JOURNAL OF SOLID STATE CHEMISTRY **74**, 239–246 (1988)

Direct Observation of Molecular Images of Lanthanide Phthalocyanines

I. Molecular, Crystal, and Twin Structures

W. P. ZHANG

College of Chemical Engineering, Dalian Institute of Technology, Dalian, People's Republic of China

K. H. KUO

Laboratory of Atomic Imaging of Solids, Institute of Metal Research, Academia Sinica, 110015 Shenyang, People's Republic of China

Y. F. HOU

College of Chemical Engineering, Dalian Institute of Technology, Dalian, People's Republic of China

AND J. Z. NI

Changchun Institute of Applied Chemistry, Academia Sinica, Changchun, People's Republic of China

Received July 13, 1987

Lanthanide phthalocyanine ($Ln\mathrm{Pc_2H}$: Ln = Nd, Tb, Er, Tm, Yb, and Lu) thin films prepared epitaxially on KCl and NaCl crystals have been studied at the molecular level by means of high-resolution electron microscopy. Both tetragonal and orthorhombic structures have been found. It is revealed that the interaction between substrates and molecules, the existence of geometric isomers, the anisotropy of molecular shapes, and the intermolecular forces play important roles in molecular stacking. Twins occur abundantly in the films grown on KCl and the twin relationship can be understood from the geometry of molecular shapes and their arrangement. It is suggested that the relative angle between two phthalocyanine ligands of a $Ln\mathrm{Pc_2H}$ molecule may vary within a limited angle range.

Introduction

Lanthanide phthalocyanine complexes have attracted much attention recently since these complexes exhibit interesting electrochromic properties. A full spectral range of color, for instance, can be generated by $\mathrm{LuPc_2H}$ films deposited on the surface of electrodes when the applied voltage varies from −1.0 to 1.2 V. These electrochromic materials must have prospect for application in full-color imaging and graphic display as well as alphanumerics. Meanwhile, $Ln\mathrm{Pc_2H}$ films have also been used as sensors for quantitative measurement of acidic gases.

0022-4596/88 $3.00

A structural study of these new materials will provide useful information needed in the correlation of their properties and will also be useful in the study of their nature. X-ray structural analysis of $NdPc_2H$ (*1*) and $LuPc_2H$ (*2*) has already been carried out by some research groups. It has been pointed out that $NdPc_2H$ and $LuPc_2H$ belong to the sandwich-type complexes, Nd or Lu cation occupying the central position between two phthalocyanine ligands which are staggered by 45° with respect to each other. Thus, Nd or Lu cation is eightfold coordinated with the nitrogen atoms of two phthalocyanine rings, and the coordination polyhedron of the metal ion is a square antiprism. Both crystals were prepared by recrystallization from solvents and monosolvated by dichloromethane, this property can affect the structures of $NdPc_2H$ and $LuPc_2H$. It has been concluded from a structural study of $NdPc_2H$ by other authors (*3*) that the rotation angle between two ligands is 38° so that the coordination polyhedron of Nd cation becomes a deformed square antiprism. The present authors believe that a high-resolution electron microscopic (HREM) study of $LnPc_2H$ thin films may provide useful structural information to improve their properties and to explain their action mechanism.

Since Menter's pioneer work in 1956 (*4*) metal complexes of phthalocyanine have been repeatedly studied by means of HREM (*5*, *6*). The molecular image of chlorinated copper phthalocyanine at atomic level and the crystal defects of thorium phthalocyanine have been observed by Uyeda *et al.* (*7*, *8*). No X-ray structural result of $LnPc_2H$ other than $NdPc_2H$ and $LuPc_2H$ has been published, and no HREM study on $LnPc_2H$ has been made.

During crystal growth, planar molecules with π-electron orbit parallel to each other on account of anisotropic intermolecular forces. Such columns are arranged with their axes parallel to each other to produce a crystal. Molecular images can be obtained if the micrographs are taken with the electron beam parallel to the column axis.

