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Structural characterization and Raman spectrum of Cs[OCN]

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Abstract: The compound Cs[OCN] has been synthesized and its crystal structure and Raman spectrum were determined on selected single crystals. As postulated in earlier work, the title compound crystallizes isopointal to KN_3 exhibiting the space group $I4/mcm$ (no. 140, $Z = 4$) with the lattice parameters $a = 653.79(2)$ and $c = 799.42(5)$ pm. The Raman spectrum verified the nature of the triatomic moiety and shows the frequencies typical for an $[OCN]^-$ anion with Fermi resonance between the 2δ and the ν_{sym} vibrations. The undisturbed frequencies and the resulting force constants have been calculated and compared to those of other alkali metal compounds containing comparable linear triatomic anions.

Keywords: caesium; cyanate; disordered anion; force constants; structure elucidation; Raman spectroscopy.

Dedicated to: Professor Arndt Simon on the occasion of his 80th birthday.

1 Introduction

Some 60 years ago, structural information and IR spectra of pseudo-binary alkali metal cyanates with the stoichiometry $A[OCN]$ (A = Na, K, NH_4, Rb, Tl, Ag and Cs) [1] have been reported and their crystal structures postulated on the basis of their respective X-ray powder diffraction patterns assuming the alkali metal cyanates to be isopointal to the corresponding azides. Complete crystal structure determinations were carried out only recently for Li[OCN] [2], Na[OCN] [3] and K[OCN] [4], but no research was performed on Rb[OCN] and Cs[OCN]. Considering the fact that it has been doubted that Cs[OCN] crystallizes isopointal to KN_3 [5] because its vibrational spectra resembled more that recorded for Na[OCN] [6, 7], we decided to have a closer look into this matter. Following the synthesis described briefly in [1], we were able to gather some hygroscopic material of the title compound, which was used to determine its crystal structure and Raman spectrum. The acquired data and those from Raman spectra of other alkali metal cyanates have been used to calculate the undisturbed fundamental frequencies and to determine the force constants of the bonds in the cyanate anion. These values are compared to force constants of other alkali metal compounds containing similar linear triatomic unities.

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2 Experimental section

2.1 Synthesis

Following the ideal reaction

$$2\ Cs_2[CO_3] + 2\ CO(NH_2)_2 \rightarrow 2\ Cs[OCN] + 2\ CO_2 + 2\ NH_3 + H_2O$$

0.33 g (1.01 mmol) of $Cs_2[CO_3]$ (Alfa-Aesar, powder, 99%, Ward Hill, MA, USA) and a slight excess (0.14 g, 2.40 mmol) of urea, $CO(NH_2)_2$ (Sigma-Aldrich, crystals, purissimum, Steinheim, Germany) were filled into a 20 cm long silica ampoule (diameter: 1.0 cm) which was sealed before on one side. The ampoule was fixed upright with the open end on top and heated gently with a handheld propane-oxygen torch until effervescence had ceased and a clear liquid remained. The temperature conditions were not controlled with a thermometer, but the melting of the reaction mixture and the remaining clear liquid indicated the reaction to be complete and making the reaction reproducible just by the looks. After cooling, the colorless, opaque ingot was crushed and the powder was placed into a screw-top vial with 10 mL ethanol (Pharmco, Brookfield, CT, USA). After six hours, the liquid part was filtered off and the solvent was evaporated in a drying oven at $T = 353$ K (80°C) leaving feather-like crystal aggregates behind. Applying pressure on crystals with a preparation needle resulted mostly in cleavage perpendicular to the apparent growth axes and in thin plates.

Due to atmospheric moisture, leaving a sample exposed to normal atmosphere resulted in small puddles containing the dissolved product. This process is reversible just by placing the sample back into the drying oven held at $T = 353$ K (80°C) without any signs of decomposition.

