Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Recent Developments of X-ray Crystal Structure Analysis by a New Diffractometer for Rapid Data Collection

Hidehiro Uekusa [a] & Yuji Ohashi [a]
[a] Department of Chemistry, Tokyo Institute of Technology, Ookayama, Tokyo, 152, JAPAN
Version of record first published: 04 Oct 2006.

To cite this article: Hidehiro Uekusa & Yuji Ohashi (1996): Recent Developments of X-ray Crystal Structure Analysis by a New Diffractometer for Rapid Data Collection, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 279:1, 285-289

To link to this article: http://dx.doi.org/10.1080/10587259608042197

Mol. Cryst. Liq. Cryst., 1996, Vol. 279, pp. 285–289
Reprints available directly from the publisher
Photocopying permitted by license only

RECENT DEVELOPMENTS OF X-RAY CRYSTAL STRUCTURE ANALYSIS BY A NEW DIFFRACTOMETER FOR RAPID DATA COLLECTION

HIDEHIRO UEKUSA and YUJI OHASHI
Department of Chemistry, Tokyo Institute of Technology, Ookayama, Tokyo 152, JAPAN

Abstract A new non-screen Weissenberg type diffractometer with imaging-plate as the detector has been designed and made for rapid data collection. Successful structure determinations have been carried out for the crystals which are sensitive to X-ray exposure and which are easily decomposed by loss of solvent molecules, and, moreover, of which the diffraction spots are elongated.

INTRODUCTION

Recently, more than ten thousands of crystal structures are determined in one year by X-ray single crystal diffraction technique using the four-circle diffractometer. Although the four-circle diffractometer is easy to use and reliable to collect the diffraction data, it has several limits. The most serious limit is that it needs about 2 to 5 days to collect the three dimensional intensity data. However, it was recently found that several crystalline-state reactions proceeded within a day. For such fast reactions, the data collection should be carried out within a few hours in order to observe the structures at initial and intermediate stages. Another limit is the data collection for the crystals with elongated or splitted diffraction spots. It may be very difficult to obtain the reliable intensity data using a scintillation counter.

In order to overcome these limits, a new diffractometer with non-screen type Weissenberg camera with imaging-plates as the detector is designed and made to collect the two dimensional data at a time. The details of the diffractometer has been reported[1].

STRUCTURE DETERMINATION BY THE NEW DIFFRACTOMETER

Data Collection during the reaction occurred by X-ray exposure

Recently Mori et al. reported that the crystal of tri-cyclooctane derivative as shown in Figure 1 showed the ring cleavage when they measured the three dimensional intensity data by X-rays. Although the NMR data indicated the molecule has a tri-cyclooctane moiety before irradiation, the analyzed structure with the conventional four-circle diffractometer has a cyclooctadiene moiety[2].

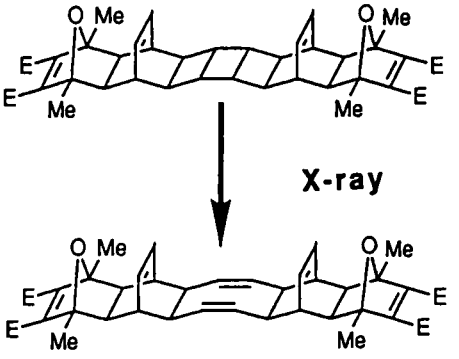

FIGURE 1. Ring cleavage reaction of tricyclooctane derivative

In order to determine the initial molecular structure and intermediate structures during the reaction, the crystal is mounted on the new diffractometer at room temperature. The three dimensional reflection data were recorded on 15 Weissenberg photographs, the total exposure time to X-rays being 140 minutes. The analyzed structure clearly showed the molecular has tri-cyclooctane moiety without extra peaks around it.

The additional three data sets were obtained using the same crystal in order to observe the progress of the crystalline state reaction. From these data sets, the extra peaks attributable to the atoms of the eight-membered ring due to the ring cleavage were observed near the four-membered ring. The occupancy factors of the four- and eight-membered ring were obtained for the three data sets. As shown in Table 1, As the ring cleavage proceeds, the occupancy factors of the four- and eight-membered rings decreases and increases, respectively. Thus, the new type of diffractometer is very useful for the observation of fast reaction occurred in the crystal.

	data set 1 140(min)	data set 2 280(min)	data set 3 420(min)	data set 4 560(min)
Initial (4 mem.)	> 90	80	73	65
Final (8 mem.)	< 10	20	27	35

TABLE 1. Change of occupancy factors for two rigs

Data collection without sealing in a glass capillary

Recently, Yano et al. synthesized a new complexes of cobalt(II) ion with N-glycoside as a ligand to investigate the molecular recognition of metal containing enzymes. The crystal of $[Co((L\text{-}Rha)_3\text{-}tren)]Br_2$ (Rha = rhamnose and tren = tris(2-aminoethyl)amine) contained two methanol molecules as a solvent. Since the crystal was easily decomposed by X-ray exposure and moreover the solvent methanol molecules are easily lost from the crystal. After several unsuccessful attempts to seal the crystal in a glass capillary with methanol, the three-dimensional intensity data were collected within 160 minutes using the new type of diffractometer without sealing at room temperature. Only eight Weissenberg photographs were necessary.

A successful structure analysis is converged to the R value of 0.073 for 2804 observed reflections. The molecular structure, as shown in Figure 2, showed a "close flower", which has a local three-fold symmetry.

