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The Structures of Some Inorganic Cyanamides. I. Preparation of Single Crystals and Preliminary Studies

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The preparation of single crystals of sodium, thallous, silver and lead cyanamides is described. Preliminary crystallographic data on these compounds are reported.

Introduction

A detailed study has recently been made of the physical properties, molecular structure and thermal and radiation stability of a number of inorganic cyanamides (Sole, 1963; Sole & Yoffe, 1964). Crystallographic studies of these compounds have therefore been undertaken in order to correlate the physical properties with the detailed crystal structures. The compounds investigated, namely sodium, thallous, silver and lead cyanamides, are fairly readily available as polycrystalline or amorphous powders and methods for their preparation in this form have been described previously (Shushunov & Pavlov, 1955; Deb & Yoffe, 1959; Bolis-Caunella & Costa, 1953). However the single crystals required for the above investigations are difficult to prepare and the methods used are therefore described in some detail in this paper. Preliminary crystallographic data are also reported.

Sodium cyanamide

An attempt to prepare sodium cyanamide by the method of Shushunov & Pavlov (1955) was unsuccessful and from infrared and X-ray analyses the product appeared to be mainly sodium acid cyanamide. Accordingly sodium cyanamide in the form of fused ingots was obtained from Bios Laboratories Incor-

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porated, New York. This material was extremely hygroscopic and soluble in polar solvents. Attempts were therefore made to recrystallize the compound from water and from methanol but unfortunately solvolysis resulted in the formation of sodium acid cyanamide and/or sodium carbonate monohydrate. Recrystallization from the melt (m.p. Na_2CN_2: *ca.* 560 °C) is possible in an atmosphere of nitrogen; in air some thermal decomposition takes place (Sole, 1963). Although some crystals were obtained by this method, their extreme deliquescence precluded any single-crystal measurements.

A sample of sodium cyanamide powder was sealed in a capillary tube and a powder photograph was taken with Fe $K\alpha$ radiation, using the Straumanis film mounting. This photograph was successfully indexed on the basis of an orthorhombic unit cell and the unit-cell dimensions were refined by a least-squares program for EDSAC II written by Dr C. H. Kelsey. The values obtained were:

$$a=10\cdot31\pm0\cdot08,\ b=9\cdot15\pm0\cdot07,\ c=7\cdot20\pm0\cdot04\ \text{Å}\ .$$

Data for the first twenty powder lines are listed in Table 1. Systematic absences indicate the space group $P222_1$ and the density is estimated to be about 2·5 g.cm^{-3}, corresponding to 12 formula units per unit cell.

Table 1. *Powder data for* Na_2CN_2

$\sin^2\theta/\lambda^2$ observed	$\sin^2\theta/\lambda^2$ calculated	Index	Relative intensity
0·00241	0·00235	100	*ms*
0·00299	0·00299	010	*ms*
0·00718	0·00717	101	*ms*
0·00790	0·00780	011	*m*
0·00960	0·00941	200	*ms*
0·01049	0·01015	111	*w*
0·01745	0·01721	211	*vw*
0·01917	0·01911	121	*w*
	0·01926	002	
0·02135	0·02135	220	*vw*
	0·02117	300	
0·02414	0·02416	310	*vw*
0·02706	0·02687	030	*vw*
0·02880	0·02867	202	*s*
	0·02897	311	
0·03130	0·03120	022	*m*
0·03274	0·03311	320	*vw*
0·03485	0·03404	131	*w*
0·03729	0·03764	400	*w*
0·03826	0·03794	321	*vs*
0·04022	0·04043	302	*s*
0·04209	0·04245	401	*ms*
0·04455	0·04544	411	*ms*

vs = very strong　*s* = strong　*ms* = medium-strong
m = medium　*w* = weak　*vw* = very weak

The instability of this compound was demonstrated by the occurrence of extra lines on powder photographs from samples which were not sufficiently well sealed from the atmosphere.

Thallous cyanamide

Good crystals of thallous cyanamide were prepared by the following method, based on the procedure suggested by Deb & Yoffe (1959). About 12·5 g of thallous sulphate was dissolved in about 250 ml of boiling distilled water and a few drops of the surface active agent Lissapol-N were then added, followed by a solution of 2·5 g of sodium cyanamide in 25 ml of water. An orange-red precipitate formed, which redissolved when the solution was reheated to boiling, just sufficient water being added, if necessary, to achieve this. The solution was then allowed to cool slowly, when needle plates (typical dimensions: $500\mu\times200\mu\times10\mu$) crystallized out. The solution was filtered while still warm (*ca.* 35–40 °C) and the crystals washed as quickly as possible with a minimum amount of water and then alcohol. They were quickly dried and stored over phosphorus pentoxide *in vacuo.* Most of the crystals were twinned about the needle axis of the plate and were cleaved before use. Thallous cyanamide should not be kept in solution for longer than about 30 minutes since there is a tendency for hydrolysis to occur with the formation of thallous hydroxide.

The structure of thallous cyanamide has previously been reported to be hexagonal with

$$a=10\cdot28,\ c=6\cdot85\ \text{Å}$$

on the basis of electron diffraction and X-ray powder data (Deb & Yoffe, 1959). However, Laue, oscillation and Weissenberg photographs from single crystals with Cu $K\alpha$ and Mo $K\alpha$ radiation showed that the unit cell is in fact triclinic. Decomposition of the crystals occurred unless they were protected from water vapour and this decomposition was apparently accelerated by X-radiation. It is therefore possible that hydrolysis to the hydroxide may have occurred in the earlier work.