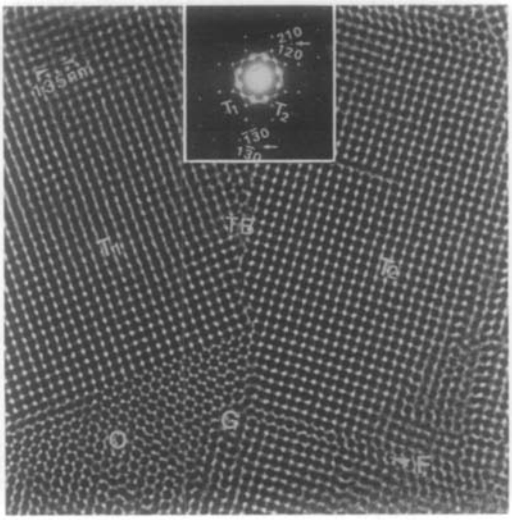

FIG. 1. A [001] molecular image of $ErPc_2H$ grown on KCl to show the tetragonal T_1 and T_2 crystallites in twin positions as well as the orthorhombic crystallites O. TB and *G* are twin and phase boundaries, respectively. *F* is a stacking fault. The corresponding [001] EDP from the tetragonal twins T_1 and T_2 has two pairs of coincident spots marked with arrows.

Both tetragonal and orthorhombic phases, ordered twins, grain boundaries, and various defects have been found in our HREM observation of $LnPc_2H$ thin films. It is suggested that the relative twist angle between two ligands of the $LnPc_2H$ molecule can vary within a limited range according to the molecular arrangement at grain boundaries. A structural image and the related electron diffraction pattern of $ErPc_2H$ grown on KCl are presented in Fig. 1. Each black disk in the HREM image corresponds to the projection of a molecular column, which has the same shape as a single molecule in a crystal. A tetragonal lattice is composed of two orthogonal sets of black rows of equal spacing, whereas an orthorhombic form (O) also exists in the film. The tetragonal twins consist of two differently oriented tetragonal structures (T_1 and T_2), and the twin boundary (TB) can clearly be seen. The boundary between orthorhombic and tetragonal structures is indicated by *G*, and the stacking fault in the tetragonal lattice by *F*. The molecular, crystal, and twin structures will be reported in this paper, and the structural defects will be discussed in a forthcoming publication.

Experimental

A mixture of 1,2-dicyanobenzene and lanthanide acetate in an unsealed test tube was heated to 573 K at a heating rate of 100 K per hour and kept at 573 K for half an hour. The product was washed repeatedly with acetic anhydrite, acetone, and *N*,*N*-dimethylformamide. The purification of the product was carried out by sublimation.

The thin films of *Ln*Pc$_2$H for the present electron microscopic study were prepared by epitaxial growth. The purified materials were deposited onto the (001) face of KCl or NaCl held at 433 K under a vacuum of 2×10^{-6} Torr. The films were backed with a thin layer of carbon to increase their mechanical strength. The specimens were floated on the surface of pure water by dissolving the substrate and then supported on copper microgrids. The HREM observation was made with a JEM-200CX electron microscope equipped with a top entry stage and high-resolution pole pieces. The images were taken at a direct magnification of 200,000 times.

Molecular and Crystal Structures

Organic molecules are generally bound together by van der Waals forces, and the molecular arrangement in a crystal is governed by a close packing of these molecules. The anisotropy of molecular shapes and intermolecular forces results in the anisotropy of crystals. These characteristics of organic crystals can be realized fully from the molecular stacking in *Ln*Pc$_2$H thin films.

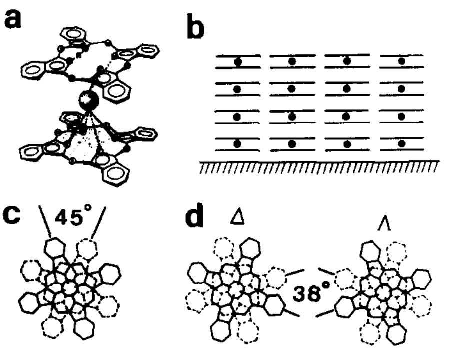

FIG. 2. (a) Sandwich structure of a *Ln*Pc$_2$H molecule with the *Ln* cation located at the center between the Pc ligands (see *1* or *12*). (b) Side view of *Ln*Pc$_2$H molecules on KCl or NaCl substrate; Pc ligands are drawn as bars and *Ln* cations as filled circles. (c) Top view of *Ln*Pc$_2$H; two ligands are rotated by an angle of 45°. (d) Top view of two geometric isomers; the relative twist angle between two ligands (solid line, above; dotted line, below) is somewhat smaller than 45°, for instance, 38° (*8*).

