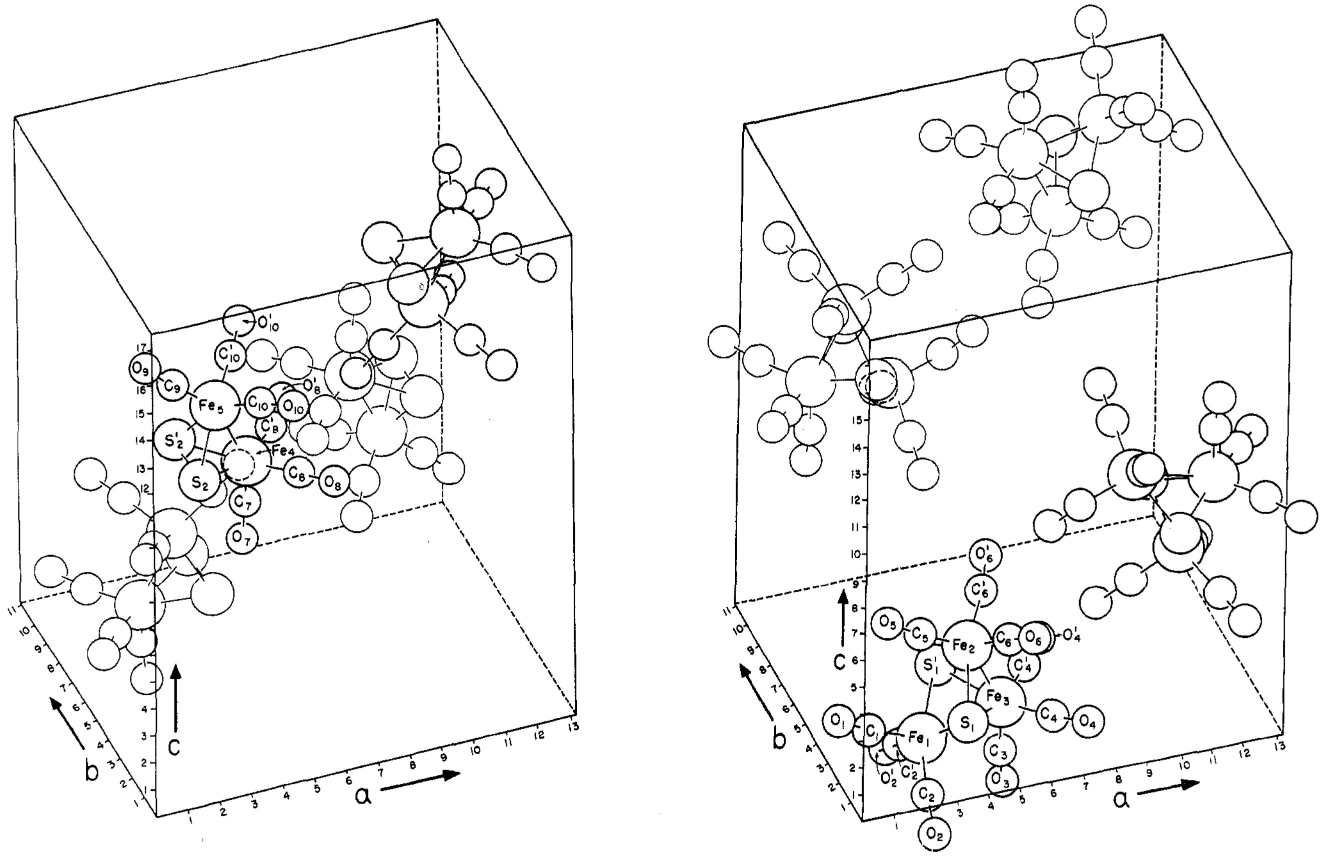

Figure 5.—Packing diagrams of the 1:1 mixture of four $S_2Fe_2(CO)_6$ species (left side) and four $(S_2Fe_3(CO)_9$ species (right side) in the unit cell.

the symmetry-related trinuclear species. All intermolecular contact distances are greater than 3.1 Å., which indicates that this molecular crystal is held together mainly by van der Waals forces.

