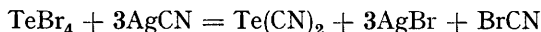


253. *The Tellurocyanate Ion, TeCN<sup>-</sup>.*

By N. N. GREENWOOD, R. LITTLE, and M. J. SPRAGUE.

Attempts to prepare the previously unknown tellurocyanate ion are described. To facilitate detection of this ion its fundamental vibration frequencies have been calculated from force constants predicted from a newly evaluated set of self-consistent force constants for the cyanate, thiocyanate, and selenocyanate ions. Comparison with the isoelectronic molecule, iodine cyanide, and other cyanogen halides is included.

THERE is some confusion in the literature concerning the existence of potassium tellurocyanate. This compound has been mentioned in several recent advanced texts,<sup>1-3</sup> though the only claim to have prepared it<sup>4</sup> was subsequently withdrawn.<sup>5</sup> It is possible that the compound exists at low temperatures in liquid ammonia solution since tellurium dissolves slowly in a solution of potassium cyanide in liquid ammonia; however, evaporation of the solvent left a residue containing only potassium cyanide and tellurium.<sup>6</sup> No reaction was observed between potassium polytelluride and potassium cyanide under conditions which converted potassium polysulphide and polyselenide into thiocyanate and selenocyanate.<sup>6</sup> It appears that the only authentic compound containing the TeCN group is tellurium dicyanide which was prepared<sup>7</sup> by treating tellurium tetrabromide with silver cyanide in benzene.



The reaction between tellurium and potassium cyanide has now been investigated under a variety of conditions in an attempt to prepare the tellurocyanate ion but no evidence for this species was found in the products. Thus, powdered tellurium was fused with potassium cyanide for 30 minutes and the finely powdered product extracted with acetone (in which both potassium thiocyanate and selenocyanate are soluble). Powdered tellurium did not react with fused sodium cyanide-potassium cyanide eutectic, with aqueous or methanolic potassium cyanide under reflux, or with a suspension of potassium cyanide in acetone. Similarly, tellurium dicyanide did not react with potassium telluride in acetonitrile [ $\text{Te}(\text{CN})_2 + 2\text{K}_2\text{Te} \neq 2\text{KTeCN}$ ].

To facilitate detection of small amounts of tellurocyanate ion in solution, the expected vibration frequencies of this ion were calculated. The calculation required accurate spectroscopic data for the cyanate, thiocyanate, and selenocyanate ions and a self-consistent set of force constants. The infrared spectra of potassium cyanate, thiocyanate, and selenocyanate were therefore redetermined and the results are presented in Table I which

TABLE I.  
Fundamental vibration frequencies (cm.<sup>-1</sup>).

Compound	$\nu_1(\text{C}\equiv\text{N})$	$\nu_2(\text{C}-\text{X})$	$\nu_2(\text{bend})$	$2\nu_2$
KOCN .....	2160	1205	637, 625	1294
KSCN .....	2048	747	485, 470	968, 949
KSeCN .....	2070	561	426, 417	847, 832
NaSeCN .....	2079	535	426, 413	847, 833
KSeCN (Raman) .....	2078	564	—	—

also includes data on the infrared spectrum of sodium selenocyanate and the Raman spectrum of an aqueous solution of potassium selenocyanate. The numerical values

<sup>1</sup> Remy, "Treatise on Inorganic Chemistry," translated by J. S. Anderson, Elsevier, 1956, p. 746.

<sup>2</sup> Cotton and Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, 1962, p. 465.

<sup>3</sup> Heslop and Robinson, "Inorganic Chemistry," 2nd Edn., Elsevier Publishing Co., 1963, p. 421.

<sup>4</sup> Birckenbach and Kellermann, *Ber.*, 1926, **58**, 786.

<sup>5</sup> Birckenbach and Huttner; *Z. anorg. Chem.*, 1930, **190**, 1 (see footnote on p. 10).

<sup>6</sup> Bergstrom, *J. Amer. Chem. Soc.*, 1926, **48**, 2319.

<sup>7</sup> Cocksedge, *J.*, 1908, **23**, 2175.

compare well with the literature.<sup>8-10</sup> The stretching force constants  $k_{C\equiv N}$  and  $k_{C-X}$  ( $X = O, S, Se$ ) and the interaction force constant  $k_{12}$  were then calculated by Orville Thomas's method for linear triatomic species.<sup>11</sup> The results are shown in Fig. 1 which plots the force constants in terms of the mixing parameter  $\rho$ . To determine  $\rho$  it is necessary to know one force constant in the series independently. Gordy's relation<sup>12</sup> is insufficiently accurate to estimate this, particularly since no precise bond distances are known for these ions. However, for the cyanate ion, data obtained from isotopic species have given enough information for all the force constants of this ion to be determined absolutely.<sup>8</sup> This gives  $k_{C\equiv N}$  15.88,  $k_{C-O}$  11.00,  $k_{12}$  1.42 mdyne/Å. Furthermore, in the series FCN, ClCN, BrCN, and ICN which is isoelectronic with the ions being considered, the force constant  $k_{C\equiv N}$  varies little (17.44, 17.61, 17.80, and 17.9 mdyne/Å, respectively), whereas, as expected,  $k_{C-X}$  and  $k_{12}$  are more variable because of the change in the halogen atom X.<sup>13</sup> Three separate values of  $\rho$  for the thiocyanate series were therefore estimated on the basis of three separate