Two phthalocyanine ligands are parallel in each *Ln*Pc$_2$H molecule and lanthanide ion (III) is sandwiched between them (Fig. 2a). The stacking of these molecules on KCl or NaCl substrate along the [100] direction of the tetragonal or orthorhombic lattice is shown in Fig. 2b. According to previous results of other authors the relative angle between two phthalocyanine ligands of different metal phthalocyanine molecules (*M*Pc$_2$H or *M*Pc$_2$) is as follows: NdPc$_2$H (*1*) and LuPc$_2$H (*2*), 45°, as exhibited in Fig. 2c; SnPc$_2$ (*9*), 42°; β-NdPc$_2$H (*3*), ThPc$_2$, and UPc$_2$ (*10*), 38° (see Fig. 2d); and UPc$_2$ (*11*), 37°. Owing to the different sense of rotation of two ligands, two geometric isomers, which are named as Δ- and Λ-forms, respectively (*8*), exist in the latter three cases, for instance, the 38° case as shown in Fig. 2d in which the upper and lower ligands are drawn with solid and dashed lines, respectively. These molecular structures are similar but the metal cation differs for different derivatives. The char-

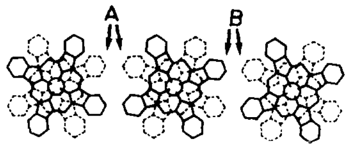

FIG. 3. Different isomers cannot be packed in a tetragonal lattice of 1.35 nm because of the steric hindrance between phenyl groups on neighboring molecules as indicated by A. Isomers of the same type can be arranged in this way because Pc ligands lie at different levels.

acteristic rotation angle between two ligands is different for various complexes probably because different crystal growth conditions have been used. This means that the rotation angle can vary within a small range. This implies that the ligand bonds between the central metal ion and the two ligands are both covalent and ionic. The covalent property of the ligand bonds is proved by the stability of the molecules even at the sublimation temperature, and the ionic property is confirmed by the change of the relative angle between two ligands. For a single molecule, it is most stable when two ligands have a relative twist of 45° because of their symmetrical distribution in space. But some close packing structures with lower lattice energies may sometimes emerge when the rotational angle of a molecule in crystals is not 45°. The energy increase caused by a deviation of 45° is compensated by the reduction in lattice energy. It is obvious that such a deviation depends on the type of molecular arrangements in the crystal under consideration.

*Ln*Pc$_2$H thin films grown on KCl consist of many crystallites, most of them having tetragonal structures as indicated by T_1 and T_2, respectively, in Fig. 1. The lattice parameter a of this tetragonal phase is 1.35 nm, similar to that of ThPc$_2$ (*8*). It is supposed that the *Ln*Pc$_2$H molecule in this tetragonal lattice, being the same as ThPc$_2$, also has a relative rotation of about 38° between two ligands. In such a case, two geometric isomers, as shown in Fig. 2d, may appear. The existence of isomers and their different arrangements may lead to polymorphs, twins, and various structural defects. As pointed out by Kobayashi *et al.* (*8*), different isomers cannot be arranged in the tetragonal lattice of 1.35 nm because of the steric hindrance between the phenyl groups in neighboring molecules as marked by A in Fig. 3. Isomers of the same type can be stacked in this way as shown in Fig. 4a since the phenyl groups in adjacent molecules lie at different levels and the steric hindrance is thus removed as designated by B in Fig. 3.

In an investigation of ThPc$_2$ Kobayashi *et al.* (*8*) have pointed out that a half-period translation is necessary at a grain boundary between two tetragonal crystallites composed of different isomers. They have even pointed out that if such an alternate arrangement of different isomers repeats itself, a new polymorph results. But in their article, no electron diffraction pattern and lattice parameters of this polymorph have been reported.

Such an orthorhombic structure has been found in all six *Ln*Pc$_2$H investigated by us. It is interesting to note that the thin films prepared on KCl consist mainly of the tetragonal phase, but those on NaCl mainly of the orthorhombic lattice. The molecular

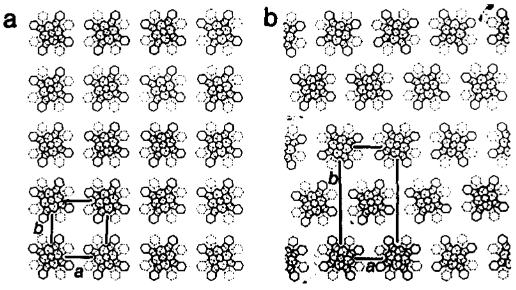

FIG. 4. Schematic diagrams of a tetragonal lattice consisting of isomers of the same type (a) and an orthorhombic phase composed of different types of isomers (b) (after Kobayashi *et al.* (*8*)).