2.2 Crystallographic studies

Samples of the compound were immerged into polybutene oil (Aldrich, $M_n \sim 320$, isobutylene >90%). A suitable single crystal of Cs[OCN] was selected under a polarization microscope, mounted in a drop of polybutene sustained in a MiTeGen loop, and placed onto the goniometer. This ensemble was cooled with a stream of nitrogen in a matter of seconds to $T = 253(2)$ K. This temperature was kept steady during the whole intensity measurement. Data was collected on a Rigaku XtaLAB diffractometer coupled to a Rigaku HyPix detector with Mo$K\alpha$ radiation ($\lambda = 71.073$ pm), from a PhotonJet microfocus X-ray source. The diffraction images were processed and scaled using the CrysAlis Pro (version 1.171.40.58a) software [8]. The positional parameters known for KN_3 [5] were used for a starting model. In the latter case, the end atoms share the same crystallographic position. To achieve this here, the oxygen and nitrogen atoms were constrained not only to be refined on the same crystallographic position, but also to have the same displacement parameters. The refinements of the structure were performed by full-matrix least-squares techniques using Shelxl-97 [9, 10]. After further refinement cycles, the refinement converged into a stable model. Additional crystallographic details are described in Table 1. Atomic coordinates and equivalent isotropic displacement coefficients are shown in Table 2, Table 3 displays selected bond lengths of alkali metal cyanates.

Crystallographic data (excluding structure factors) for the structure of Cs[OCN] have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Further details oft the crystal structure investigation may be obtained free of charge from the joint CCDC/ICSD Karlsruhe online

Table 1: Summary of X-ray single-crystal structure determination data on Cs[OCN].

Compound	Cs[OCN]
CCDC number	1951805
T, *K*	253(2)
M_r	174.93
Space group (no.), *Z*	*I*4/*mcm* (140), 4
Lattice parameters	
a, pm	651.85(1)
c, pm	799.42(3)
V, Å³	339.68(2)
F(000), *e*	304.0
D_{calcd}, g cm^{-3}	3.42
Crystal system	Tetragonal
Crystal color	Transparent colorless
Crystal shape	Rectangular, thin plate
Crystal size, mm³	0.06 × 0.04 × 0.01
Diffractometer	Rigaku XtaLAB Synergy with a Hybrid Pixel Array Detector
Radiation/λ, pm	Mo$K\alpha$/71.073
Ranges *hkl*/$2\theta_{max}$, deg	−8 → 9, −8 → 9, ±11/62.62
Data correction	Lp, multiscan (CrysAlis Pro, 1.171.40.58a) [8]
μ, mm^{-1}	10.7
Reflections: measured/unique	7409/162
R_{int}/R_σ	0.0573/0.0117
Unique reflections with $F_o > 4\,\sigma(F_o)$	132
Refined parameter	11
Weight factors *x*/*y*	0.0116/0.1357
*R*1[a]/*wR*2[b]/GooF[c] (all refl.)	0.0145/0.0255/1.245
Max. shift/esd, last refinement cycle	<0.0005
$\Delta\rho_{fin}$ (max/min), *e* Å^{-3}	0.36 (86 pm to N/O)/−0.46 (170 pm to C)

[a]$R1 = \Sigma\,||F_o| - |F_c||/\Sigma\,|F_o|$; [b]$wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$ with $P = [(F_o^2) + 2F_c^2]/3$; [c]GooF $(S) = [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$, with *n* being the number of reflections and *p* being the number of refined parameters.

Table 2: Atomic coordinates, anisotropic[a] and equivalent isotropic[b] displacement parameters (all given in pm²) of Cs[OCN].

Atom	Wyckoff site	*x*	*y*	*z*	$U_{11}=U_{22}$	U_{33}	U_{12}	U_{eq} [b]
Cs	4*a*	0	0	1/4	282(2)	231(2)	0	265(1)
C	4*d*	0	1/2	0	256(12)	243(20)	0	252(8)
O/N	8*h*	0.1304(3)	*x*+1/2	0	327(7)	548(15)	−25(12)	401(6)

[a]The anisotropic displacement factor takes the form: $U_{ij}=\exp[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2klb^*c^*U_{23}+2hla^*c^*U_{13}+2hka^*b^*U_{12})]$. [b]$U_{eq}$ is defined as a third of the orthogonalised U_{ij} tensors.

Table 3: Selected results of single crystal structure determinations of alkali metal cyanates *A*[OCN] (temperatures, atomic distances and sums of ionic radii [11]).

Compound	*T* (in K)	*d*(C–N/O)	*d*(*A*–N/O)	*d*(*A*–N)/*d*(*A*–O) Sum of ionic radii [11]	Ref.
Li[OCN]	293	120.5(1)	6× 220.3(1)	*222/214*	[2]
Na[OCN]	170	121.1(2)	6× 244.1(1)	*248/240*	[3]
K[OCN]	293	119.88(4)	8× 294.23(6)	*297/289*	[4]
Cs[OCN]	253	120.3(3)	8× 324.35(9)	*320/312*	This work

All distances are given in pm; all (N–C–O) angles are set by symmetry to 180°.

