]$ $1/2\,H_2O$

and $[Co(DMGH)_2(NH_3)_2Cl \cdot 5\ H_2O$, where (DMGH) stands for the dimethylglyoximato ion.

The reactant $K[Co(DMGH)_2(CN)_2]\ 12\ H_2O$ (here in after A_1) was prepared by using the methods described by Maki. 0.044 g. of this salt were dissolved in 20 ml of a sodium metasilicate (Merck) solution with specific gravity 1.059 g/cm³ and *p*H 11.2, and afterwards silica gel was produced by acidifying this solution with CH_3COOH [1 N] up to the desired *p*H. Gelling was carried out in two different crystallization apparatus:

a) Glass test tube of 12 mm inner diameter and 169 mm long.

b) Glass cassettes which are described in Figure 1.

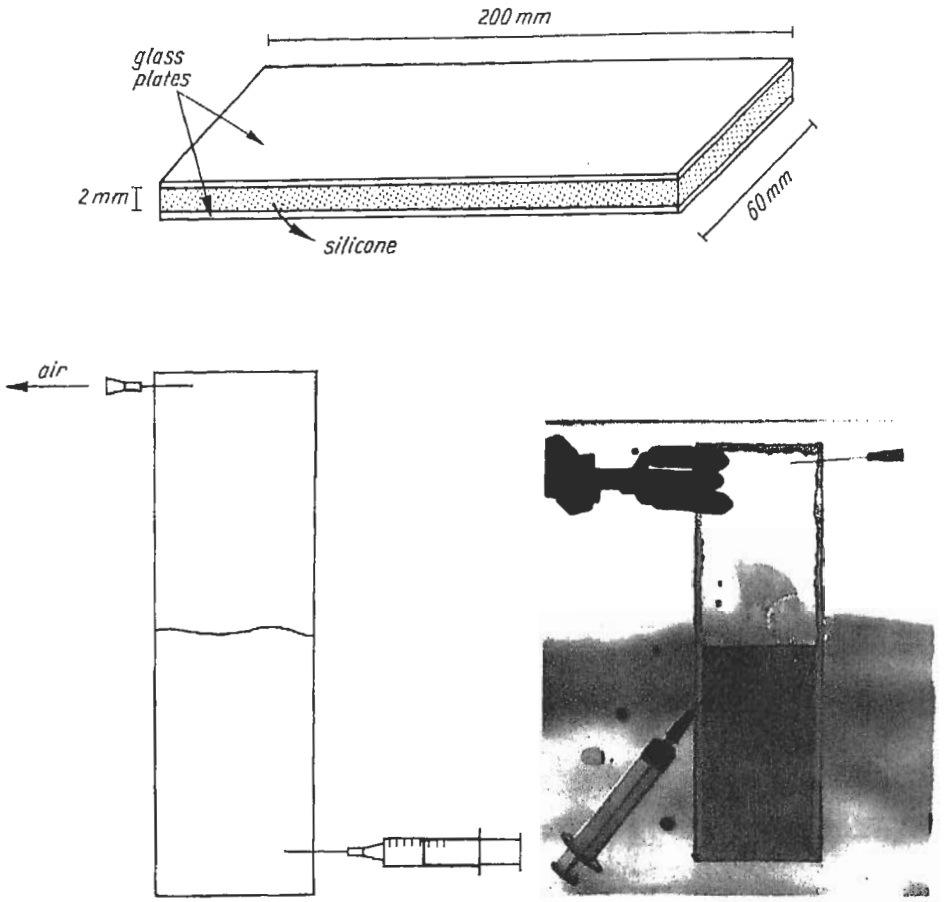

Fig. 1. Glass cassettes for crystal growth by difussion techniques. a) Typical dimensions used in this work. b) Diagram and picture showing the use of xeringes for filling the cassette. This new device let us a better observation of the growth processes

Gelling time is *p*H dependent (Henisch (75′ ± 5′ for *p*H 6). After gelling a solution formed by standard sodium metasilicate and $[Co(DMGH)_2(NH_3)_2]\ Cl \cdot 5\ H_2O$ (0.07 M) (here in after A_2) the *p*H of which was adjusted at the same value as the previously described solution, was poured on the gel. In order to optimize growth conditions ten different initial gel *p*H were used: 7,0; 6.5; 6.0; 5.5; 5.0; 4.5; 4.0; 3.5; 3.0 and 2.3. It is important to note that the *p*H value do not change throughout the experiment. Twice-distilled water and analytical reagent grade chemical were used throughout this study. Experiments were performed at room temperature (about 25 °C).

