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# Synthesis, Spectroscopic, and Structural Investigation of Ytterbium Potassium Hexacyanoferrate (II), $YbKFe(CN)_6 \cdot 3.5H_2O$

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Single crystals of the title compound are prepared by the U-tube slow diffusion method. The orthorhombic form of $YbKFe(CN)_6 \cdot 3.5H_2O$ crystallizes in space group *Cmcm* (No. 63, $D_{2h}^{17}$ with $a = 7.186(3)$, $b = 12.544(2)$, $c = 13.433(3)$ Å, $Z = 4$, $D_m = 2.6(1)$ Mg m$^{-3}$, and $D_x = 2.67$ Mg m$^{-3}$. The lattice constants were obtained from powder diffraction data, $F(34) = 24(0.013, 106)$ and $M20 = 22.0$. The final least-squares full-matrix refinement based on 1316 unique reflections has yielded $R = 0.041$ and $R_w = 0.046$. Cyanide bridges link the nine-coordinated (TTP) $YbN_6(H_2O)_3$ groups to the octahedral $FeC_6$ groups. Cavities within the structure are occupied by uncoordinated zeolitic water molecules and potassium ions. Important mean bond lengths are: Yb—N = 2.337; Yb—O = 2.467; Fe—C = 1.891; and C≡N = 1.155 Å.

## Introduction

The ferro- and ferricyanides of the lanthanide series exhibit ion-exchange and semipermeable membrane properties. The manner in which the water molecules are structurally maintained in these compounds can be further understood when one of the water molecules is replaced by an alkali metal ion such as sodium or potassium. Of particular interest is the physical characteristics and structural arrangement of the cavities in which the water molecules and alkali ions are held. A crystallographic study related to the physiochemical and structural properties of potassium-lanthanide ferrocyanides would determine the amount of water and potassium ions and the positions of these species within the cavities of the lattice.

The first double salt ferrocyanide containing a lanthanide atom was prepared by Robinson (*1*), $CeKFe(CN)_6$. Prandtl and Mohr (*2*) reported the preparation of lanthanide ferrocyanides containing sodium and potassium and the number of water molecules associated with these alkali-lanthanide ferrocyanide compounds. The structural features were not adequately described. Single-crystal X-ray analyses of $LnKFe(CN)_5 \cdot 4H_2O$ have shown that the first four members of the lanthanide series (*Ln* = La, Ce, Pr, and Nd) crystallize in the hexagonal space group $P6_3/m$ (*3*) and are structurally isomorphous with $LaFe(CN)_6 \cdot 5H_2O$ (*4*), the only difference is the replacement of a water molecule with a potassium ion. However, the next basic member of the series, $SmKFe(CN)_6 \cdot 3H_2O$, crystallizes in the monoclinic space group $P2_1/m$ (*5*). The space group symmetry was verified by employing the program MISSYM (*6*). For this reason, it was deemed necessary to continue structural investigations of other members

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of the series. $YbKFe(CN)_6 \cdot 3.5H_2O$ was chosen because of its position in the lanthanide series. If the monoclinic lattice persisted from samarium onward in the series or if a change were to be found, it would be observed by studying ytterbium potassium hexacyanoferrate (II).

## Experimental

Clear colorless crystals of the titled compound were synthesized by employing the U-tube slow diffusion method. Starting materials, $YbCl_3$ and $K_4Fe(CN)_6$, were obtained commercially (reagent grade) and used without further purification. The flotation technique was used to obtain the experimental density, 2.6(1) Mg $m^{-3}$ ($D_x$ = 2.67 Mg $m^{-3}$). A Perkin–Elmer TGS-1 thermobalance, operated at 2.5°C $min^{-1}$ while being purged with nitrogen (20 cm $min^{-1}$), was used to determine the thermal dehydration, 3.52(3) water molecules-formula $unit^{-1}$. An infrared spectrum obtained over a frequency range of 4000 to 450 $cm^{-1}$ using the pressed-disk method (KBr pellet) on a Mattson Fourrier Transform analyzer displays a sharp peak at 3610 $cm^{-1}$ and a very broad peak with a distinctive shoulder between 3505 and 3150 $cm^{-1}$, which are attributed to coordinated water molecules and hydrogen bonded zeolitic water molecules, respectively. An extremely sharp cyanide band is located at 2082 $cm^{-1}$ as well as a sharp H–O–H deformation at 1598 $cm^{-1}$. Two respective metal carbon peaks at 603 and 486 $cm^{-1}$, Fe—CN ($\delta$) and Fe—C ($\nu$), are also observed.

