591. *Infrared Spectra and Structures of Perthiocyanic Acid, its Barium Salt,* $(SCN)_4Cl_2$, *and* $(ClSCN)_5$.

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The infrared spectrum of perthiocyanic acid, $(SCN)_2,H_2S$, strongly supports the cyclic structure proposed on chemical grounds by Hantzsch and Wolfenkamp. The barium salt of this acid and $(SCN)_4Cl_2$ have very similar infrared spectra that are consistent with the structure suggested on chemical grounds for the latter by Söderbäck. The polymer $(ClSCN)_5$ has an infrared spectrum consistent with the structure $[-CCl=N-S-]_5$.

In the preceding paper [1] we discussed the infrared spectrum of isoperthiocyanic acid and some related compounds with respect to some *X*-ray-diffraction crystal-structure determinations and their chemical properties. The compounds were assigned precise structures, which involved a slight modification of that originally proposed by Freund [2] and supported strongly on chemical grounds by Hantzsch and Wolfenkamp.[3] The latter authors, and

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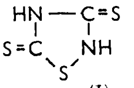
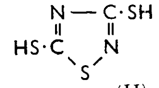
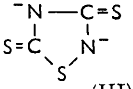
[1] Emeléus, Haas, and Sheppard, preceding paper.
[2] Freund, *Annalen*, 1895, **285**, 154.
[3] Hantzsch and Wolfenkamp, *Annalen*, 1904, **331**, 265.

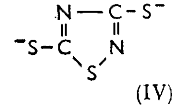
also Klason,[4] had suggested the formula (II) for the isomeric compound perthiocyanic acid and this and the alternative structure (I) will be considered in this paper in the light of infrared spectroscopic data. The structure of barium perthiocyanate and the compounds $(SCN)_4Cl_2$ and $(SCNCl)_x$ will also be considered.

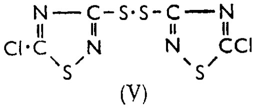
There are two possible canonical forms (III, IV) for the ion of the barium salt. These are related to (I) and (II) and, on chemical grounds (reaction with ethyl iodide[4]), a structure approximating more to (IV) is indicated. Söderbäck[5] proposed the structure


(I)


(II)


(III)


(IV)


(V)

(V) for the compound $(SCN)_4Cl_2$, which is related in its ring formula to (II) of perthiocyanic acid.

Chemical evidence[5] in favour of structure (V) is its ready reaction with mercury to form the compound $Hg[(SCN)_2Cl]_2$ and the latter's reconversion by iodine into the original compound. On treatment with hydrogen bromide, the disulphide (V) gave a compound $(SCN)_2,2HBr$, which resembles the compound $(SCN)_2,2HCl$ of the isoperthiocyanic acid series.[5] However, the ring transformation implied by this reaction is readily explicable as being analogous to the reversible formation of isoperthiocyanic acid discussed by Hantzsch and Wolfenkamp.[3] It is clear from the infrared spectrum of the polymer $[SCNCl]_x$ that its structure is quite different from those of the other compounds and that it is related to open-chain compounds of the type $SCNCl_3$ discussed most recently by Bacon, Irwin, Pollock, and Pullin.[6]

The Infrared Spectra of Perthiocyanic Acid, its Barium Salt, and $(SCN)_4Cl_2$.—The spectra are presented in the Figure and the detailed frequencies of the absorption bands are listed in the Experimental section. The spectra show a family resemblance, particularly in the region 1300—800 cm.$^{-1}$ and, apart from the multiplicity of certain bands for $(SCN)_4Cl_2$, the resemblance is extremely close in this region for this chloro-compound and the barium salt. It was impossible to free the barium salt from water of crystallisation, and this accounts for the additional absorption bands indicated with asterisks.

In the spectrum of perthiocyanic acid, the strong bands at 3010 and 2830 cm.$^{-1}$ must be assigned to stretching vibrations of NH groups and on these grounds alone formula (I) is strongly preferred over (II), which would have been expected to give SH bands of medium strength in the 2600 cm.$^{-1}$ region. The absence of a strong band at about 1620 cm.$^{-1}$ shows that there are no NH_2 groups, as there are in isoperthiocyanic acid.[1] Other possible vibrational assignments for the strongest bands, based mainly on the work of Mecke and Mecke[7] on cyclic thioamides and cyclic thioureas, are as follows: 1495 (NH in-plane deformation), 1395 (skeletal, involving C–N stretching), 1171 and 1066 (coupled C=S stretching vibrations), 770 and perhaps 620 cm.$^{-1}$ (broad) (NH out-of-plane deformation). The main features of the spectrum can thus be accounted for by formula (I), which is strongly supported.

