

499. Lattice Parameters and Infrared Spectra of Some Inorganic Cyanates.

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The lattice parameters of rubidium, caesium, thallos, argentous, and ammonium cyanates and the infrared spectra of these salts, as well as those of sodium and potassium, are reported.

THE crystal structures of sodium and potassium cyanates have previously been investigated. Sodium cyanate¹ is isomorphous with sodium azide and has a body-centred rhombohedral lattice, space group $R_{\bar{3}m}$. Potassium cyanate² is isomorphous with potassium azide and has a body-centred tetragonal lattice, space group $I4/mcm$. X-Ray powder photography has shown that rubidium, caesium, and thallos cyanates all have the body-centred tetragonal lattice of potassium cyanate. Silver cyanate has an orthorhombic lattice with four molecules to the unit cell, similar to that of silver azide, space group $Ibam$. However the structure of the ammonium cyanate lattice is quite different from that of ammonium azide; it has a tetragonal lattice differing from that of the alkali-metal cyanates. The lattice parameters of the cyanates together with those of the corresponding azides for comparison are given in Table 1.

TABLE 1. Crystal structures of the cyanates and azides.

Salt	Class *	Space group	Unit-cell dimensions				Moles/unit cell	Ref.
			<i>a</i>	<i>b</i>	<i>c</i>	α		
NaNCO	R	$R_{\bar{3}2}$ or $R_{\bar{3}m}$	5.44			$38^{\circ} 37'$	1	1
KNCO	T	$I4/mcm$	6.07		7.03		4	2
RbNCO	T	"	6.35		7.38		4	
CsNCO	T	"	6.71		8.04		4	
TlNCO	T	"	6.23 ₂		7.32 ₀		4	
AgNCO	O	$Ibam$	6.37	6.82	5.48		4	
NH ₄ NCO	T	—	3.64		5.57 ₉ †		1	
NaN ₃	R	$R_{\bar{3}2}$ or $R_{\bar{3}m}$	5.488			$38^{\circ} 43'$	1	2
KN ₃	T	$I4/mcm$	6.096		7.056		4	3
RbN ₃	T	"	6.36		7.41		4	4
CsN ₃	T	"	6.72		8.04 ₅		4	5
TlN ₃	T	"	6.23		6.88		4	5, 6
AgN ₃	O	—	5.59	5.91	6.01		4	7, 8, 9
NH ₄ N ₃	O	$Pman$	8.93 ₀	8.64 ₂	3.80 ₀		4	3

* R, rhombohedral; T, tetragonal; O, orthogonal. † This is probably a pseudo-unit cell, see Figure.

The two most striking differences between the structures of the cyanates and the isoelectronic azides are observed in the silver and ammonium salts. The molecular volume of silver cyanate is 59.5 \AA^3 , compared with a molecular volume of 49.7 \AA^3 for silver azide. The molecular volumes of the potassium salts are KNCO, 64.3 \AA^3 ; KN₃, 65.6 \AA^3 . The large difference for the silver salts and the much smaller value for silver azide must reflect a larger non-ionic contribution to the binding energy in that salt than in silver cyanate. Thallos azide too appears to have a larger non-ionic contribution to the binding energy than thallos cyanate. The azide is insoluble in water whereas the cyanate is quite soluble. The reason why the cyanates are more ionic than the azides is probably the greater electron affinity of the cyanate ion (*ca.* 90 kcal. mole⁻¹)¹⁰ than that of the azide ion

¹ Bassière, *Compt. rend.*, 1938, **206**, 1309.

² Hendricks and Pauling, *J. Amer. Chem. Soc.*, 1925, **47**, 2904.

³ Frevel, *Z. Krist.*, 1936, **94**, 197.

⁴ Gunther, Porget, and Rosbaud, *Z. phys. Chem.*, 1930, *B*, **6**, 459.

⁵ Waddington, Ph.D. Thesis, University of Cambridge, 1955.

⁶ Gray and Waddington, *Chem. and Ind.*, 1955, 1555.

⁷ West, *Z. Krist.*, 1936, **95**, 421.

⁸ Pfeiffer, Ph.D. Thesis, California Institute of Technology, 1948.

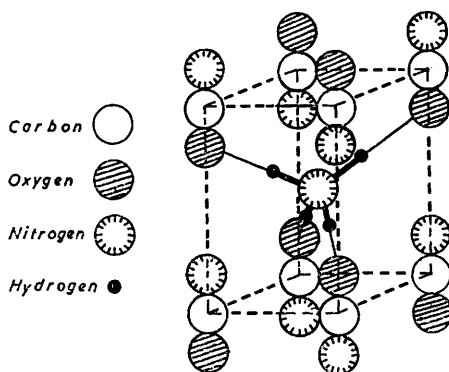
⁹ Bassière, *Compt. rend.*, 1935, **201**, 735.