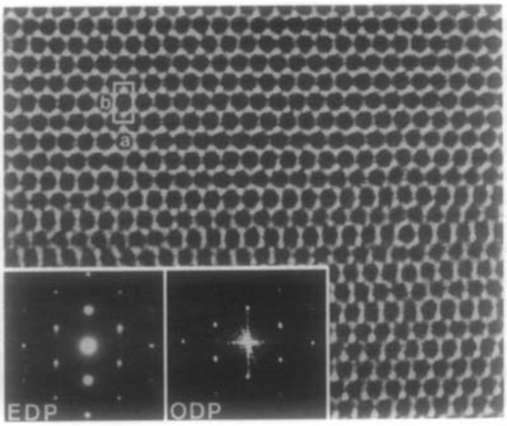

FIG. 5. Structural image, EDP, and ODP of the orthorhombic phase of $LuPc_2H$ grown on NaCl.

image, electron diffraction pattern (EDP), and optical diffraction pattern (ODP) of the $LuPc_2H$ grown on NaCl are shown in Fig. 5. The ODP obtained from the HREM image is identical to the EDP from a crystal. Lattice parameters obtained from the EDP are $a = 1.35$ nm, $b = 2.63$ nm. The length of the a axis in both the tetragonal and orthorhombic structures is the same, indicating that the molecular arrangements along the [100] direction in both phases are possibly alike and the molecular structures are probably identical in both crystal structures. Molecular arrangements of different isomers in the orthorhombic lattice are explained schematically in Fig. 4b and the steric hindrance between the phenyl groups of isomers either of the same or different type is avoided in this model. Molecules are packed more closely in the orthorhombic lattice than in the tetragonal one.

Molecular stacking in the [001] direction of both phases should be the same, and the length of the c axis is the same as the thickness of one molecular layer. According to Darovskikh *et al.* (*3*), the thickness of one molecular layer of $NdPc_2H$ in α-phase, which is similar to the tetragonal crystal in this paper, is 0.6581 nm. It is proposed that the c axial length of both the tetragonal and the orthorhombic structures is also about 0.66 nm. Because of the different radii of various lanthanide ions, the lattice parameters of different $LnPc_2H$ are expected to differ slightly.

Twin Morphology

Ordered tetragonal twins are common in the films grown on KCl and a few orthorhombic twins also exist in these films, but it is rather difficult to find twins in the films prepared on NaCl. EDPs of tetragonal twins in six different $LnPc_2H$'s grown on KCl are identical to that shown in Fig. 1. Two tetragonal lattices are delineated by the diffraction streaks passing through the diffraction spots. The 120 diffraction spot of one crystal overlaps the 210 spot of the other, indicating that the angle between the twins is 53.1°. The twins are reflection ones across the (120) mirror plane, but not of a rotation of 53.1° around the [001] direction since the twins are produced by two tetragonal crystals consisting of different isomers. The twin formation results from the interaction between the molecules and the substrate as well as the existence of different geometrical isomers. A detailed interpretation will be presented in another paper. Figure 6 is the HREM image and its schematic diagram of 53.1° tetragonal twins of $ErPc_2H$, in which the regular arrangements of molecules at the TB can clearly be seen. The molecules marked by arrows are located at the approximate coincident points of the twin boundary, and they match well to both of the crystals on each side of the twin boundary so that it is difficult to distinguish which crystal they really belong to. Being different from the molecules inside the crystals, the two ligands of these molecules possibly have a 45° angle between them and they are symmetrical with respect to the two crystals in twin positions. The interstices between the mole-

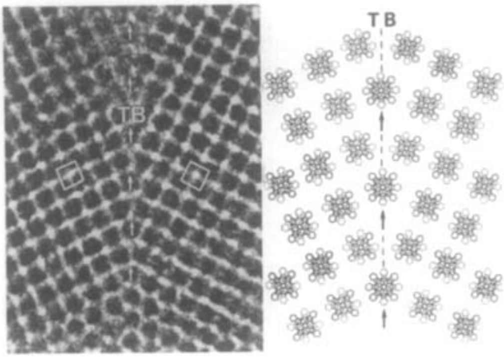

FIG 6. Molecular image and schematic diagram of the 53.1° tetragonal twin of $ErPc_2H$ grown on KCl. The rotation angle of coincident molecules marked by arrows is 45° instead of 38°.

cules close to the twin boundary are somewhat larger, and the molecules adjacent to the twin boundary may have some freedom to adjust themselves either in their positions or in the angle of rotation between the two ligands in them. It is possible that the rotation angle between two ligands of a molecule varies gradually from 38° to 45° at the twin boundary. There are similar coincident relationships at all such twin boundaries. The molecules at the boundaries are packed in this way with the result that a minimum boundary energy is realized.