A Debye–Scherrer cylindrical camera (114.6 mm) using nickel-filtered Cu$K\bar{\alpha}$ radiation ($\lambda_{mean}$ = 1.54184 Å) under vacuum at 293 K was used to obtain the X-ray powder diffraction data from which the unit cell parameters were determined, see Table I. Yb $KFe(CN)_6 \cdot 3.5H_2O$ crystals were finely ground and placed into a 0.2-mm capillary. Characterization was based on 34 lines which were refined by placing measured $S$ values into a least-squares X-ray powder diffraction data program designed by Roof (*7*). The employed measuring tests for rating the quality and assessment of the reliability of the powder-pattern indexing are the figures of merit $F_N$ and $M_{20}$. The quantitative figure of merit $F_N$ (*8*) reveals accuracy and completeness of measured interplanar spacings. The figure of merit $M_{20}$ (*9*) rates the reliability of the unit cell and indexing. In this work, $F_{34}$ = 24(0.013,106) [$F_{20}$ = 29(0.013,53)] with an average $\Delta 2\theta$ percentage deviation of 0.033 and $M_{20}$ = 22.0. The observed and calculated $2\theta$ values with associated Miller indices, the visual estimated relative intensities based on 100 as the intensity for the strongest observed reflection and the observed $d$-spacing values in Å are presented in Table II. The mean deviation between the observed and the calculated $d$-spacing values is 0.13 percent.

A single crystal of ytterbium potassium iron (II) hexacyanide (0.19 × 0.16 × 0.11 mm) was chosen on the basis of optical purity. Using a Zeiss Photomicroscope (II), the biaxial nature of the system was verified by a conoscopic study which also negated any possibility of the system being considered hexagonal (a uniaxial system). The selected crystal was mounted on an Enraf-Nonius CAD-4F automated diffractometer equipped with a dense graphite monochromator (take-off angle, 5.8°). The orientation matrix and lattice parameters, which are in good agreement with the X-ray powder diffraction results (see Table I), were obtained using 25 well-centered reflections acquired through the application of CAD4 subroutines SEARCH, PHOTO, and INDEX (*10*). Intensity data were collected using Mo$K\bar{\alpha}$ radiation ($\lambda_{mean}$ = 0.71073 Å) at a temperature of 294 K employing the $\omega$-$2\theta$ scan technique with a variable scan rate (0.38–3.35° $min^{-1}$) determined by a fast prescan of 3.35° $min^{-1}$ and a scan angle of $1.30 + 0.35 \tan \theta$ over a $2\theta$ range of 3.0 to 70.0°. The variance