¹⁰ Waddington, unpublished results.

(70—80 kcal. mole⁻¹).^{11,12} Because of this the cyanate ion is less likely to participate in electron sharing with a given metal ion than is the azide.

The molecular volumes of ammonium cyanate and ammonium azide are almost identical: NH_4NCO , 74.1 Å³; NH_4N_3 , 73.3 Å³, though the structures of the two compounds are so very different. An explanation for the structural difference may perhaps be that in the cyanate the hydrogen atoms of the ammonium ion are hydrogen-bonded only to the oxygen end of the cyanate ion, as it is the more electronegative, whereas they are hydrogen-bonded to both ends of the azide ion in ammonium azide. This will give ammonium cyanate a structure similar to that of ammonium cyanide,¹³ with the cyanate ions along the tetrad axis, as shown in the Figure.

Inferred crystal structure of ammonium cyanate.



Though the infrared spectrum of aqueous potassium cyanate was investigated by Williams¹⁴ and the Raman spectra of aqueous potassium cyanate by Cleveland,¹⁵ Williams's results and assignment of vibration frequencies are at variance with the earlier work of Goubeau¹⁶ who investigated the Raman spectra of solid KNCO , AgNCO , $\text{Hg}_2(\text{NCO})_2$, and $\text{Pb}(\text{NCO})_2$. Miller and Wilkins¹⁷ have recently investigated the infrared spectra of solid KNCO and AgNCO in the sodium chloride region but have not assigned vibration frequencies. Accordingly the infrared spectra of NaNCO , KNCO , RbNCO , CsNCO , AgNCO , TlNCO , and NH_4NCO have been measured in the sodium chloride and potassium bromide regions. The data and assignments are in Table 2.

TABLE 2. *Infrared spectra of the cyanates (cm.⁻¹).*

	ν_2'	ν_2	$2\nu_2$	ν_1	ν_3
NaNCO		620	1216	1305	2220
KNCO	626	636	1205	1300	2170
RbNCO	627	637	1205	1293	2210
CsNCO	627	635	1217	1307	2160
AgNCO	605	632	1203 *	1300 *	2145
TlNCO	617	627	1203	1292	2130
NH_4NCO		640	1293	1334	2190

* These lines were taken from Goubeau's Raman data; they were not observed by the author in the infrared spectrum of AgNCO .

The isolated cyanate ion should have three fundamental vibration frequencies, all active in the infrared region. They are the symmetric stretching frequency, ν_1 , a degenerate bending frequency, ν_2 (with two degrees of freedom at right angles), and an asymmetric

¹¹ Gray and Waddington, *Proc. Roy. Soc.*, 1956, *A*, **235**, 481.

¹² Franklin, Dikeler, Reese, and Krauss, *J. Amer. Chem. Soc.*, 1958, **80**, 298.

¹³ Lely and Bijvoet, *Rec. Trav. chim.*, 1944, **63**, 39.

¹⁴ Williams, *J. Amer. Chem. Soc.*, 1940, **62**, 2442.

¹⁵ Cleveland, *J. Amer. Chem. Soc.*, 1941, **63**, 622.

¹⁶ Goubeau, *Ber.*, 1935, **68**, 912.

¹⁷ Miller and Wilkins, *Ind. Eng. Chem. Anal.*, 1952, **24**, 1253.

stretching vibration, ν_3 . Because of the way the cyanate ions are packed in the lattices of the potassium, rubidium, caesium, thallous, and silver salts, the degeneracy of ν_2 will be removed and two infrared bands should be found owing to the bending vibrations of the ion. In sodium cyanate the cyanate ions lie along the hexad axis of the crystal and so the degeneracy will be preserved. If the crystal structure assigned above to ammonium cyanate is correct and the cyanate ions lie along the tetrad axis of the crystal then the degeneracy will be preserved and only one vibration frequency should be observed. This is found to be so, and the position of the cyanate ion in the lattice confirmed. This is in marked contrast to orthorhombic ammonium azide, where the site symmetry destroys the degeneracy of the bending vibration of the azide ion and two infrared-active bands due to bending are observed.^{18,19}

Because of the closeness of $2\nu_2$, the first harmonic of the bending frequency, to ν_1 , its intensity will be raised by Fermi resonance and it will appear as a fairly strong infrared band, just as it does in the Raman spectra of CO_2 and N_3^- .²⁰ Other, but much weaker, bands occur as a result of the interactions of these vibrations of the cyanate ion with the vibrations of the crystal lattice. Some of these vibrations have been observed but they are not recorded in Table 2.