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The Crystal Structure of Potassium Selenocyanate

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The crystal structure of KSeCN has been determined. The compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 4.59$ Å., $b = 7.64$ Å., $c = 11.89$ Å., and $\beta = 101.13°$. The structure contains the linear $SeCN^-$ ion with a C–N distance of 1.12 Å. and a Se–C distance of 1.83 Å.

Introduction

Recently Morgan[1] has investigated the infrared spectrum of solid KSeCN. His study indicated the existence of the linear $SeCN^-$ ion which was slightly perturbed by the influence of the crystal lattice. Although the $SeCN^-$ ion is isoelectronic (in the valence electrons) with the better-known OCN^- and SCN^- ions, a crystallographic study of the $SeCN^-$ ion had not been made. Because of a theoretical interest in the electronic structure of linear triatomic molecules and ions, it was decided to study the crystal structure of

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[1] H. W. Morgan, *J. Inorg. Nucl. Chem.*, **16**, 367 (1961).

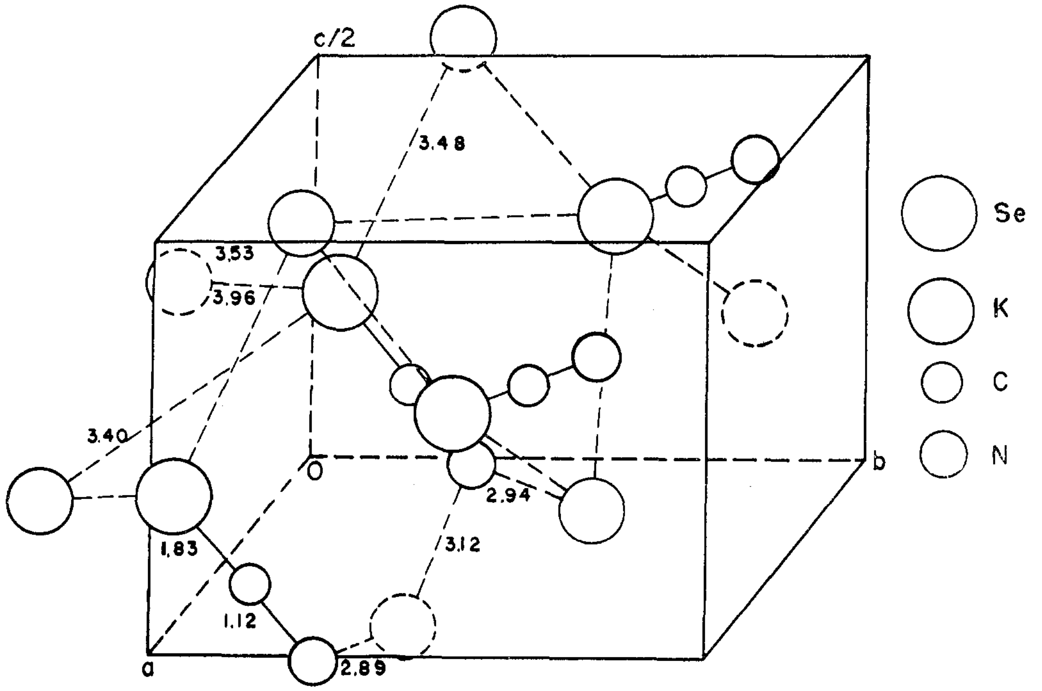

Figure 1.—Illustration of the structure of KSeCN.