TABLE I

EXPERIMENTAL AND STATISTICAL SUMMARIES

| | Powder | Single crystal |
|---|---|---|
| $a$ (Å) | 7.186(3) | 7.189(2) |
| $b$ (Å) | 12.544(2) | 12.544(6) |
| $c$ (Å) | 13.433(3) | 13.430(6) |
| $V$ (Å$^3$) | 1210.9 | 1211.1 |
| $M_r$ | 487.18 | 487.18 |
| $Z$ | 4 | 4 |
| $D_m$ (Mg m$^{-3}$) | 2.6(1) | 2.6(1) |
| $D_x$ (Mg m$^{-3}$) | 2.67 | 2.67 |
| Radiation | Cu$K\bar{\alpha}$ | Mo$K\bar{\alpha}$ |
| Space group | $Cmcm$ (No. 63, $D_{2h}^{17}$) | |
| Systematic abs. | $hkl$, $h + k = 2n + 1$<br>$h0l$, $h,l = 2n + 1$ | |
| $F(000)$ (e$^-$) | | 911 |
| $\mu$ (Mo$K\bar{\alpha}$)(mm$^{-1}$) | | 9.212 |
| $g$(e$^{-2}$)(10$^{-7}$) | | 7.1(11) |
| $\Delta\omega$ (°) ($\omega$-2$\theta$ scan) | | 1.30 + 0.35 tan $\theta$ |
| $\Delta\theta$ (°) | | 1.5–35.0 |
| Scan limits (°min$^{-1}$) | | 0.38–3.35 |
| Unique reflections (>3$\sigma(I)$) | | 1316 |
| $R_{\text{int}}$ | | 0.034 |
| $R$, $R_w$ | | 0.041, 0.046 |
| Gnft ($\Sigma_2$) | | 1.44 |
| Transmission coefficient range | | |
| Maximum | | 0.4524 |
| Minimum | | 0.1467 |
| Average | | 0.3390 |
| Abscission value [$\Delta\xi_i/\sigma(\xi_i)$] | | |
| Maximum (10$^{-4}$) | | 3.53 |
| Average (10$^{-5}$) | | 3.7 |
| Residual density (e Å$^{-3}$) | | |
| Maximum | | 3.0(2) |
| Minimum | | −3.4(2) |

in intensity of the two check reflections (232,231) was less than 0.3% throughout the entire data collection, verifying crystal stability and instrument reliability. Lorentz and polarization corrections were applied to the data. An absorption correction ($\mu$ = 9.212 mm$^{-1}$) based on the crystal shape and dimensions was applied to the data. The numerical absorption correction (*10*) is based on Gaussian integration techniques described by Coppens *et al.* (*11*). After averaging redundant data, 1316 reflections were found to be greater than 3$\sigma(I)$ and were used in the full-matrix least-squares refinement. Experimental and statistical summaries are presented in Table I.

Initial lattice parameters revealed a pseudo-hexagonal ($a \approx b \neq c$, $\alpha = \beta = 90°$, and $\gamma = 120.0$) system. Since, as mentioned in the introduction that SmKFe(CN)$_6$ · 3H$_2$O was also pseudohexagonal and in the experimental section that YbKFe(CN)$_6$ · 3.5H$_2$O was biaxial, the lattice constants were transformed to the monoclinic system ($a \neq b \neq c$, $\alpha = \gamma = 90.0°$, $\beta = 119.82$) and the data were collected accordingly. Collecting the

