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# Potassium carbamoyldicyanomethanide

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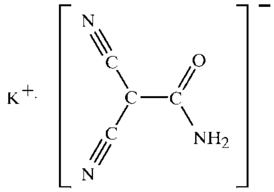
The crystal structure of the title compound, K[(CN)$_2$CC(O)NH$_2$)] or $K^+ \cdot C_4H_2N_3O^-$, conventionally abbreviated as Kcdm, where cdm is carbamoyldicyanomethanide, is described. The bond lengths and angles of the cdm cation are comparable to those reported previously for [*M*(cdm)$_2$(H$_2$O)$_4$]·2H$_2$O (*M* = Ni, Mn and Co). The K atoms are coordinated to four nitrile N atoms and two carbonyl O atoms in a distorted trigonal prismatic fashion, with two further N atoms semicoordinated through the centers of two prism side faces. This coordination leads to the formation of mixed anion–cation sheets parallel to the *ab* plane, which are joined together *via* hydrogen-bonding interactions. The cdm anion is potentially useful for the formation of transition metal coordination polymers, in which magnetic superexchange could occur through a bidentate cdm bridge. Kcdm provides a model compound by which the molecular geometry of the cdm anion can be analyzed.

## Comment

The structural and magnetic properties of coordination polymers containing cyano-based anions have received increased attention over the past decade. The dicyanamide (dca) anion, N(CN)$_2^-$, has been shown to be an effective magnetic superexchange ligand, with Ni(dca)$_2$ exhibiting ferromagnetism at 21 K (Kurmoo & Kepert, 1998). A logical extension of this research is to include cyanocarbon anions as molecular building blocks for the construction of magnetic solids. Tricyanomethanide (tcm), C(CN)$_3^-$, is one of the simplest cyanocarbon anions that is capable of forming polymeric structures. The *M*(tcm)$_2$ (*M* = Cu, Mn and Zn) crystal structures are characterized by the interpenetration of two identical rutile-like lattices, in which the tcm anion is $\mu_3$-bonded to three $M^{II}$ ions (Batten *et al.*, 1991; Manson *et al.*, 1998; Hoshino *et al.*, 1999). The carbamoyldicyanomethanide (cdm) anion, (CN)$_2$CC(O)NH$_2^-$, is a derivative of tcm in which one nitrile group is replaced with C(O)NH$_2$. The cdm anion is therefore a candidate for forming coordination polymers (Trofimenko *et al.*, 1962). Unfortunately, structures in which the cdm anion bridges transition metal centers are yet unknown. Single-crystal X-ray diffraction studies have revealed that Ni (Shi *et al.*, 2001), Co (Shi, Yin *et al.*, 2002) and Mn (Schlueter *et al.*, 2003) form isomorphous mononuclear complexes, [*M*(cdm)$_2$(H$_2$O)$_4$]·2H$_2$O, in which the metal atom is octahedrally coordinated by the nitrile N atoms of two cdm anions and the O atoms of four water molecules. In this study, the crystal structure of Kcdm was examined in an attempt to understand why tcm has a tendency to form polymeric networks while cdm preferentially forms molecular species.



Kcdm

The geometry of the cdm anion in the Kcdm salt is essentially identical to that found in [*M*(cdm)$_2$(H$_2$O)$_4$]·2H$_2$O. The anion is very nearly planar (the r.m.s. deviation is 0.009 Å), the greatest deviation from planarity being 0.017 (1) Å for methanide atom C3 (Fig. 1). As expected, the C—C—C angles about the methanide C atom [117.6 (1), 120.2 (1) and 122.2 (1)°] sum to 360.0°, indicating nearly complete $sp^2$ hybridization. A distorted trigonal prismatic inner coordination sphere exists about the potassium cation, consisting of two carbonyl O atoms and four nitrile N atoms of six different cdm anions. The outer coordination sphere of potassium contains one amide and one nitrile N atom whose K—N distances are about 0.4 Å longer than the inner-sphere K—N bond lengths.

