Crystal Structures and Thermal Behavior of Alkaline Earth Tricyanomethanides

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The alkaline earth tricyanomethanides $Mg(tcm)_2 \cdot 2H_2O$, $Ca(tcm)_2$, $Sr(tcm)_2 \cdot H_2O$ and $Ba(tcm)_2 \cdot 2H_2O$ were prepared from aqueous solutions of the respective chlorides and silver tricyanomethanide. Their IR spectra and thermal behavior are described. The crystal structures of $Ca(tcm)_2$ and $Ba(tcm)_2 \cdot 2H_2O$ were determined by single crystal X-ray diffraction. The structure of $Ca(tcm)_2$ is of the type found for several transition metal tricyanomethanides [1], containing two independent interpenetrating networks. $Ba(tcm)_2 \cdot 2H_2O$ has a unique crystal structure corresponding to a three-dimensional coordination polymer with nine fold coordinated Ba atoms connected by water molecules and tricyanomethanide anions.

Key words: Pseudohalides, Alkaline Earth Tricyanomethanides, X-Ray Crystal Structures, Thermoanalysis

Introduction

With its three terminal nitrogen donors, the anion $C(CN)_3^-$ offers a variety of coordination modes as a terminal, 1,5-bridging or 1,5,7-bridging ligand. Its rigid trigonal planar geometry leads to the formation of interesting networks of coordination polymers [1, 2]. A large number of binary and more complex transition metal tricyanomethanides have been described and structurally characterized [3, 4], however, binary tricyanomethanides of the main group elements have received little attention. Earlier work has revealed basic structural information for the Na and K salts [5, 6]. More recently the crystal structure of lead(II) tricyanomethanide was determined [7].

Experimental Section

Materials and methods

Reagents were used as purchased from commercial suppliers. Silver tricyanomethanide was prepared according to Trofimenko [8]. The infrared spectra were recorded from Nujol mulls on a Bomem 100 FT-IR spectrometer in the range 400 – 4000 cm^{-1}. The thermogravimetric analyses were performed on a Shimadzu thermogravimetric analyzer TGA-50 in alumina crucibles at a heating rate of 10 °C min^{-1} in air. Crystallographic data were collected on a Bruker SMART CCD diffractometer. The structures were solved by Direct Methods [9] and refined by full-matrix least-squares on F^2 [10] with anisotropic displacement parameters for the non-hydrogen atoms. Hydrogen atoms were placed in idealized positions and treated with the 'riding model' option of SHELXL-97. Crystal data and details of the data collection and structure refinement are given in Table 1.

Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CSD numbers CCDC 650413 and CCDC 650414. These data can be obtained, free of charge *via* www.ccdc.cam.ac.uk/data_request/cif.

Preparation of the tricyanomethanides $M(tcm)_2$ (M = Mg, Ca, Sr and Ba)

Aqueous solutions of the chlorides MCl_2 are stirred at r. t. for 6 h with a 50 % excess of silver tricyanomethanide. The insoluble silver salts are filtered off, and the filtrates are slowly evaporated to dryness at 25 °C to leave the crystalline tricyanomethanides in quantitative yield.

Results and Discussion

Infrared spectra

The IR spectra of the title compounds show the expected features of the tricyanomethanide ion [11].

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Table 1. Crystal data and structure refinement for $Ca(tcm)_2$ and $Ba(tcm)_2 \cdot 2H_2O$.