TABLE II

X-RAY POWDER DIFFRACTION DATA FOR $YbKFe(CN)_6 \cdot 3.5\ H_2O$

| $h$ | $k$ | $l$ | $2\theta_{obs}$(°) | $2\theta_{cal}$(°) | $I/I_0$ | $d_0$(Å) |
|---|---|---|---|---|---|---|
| 0 | 0 | 2 | 13.18 | 13.18 | 10 | 6.72 |
| 1 | 1 | 0 | 14.19 | 14.19 | 10 | 6.24 |
| 0 | 2 | 1 | 15.60 | 15.60 | 95 | 5.68 |
| 0 | 2 | 2 | 19.38 | 19.38 | 95 | 4.58 |
| 1 | 1 | 3 | 24.50 | 24.48 | 100 | 3.633 |
| 1 | 3 | 1 | 25.52 | 25.52 | 5 | 3.490 |
| 0 | 0 | 4 | 26.55 | 26.54 | 5 | 3.357 |
| 0 | 4 | 0 | 28.47 | 28.46 | 5 | 3.135 |
| 2 | 2 | 0 | 28.65 | 28.63 | 5 | 3.116 |
| 2 | 2 | 1 | 29.40 | 29.41 | 5 | 3.038 |
| 1 | 1 | 4 | 30.24 | 30.22 | 5 | 2.955 |
| 0 | 4 | 2 | 31.52 | 31.48 | 20 | 2.838 |
| 0 | 4 | 3 | 34.95 | 34.93 | 90 | 2.567 |
| 0 | 2 | 5 | 36.40 | 36.37 | 80 | 2.468 |
| 1 | 5 | 1 | 38.59 | 38.59 | 50 | 2.333 |
| 0 | 4 | 4 | 39.33 | 39.31 | 3 | 2.291 |
| 0 | 0 | 6 | 40.32 | 40.28 | 60 | 2.237 |
| 1 | 1 | 6 | 42.92 | 42.92 | 50 | 2.1070 |
| 0 | 6 | 0 | 43.28 | 43.28 | 20 | 2.0907 |
| 0 | 4 | 5 | 44.40 | 44.40 | 20 | 2.0403 |
| 3 | 3 | 2 | 45.70 | 45.69 | 3 | 1.9853 |
| 1 | 3 | 6 | 47.80 | 47.79 | 10 | 1.9028 |
| 1 | 1 | 7 | 49.72 | 49.71 | 10 | 1.8336 |
| 2 | 2 | 6 | 50.18 | 50.17 | 10 | 1.8182 |
| 2 | 6 | 1 | 51.00 | 50.99 | 5 | 1.7907 |
| 1 | 5 | 5 | 51.45 | 51.43 | 20 | 1.7761 |
| 2 | 6 | 2 | 52.45 | 52.44 | 5 | 1.7446 |
| 1 | 7 | 1 | 53.12 | 53.11 | 10 | 1.7240 |
| 1 | 3 | 7 | 54.12 | 54.11 | 3 | 1.6945 |
| 0 | 0 | 8 | 54.68 | 54.66 | 10 | 1.6787 |
| 0 | 4 | 7 | 56.22 | 56.20 | 15 | 1.6361 |
| 2 | 4 | 6 | 56.65 | 56.64 | 5 | 1.6248 |
| 2 | 6 | 4 | 57.97 | 57.95 | 5 | 1.5908 |
| 0 | 8 | 1 | 59.35 | 59.34 | 5 | 1.5572 |

data using a lower symmetry (monoclinic) system provided the option of solving the titled compound in either the monoclinic system or a higher symmetry system. Even though a hexagonal lattice was not considered possible, the data were transformed to a hexagonal system. Then, after rejecting a hexagonal lattice due to nonequivalent cyclic permutations of *hk*0 reflections, the data were returned to the monoclinic $P2_1/m$ (No. 11) space group as was done with $SmKFe(CN)_6 \cdot 3H_2O$ (*5*). Take note, the data for $SmKFe(CN)_6 \cdot 3H_2O$ was tested using the program MISSYM (*6*), which verified no additional symmetry. The data of the title compound also fitted the $P2_1/m$ model especially well, yielding respectable reliability factors ($R = 0.042$, $R_w = 0.042$) and the resultant bond distances and angle provided a solution comparable to that of $SmKFe(CN)_6 \cdot 3H_2O$. However, after subjecting the data to the MISSYM program (*6*), additional symmetry was found, an orthorhombic system (*Cmcm*, No. 63). Since the data fitted both models ($P2_1/m$ and *Cmcm*) equally well with equivalent solutions, the higher symmetry model was chosen.

The initial atomic positions for the iron and ytterbium ions were chosen based on isomorphic substitution using $SmFe(CN)_6 \cdot 4H_2O$ (an orthorhombic system, *Cmcm*) as a guide (*12*). The positions of the remaining nonhydrogen atoms were obtained from difference Fourier mapping. Full-matrix least-squares refinement using secondary extinction corrections ($g$) yielded final reliability factors, $R = \Sigma\Delta F/\Sigma\ |F_0| = 0.041$ and $R_w = \Sigma\sqrt{w}\Delta F/\Sigma\sqrt{w}\ |F_0| = 0.046$ where $\Delta F = |\,|F_0| - |F_c|\,|$ and $w = \sigma^{-2}(|F_0|)$. A final electron density map revealed some density in the vicinity of the Yb atom, which is common for heavy metals. Elsewhere, the map was virtually featureless, revealing only a random fluctuation in the background. Atomic scattering factors and anomalous dispersion correction factors were taken from the "International Tables" (*13*). Table III list the final atomic coordinates and equivalent isotropic thermal parameters. Full listings of anisotropic thermal parameters and observed and calculated structure factors are available from the authors (D.F.M.).