In discussing the infrared spectrum of $(SCN)_4Cl_2$ the splitting of the strong bands in the vicinity of 1210, 1070, 805, 685, and 480 cm.$^{-1}$ will be ignored as it will be assumed that this is caused by weak coupling of related vibrations of the two rings across the S–S bridge plus, in some cases, interaction between more than one $(SCN)_4Cl_2$ molecule in the unit cell of the crystal structure. In view of the possibility [not indicated in formula (V)]

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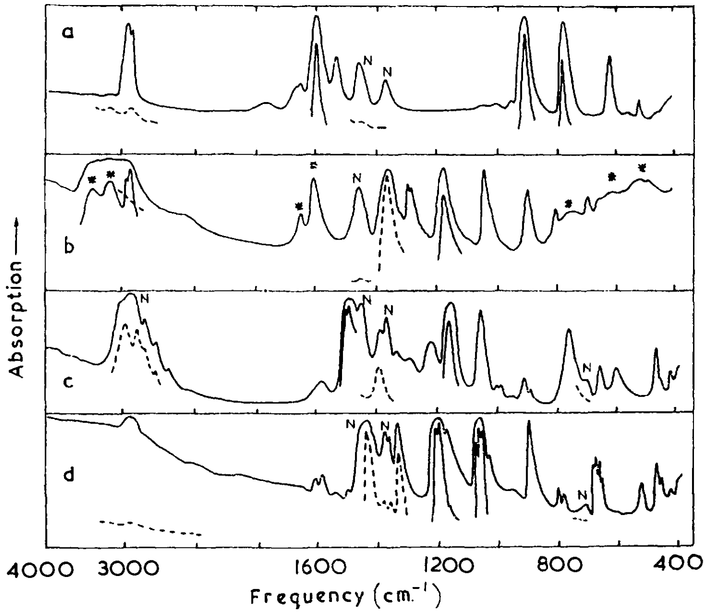
[4] Klason, *J. prakt. Chem.*, 1888, **38**, 366.

[5] Söderbäck, *Annalen*, 1928, **465**, 184.

[6] Bacon, Irvin, Pollock, and Pullin, *J.*, 1958, 764.

[7] Mecke and Mecke, *Chem. Ber.*, 1956, **89**, 343.

that the C–S and S–N bonds in a single five-membered ring may have some double-bond character caused by participation of lone-pair electrons or vacant *d*-orbitals on the sulphur atoms in the π-electron system of the rest of the ring, four or five skeletal stretching fundamentals with frequencies greater than 800 cm.$^{-1}$ might be expected. The strong bands at **1445**, **1340**, **1214**—**1205**, **1082**—**1071**—**1065**, and **904** cm.$^{-1}$ are probably to be assigned in this fashion, the two highest frequencies probably corresponding most closely to the two C=N stretching vibrations in the conjugated ring system. That the highest frequency of this type is not found above **1445** cm.$^{-1}$ calls for comment in view of the fact that C=N bonds in the five-membered ring of isoperthiocyanic acid absorb above **1500** cm.$^{-1}$ (at **1515** cm.$^{-1}$). All that can be said is that the additional strain caused by the two conjugated double bonds in the ring should lower the frequency further and that π-electron delocalisation in the ring would have an effect in the same direction. It is concluded that



Infrared spectra of perthiocyanic acid, its barium salt, $(SCN)_4Cl_2$, and $(ClSCN)_5$.

(——) Nujol mulls; (– – –) hexachlorobutadiene mulls; (N) Nujol absorptions.
(a) $(ClSCN)_5$; (b) $BaC_2N_2S_3$,aq.; (c) $H_2C_2N_2S_3$; (d) $(SCN)_4Cl_2$.

the infrared spectrum of $(SCN)_4Cl_2$ is in satisfactory agreement with structure (V) suggested on chemical grounds but, in the absence of characteristic group frequencies associated with hydrogen atoms, the spectroscopic evidence is less definite than for perthiocyanic acid.