Table I

Parameters for KSeCN[a,b]

Parameter	Se	K	C[c]	N[c]
x	0.0273 (0.0006)	0.6198 (0.0014)	0.1580 (0.0056)	0.2336 (0.0056)
y	0.0434 (0.0004)	0.2007 (0.0008)	0.2200 (0.0032)	0.3726 (0.0031)
z	0.1973 (0.0002)	0.3995 (0.0005)	0.1157 (0.0021)	0.0645 (0.0020)
β_{11}	0.0455 (0.0015)	0.0390 (0.0035)	0.0372 (0.0097)	0.0542 (0.0102)
β_{22}	0.0115 (0.0004)	0.0147 (0.0011)	0.0129 (0.0034)	0.0188 (0.0036)
β_{33}	0.0068 (0.0002)	0.0077 (0.0005)	0.0056 (0.0015)	0.0081 (0.0016)
β_{12}	−0.0022 (0.0008)	−0.0031 (0.0015)	0.0	0.0
β_{13}	0.0075 (0.0004)	0.0068 (0.0010)	0.0028 (0.0008)	0.0040 (0.0008)
β_{23}	−0.0004 (0.0004)	0.0003 (0.0007)	0.0	0.0

$$R_1 = \sum_{hkl} \left| |F_o| - |F_c| \right| / \sum_{hkl} |F_o| = 0.066$$

$$R_3 = \sum_{hkl} w(|F_o| - |F_c|)^2 / \sum_{hkl} w|F_o|^2 = 0.086$$

[a] Standard deviations are given in parentheses. [b] The β_{ij} are defined by $T = \exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl)$. [c] Anisotropic temperature factors not varied.

KSeCN to verify the linearity of the SeCN ion and to determine the symmetry, if any, required of the ion in the crystalline state.

Experimental

The compound KSeCN was prepared in the manner described by Waitkins and Schutt.[2] The compound crystallized as needles with the a axis parallel to the needle axis. The material is very hygroscopic and decomposes in air to form red selenium and potassium cyanide. Consequently the crystals were placed in Lindemann glass capillaries while the crystallographic data were obtained.

The lattice constants for KSeCN, determined from Weissenberg and precession camera photographs using Cu Kα radiation (1.5418 Å.), are $a = 4.59 \pm 0.02$ Å, $b = 7.64 \pm 0.01$ Å., $c = 11.89 \pm 0.01$ Å., and $\beta = 101.13 \pm 0.08°$. Systematic extinctions ($l = 2n + 1$ for $h0l$ reflections, and $k = 2n + 1$ for $0k0$ reflections) imply the space group $P2_1/c$. The observed density, measured by a flotation technique, is 2.35 g./cc. The calculated density, for $Z = 4$, is 2.30 g./cc.

Intensity data were collected on a Weissenberg camera with Zr-filtered Mo Kα radiation using a combination of multiple film and timed exposure techniques. The zeroth through the third layer were recorded while rotating about the $\langle 100 \rangle$ direction. In this manner, the intensities of 491 reflections were recorded. The relative intensities were estimated visually against a set of standard intensities and converted to structure factor magnitudes in the usual manner. Absorption corrections[3] were also applied to the structure factor magnitudes.

Determination of Structure

The Patterson projection onto (100) was calculated first to determine the heavy atom y and z parameters. The largest peaks were assigned as selenium–selenium vectors. Selenium–potassium vector peaks also appeared quite distinctly on the Patterson map. A two-dimensional Fourier projection onto (100), based on the postulated Se and K positions, confirmed their assignment. The C and N atoms appeared, though they were not well-resolved at this point. The x parameters for the Se and K atoms were determined from Patterson projections onto (100) modified by $\cos(2\pi u)$; cos

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[2] G. R. Waitkins and R. Schutt, *Inorg. Syn.* **2**, 186 (1946).

[3] International Tables for Crystallography, Vol. II, The Kynoch Press, Birmingham, England, 1959, pp. 295–298.