## Discussion

$YbKFe(CN)_5 \cdot 3.5H_2O$ crystallizes in the orthorhombic space group *Cmcm* and is

TABLE III

ATOMIC POSITIONAL PARAMETERS (× $10^4$) AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS (× $10^3$)

| Atom | Occupancy | *x* | *y* | *z* | $U_{eq}$(Å$^2$)[a] |
|---|---|---|---|---|---|
| Yb | 1.00 | 0000 | 3397.5(2) | 2500 | 13.06(6) |
| Fe | 1.00 | 0000 | 0000 | 0000 | 1060(10)[b] |
| C(1) | 1.00 | 3140(10) | 4364(5) | 779(5) | 70(1) |
| C(2) | 1.00 | 0000 | 1192(5) | 882(6) | 23(1) |
| N(1) | 1.00 | 2030(10) | 3974(6) | 1273(6) | 164(2) |
| N(2) | 1.00 | 0000 | 1927(5) | 1406(6) | 30(1) |
| K | 0.50(1) | 0000 | 6674(4) | 799(6) | 85(3)[c] |
| O(1) | 0.50(1) | 0000 | 6620(10) | 880(20) | 73(8)[c] |
| O(2) | 1.00 | 3170(20) | 2730(10) | 2500 | 55(3) |
| O(3) | 0.75(1) | 0000 | 5400(10) | 2500 | 230(20)[d] |

[a] Isotropic equivalent thermal parameter ($U_{eq}$) is defined as one-third the trace of the orthogonalized $U_{ij}$ tensor.

[b] Fe was refined isotropically and the thermal parameter is in the conventional isotropic B form.

[c] O(1) and K atoms were refined at one-half occupancy.

[d] O(3) atom was refined at three-fourths occupancy.

structurally similar to other lanthanide potassium hexacyanoferrates (*3, 5, 14, 15*). The 9-coordinated ytterbium ion is bonded to six nitrogen atoms in apical positions (three above and three below the central ion) and to three water molecules which are equatorially positioned forming a distorted tricapped trigonal prism (TTP). The distortion, which is quite common for lanthanide compounds, is evidenced by the dihedral angle between the apical planes (7.95°) and the dihedral angles between the equatorial plane and the apical planes (3.97°). The average Yb—N and Yb—O bond distances of 2.337 and 2.467 Å, respectively, are in good agreement with published values found in BIDICS (*16*). Figure 1 displays a projected view of the nitrogen atoms and the water molecules about the ytterbium ion and the $FeC_6$ octahedral arrangement and Fig. 2 presents a stereoview of the unit cell. The iron ion is 6-coordinated to carbon atoms forming the octahedral $FeC_6$ groups with an average C—Fe—C angle of 90.3° and an average Fe—C bond distance of 1.891 Å, see BIDICS (*16*). The cyanide linkage of the $FeC_6$ and $YbN_6(H_2O)_3$ groups is close to being linear (mean Fe—C≡N = 179.0° and mean Yb—N≡C = 174.0°). The average Fe—C≡N bond angle shows strong directional bonding related to the interaction of the Fe 3*d* orbitals and the CN orbitals. The