Oscillation and Weissenberg photographs provided the following data:

$$\begin{aligned} a^* &= 0\cdot1078\pm0\cdot0002\ \text{Å}^{-1} & \alpha^* &= 66\cdot5\pm0\cdot5^\circ \\ b^* &= 0\cdot1700\pm0\cdot0005 & \beta^* &= 76\cdot0\pm0\cdot5^\circ \\ c^* &= 0\cdot2110\pm0\cdot0007 & \gamma^* &= 76\cdot5\pm0\cdot5^\circ \end{aligned}$$

$$\begin{aligned} a &= 9\cdot99\pm0\cdot05\ \text{Å} \\ b &= 6\cdot57\pm0\cdot05 \\ c &= 5\cdot39\pm0\cdot05 \end{aligned}$$

and the remaining parameters of the unit cell were calculated from these to be:

$$\alpha=111\cdot9\pm0\cdot7^\circ,\ \beta=99\cdot7\pm0\cdot8^\circ,\ \gamma=98\cdot2\pm0\cdot8^\circ.$$

The needle axis is c and the plane of the plates (010). The density is approximately 7 g.cm^{-3} which corresponds to three formula units per unit cell.

Silver cyanamide

Silver cyanamide powder was prepared by the method of Deb & Yoffe (1959) and crystals in the form of needle plates (typical dimensions: $200\mu \times 60\mu \times 25\mu$) were then obtained by an arbitrary procedure based on one first suggested by Montagu-Pollock (1962) for the preparation of very small crystals. About 0·5 g of silver cyanamide powder was dissolved in 2 ml of a solution of concentrated nitric acid diluted 1:1 with water. 100 ml of 0·880 ammonia solution was quickly added, together with another 2 ml of the nitric acid solution. Finally a further 50 ml of ammonia and 10 ml of 0·1% Flash solution† were added. After filtration the solution was allowed to stand in a 6″ diameter Petri dish for about 30 hours, in a closed cupboard. During this time crystals formed as the ammonia evaporated. The crystals were found to be twinned about the needle axis (*b*) and the plane of the plates was (100). In the presence of other additives or under differing conditions of concentration crystals of other habits were formed.

The structure of silver cyanamide has been examined previously (Montagu-Pollock, 1962). The unit cell is monoclinic with:

$$a=7{\cdot}26,\ b=5{\cdot}92,\ c=6{\cdot}61\ \text{Å};\ \beta=102°\ 21'.$$

The density is 5·96 g.cm^{-3} with 4 formula units per unit cell. The space group is $P2_1/c$ and the positions of the silver atoms only have been determined.

Lead cyanamide

Lead cyanamide powder is normally prepared by double decomposition and in this case equivalent amounts of sodium cyanamide and lead acetate were mixed in aqueous solution. The reaction is as follows:

$$Na_2CN_2+PbAc_2 \rightarrow PbCN_2\downarrow +2NaAc\ .$$

The bulky yellow precipitate was filtered off and then redissolved in dilute acetic acid. Insoluble sulphide impurities were removed by filtration. Lead cyanamide was reprecipitated by the addition of ammonium hydroxide and was then washed and dried.

Under some circumstances, not yet fully established, a slightly darker yellow compound was formed on mixing sodium cyanamide and lead acetate solutions. This unknown compound gave an infrared absorption spectrum similar to that of lead cyanamide, but the X-ray powder pattern was completely different and it is thought that the compound is possibly a basic cyanamide.

Crystals of lead cyanamide (typical dimensions: $400\mu \times 50\mu \times 10\mu$) were prepared by a similar procedure which depends for its success on the slow diffusion of ions. The method was as follows. 5 to 10 ml of a freshly prepared 2*M* solution of sodium cyanamide was carefully added to a similar volume of 1*M* lead acetate solution, contained in a test tube in order to avoid overmixing of the two solutions. Immediate precipitation occurred at the interface and the bulky precipitate then acted as a semipermeable membrane and so retarded further reaction. The mixture was then left undisturbed for between 16 and 36 hours. Finally the liquid was decanted and the precipitate washed with water and alcohol. The test tube was crushed and the fragments examined under a microscope. Crystals of yellow lead cyanamide were usually to be found adhering to the glass, which had acted as a nucleating surface. These were clearly distinguishable by their colour from the white crystals of a basic lead salt which were also formed.

Laue, oscillation and Weissenberg photographs from single crystals with Cu $K\alpha$ and Mo $K\alpha$ radiation showed that the unit cell is orthorhombic with:

$$a=5{\cdot}54\pm0{\cdot}04,\ b=11{\cdot}69\pm0{\cdot}04,\ c=3{\cdot}86\pm0{\cdot}02\ \text{Å}\ .$$

A powder photograph taken with Cu $K\alpha$ radiation was successfully indexed on the basis of this unit cell, showing that the powder was also lead cyanamide. The *d* spacings derived from this photograph were in good agreement with those listed in the ASTM Index.

Structure analysis

The determination of the detailed structure of lead cyanamide is described in part II (Cooper, 1964). Determination of the structure of thallous cyanamide is in progress and it is also hoped that additional data will be collected to permit the location of the light atoms in silver cyanamide. No further structural work on sodium cyanamide is contemplated.

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† Flash is a household detergent manufactured by Thos. Hedley and Co. Ltd., Newcastle-upon-Tyne, England.