The plane of the cdm ligand lies at an angle of 26.79 (2)° with respect to the *ac* plane. The angle between cdm molecular planes related by the screw axis is twice as large. The potassium coordination links the cdm anions into bi-bridged sheets parallel to the *ab* plane (Fig. 2). Intersheet hydrogen bonding is observed between amine atom H3*A* and the carbonyl O atoms. The second amine H atom, H3*B*, has a significantly

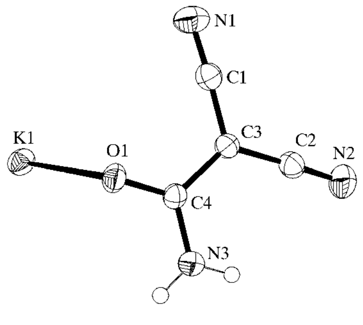


**Figure 1**
A view of the molecular structure of Kcdm, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level, and H atoms are shown as small spheres of arbitrary radii.

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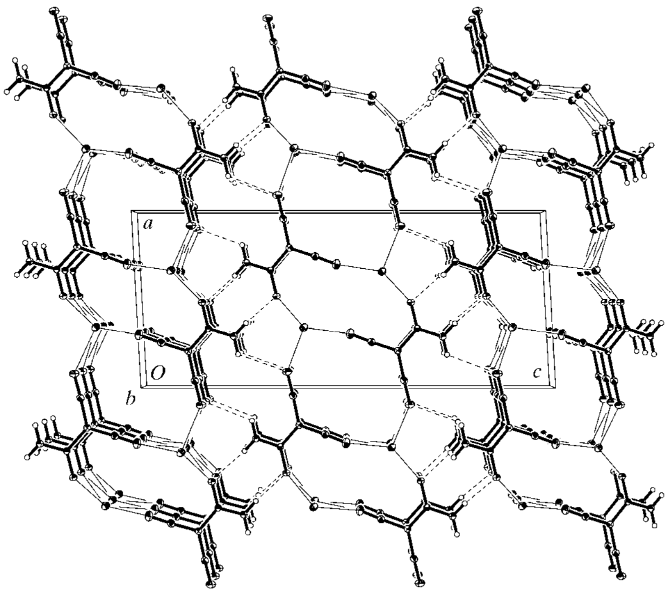

**Figure 2**
A packing diagram for Kcdm, projected approximately along the *b* axis. Displacement ellipsoids are drawn at the 20% probability level. Intersheet hydrogen bonds are depicted as dashed lines.

weaker hydrogen-bonding interaction because of the lack of good acceptor sites, the nearest acceptor being nitrile atom N2.

The geometry of the dicyanomethanide moiety of the cdm anion is essentially identical to that observed in Ktcm (Witt & Britton, 1971). The reason that the cdm anion has not formed polymeric structures with transition metals through bidentate bridging of the nitrile groups may simply be a result of the subtle steric effects related to the carbamoyl moiety. It is noted that cdm forms a two-dimensional polymeric structure with europium (Shi, Xu *et al.*, 2002), but in this case, the bridge is completed through the bonding of the carbonyl O atom to the oxophilic rare earth atom. Crystallization in non-aqueous solvents may be necessary in order to form polymeric transition metal complexes with cdm, because the formation of $[M(\mathrm{cdm})_2(\mathrm{H_2O})_4]\cdot 2\mathrm{H_2O}$ compounds appears to be thermodynamically favorable as a result of cdm having a better hydrogen-bonding capability than tcm.

## Experimental

Potassium carbamoyldicyanomethanide was prepared by a modification of the procedure described by Trofimenko *et al.* (1962). Malononitrile (6.6 g, 0.1 mol; Aldrich) was added to a slurry containing powdered potassium cyanate (8.1 g, 0.1 mol; Aldrich) in *N*,*N*-dimethylformamide (150 ml). After heating at reflux for 1 h, the resulting red–orange solution was filtered while hot and the filtrate was cooled to 273 K overnight. Diethyl ether (100 ml) was added, precipitating a yellow powder that was recovered by filtration. The crude product was recrystallized by dissolution in warm methanol (1.5 l) followed by precipitation with hexane (1 l). Crystals of Kcdm were formed while attempting to crystallize an adduct of $[\mathrm{Mn(cdm)_2(H_2O)_4}]\cdot 2\mathrm{H_2O}$, in which the coordinated water molecules would be replaced with pyrimidine. Pyrimidine (340 mg, 4 mmol; Aldrich) was added to a solution of Kcdm (588 mg, 4 mmol) in water (20 ml). This solution was layered on top of a solution of manganese(II) nitrate (2 mmol, 358 mg; Aldrich) in water (10 ml). After one month, colorless rod-like crystals of Kcdm were collected, and after these were removed, crystals of $[\mathrm{Mn(cdm)_2(H_2O)_4}]\cdot 2\mathrm{H_2O}$ formed from the filtrate (Schlueter *et al.*, 2003).