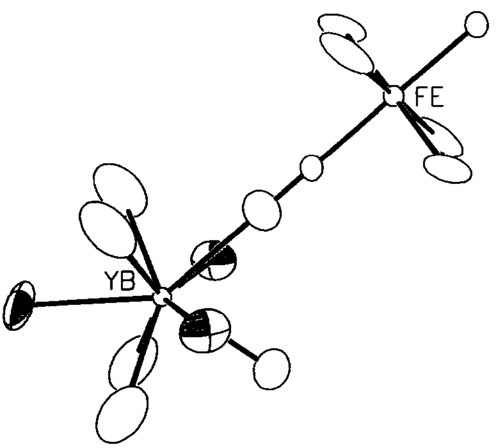

FIG. 1. A projected view of the 9-coordinated ytterbium atom and the $FeC_6$ octahedral arrangement.

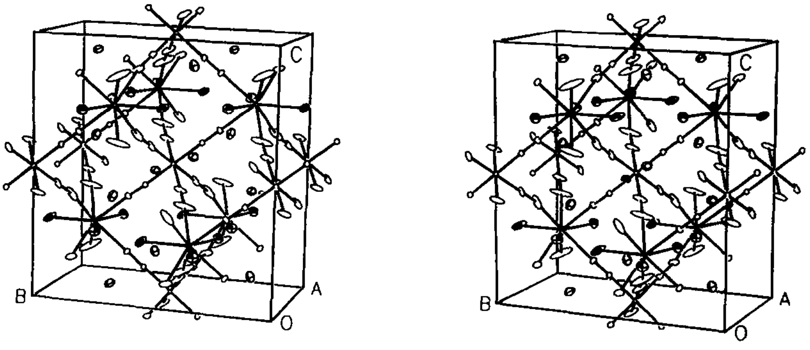

FIG. 2. A stereodrawing of the unit cell showing the arrangement of the $YbN_6(H_2O)_3$ and the octahedral $FeC_6$ with the cyanide bridges. Note the arrangement of the potassium ions and the water molecules.

average C≡N bond distance of 1.155 Å is in excellent agreement with the values found in the literature (*16*) as well as with the summation of the involved triple bond radii of carbon (0.603 Å) and nitrogen (0.55 Å) atoms which are found in the work of Pauling (*17*), 1.153 Å. Additional selected bond and contact distances and bond angles are listed in Table IV.

The zeolitic type water molecules and potassium ions are found within cage-like cavities in the structure. These uncoordinated water molecules, O(1), are within range of hydrogen bounding to the coordinated water molecules, O(2) and O(3), 2.90(2) and 2.66(2) Å, respectively. These intermoiety O···O contact distances are significantly different, which infers that two

TABLE IV

TABLE OF BOND DISTANCES (Å) AND ANGLES (°) FOR $YbKFe(CN)_6 \cdot 3.5\,H_2O$

| | | | |
|---|---|---|---|
| Fe–C(1) | 1.874(5) | Yb–N(1) | 2.315(6) |
| Fe–C(2) | 1.908(6) | Yb–N(2) | 2.358(6) |
| avg. | 1.891 | avg. | 2.337 |
| Yb–O(2) | 2.427(10) | C(1)–N(1) | 1.151(8) |
| Yb–O(3) | 2.507(10) | C(2)–N(2) | 1.160(8) |
| avg. | 2.467 | avg. | 1.155 |
| O(1)–O(2) | 2.90(2) | K–O(2) | 2.950(6) |
| O(1)–O(3) | 2.66(2) | K–O(3) | 2.790(6) |
| N(1)–Yb–N(1) | 78.0(7) | C(1)–Fe–C(1) | 90.8(7) |
| N(1)–Yb–N(1)′ | 90.7(5) | C(1)–Fe–C(1)′ | 89.2(7) |
| N(1)–Yb–N(2) | 78.5(2) | C(1)–Fe–C(2) | 90.7(2) |
| N(1)–Yb–O(2) | 61.2(4) | avg. | 90.3 |
| N(1)–Yb–O(3) | 71.8(3) | | |
| N(2)–Yb–N(2) | 77.1(3) | Fe–C(1)–N(1) | 179.0(10) |
| N(2)–Yb–O(2) | 74.3(2) | Fe–C(2)–N(2) | 179.0(6) |
| N(2)–Yb–O(3) | 141.5(2) | | |
| O(2)–Yb–O(2) | 139.6(6) | Yb–N(1)–C(1) | 169.2(7) |
| O(2)–Yb–O(3) | 110.2(3) | Yb–N(2)–C(2) | 178.8(6) |