	$Ca(tcm)_2$	$Ba(tcm)_2 \cdot 2H_2O$
Empirical formula	C_8N_6Ca	$C_8H_4N_6O_2Ba$
M_r	220.22	353.51
Crystal size, mm^3	0.29×0.24×0.06	0.31×0.11×0.10
T, K	293(2)	293(2)
Radiation, λ, Å	MoK_α, 0.71073	MoK_α, 0.71073
Crystal system	orthorhombic	monoclinic
Space group	*Pnma*	$P2_1/n$
a, Å	8.0881(3)	6.9553(2)
b, Å	5.5645(3)	10.7462(3)
c, Å	10.9514(5)	17.5447(5)
β, deg	90	97.407(2)
V, Å^3	492.88(4)	1300.40(6)
Z/D_{calcd}, g cm^{-3}	2 / 1.49	4 / 1.81
μ(MoK_α), cm^{-1}	0.6	3.1
F(000), e	220	664
θ range, deg	3.66 – 28.27	3.01 – 27.48
hkl range	$-6 \le h \le 7$ $-10 \le k \le 10$ $-12 \le l \le 14$	$-9 \le h \le 8$ $-13 \le k \le 13$ $-22 \le l \le 21$
Refl. coll. / unique	2594 / 590	8893 / 2995
Transm. (max. / min.)	0.96 / 0.82	0.79 / 0.56
Data / param.	590 / 41	2995 / 154
Goodness-of-fit (F^2)	1.112	1.157
$R_1(F)/wR_2(F^2)$ $[I \ge 2\sigma(I)]$[a]	0.0458 / 0.1117	0.0332 / 0.0730
$R_1(F)/wR_2(F^2)$ (all data)	0.0557 / 0.1245	0.0385 /0.0754
$\Delta\rho_{\text{fin}}$ (max/min), e Å^{-3}	0.41 / −0.38	0.92 / −1.02

[a] $R_1 = \|F_o| - |F_c\|/|F_o|$; $wR_2 = [w(F_o{}^2 - F_c{}^2)^2/(wF_o{}^2)]^{-1/2}$.

Table 2. Infrared data (wavenumbers in cm^{-1}) obtained on Nujol mulls of the alkaline earth tricyanomethanides.

	$Mg(tcm)_2 \cdot 2H_2O$	$Ca(tcm)_2$	$Sr(tcm)_2 \cdot H_2O$	$Ba(tcm)_2 \cdot 2H_2O$
ν (H_2O)	3418 vs, br	—	3391 vs, br	3450 vs, br 3360 vs, br
ν (C≡N)	2205 vs 2179 s	2190 vs	2223 sh 2198 vs	2230 sh 2194 vs 2167 s
δ (H_2O)	1642 m	—	1665 m 1625 w	1667 w 1631 m
ν (C–C)	1253 w	1262 w	1277 vw 1248 w	1277 vw 1250 w
δ (C–C≡N i.p.)	614 w	617 w	618 vw	614 vw
δ (C–C≡N o.p.)	564 m	566 m	571 m	570 m
δ ($C–C_3$ i.p.)	480 vw	480 vw	509 w 491 vw	516 w 456 w

Selected IR frequencies are summarized in Table 2. The C≡N stretching modes are observed as strong absorption bands in the range from 2167 to 2223 cm^{-1}. The C≡N absorptions of the hydrated tricyanomethanides of Mg, Sr and Ba show splitting, whereas a unique C≡N band is found for $Ca(tcm)_2$ due to its highly symmetric structure. The H_2O stretching modes appear as very intense and broadened bands at 3360 to 3450 cm^{-1}, indicating strong hydrogen bonding.

Table 3. Thermogravimetric data for the alkaline earth tricyanomethanides.

	$Mg(tcm)_2 \cdot 2H_2O$	$Ca(tcm)_2$	$Sr(tcm)_2 \cdot H_2O$	$Ba(tcm)_2 \cdot 2H_2O$
Temp. for H_2O loss, °C	135	—	66	79
Loss of H_2O, %	13.35	—	5.34	9.99
Calcd., %	14.98	—	6.30	10.19
Max. dec. rate, °C	478	533	496	450
Total weight loss up to 800 °C, %	80.28	53.87	47.82	44.19
Calcd. for MCO_3 as residue, %	83.24 (for MgO)	54.55	48.34	44.17

Thermal behavior

Thermogravimetric analyses reveal the expected values of weight loss up to 140 °C due to evaporation of crystal water. Thermal degradation of the tricyanomethanide starts at 380 – 400 °C with maximum decomposition rates from 450 to 534 °C. Thermal stability increases in the sequence $Ba < Mg < Sr < Ca$. The total weight losses up to 800 °C correspond to the values expected for $CaCO_3$, $SrCO_3$, $BaCO_3$ and MgO as final residues. More detailed TGA data are given in Table 3.