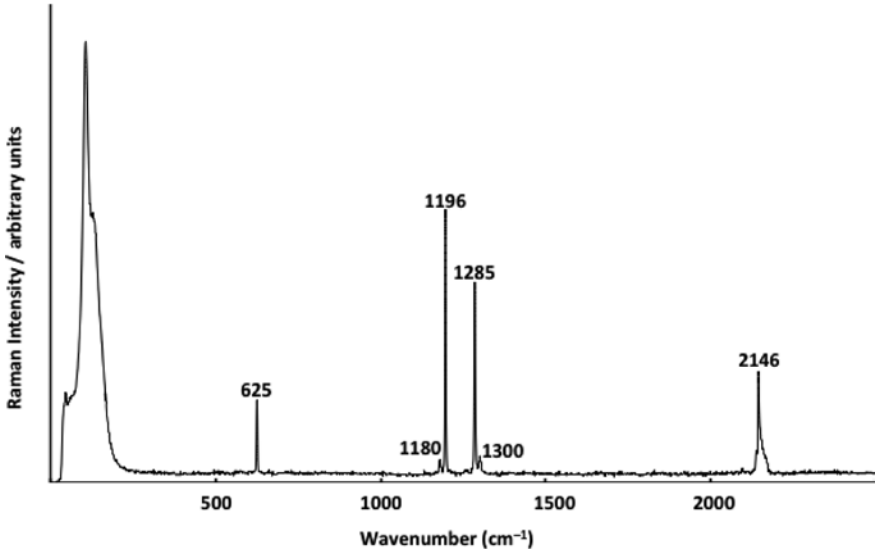

Fig. 1: Raman spectrum of Cs[OCN].

deposition service: https://www.ccdc.cam.ac.uk/structures by quoting the deposition number CCDC 1951805.

2.3 Raman spectrum and force constant calculations

Raman investigations (microscope laser Raman spectrometer: Jobin Yvon, 1 mW, excitation line at $\lambda = 632.817$ nm (HeNe laser), grating: 1800 lines/mm, 100× magnification, samples in glass capillaries, 10 × 90 s accumulation time) were performed on the same specimen used for the single crystal measurement. The result of the Raman measurement is displayed in Fig. 1.

The undisturbed frequencies are calculated with the following expression [12, 13]:

$$\nu_{corr.} = \frac{\nu_a + \nu_b}{2} \pm \frac{\nu_a - \nu_b}{2} \cdot \frac{I_a - I_b}{I_a + I_b}$$

The measured and corrected frequencies are displayed in Table 4. The corrected modes were assigned in

Table 4: Fundamental frequencies (cm^{-1}) for alkali metal cyanates obtained by Raman measurements and by IR data for Rb[OCN] [1, 7].

Compound	δ	2δ	ν_{sym}	ν_{as}	Ref.
Li[OCN]	645	1320	1221	2180	[2]
		1275	**1266**		
Na[OCN]	637	1305	1215	2178	[3]
		1277	**1258**		
K[OCN]	638	1300	1207	2167	[12]
		1272	**1236**		
Rb[OCN]	626/637	1293	1205	2210	[1]
Rb[OCN]	627/633	1290	1202	2163	[7]
Cs[OCN]	628	1286	1197	2146	[7]
		1245	**1238**		
Cs[OCN]	625	1285	1196	2146	This work
		1247	**1234**		

Corrected values are given in bold print.

Table 5: Force constants of alkali metal compounds containing triatomic anionic units given in N cm^{-1}.

	A[OCN]		$A_2[CN_2]$	$A[N_3]$	Ref.
	f_{C-O}	f_{C-N}	f_{C-N}	f_{N-N}	
Li^+	13.67	12.49	12.43	13.75	
Na^+	13.56	12.40	11.35	13.33	
K^+	13.21	12.11	10.87	13.12	
Rb^+	–	–	10.85	13.06	
Cs^+	13.23	12.10	–	12.90	
Cs[OCN]	13.10	11.98	–	–	This work
K[OCN] (IR in KBr)	15.88	11.00	–	–	[15]
K[OCN] (IR in KI)	15.51	11.03	–	–	[15]

Spectroscopic data from were taken from Table 4 for the cyanates; for carbodiimides and azides corresponding data from Ref. [14] were used for the calculations.

analogy to the spectrum of K[OCN] and the general rules mentioned in the literature [12, 13]. The force constants were calculated using the fundamental vibrations following the equations given in [13]. The corrected values were used to calculate the valency force constant with the acquired data, but also with previously reported data [14]. The results are displayed in Table 5. Incomplete sets of fundamental vibrations and/or lacking peak intensities for the spectra of Rb[OCN] and $Rb_2[CN_2]$ prevented performing the aforementioned calculations for these compounds.