The as-grown crystals were mechanically separated from the gel and washed with twice distilled water. These crystals were identified by infrared spectra, using KBr tablets. The morphological study was carried out under binocular lens, optical and scanning electron microscopes. Specimens for S.E.M. were fixed on an aluminium basis using double adhesive tape. Gold metallization was used. To determine Miller indices of the as grown crystal faces, the interfacial angles were measured by using a two-circle optical goniometer. Lattice constants and space group was investigated by X-ray diffraction in an automatic diffractometer CAD4F.

3. Results

3.1. Identification

The orange crystals obtained by the technique described above were identified by elemental analysis (Table 1) as well as the infrared spectra. The first ones were carried out at the "Instituto de Química Bio-orgánica" (C.S.I.C.) of Barcelona by using a microanalizer Carlo Erba 1106. The infrared spectra was recorded in a Beckman IR 20 A spectrophotometer in the range 4000 — 259 cm^{-1}. The spectra in the CN stretching region (2300 — 1900 cm^{-1}) was obtained under higher resolution conditions and calibrated against polystyrene film giving an average precision better than 2 cm^{-1}. It shows the characteristic bands of trans-bis-(dimethylglyoximate) cobalt (III) derivatives and stretching band (2139 cm^{-1}) of the CN^- group (Fig. 2).

Table 1
Elemental analysis of bis-dimethylglyoximate Co(III) single crystals

	calc.	found
% C	32.51	32.46 32.49
% N	25.29	25.18 25.22
% H	5.12	5.15 5.17

3.2. Growth features

In the range of *p*H investigated in this work, well-crystallized $[Co(DMGH)_2(NH_3)_2]$ $[Co(DMGH)_2(CN)_2]$ has been obtained in gels of *p*H 5, 5.5, and 6. In other experimental runs with different *p*H values, no precipitate appears even after a length of the experiment of four months. Incubation time (T_1: the time elapsed from setting the experiments up to first crystals can be observed by using a binocular lens — × 100-) was minimum (46 ± 2 hours) for *p*H = 6. At *p*H = 5.5 and 5, T_1 took the values 56 ± 2 and 90 ± 2 hours, respectively. Crystal size was optimum (8 mm in length) for crystals grown from gels of *p*H 6. It was observed that on increasing the *p*H value, the number of crystals increased too (Fig. 3). No cups cavities were observed around the crystals.

In all cases, precipitations zones are usually restricted to the interface between both gels. At *p*H 6, the precipitation zone moves from the interface to the gel containing A_2 reactant, up to a maximum distance of 8 mm, showing in this zone crystals larger in size. This behaviour can be understood by considering the large molecular

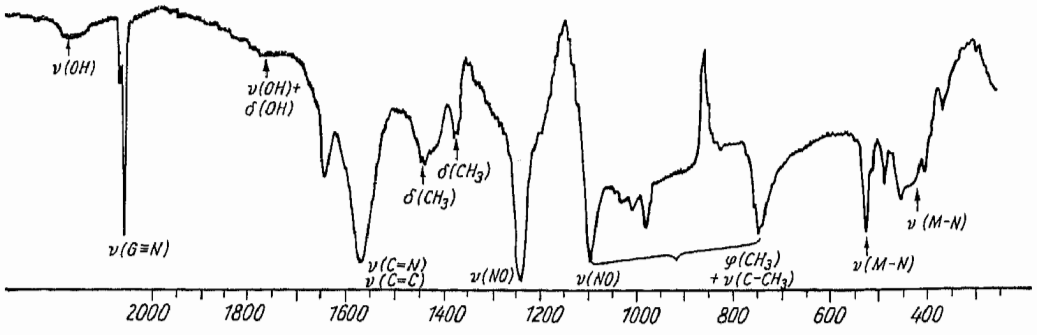

Fig. 2. Infrared spectra of bis-dimethylglyoximate crystals obtained in this work