$(2\pi 2u)$, and $[1 + \cos (2\pi u)]$. From these parameters, a trial structure was deduced and refined, the carbon and nitrogen positions being assigned on chemical grounds. A three-dimensional Fourier map confirmed the structure. The Sly, Shoemaker, and Van den Hende ERFR2 IBM 709/7090 program[4] was used for the Fourier computations. Atomic positions obtained from these projections were refined with isotropic temperature factors and refinement proceeded rapidly to a value of $R_1 = 0.082$ for observed reflections only. Refinement of the anisotropic temperature factors (with the exception of the lighter nitrogen and carbon atoms) further reduced the value of R_1 to 0.066 for observed reflections only and to 0.130 for all reflections. The Busing, Martin, and Levy 709/7090 Fortran crystallographic least-squares[5] program was used to minimize the function R_3 as defined in Table I. The intensities for unobserved reflections were assigned one-half the minimum observable intensity and were omitted from the refinement if the calculated structure factor was less than the observed structure factor. A modified version of the Hughes weighting scheme was used as described previously.[6] Atomic form factors for K^+, C, and N were used as computed from SCF wave functions with exchange effects included,[7] and the atomic form factor for Se was used as computed from the Thomas–Fermi–Dirac statistical method.[8] Final parameters are listed in Table I and a list of the observed and calculated structure factors is given in Table II.[9] Bond distances and angles were computed using the Busing, Martin, and Levy 709/7090 Fortran function and error program.[10]

Discussion

This structure contains $SeCN^-$ ions which are linear (178.8 ± 2.5°) to within the accuracy of our determination. The C–N distance is found to be quite short at 1.117 ± 0.026 Å., but because of the high standard deviation it cannot be considered significantly different from a normal C–N triple bond of 1.16 Å. The Se–C distance of 1.829 ± 0.025 Å. is considerably shorter than the normal single bond length of 1.94 Å., indicating some multiple bond contribution. This $SeCN^-$ ion is isoelectronic in the valence electrons with the OCN^- and SCN^- ions; however, because of the decreased electronegativity of the selenium atom, it is expected that the π-bonds will be essentially localized between the carbon and nitrogen atoms.

The C–N stretching frequency is smaller for SCN^- (2048 $cm.^{-1}$) than for either OCN^- (2160 $cm.^{-1}$) or $SeCN^-$ (2070 $cm.^{-1}$),[11] which is not in the order ($SeCN^- < SCN^- < OCN^-$) expected from electronegativity arguments. However, it may well be that the force constants, which give a more accurate estimation of bond order, will be in the expected order.

Each selenium atom is coordinated to four potassium ions forming a very shallow, distorted rectangular pyramid with the selenium at the apex. The Se–K distances range from 3.4 to 4.0 Å. Each nitrogen atom has three potassium ions as next nearest neighbors with distances ranging from 2.6 to 3.1 Å., as illustrated in Figure 1.

[4] W. G. Sly, D. P. Shoemaker, and J. H. Van den Hende, Esso Research and Engineering Co., Report CBRL-22M-62 (1962).

[5] W. R. Busing, K. O. Martin, and H. A. Levy, U. S. Atomic Energy Commission Report ORNL-TM-305 (1962).

[6] See R. D. Willett, C. Dwiggens, Jr., R. Kruh, and R. E. Rundle, *J. Chem. Phys.*, **38**, 2429 (1963). K_1 was chosen as the average intensity for each layer and K_2 as twice the minimum observable intensity.

[7] International Tables for Crystallography, Vol. III, The Kynoch Press, Birmingham, England, 1962, pp. 202–209.

[8] Reference 7, pp. 210–212.

[9] Table II has been deposited as Document No. 8197 with the ADI Auxiliary Publications Project, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $1.25 for photoprints or $1.25 for 35-mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

[10] W. R. Busing, K. O. Martin, and H. A. Levy, U. S. Atomic Energy Commission Report ORNL-TM-306 (1964).

[11] N. N. Greenwood, R. Little, and M. J. Sprague, *J. Chem. Soc.*, 1292 (1964).