Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.

Acta Cryst. (1971). B27, 1835

The crystal structure of potassium tricyanomethide KC(CN)₃. By JERRY R. WITT, Department of Chemistry, Winona State College, Winona, Minnesota, U.S.A. and DOYLE BRITTON, Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, U.S.A.

(Received 24 February 1971)

Potassium tricyanomethide, KC(CN)₃, is triclinic, space group *P*T, with a=8.665 (8), b=8.873 (8), c=3.89 (1) Å, $\alpha=86.7$ (3), $\beta=90.1$ (3), $\gamma=105.0$ (3)°, Z=2, and measured and calculated densities of 1.49(1) and 1.487(5) g.cm⁻³, respectively. The structure was determined from 457 visually estimated intensities from Weissenberg films and was refined by least-squares methods to an *R* value of 0.11. The tricyanomethide group has approximate D_{3h} symmetry with C-C bond distances averaging 1.39 (2) Å and C-N distances averaging 1.17 (1) Å. The central C atom is 0.026 Å above the plane of the three N atoms. The potassium ion is surrounded by seven N atoms at 2.86 to 2.98 Å.

A preliminary report of the structure of KC(CN)₃ was made by Andersen & Klewe (1963). They did not complete their study when they learned that we were determining this same structure, but they did determine the structure of $NaC(CN)_3$ (Andersen, Klewe & Thom, 1967). These studies were undertaken to determine whether the $C(CN)_3^-$ ion is planar or pyramidal, *i.e.* whether the C-C-C angles averaged 120° or some lesser value. Spectroscopic studies by Long, Carrington & Gravenor (1962) and by Miller & Baer (1963) indicated the planar form to be the more likely one. The structure of NH₄C(CN)₃ (Desiderato & Sass, 1965) was determined with the same question in mind. The structures of Cu[C(CN)₃]₂ (Biondi, Bonamico, Torelli & Vaciago, 1965) and AgC(CN)₃ (Konnert & Britton, 1966) were also determined. We report here the details of the $KC(CN)_3$ structure.

Potassium tricyanomethide was prepared by the method of Cox & Fontaine (1954). Twinned, acicular crystals were prepared by recrystallization from ethanol. The twin pairs were related by a 180° rotation about the *c* axis. An infrared spectrum showed no solvent incorporated in the compound.

The unit cell is triclinic with a = 8.665 (8), b = 8.873 (8),

c=3.89 (1) Å, $\alpha=86.7$ (3), $\beta=90.1$ (3), and $\gamma=105.0$ (3)°. The *a* and *b* dimensions were measured from a powder photograph taken with Cr K α radiation ($\lambda=2.2909$ Å); *c* was measured from an oscillation photograph taken with Cu K α radiation ($\lambda=1.5418$ Å); angles were determined from *hk*0, 0*kl*, and *h*0*l* precession photographs. All measurements were made at room temperature. Cell volume is 288 Å³; calculated density, assuming Z=2, is 1.487 (5) g.cm⁻³; density measured by flotation is 1.49 (1) g.cm⁻³. Values given by Andersen & Klewe for KC(CN)₃, when converted to our orientation, are a=8.62, b=8.90, c=3.87Å, $\alpha=86.7$, $\beta=89.7$, $\gamma=104.9^\circ$, and $d_{calc}=d_{exp}=1.50$ g.cm⁻³. The solved structure shows the space group to be *P*I.

A cylindrical crystal, 0.10 mm thick and 1.0 mm long, was mounted with the needle axis, c, as the rotation axis. Multiple-film Weissenberg data from levels hk0 to hk2 were collected using Cu Ka radiation. Intensities of 457 reflections were estimated visually. In the same region of reciprocal space, 157 reflections had intensities too weak to be observed. The quality of the precession photographs was not good enough for use in correlating the Weissenberg layers; initially, the layer correlation factors were estimated from exposure times and were later refined by least-squares

Table 1. Observed and calculated structure factors (in electrons)

methods. The usual Lorentz and polarization corrections were made,^{*} but no absorption corrections were made (linear absorption coefficient, μ , for KC(CN)₃ is 66 cm⁻¹ for Cu K α radiation).

Approximate locations of all atoms were found from Patterson and Fourier maps. After several cycles of least-squares refinement, using isotropic thermal parameters and including refinement of the layer scaling factors, agreement factors converged to R=0.100 and r=0.040.[†]

The F_o and F_c values on an absolute scale are listed in Table 1, final atomic parameters in Table 2, and final interatomic distances and angles in Table 3. The structure is shown in Fig. 1.

Table 2. Final atomic coordinates and temperature factors§

| | x | у | z | B (Å2) |
|-----------------|------------|------------|-------------|-----------|
| к | 0.1724 (2) | 0.2020 (2) | 0.2116 (5) | 1.77 (2) |
| N(1) | 0.2272 (8) | 0.4513 (8) | 0.6918 (19) | 4.41 (15) |
| N(2) | 0.6038 (7) | 0.8521 (7) | 0.2730 (18) | 3.63 (14) |
| N(3) | 0.0887 (7) | 0.8656 (7) | 0.2669 (17) | 3.26 (13) |
| $\mathbf{C}(1)$ | 0.2623(8) | 0.5779 (8) | 0.5680 (21) | 2.79 (15) |
| C(2) | 0.4683 (8) | 0.7968 (8) | 0.3375 (21) | 2.76 (14) |
| C(3) | 0.1902 (8) | 0.8049 (8) | 0.3329 (20) | 2.38 (14) |
| C(4) | 0.3062 (7) | 0.7256 (7) | 0.4151 (19) | 1.96 (13) |

§ Standard deviations (in parentheses) occur in the last digit.