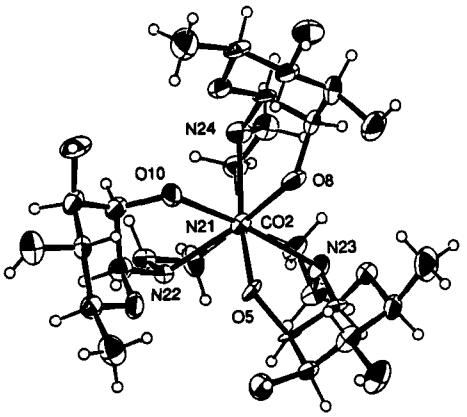

FIGURE 2. Molecular structure of $[Co((L\text{-}Rha)_3\text{-}tren)]^{2+}$

Data collection of broad diffraction spots

Recently $[NBu^n_4]$ $[Gd(III)Pc_2]$ (Bu^n = n-butyl, Pc = phthalocyaninato) was synthesized and its crystal structure analysis was attempted in order to investigate the relation between the electrochemical property and molecular structure, since the $[Ln(III)Pc_2]^-$ (Ln = Lanthanide) complexes draw much interests as a molecular semiconductors and optical nonlinear materials[3]. Due to the relatively weak and broad diffraction peaks, enough number of reflections had not been collected with the conventional four-circle diffractometer. Then the intensity measurement was attempted using the new diffractometer. Figure 3 shows one of the Weissenberg photograph. The elongated and diffused diffraction spots indicate that the crystallinity is not so good, which may be due to the disordered structure. For such broad peaks we must use wide slit and wide scan range for the scintillation counter. However, this severely increases back ground counts. The number of the significant data may be decreased.

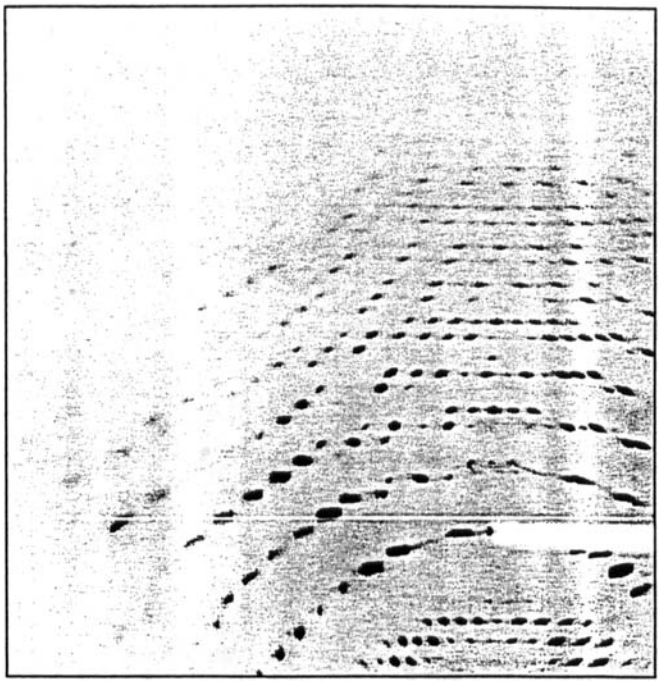

FIGURE 3. Part of Weissenberg photograph of $[NBu^n_4][Gd(III)Pc_2]$

A total of 12 Weissenberg photographs were taken in 240 minutes. The structure was converged in R value of 0.077 for 1932 observed reflections and it revealed a "sandwich type" molecular structure having four-fold symmetry as shown in Figure 4.

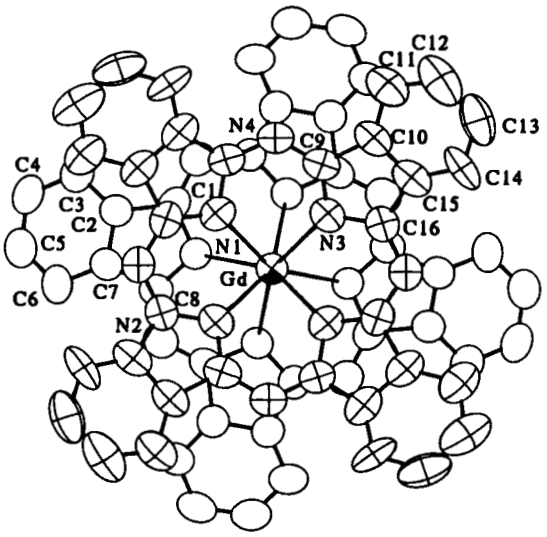

FIGURE 4. Molecular structure of $[NBu^n_4][Gd(III)Pc_2]$ (view along four-fold axis)

CONCLUSION

All the results suggest that the newly developed Weissenberg type diffractometer is very effective to investigate the rapid data collection. Reaction process occurred in a crystal and unstable structure before decomposition will be clarified. Moreover, the structure of the crystal with weak and broad diffraction spots will be analyzed. Thus this equipment will be a very powerful tool to observe the structures not only of the unstable crystal but also of stable one.

REFERENCES

1. Y. Ohashi, and H. Uekusa, J. Mol. Struct., (1995) in print.
2. A. Mori, N. Kato, H. Takeshita, Y. Kurahashi, and M. Ito, J. Chem. Soc., Chem.Commun., 1994, 869.
3. N. Koike, H. Uekusa, Y. Ohashi, C. Harnoode, F. Kitamura, T. Ohsaka, and K. Tokuda, to be submitted to Inorg. Chem., (1996).