There are another type of tetragonal twins in $Ln$$Pc_2H$ films grown on KCl. The $\bar{1}30$ electron diffraction spot of one crystal superposes on the $1\bar{3}0$ spot of the other, as shown in the EDP in Fig. 1. The angle between these twins is 36.9°. Similar to the 53.1° twins, the 36.9° twins are composed of different isomers having the (130) mirror reflection. In fact, both kinds of tetragonal twins can coexist and have the same EDP because the tetragonal lattice has a fourfold symmetry. However, the molecular arrangements at the boundaries of two tetragonal twins differ materially. The molecular image and a schematic diagram of 36.9° tetragonal twins are given in Fig. 7. The molecule at the coincident site is marked by an arrow. It is clear that the coincident relationship similar to Fig. 6 does not exist at the twin boundary here (TB). The misfit at the junction of two crystals is so big that the molecules near the boundary are displaced from their regular positions. It is possible that these molecules can shift, twist, and change the rotation angle between two ligands to adjust themselves so as to reduce the steric hindrance. Very often the 53.1° and 36.9° tetragonal twins occur side by side though the formation of 53.1° twins is favored according to the molecular arrangement at the twin boundary. It can be explained as follows: first, both kinds of tetragonal twins may coexist because of the fourfold symmetry of the tetragonal lattice, and this is a common phenomenon in HREM images; second, 36.9° twins are also stable since the energy difference between these two kinds of tetragonal twins is not significant. The grain boundary (G) between tetragonal and orthorhombic structures is indicated by the continuous black dots in Fig. 7. In this situation, some molecules match well with each other, but some do not.

Although orthorhombic crystallites occur much less frequently than the tetragonal ones in the films grown on KCl, some orthorhombic twins can sometimes still be

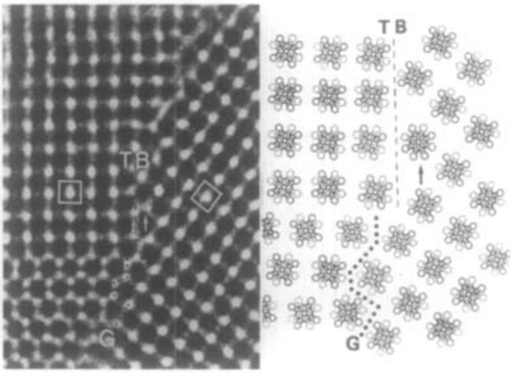

FIG. 7. Molecular image and schematic diagram of the 36.9° tetragonal twins of $ErPc_2H$ grown on KCl.

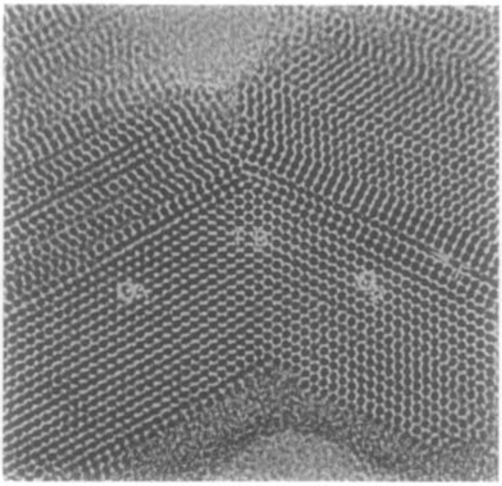

FIG. 8. Molecular image of orthorhombic twins of $LuPc_2H$ grown on KCl.