Since the internuclear distances in the cyanate ion are not known the bending force constant cannot be calculated. There are also insufficient data (only two lines ν_1 and ν_3) to apply a general quadratic force field to calculate the stretching force constants of the ion. The application of the simple valence force field yields complex values for k_1 and k_2 and thus cannot be used. However, a comparison can be made of the actual vibration frequencies of the cyanate ion with those of some isoelectronic molecules. In particular the series CO_2 , NCO^- , CN_2^{2-} is of interest as here the oxygen atoms are replaced stepwise by N^- . The data for N_2O are also included in Table 3.

TABLE 3. *Vibration frequencies of the cyanate ion and some isoelectronic molecules and ions (cm.⁻¹).*

Molecule or ion	ν_1	ν_2	ν_3	Ref.
CO_2	1337	667	2349	20
NCO^-	1300	630	2170	*
CN_2^{2-}	1230	600	2150	21 †
NNO	1285	589	2224	20
$(\text{HN})\text{-C-O}$	1327	670	2274	22

* This work; an average value for the alkali metal salts.

† An approximate average for the data on the sodium and calcium salts.

Hydrogen isocyanate, a non-linear tetratomic molecule, has six fundamental vibration frequencies,²² three of which arise principally from the internal motions of the $-\text{NCO}$ group. These may be compared with the corresponding modes in CO_2 , from which HNCO can be regarded as being derived by the replacement of an oxygen by NH , and the cyanate ion. This is done in Table 3.

EXPERIMENTAL

Materials.—Sodium cyanate was prepared by heating anhydrous sodium hydrogen carbonate with the stoichiometric quantity of urea. When effervescence had ceased the molten solid was tested for carbonate by withdrawing a little with a glass rod, dissolving it in water and adding barium chloride solution. A little more urea was added and the test repeated till no carbonate could be detected. The melt was then allowed to cool and solidify, and dissolved in the minimum of water. The solid salt was precipitated by addition of absolute ethyl alcohol, washed with alcohol, and dried *in vacuo*. Potassium cyanate was made from potassium hydrogen carbonate in the same way, and rubidium and caesium cyanates from the carbonates.

¹⁸ Dows, Whittle, and Pimentel, *J. Chem. Phys.*, 1955, **23**, 1475.

¹⁹ Gray and Waddington, *Trans. Faraday Soc.*, 1957, **53**, 901.

²⁰ Herzberg, "Infra-Red and Raman Spectra," Van Nostrand, New York, 1945.

²¹ Deb and Yoffe, *Trans. Faraday Soc.*, 1959, **55**, 106.

²² Herzberg and Reid, *Discuss. Faraday Soc.*, 1950, **9**, 92.

Thallos cyanate, which is soluble in water, was made by mixing aqueous solutions of sodium cyanate and thallos acetate and adding absolute alcohol. Silver cyanate was precipitated by mixing aqueous solutions of silver nitrate and sodium cyanate. Single crystals were grown by slow recrystallization from ammoniacal solution. To make ammonium cyanate, an ethereal solution of isocyanic acid was first prepared by heating cyanuric acid and passing the isocyanic acid vapour so obtained into cold dry ether. Dry ammonia was then passed into the ethereal solution and ammonium cyanate was precipitated as it formed. The precipitate was filtered off, washed with ether, and dried *in vacuo*.

Apparatus and Method.—X-Ray powder photographs of KNCO, RbNCO, CsNCO, TINCO, AgNCO, and NH₄NCO were taken in 19 cm. Debye-Scherrer cameras with Cu-K_α radiation. The powdered salts were filled into thin-walled glass capillaries which were then sealed with picein wax. Single crystal rotation-oscillation photographs of silver cyanate were taken perpendicular to the three morphological axes of the crystal. The density of ammonium cyanate was measured by the density-gradient tube method; $\rho_{\text{obs.}} = 0.712$, $\rho_{\text{calc.}}$ (1 molecule/unit cell) = 0.713_g.

The infrared spectra of the solid cyanates were taken with a Perkin-Elmer 21, double-beam, continuously recording spectrophotometer. A rock-salt prism was used in the range 4000—650 cm.⁻¹ and a potassium bromide prism in the range 800—400 cm.⁻¹. In all cases the solid was finely powdered and made into a mull, either with Nujol or with hexachlorobutadiene. The mull was then smeared between rock-salt or potassium bromide plates.

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