Crystal structures

In both structures (Figs. 1 and 2) the tcm ion shows only very slight distortion from the ideal trigonal planar geometry. The crystal structure of $Ca(tcm)_2$ is isomorphous with those of the tricyanomethanides of divalent transition metals, containing two inter-

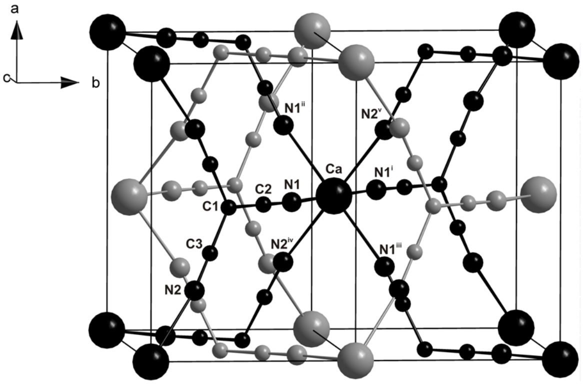

Fig. 1. A view of the expanded unit cell of $Ca(tcm)_2$ showing the two interpenetrating networks [12]. For symmetry transformations see the footnote to Table 4.

Table 4. Selected bond lengths (Å) and angles (deg) for $Ca(tcm)_2$[a].

Bond lengths		Bond angles	
Ca–N(1)	2.431(1)	Ca–N(1)–C(2)	170.55(1)
$Ca–N(2)^{iv}$	2.455(2)	Ca^{vi}–N(2)–C(3)	165.94(2)
C(1)–C(2)	1.400(2)	C(1)–C(2)–N(1)	179.45(2)
C(1)–C(3)	1.405(3)	C(1)–C(3)–N(2)	179.7(2)
C(2)–N(1)	1.150(2)	$C(2)–C(1)–C(2)^{vii}$	118.9(2)
C(3)–N(2)	1.146(3)	C(2)–C(1)–C(3)	120.5(1)

[a] Symmetry transformations: ^{iv} $-x-0.5, -y+1, z-0.5$; ^{vi} $-x-0.5, -y+1, z+0.5$; ^{vii} $-x-1, y, z$.

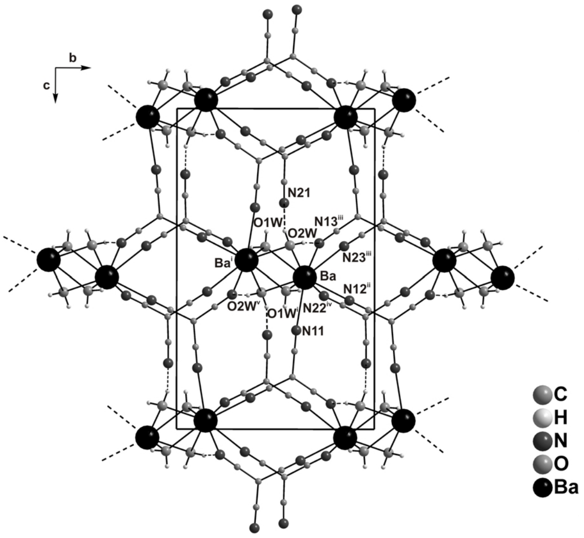

Fig. 2. Projection of the crystal structure of $Ba(tcm)_2$ parallel to the crystallographic *bc* plane [12]. For symmetry transformations see the footnote to Table 5.

penetrating networks, generated by octahedral six-connecting metal ions and trigonal three-connecting tcm^- anions [1] (see this reference for a detailed discussion of this structure type). Two slightly different Ca–N distances are observed with 2.431(1) and 2.455(2) Å. Steric interaction between the two interpenetrating frameworks causes two types of major distortion. One of them is the angular deformation of the coordination octahedron, with N–Ca–N angles varying from 80.61(7) to 99.39(7)°. The second one is a significant bending of the C–N–Ca angles (165.9(2) and 170.5(1)°) out of the $C(CN)_3$ plane. Relevant bond lengths and angles are given in Table 4.

