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$Cs_2K[Mn(CN)_6]$ at 293, 85 and 10 K

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The crystal structure of dicaesium potassium hexacyanomanganese(III) has been determined by X-ray diffraction at 293, 85 and 10 K. The Mn and K atoms lie on inversion centres and the Cs atom is in a general position. The accurate and extensive data sets collected should be suitable for charge–density analysis studies.

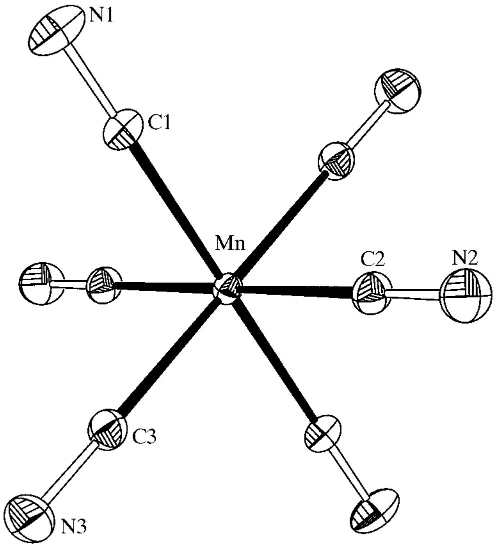

Figure 1
Conventional atomic numbering of the $[Mn(CN)_6]^{3-}$ octahedron with 50% probability displacement ellipsoids for the structure determined at 85 K.

Comment

The trivalent first transition series metals from Cr to Co and some second and third series elements form complexes of formulation $Cs_2M^I[M^{III}(CN)_6]$ (M^I = Li–Cs) with the elpasolite structure. They crystallize well and are of interest in inorganic chemistry as classical coordination complexes involving the most covalently bonding of ligands, the cyanide ion, and for which the physical properties are well defined. There are previous structural studies of these elpasolites by X-ray and neutron diffraction both at room temperature and at lower temperatures, for example, $Cs_2K[Cr(CN)_6]$ (Figgis *et al.*, 1983; Brown *et al.*, 1987), $Cs_2K[Mn(CN)_6]$ (Ziegler *et al.*, 1989; Blake *et al.*, 1994) and $Cs_2K[Fe(CN)_6]$ (Fletcher & Gibb, 1977; Herren *et al.*, 1979; Figgis *et al.*, 1990).

In particular, for M^I = K, magnetic susceptibility and polarized neutron diffraction experiments have been performed on their single crystals (Figgis *et al.*, 1985; Brown *et al.*, 1987; Figgis & Reynolds, 1987; Reynolds *et al.*, 1992; Blake *et al.*, 1994). Also, for M^I = Li, the complexities of thermal motion have received attention; see, for example, Chadwick *et al.* (1988) and Ryan & Swanson (1974).

We have determined by X-ray diffraction the crystal structure of $Cs_2K[Mn(CN)_6]$ at 293, 85 and 10 K. Salts of this type are made up of Cs^+ and K^+ cations and $[M(CN)_6]^{3-}$ anions, and this anion is illustrated in Fig. 1. The structural features have been described before and the present case presents no unusual results. Selected bond lengths and angles for the $[Mn(CN)_6]^{3-}$ ion at the three temperatures are given in Table 1. The results for the 293 K study are very similar to those of Ziegler *et al.* (1989) at ambient temperature, but with s.u.'s lower by a factor approaching 2.

The $[Mn(CN)_6]^{3-}$ ion is very close to regular octahedral stereochemistry at each of the temperatures, with the bond from Mn to C3 just significantly shorter than those to C1 and C2. All the C—Mn—C angles for adjacent ligands differ from 90° by *ca* 0.15°, and the C—Mn—N angles are all *ca* 1.5° off the linear configuration. The Mn—C bond lengths are essentially independent of temperature although the C—N bonds apparently lengthen significantly, presumably due to reduced libration, as the temperature is lowered from 293 to 10 K. The mean Mn—C bond length at 85 K [1.989 (4) Å] lies between those in the $[Cr(CN)_6]^{3-}$ ion [2.066 (4) Å; Figgis & Reynolds, 1987] and those in the $[Fe(CN)_6]^{3-}$ ion (1.932 Å; Figgis *et al.*, 1990), while the average C—N separation of 1.159 (1) Å matches that for the Cr salt [1.160 (1) Å] and is slightly lower than for the Fe salt [1.166 (2) Å]. The Mn (d^4) and Fe (d^5) cases are low spin and have orbitally degenerate ground states and so are formally Jahn–Teller unstable. On the other hand, the Cr (d^3) case has an orbital singlet ground state and is Jahn–Teller stable. However, the bond lengths within the respective $[M(CN)_6]^{3-}$ ions do not show the differences which might be expected on that account. The Cs atomic displacement parameters (adp's) are quite isotropic at all temperatures. This contrasts with the results for the Cs adp's of $Cs_2K[Cr(CN)_6]$ at 120 K and, to a lesser extent, of $Cs_2K[Fe(CN)_6]$ at 85 K, where apparent anomalies in the thermal motion placed limitations on the interpretation of the X-ray data in terms of valence orbital parameters in a charge–density analysis. Such anomalies appear to an even greater degree in the analagous Co salt (Figgis & Sobolev, 2000) and preclude its use in a charge–density study.

Experimental

$Cs_2K[Mn(CN)_6]$ was prepared by a standard procedure (Brauer, 1963). Single crystals of the complex were obtained by recrystallization from aqueous solution. The room temperature and very low-temperature data sets were collected on a locally assembled Huber 512 goniometer equipped with a Displex 202D cryogenic refrigerator (Henricksen *et al.*, 1986; Larsen, 1995). The 85 K data were collected on a Syntex *P*21 diffractometer equipped with a locally developed nitrogen gas stream cooling device.