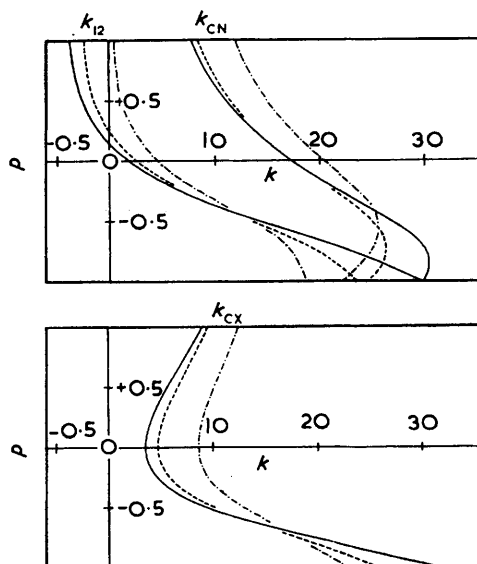


FIG. 1. Variation of force constant with mixing parameter.

—  $SeCN^-$ , - - - -  $SCN^-$ , - . - . -  $OCN^-$ .

assumptions about  $k_{C\equiv N}$  and from these, three separate values for  $k_{C-X}$  and for  $k_{12}$  for each ion were read off from the graphs in Fig. 1. The assumptions were (a)  $k_{C\equiv N}$  does not vary at all in the series  $OCN^-$ ,  $SCN^-$ , and  $SeCN^-$ ; (b)  $k_{C\equiv N}$  increases with atomic weight of X at the same rate as in the isoelectronic cyanogen halides; (c)  $k_{C\equiv N}$  increases twice as rapidly as in the isoelectronic halides. The results are summarised in Table 2, together with previously calculated force constants for these ions. The same assumptions lead to the three values of  $k_{C\equiv N}$  for the unknown tellurocyanate ion shown in Table 2 but, since no experimental vibration frequencies are available, it is not possible to calculate  $\rho$  and hence  $k_{C-Te}$  and  $k_{12}$  as with the preceding ions. Values for  $k_{C-Te}$  were therefore obtained by utilising the observation that  $k_{C-X}$  is a linear function of the ionisation potential of X where  $X = O, S, \text{ and } Se$ . Use of the values of  $k_{C-X}$  in Table 2 and extrapolation by the method of least squares leads to the three values of  $k_{C-Te}$  in Table 2. Values for the interaction force constant  $k_{12}$  for the tellurocyanate ion were obtained by extrapolating the values of  $k_{12}$  in Table 2 as a function of atomic weight of O, S, and Se. When these three sets of values

<sup>8</sup> Maki and Decius, *J. Chem. Phys.*, 1959, **31**, 772.

<sup>9</sup> Jones, *J. Chem. Phys.*, 1956, **25**, 1069.

<sup>10</sup> Morgan, *J. Inorg. Nuclear Chem.*, 1961, **16**, 367.

<sup>11</sup> Orville Thomas, *J. Chem. Phys.*, 1951, **19**, 1162.

<sup>12</sup> Gordy, *J. Chem. Phys.*, 1946, **14**, 305; 1947, **15**, 305.

<sup>13</sup> Aynsley and Little, *Spectrochim. Acta*, 1962, **18**, 667.

TABLE 2.  
Estimated force constants (mdyne/Å).

Ion	$\rho$	$k_{\text{C}\equiv\text{N}}$	$k_{\text{C-X}}$	$k_{12}$	Ref.
$\text{OCN}^-$ .....	—	15.88	11.00	1.42	8
	0.378	15.88	9.59	1.59	this work
	0.100	15.88	4.85	1.27	assumption (a)
$\text{SCN}^-$ .....	0.090	16.03	4.82	1.39	assumption (b)
	0.079	16.19	4.80	1.50	assumption (c)
	—	$15.95 \pm 0.45$	$5.18 \pm 0.15$	$0.9 \pm 0.5$	9
$\text{SeCN}^-$ .....	0.095	15.88	3.76	0.63	assumption (a)
	0.072	16.21	3.71	0.90	assumption (b)
	0.050	16.54	3.69	1.22	assumption (c)
$\text{TeCN}^-$ .....	—	15.1	3.88	0 (assumed)	10
	—	15.88	2.75	0.18	assumption (a)
	—	16.34	2.69	0.52	assumption (b)
	—	16.79	2.67	0.93	assumption (c)

for the three force constants were substituted in the appropriate equations<sup>11</sup> the following sets of fundamental vibration frequencies for the tellurocyanate ion were obtained:

assumption (a)	$\nu_{\text{C}\equiv\text{N}} = 2083 \text{ cm}^{-1}$	$\nu_{\text{C-Te}} = 456 \text{ cm}^{-1}$ .
assumption (b)	2086	455
assumption (c)	2086	457