Table 3. Final interatomic distances and angles

| K-N(1) | 2·92 (1) Å | N(1)-C(1)-C(4) | 178.3 (15) |
|-------------------------------|------------|--------------------|------------|
| | 2·85 (1) | N(2)-C(2)-C(4) | 178.2 (15) |
| | | N(3)-C(3)-C(4) | 177.3 (15) |
| K-N(2) | 2.88 (1) | N(1)-C(4)-N(3) | 119.2 (7) |
| | 2.87 (1) | N(1)-C(4)-N(2) | 118.6 (7) |
| | | N(2) - C(4) - N(3) | 122.1 (10) |
| K-N(3) | 2.88(1) | C(1) - C(4) - C(3) | 120.0 (6) |
| | 2.88(1) | C(2) - C(4) - C(3) | 120.2 (10) |
| | 2.98 (1) | C(1) - C(4) - C(2) | 119.8 (10) |
| | | | |
| N(1)-C(1) | 1.16 (1) | | |
| N(2) - C(2) | 1·17 (1) | | |
| N(3) - C(3) | 1.17 (1) | | |
| C(1) - C(4) | 1.37 (1) | | |
| C(2) - C(4) | 1.41 (1) | | |
| $\tilde{C}(3) - \tilde{C}(4)$ | 1.40 (1) | | |
| | (1) | | |

The average C–C distance in the tricyanomethide anion is 1·39 (2) Å, in agreement with the distance of 1·38 Å we would expect for a $C_{sp}-C_{sp2}$ bond with a bond order of $\frac{4}{3}$ (Bent, 1961). The average C–N distance, 1·17 (1) Å, is not significantly greater than the usual 1·156 Å for the C–N distance in nitriles (Britton, 1967). All angles about the central carbon atom are 120° and all the N–C–C angles are 180° within two e.s.d.'s. All this information is in substantial agreement with the results for NaC(CN)₃ and NH₄C(CN)₃.

Atoms C(1), C(2), C(3), and the central C(4) atom are calculated to be 0.026, 0.020, 0.018, and 0.026 Å, respect-

† $[R=\sum ||F_o|-|F_c||/\sum |F_o|; r=\sum w(|F_o|^2-|F_c|^2)^2/\sum w|F_o|^4; w$ =1 for $F_o \le 4.0$, $w=(4.0/F_o)^4$ for $F_o > 4.0$. Numerator of r is the function refined.





ively, above the plane through the N atoms. Thus, the four carbon atoms are coplanar within experimental error; yet there does seem to be a slight, but real difference, between the plane of the carbon atoms and the plane of the nitrogen atoms. The same nearly planar geometry is found in NaC(CN)₃ and Cu[C(CN)₃]. There is a larger deviation from a planar anion in NH₄C(CN)₃, and probably also in AgC(CN)₃. Steric arguments have been used to explain the distortions in the latter two cases.

The potassium ion has seven near nitrogen neighbors at 2.86 to 2.98 Å away. It is at the center of an imaginary tetragonal prism of dimensions $3.39 \times 3.39 \times 3.89$ Å; six N atoms are at the corners of the imaginary prism and the 7th is on the edge between the unoccupied corners. A comparison of the cation environment in KC(CN)₃, NH₄C(CN)₃, and NaC(CN)₃ is given in Fig. 2 of the article on the NaC(CN)₃ structure (Andersen, Klewe & Thom, 1967). The same illustration (plus an extensive discussion of these compounds) is also given in the review article by Andersen (1967).

We thank the National Science Foundation for their support of this work, and Dr Carol Mahon for her assistance.

References

- ANDERSEN, P. (1967). In Selected Topics in Structure Chemistry, p. 125. Ed. P. ANDERSEN et al. Oslo: Universitetsforlaget.
- ANDERSEN, P. & KLEWE, B. (1963). Nature, Lond. 200, 464.
- ANDERSEN, P., KLEWE, B. & THOM, E. (1967). Acta Chem. Scand. 21, 1530.
- BENT, H. A. (1961). Chem. Rev. 61, 275.
- BIONDI, C., BONAMICO, M., TORELLI, L. & VACIAGO, A. (1965). Chem. Commun. 10, 191.
- BRITTON, D. (1967). Perspectives Struct. Chem. 1, 109.
- Cox, E. & FONTAINE, A. (1954). Bull. Soc. Chim. Fr. 948.
- DESIDERATO, R. & SASS, R. L. (1965). Acta Cryst. 18, 1.
- KONNERT, J. & BRITTON, D. (1966). Inorg. Chem. 5, 1193.
- LONG, D. A., CARRINGTON, R. A. & GRAVENOR, R. B. (1962). Nature, Lond. 196, 371.
- MILLER, F. A. & BAER, W. K. (1963). Spectrochim. Acta, 19, 73.

^{*} These and most subsequent calculations were made on a Univac 1103 computer with programs developed by Professor W. N. Lipscomb and co-workers at the University of Minnesota. Final refinements were made with programs, supplied by Professor R. Jacobson of Princeton University, for a CDC 1604 computer. Plane calculations were made with a local program (PLANE) on a CDC 6600 computer. All calculations were made at the University of Minnesota Computer Center.