$Cs_2K[Mn(CN)_6]$ at 293 K

Crystal data

$Cs_2K[Mn(CN)_6]$
$M_r = 515.98$
Monoclinic, $P2_1/n$
$a = 11.207$ (2) Å
$b = 8.210$ (1) Å
$c = 7.696$ (1) Å
$\beta = 90.25$ (1)°
$V = 708.1$ (2) Å^3
$Z = 2$
$D_x = 2.420$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 12 reflections
$\theta = 15.2–16.4°$
$\mu = 6.275$ mm^{-1}
$T = 293$ (2) K
Prism, dark red–brown
0.36 × 0.23 × 0.23 mm

Data collection

Huber 512 goniometer diffractometer
$\omega–2\theta$ scans
Absorption correction: Gaussian (*Xtal*3.4; Hall *et al.*, 1995)
$T_{min} = 0.197$, $T_{max} = 0.268$
4814 measured reflections
1254 independent reflections
1217 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 25.04°$
$h = -13 \rightarrow 13$
$k = -9 \rightarrow 9$
$l = -9 \rightarrow 9$
3 standard reflections every 100 reflections intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.060$
$S = 1.117$
1254 reflections
77 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0311P)^2 + 0.9408P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.48$ e Å^{-3}
$\Delta\rho_{min} = -1.02$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0512 (16)

$Cs_2K[Mn(CN)_6]$ at 85 K

Crystal data

$Cs_2K[Mn(CN)_6]$
$M_r = 515.98$
Monoclinic, $P2_1/n$
$a = 11.084$ (2) Å
$b = 8.213$ (1) Å
$c = 7.617$ (1) Å
$\beta = 90.77$ (1)°
$V = 693.3$ (2) Å^3
$Z = 2$
$D_x = 2.472$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 14 reflections
$\theta = 16.25–20.25°$
$\mu = 6.409$ mm^{-1}
$T = 85$ (2) K
Prism, dark red–brown
0.41 × 0.27 × 0.23 mm

Data collection

Syntex *P*21 diffractometer
$\omega–2\theta$ scans
Absorption correction: Gaussian (*Xtal*3.4; Hall *et al.*, 1995)
$T_{min} = 0.192$, $T_{max} = 0.323$
39 456 measured reflections
7328 independent reflections
6386 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 50.21°$
$h = -21 \rightarrow 23$
$k = -17 \rightarrow 17$
$l = -16 \rightarrow 16$
6 standard reflections every 100 reflections intensity decay: 2%

Table 1
Selected bond lengths (Å) and angles (°) for the $[Mn(CN)_6]^{3-}$ ion at 293, 85 and 10 K.

	293 K	85 K	10 K
Mn–C1	1.999 (3)	1.989 (1)	1.991 (1)
Mn–C2	1.999 (3)	1.996 (1)	1.998 (1)
Mn—C3	1.991 (3)	1.982 (1)	1.988 (2)
C1—N1	1.142 (5)	1.160 (2)	1.164 (2)
C2—N2	1.146 (5)	1.158 (2)	1.162 (2)
C3—N3	1.149 (5)	1.159 (2)	1.165 (2)
C1—Mn—C2	90.1 (1)	90.29 (5)	90.15 (5)
C2—Mn—C3	89.9 (1)	90.00 (5)	89.91 (6)
C3—Mn—C1	90.1 (1)	89.86 (5)	89.94 (6)
N1—C1—Mn	178.8 (3)	178.7 (1)	178.6 (1)
N2—C2—Mn	178.9 (3)	178.9 (1)	178.8 (1)
N3—C3—Mn	178.0 (3)	178.2 (1)	178.2 (1)

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.079$
$S = 1.087$
7328 reflections
77 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0369P)^2 + 0.4475P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 2.95$ e Å^{-3}
$\Delta\rho_{min} = -1.63$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0044 (4)

$Cs_2K[Mn(CN)_6]$ at 10 K

Crystal data

$Cs_2K[Mn(CN)_6]$
$M_r = 515.98$
Monoclinic, $P2_1/n$
$a = 11.074$ (7) Å
$b = 8.227$ (2) Å
$c = 7.6135$ (5) Å
$\beta = 90.95$ (4)°
$V = 693.5$ (5) Å^3
$Z = 2$
$D_x = 2.471$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 16 reflections
$\theta = 37.4–42.7°$
$\mu = 6.407$ mm^{-1}
$T = 10$ (2) K
Prism, dark red–brown
0.36 × 0.23 × 0.23 mm

Data collection

Huber 512 goniometer diffractometer
$\omega–2\theta$ scans
Absorption correction: Gaussian (*PROFIT*; Streltsov & Zavodnik, 1989)
$T_{min} = 0.192$, $T_{max} = 0.291$
28 154 measured reflections
7317 independent reflections
7143 reflections with $I > 2\sigma(I)$
$R_{int} = 0.039$
$\theta_{max} = 50.15°$
$h = -23 \rightarrow 23$
$k = -17 \rightarrow 17$
$l = -16 \rightarrow 16$
3 standard reflections every 100 reflections intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.077$
$S = 1.222$
7317 reflections
77 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0341P)^2 + 0.7780P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 2.18$ e Å^{-3}
$\Delta\rho_{min} = -3.75$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0535 (12)

For the 10 and 293 K determinations, data collection: local software; cell refinement: local software. For the 85 K determination, data collection: *P*3/*P*4-*PC Software* (Siemens, 1991); cell refinement: *P*3/*P*4-*PC Software*. For all three temperature determinations: data reduction: *PROFIT* (Streltsov & Zavodnik, 1989); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1983); 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: BR1288). Services for accessing these data are described at the back of the journal.

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