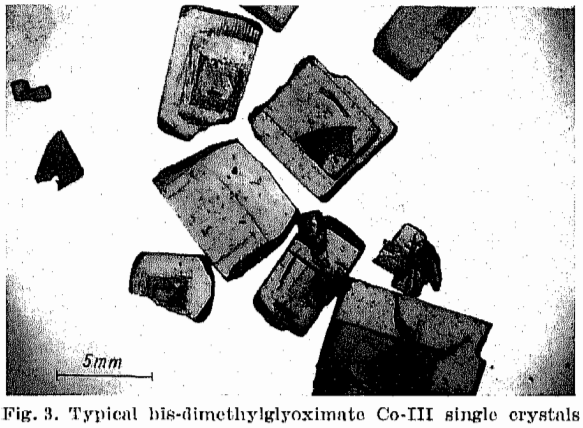

Fig. 3. Typical bis-dimethylglyoximate Co-III single crystals grown in silical gel. Optical microscopy

size (15 Å) of both reactants, which explain its low diffusivity. This is the reason why no success was obtained when using a hybrid gel technique, i.e.: both A_1 and A_2 reactants in a gelled medium separated by a thin layer of a saturated solution of (CN). In order to enhance the effect of the diffusion transport on the nucleation and crystal growth kinetics, gels with a larger porous size will be used in further experiments.

In all experiments, the concentration of the reactants have been kept constant. The use of larger concentrations is limited by the solubility of the reactants. Hence, the optimization of the crystal size must be achieved by the use of larger volumes and more porous gels.

3.3. Morphological characterization

(CN) crystals having excellent crystal faces and optical transparency were obtained with a typical volume of 80 mm^3. Figure 4 shows some of the crystals grown in silica gels at *p*H 6.

An X-ray diffraction study shows (CN) crystals to be monoclinic, space group $P\,2_1/n$ with $a = 8.432(4)$, $b = 14.147(2)$, $c = 13.746(6)$ and $\beta = 103.78(3)$. The morphology of various crystals have been examined by optical and scanning electron microscopy. No morphological differences were found as an effect of the gel *p*H. All these crystals belong to the 2/m symmetry class showing the {001} {010} {103} and {50$\bar{1}$} main forms, (Fig. 5) the pinacoidal faces (001) and (00$\bar{1}$) are the most developed and therefore (CN) crystals show a tabular morphology.

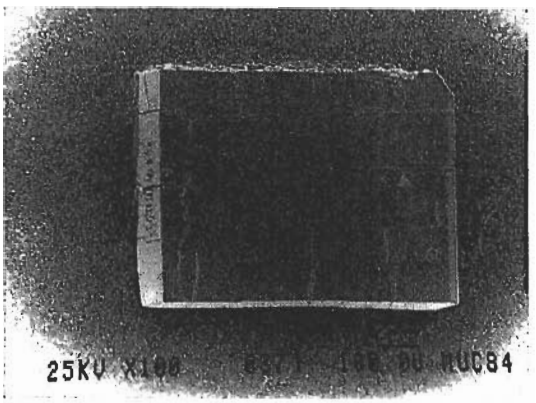

Fig. 4. SEM view of bis-dimethylglyoximate single crystals

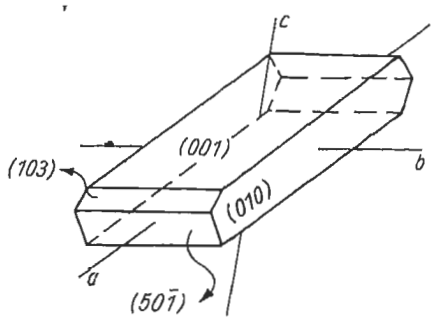

Fig. 5. A crystal of bis-dimethylglyoximate Co-III showing typical morphology with indexed faces

4. Conclusions

The feasibility of growing single crystals of bis-dimethylglioximate Co(III) by using diffusion technique at room temperature has been demonstrated. Crystals of this compound were obtained by the first time using this technique. In this study both reactants were gelled and a two-layers method (without a spacer gel) was used with success. The as-grown crystals belong to the monoclinic system, space group $P\,2_1/n$.

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