The close relation between the infrared spectra of $(SCN)_4Cl_2$ and the barium salt of perthiocyanic acid leaves no doubt that the ring structures are very similar and suggests that the canonical form (IV) may be dominant in the resonance hybrid of the ion. Here the two highest frequencies are **1369** and *ca.* **1290** cm.$^{-1}$, each considerably below the values for $(SCN)_4Cl_2$. This undoubtedly denotes a higher degree of bond delocalisation in the ring of the negative ion. Two of the other skeletal absorption bands, at **1186** and **1050** cm.$^{-1}$, are also appreciably lower in frequency; it is the overall pattern of frequencies and intensities that makes for the strong general resemblance between the two spectra.

The Infrared Spectrum of $[ClSCN]_x$.—Since its preparation in 1924 by Kaufmann and Liepe[8] there has been some confusion as to the degree of polymerisation of this compound.[9,10] Recent molecular-weight[11] and spectroscopic measurements[12] have shown that the monomer Cl·S·C≡N is formed in solution and that this then forms a polymer. The needle-like crystals of $[ClSCN]_x$ studied here crystallised from solution on storage and had a molecular weight corresponding to the formula $(ClSCN)_5$.

The infrared spectrum is completely different from those of the cyclic compounds discussed above and in particular shows a C=N absorption band (corresponding to an unconjugated double bond) at 1601 cm.$^{-1}$. The spectrum of this crystalline material is essentially that described in solution by Nelson and Pullin[12] for the "second decomposition product" of the monomer. It is also similar in type to the spectrum of $SCNCl_3$;[6] the latter compound was shown to have the structural formula $Cl_2C{=}N{\cdot}SCl$ or (ClS)ClC=NCl [ν(C=N) at 1596 cm.$^{-1}$]. Finally the spectrum of $(ClSCN)_5$ is very closely similar to that described for $Cl_2C{=}N{\cdot}S{\cdot}N{=}CCl_2$ (or ClN=CCl·S·CCl=NCl);[6] it is clearly entirely consistent with a polymeric formulation of the type $[-CCl{:}N{\cdot}S-]_5$.

EXPERIMENTAL

Recorded methods were used to prepare perthiocyanic acid,[4] its barium salt,[4] $(SCN)_4Cl_2$,[5] and $(ClSCN)_5$.[8] Elemental analyses were done on each compound. The molecular weight of $(ClSCN)_5$ was determined by a vapour-pressure method in dichloromethane solution after recrystallisation from chloroform (Found: *M*, 457. Calc. for $C_5Cl_5N_5S_5$: *M*, 467). Details of spectroscopic procedure are given in the previous paper.[1]

Infrared Spectra.—$(SCN)_2,H_2S$. 3060—2960vs(bd), 2830s, 2715m, 2560m, 1627w(sh), 1600w(bd), 1516s, 1495vs, 1395m, 1345w, 1307w, 1240m(bd), 1171vs(bd), 1066s, 1013w, 998w, 922w, 903w, 770s(bd), 667m, 620m(bd), 577m, 436w.

$(SCN)_4Cl_2$. 1615w, 1596w, 1445vs, 1380m, 1367m, 1340s, 1214s, 1205vs, 1178w(sh), 1082s, 1071vs, 1065s, 1041w(sh), 904s, 810w, 800w, 690m, 684m, 673m, 665m, 540m, 487m, 475m, 438w.

$BaS_2C_2N_2S$,aq. 3400s(bd) (H_2O), 3200s(bd) (H_2O), 1658m (H_2O), 1613s (H_2O), 1369vs, 1297m, 1285m, 1186s, 1050s, 903m, 814w, 763w(bd) (H_2O), 696w, 620m(bd) (H_2O), 520s(bd) (H_2O).

$(ClSCN)_5$. 1601s, 1536m, 912s, 771s, 615m, 520w.

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[8] Kaufmann and Liepe, *Ber.*, 1924, **57**, 923.
[9] Lecher and Joseph, *Ber.*, 1926, **59**, 2603.
[10] Baroni, *Atti R. Accad. naz. Lincei, Rend. Adun. Sol. Rome*, 1936, **23**, 871.
[11] Bacon and Irvin, *J.*, 1958, 774, 778.
[12] Nelson and Pullin, *J.*, 1960, 604.