types of hydrogen bonds are present, weak and strong. Investigations by Brown (*18*) on the geometry of hydrogen bonding have shown that oxygen–oxygen intermolecular distances of 2.73 Å (or less) are considered to be strong hydrogen bonds and that, as the contact distance increases, the hydrogen bonding becomes progressively weaker. Such reasoning is based on the assumption that there are no specific geometric constraints in the system. As mentioned in the experimental section, an ir spectrum of the title compound displayed a very broad band with a pronounced shoulder (3505–3150 $cm^{-1}$) which lends credence that there are two types of hydrogen bonds. Similar observations were confirmed by a neutron diffraction study (*19*). This suggests that neutron diffraction investigations of $YbKFe(CN)_6 \cdot 3.5H_2O$ and other members of the $LnKFe(CN)_6 \cdot nH_2O$ series could resolve whether or not two types of hydrogen bonds are present as well as the elucidation of molecular sieve properties and the weak aspects in the theories of semipermeable membranes and hydrogen bonding.

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## References

*1.* F. W. Robinson, *J. Chem. Soc.* **95,** 1353 (1907).
*2.* W. Prandtl and S. Mohr, *Z. Anorg. Allg. Chem.* **236,** 243 (1938).
*3.* D. F. Mullica and E. L. Sappenfield, *Powder Diffr.* **4**(2), 101 (1989).
*4.* W. E. Bailey, R. J. Williams, and W. O. Milligan, *Acta Crystallogr. Sect. B* **29,** 1365 (1973).
*5.* D. F. Mullica, E. L. Sappenfield, and H. O. Perkins, *J. Solid State Chem.* **78,** 301 (1989).
*6.* E. J. Gabe, Y. Le Page, J-P. Charland, and F. L. Lee, *J. Appl. Crystallogr.* **22,** 384 (1989).
*7.* R. B. Roof, Jr., LASL Report, Los Alamos Scientific Laboratory (1968).
*8.* G. S. Smith and R. L. Snyder, *J. Appl. Crystallogr.* **12,** 60 (1979).
*9.* P. M. DeWolff, *J. Appl. Crystallogr.* **1,** 108 (1968).
*10.* Enraf-Nonius, "Enraf-Nonius VAX Structural Determination Package," Delft, Holland (1982).
*11.* P. Coppens, L. Leserowitz, and D. Rabinovich, *Acta Crystallogr.* **18,** 1035 (1965).
*12.* D. F. Mullica and E. L. Sappenfield, *J. Solid State Chem.* **82,** 168 (1989).
*13.* J. A. Ibers and W. C. Hamilton, "International Tables for X-ray Crystallography," Vol. IV, 72 (1974).
*14.* G. W. Beall, D. F. Mullica, W. O. Milligan, J. Korp, and I. Bernal, *Acta Crystallogr. Sect. B* **34,** 1446 (1978).
*15.* D. F. Mullica, E. L. Sappenfield, and H. O. Perkins. *J. Solid State Chem.* **73,** 65 (1988).
*16.* "Bond Index to the Determination of Inorganic Crystal Structures," BIDICS, Institute for Material Research, Hamilton (1969–1981).
*17.* L. Pauling, "Nature of the Chemical Bond," 3rd Ed., Cornell University Press, p. 228 (1960).
*18.* I. D. Brown, *Acta Crystallogr. Sect. A* **32,** 24 (1976).
*19.* D. F. Mullica, G. W. Beall, W. O. Milligan, J. D. Korp, and I. Bernal. *J. Inorg. Nucl. Chem.* **41,** 277 (1979).