The unique crystal structure of $Ba(tcm)_2 \cdot 2H_2O$ corresponds to a coordination polymer with water molecules and tcm^- ions as connecting ligands. The barium ions coordinate to five nitrogen atoms of the tcm^- ligands and four oxygen atoms of the water molecules. The coordination polyhedron can be described as a distorted singly capped tetragonal antiprism. Pairs of Ba atoms are linked by four water molecules. The Ba–O distances lie between 2.812 and 2.912 Å. Two non-equivalent $C(CN)_3$ units are observed. One of them coordinates through all of its three nitrogen atoms, the other one leaves one nitrogen atom not coordinated. All five Ba–N distances are slightly different, varying from 2.846 to 2.989 Å. All C–N–Ba angles are strongly bent out of the $C(CN)_3$ plane by 122.0(3) to 170.55(1)°. O–H ··· N hydrogen bonds are observed between the water molecules and three of the nitrogen atoms. The planar $C(CN)_3$ anions are organized parallel to the *bc* plane. Selected bond lengths and angles are presented in Tables 5 and 6.

Table 5. Selected bond lengths (Å) and angles (deg) for $Ba(tcm)_2 \cdot 2H_2O$[a].

Bond lengths		Bond angles	
Ba–N(11)	2.898(4)	Ba–N(11)–C(11)	173.8(4)
$Ba–N(12)^{ii}$	2.846(4)	Ba^{vi}–N(12)–C(12)	164.6(4)
$Ba–N(13)^{iii}$	2.989(4)	Ba^{vii}–N(13)–C(13)	129.1(3)
$Ba–N(22)^{iv}$	2.881(4)	Ba^{viii}–N(22)–C(22)	122.0(3)
$Ba–N(23)^{iii}$	2.867(4)	Ba^{vii}–N(23)–C(23)	163.3(4)
Ba–O(1W)	2.812(3)	$Ba–O(1W)–Ba^{i}$	112.00(9)
$Ba–O(1W)^{i}$	2.8354(3)	$Ba–O(2W)–Ba^{v}$	116.06(9)
Ba–(O2W)	2.873(3)		
$Ba–O(2W)^{v}$	2.912(3)		

[a] Symmetry transformations: ^{i} $-x+2, -y, -z+2$; ^{ii} $-x+1.5, y-0.5, -z+1.5$; ^{iii} $x+0.5, -y-0.5, z+0.5$; ^{iv} $-x+0.5, y-0.5, -z+1.5$; ^{v} $-x+1, -y, -z+2$; ^{vi} $-x+1.5, y+0.5, -z+1.5$; ^{vii} $x-0.5, -y-0.5, z-0.5$; ^{viii} $-x+0.5, y+0.5, -z+1.5$.

Table 6. Hydrogen bonding distances (Å) and angles (deg) in $Ba(tcm)_2 \cdot 2H_2O$[a].

	D−H	H ··· A	D−A	D−H ··· A
O2w−H21w ··· N21	0.883(3)	2.094(5)	2.898(6)	151.0(2)
O1w−H11w ··· $N21^{i}$	0.830(3)	2.217(5)	2.887(6)	137.9(2)
O1w−H12w ··· $N22^{ii}$	0.934(3)	1.918(4)	2.833(5)	165.9(2)
O2w−H22w ··· $N13^{iii}$	0.986(3)	2.093(0)	3.012(5)	154.3(2)

[a] Symmetry operations: ^{i} $x+1, y, z$; ^{ii} $-x+1.5, y-0.5, -z+1.5$; ^{iii} $-x+1.5, y+0.5, -z+1.5$.

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