*Crystal data*

$\mathrm{K^+\cdot C_4H_2N_3O^-}$
$M_r = 147.19$
Monoclinic, $P2_1/c$
$a = 8.2495$ (3) Å
$b = 3.8591$ (1) Å
$c = 19.2181$ (6) Å
$\beta = 93.168$ (1)°
$V = 610.89$ (3) Å$^3$
$Z = 4$
$D_x = 1.600$ Mg m$^{-3$}
Mo $K\alpha$ radiation
Cell parameters from 1719 reflections
$\theta = 3.3$–28.1°
$\mu = 0.78$ mm$^{-1}$
$T = 298$ (2) K
Rod, colorless
0.50 × 0.08 × 0.06 mm

*Data collection*

Siemens SMART CCD area-detector diffractometer
$\omega$ scans
Absorption correction: integration (*SHELXTL.*; Sheldrick, 2001)
$T_{\min} = 0.801$, $T_{\max} = 0.958$
5795 measured reflections
1448 independent reflections
1286 reflections with $I > 2\sigma(I)$
$R_{\mathrm{int}} = 0.027$
$\theta_{\max} = 28.3°$
$h = -10 \rightarrow 10$
$k = -5 \rightarrow 5$
$l = -25 \rightarrow 25$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.072$
$S = 1.10$
1448 reflections
83 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0328P)^2 + 0.1783P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.020$
$\Delta\rho_{\max} = 0.27$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.20$ e Å$^{-3}$
Extinction correction: *SHELXL*97
Extinction coefficient: 0.038 (4)

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| K1—O1$^{\mathrm{i}}$ | 2.7084 (11) | C1—N1 | 1.1525 (19) |
| K1—O1 | 2.7645 (11) | C1—C3 | 1.4043 (19) |
| K1—N1$^{\mathrm{ii}}$ | 2.8499 (13) | C2—N2 | 1.153 (2) |
| K1—N2$^{\mathrm{iii}}$ | 2.9294 (15) | C2—C3 | 1.4017 (19) |
| K1—N1$^{\mathrm{iv}}$ | 2.9426 (14) | C3—C4 | 1.4396 (18) |
| K1—N2$^{\mathrm{v}}$ | 2.9696 (15) | C4—N3 | 1.3443 (18) |
| O1—C4 | 1.2521 (16) | | |
| | | | |
| N1—C1—C3 | 177.61 (16) | C1—C3—C4 | 117.60 (12) |
| N2—C2—C3 | 178.14 (16) | O1—C4—N3 | 120.38 (12) |
| C2—C3—C1 | 120.20 (12) | O1—C4—C3 | 120.91 (12) |
| C2—C3—C4 | 122.17 (12) | N3—C4—C3 | 118.71 (12) |
| | | | |
| C2—C3—C4—O1 | 179.66 (13) | C2—C3—C4—N3 | −1.1 (2) |
| C1—C3—C4—O1 | 1.7 (2) | C1—C3—C4—N3 | −179.05 (13) |

Symmetry codes: (i) $x, 1+y, z$; (ii) $1-x, 2-y, -z$; (iii) $1+x, 1+y, z$; (iv) $1-x, 1-y, -z$; (v) $1+x, y, z$.

**Table 2**
Hydrogen-bonding geometry (Å, °).

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| N3—H3$A\cdots$O1$^{\mathrm{vi}}$ | 0.86 | 2.08 | 2.9358 (15) | 171 |
| N3—H3$B\cdots$N2$^{\mathrm{vii}}$ | 0.86 | 2.63 | 3.185 (2) | 123 |

Symmetry codes: (vi) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$; (vii) $-x, y-\frac{1}{2}, \frac{1}{2}-z$.

The H atoms of the amine group were placed geometrically and treated with a riding model, with N—H distances of 0.86 Å and with $U_{iso}$(H) values constrained to be 1.2 times the $U_{eq}$ value of the carrier N atom.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1682). Services for accessing these data are described at the back of the journal.

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