The values are seen to be essentially independent of variation in the assumed values for the force constants. The third fundamental (bending) mode can be obtained roughly

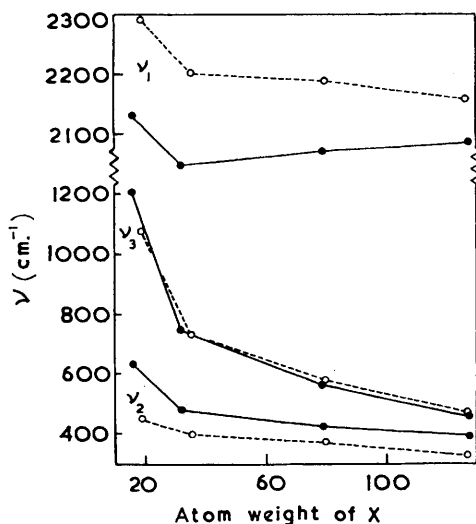


FIG. 2. Vibrational frequencies of XCN species.

—●— XCN (X = O, S, Se, Te).  
--○-- XCN (X = F, Cl, Br, I).

by extrapolating the simple plot of  $\nu_2$  for the ions  $\text{OCN}^-$ ,  $\text{SCN}^-$ , and  $\text{SeCN}^-$  against the atomic weight of the atoms O, S, and Se; this gives a value of  $\nu_2 \simeq 400 \text{ cm}^{-1}$  for the tellurocyanate ion.

The predicted values of  $\nu_{\text{C}\equiv\text{N}}$ ,  $\nu_{\text{C-Te}}$ , and  $\nu_2$  (bend) for the tellurocyanate ion are consistent with the spectrum of tellurium dicyanide in Nujol, for which bands were observed at 2176, 2169, 459, and  $403 \text{ cm}^{-1}$ . The two latter values are close to those predicted for the tellurocyanate ion; the band at  $403 \text{ cm}^{-1}$  had previously been assigned to the antisymmetric C-Te stretching mode,<sup>14</sup> but in view of the above correlation it is considered more likely to be the Te-C≡N bending mode, the band at  $459 \text{ cm}^{-1}$  representing the C-Te stretch. Likewise, the predicted value for the C≡N stretching mode is

<sup>14</sup> Fritz and Keller, *Chem. Ber.*, 1961, **94**, 1524.

also at the expected position since this is consistent with the trend in values for the ratio  $\nu_{\text{C}\equiv\text{N}}[\text{XCN}^-]/\nu_{\text{C}\equiv\text{N}}[\text{X}(\text{CN})_2]$ ; this ratio, when calculated on the basis of recent data<sup>15</sup> and the present results, has values of 0.938, 0.950, and 0.961 for X = S, Se, and Te.

Trends in the vibration frequencies of the chalcogenocyanate ions and the isoelectronic halogen cyanides are summarised in Fig. 2 from which it is clear that  $\nu_1(\text{C}\equiv\text{N})$  does not follow the same trend in the two series, whereas  $\nu_3(\text{C-X})$  and  $\nu_2(\text{bend})$  are fairly closely related. The considerably higher values for the frequencies of the fundamental modes for the first member of each series presumably reflects the greater force constants, which arise from stronger bonding with the first-row elements. The fundamental modes for the formally analogous molecule HCN<sup>16</sup> are  $\nu_{\text{C}\equiv\text{N}}$  2089,  $\nu_{\text{C-H}}$  3313, and  $\nu_2$  712  $\text{cm}^{-1}$ .

#### EXPERIMENTAL

Potassium cyanate was purified by successive precipitation from saturated aqueous solutions by dropwise addition of ethanol. Potassium thiocyanate and selenocyanate were purified similarly by precipitation from dry acetone solutions by addition of ether. Tellurium cyanide was prepared by refluxing 14.6 g. of tellurium tetrabromide with 40 g. of freshly precipitated silver cyanide in 90 ml. of dry benzene under nitrogen.<sup>7</sup> Potassium telluride was prepared<sup>17</sup> from 12.2 g. of purified potassium metal and 17.5 g. of finely powdered tellurium in 150 ml. of liquid ammonia which had previously been dried over potassium.

The infrared and Raman techniques have been described previously.<sup>15</sup>

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<sup>15</sup> Aynsley, Greenwood, and Sprague, *J.*, 1964, 704.

<sup>16</sup> Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand, 1945.

<sup>17</sup> Hugot, *Compt. rend.*, 1899, 129, 388.