found. Figure 8 is the molecular image of the orthorhombic twins of $LuPc_2H$. The TB is not obvious but the twin relationship between two orthorhombic phases (O_1 and O_2) can clearly be identified from their morphology. Similar to the above mentioned tetragonal twins, the angle between two orthorhombic lattices is also 53.1°. The approximate coincident molecules at the twin boundary are marked by arrows in Fig. 9. It seems that the coincident molecules have the same relationship to the two orthorhombic crystals. The only reasonable explanation to account for these characteristics of the image is to assume the relative angle of two ligands in each molecule at the twin boundary being 45° as illustrated in the drawing in Fig. 9. Moreover, a minimum steric hindrance can perhaps be realized if the molecules are packed in this way. It is tentatively suggested that the structure of $LnPc_2H$ molecules, i.e., the rotation angle of two ligands, inside a crystal is different from that at the grain boundaries. Analyzing the schematic diagram in Fig. 9 carefully, it is confirmed that these twins are mirror reflection ones, the symmetrical plane being perpendicular to (001) and parallel to [110] of the crystal. It is worthwhile to point out that the molecular arrangement is more compact at the twin boundary in the orthorhombic phase than those at both kinds of twin boundaries in the tetragonal phase.

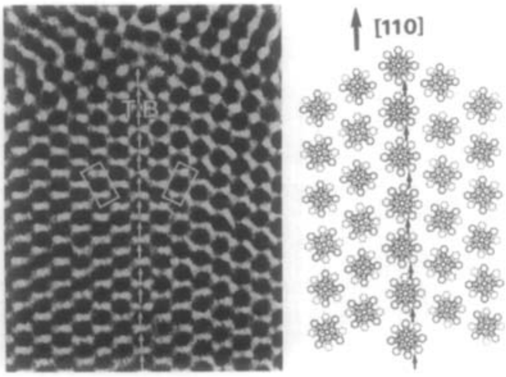

FIG. 9. An enlarged view of the molecular image and schematic diagram of orthorhombic twins and the twin boundary of $LuPc_2H$.

These six kinds of $LnPc_2H$ molecules have the same behaviors in molecular stacking. It is suggested that the same results may perhaps be obtained for other $LnPc_2H$'s in addition to those discussed above.

Conclusion

$LnPc_2H$ molecules are packed closely with their planes parallel to the (001) face of KCl or NaCl in epitaxial growth. The thin films grown on KCl, in which ordered twins exist abundantly, consist mainly of the tetragonal phase, but those on NaCl, in which few twins occur, are generally composed of the orthorhombic lattice. These characteristics are closely related with the sandwich-type structure of $LnPc_2H$ molecules and can be explained by the interaction between substrates and molecules, the molecular shape, and intermolecular forces. The dominating factor in organic crystals is that the anisotropic molecules try to pack as tight as possible provided that the steric hindrance can be avoided.

Molecular imaging by HREM is a powerful method to study molecular stacking and crystal structures in organic solids.

References

1. K. Kasuga, M. Tsutsui, R. C. Petterson, K. Tatsumi, N. Van Opdenbosch, G. Pepe, and E. F. Meyer, Jr., *J. Amer. Chem. Soc.* **102,** 4835 (1980).
2. A. De Cian, M. Moussavi, J. Fischer, and R. Weiss, *Inorg. Chem.* **24,** 3162 (1985).
3. A. N. Darovskikh, A. K. Tsytsenko, O. V. Franck-Kamenetskaya, V. S. Fundamenskii, and P. N. Moskalev, *Sov. Phys. Crystallogr. Engl. Transl.* **29,** 273 (1984).
4. J. W. Menter, *Proc. R. Soc. London Ser. A* **236,** 199 (1956).
5. Y. Murata, J. R. Fryer, and T. Baird, *J. Microsc.* **108,** 261 (1976).
6. D. J. Smith, J. R. Fryer, and R. A. Camps, *Ultramicroscopy* **19,** 279 (1986).
7. N. Uyeda, T. Kobayashi, K. Ishizuka, and Y. Fujiyoshi, *Chem. Scr.* **14,** 47 (1978–79).
8. T. Kobayashi, Y. Fujiyoshi, and N. Uyeda, *J. Crystallogr. Growth* **65,** 511 (1983).
9. W. E. Bennett, D. E. Broberg, and N. C. Baenziger, *Inorg. Chem.* **12,** 930 (1973).
10. I. S. Kirin, A. B. Kolyadin, and A. A. Lychev, *Zh. Strukt. Khim.* **15,** 486 (1974).
11. A. Gieren and W. Hoppe, *Chem. Commun.,* 413 (1971).
12. M. M. Nicholson and R. V. Galiardi, U.S. NTIS, AD Rep. AD-A039596 (1977).