3 Results and discussion

3.1 Vibrational spectra

The data acquired by the Raman measurement fit in nicely with most of the data reported before (Table 4), but the deviation from some of the frequencies reported by Waddington [1] is quite large, therefore spectroscopical data from this source was excluded here.

The calculated values for all compounds under consideration show the general trend that the force constants decrease with increasing cationic radius (Table 5). The force constants determined for K[OCN] in different matrices [15] show larger values for f_{C-O}, but smaller values for f_{C-N} if compared to values calculated here with a quite simple approach, but the average values compare quite well. The force constant f_{C-N} of the cyanate anions obtained here is in the same range as found for $A_2[CN_2]$ compounds. No comparable compounds containing linear triatomic anions with a C=O double bond were found, but the values are in the same order as $f_{N=N}$ observed for alkali metal *azide* compounds.

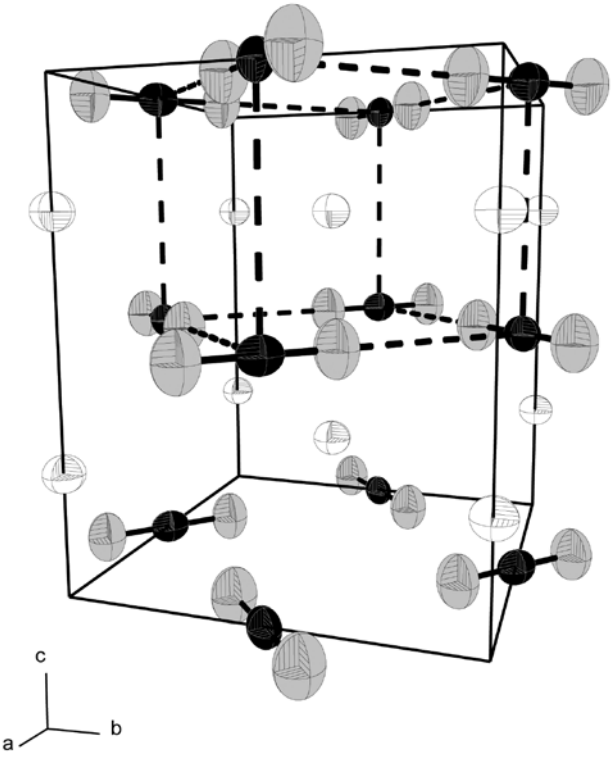

Fig. 2: Perspective view on the tetragonal unit cell of Cs[OCN] (indicated by thick lines) and the pseudo-cubic primitive unit cell (indicated by broken lines). Cs^+ cations are displayed as white octants, C and O/N atoms are displayed as black and light grey octants, respectively. Displacement ellipsoids are drawn with 70% probability.

3.2 Crystal structure

As assumed before on the basis of its powder X-ray diffraction pattern [1], the crystal structure of Cs[OCN] is isopointal to that of KN_3 [5] and isotypic to the crystal structure of K[OCN] [3]. Therefore, the title compounds crystallizes in a tetragonally distorted variant of the CsCl structure and can be described as a layered structure (as indicated by the plate-like, feathery habit of the crystals) consisting of Cs^+ and head-to-tail-disordered $[OCN]^-$. The layers are perpendicular to the crystallographic *c* axis. The Cs^+ cations are in positions exactly above each other in all layers, while the cyanate anions are placed above each other only in every second layer. In the intermediate anionic layers the cyanate anions are rotated by 90° with respect to the crystallographic *c* axis resulting in a distorted square-antiprismatic coordination of the cation by the N/O atoms of the cyanate anions (Fig. 2) with atomic distances which are very close to the sums of the ionic radii (Table 3).

4 Conclusion

The crystal structure of Cs[OCN] has been established unambigiously on the basis of single crystal data. It exhibits a head-to-tail disorder of the $[OCN]^-$ anions, isotypic to K[OCN] [4]. The triatomic anion was characterized by the Raman spectrum of the title compound. The fundamental frequencies perturbed by Fermi resonance have been corrected and used for the calculation of the force constants, which fit into the data of other alkali metal compounds containing similar triatomic pseudohalide species. The doubts voiced in the past of the crystal structure of Cs[OCN] being isotypic to K[OCN] on the base of spectroscopic data [6, 7] have been shown to be without a basis.

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