Pure Quadrupole Spectrum of Trithiazyl Trichloride

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So far we have studied pure quadrupole spectra of some heterocyclic compounds. In this connection, trithiazyl trichloride $(SNCl)_3$ was prepared[1] by chlorinating sulfur nitride $(SN)_4$. It is very unstable and reacts with moisture so easily that some precaution must be taken to preserve it. The spectrum due to ^{35}Cl was observed by the frequency-modulated super-regenerative spectrometer, and only one weak absorption line 29.842 megacycle/sec. was found at 285°K.

This result is evidently different from that of cyanuric chloride $(CNCl)_3$ which shows two adjacent lines[2], although trithiazyl trichloride might be benzene-like heterocyclic compound as well. It crystallizes in hexagonal prisms or needles, which should be closely related to the above fact. However, its crystal structure

1) A. Meuwsen, *Ber.*, **64**, 2311 (1931).
2) H. Negita and S. Satou, This Bulletin, **29**, 426 (1956).

has not yet been established.

On the other hand, it will be seen that the line situates in the neighborhood of those of thionyl chloride $SOCl_2$. This reminds us of the case of phosphonitrile chloride $(PNCl_2)_3$, where the lines are found at almost the same region as those of phosphorus oxychloride $POCl_3$. In the same way, those of cyanuric chloride are near to those of phosgene $COCl_2$. These results are summarized in Table I. When many lines are found in a compound, they are shown on an average for convenience.

TABLE I

COMPARISON OF ^{35}Cl RESONANCE ABSORPTION FREQUENCIES (ν) OF VARIOUS COMPOUNDS

Compd.	ν (Mc./sec.) at room temp.	Compd.	ν (Mc./sec.) at 77°K
$(SNCl)_3$	29.8	SO_2Cl_2	37.7[4]
		$SOCl_2$	31.9[5]
		PCl_5	32.4[6]
$(PNCl_2)_3$	27.8[2]	$POCl_3$	28.6[5]
		PCl_3	26.2[7]
$(CNCl)_3$	36.3[3]	CCl_4	40.6[7]
		$COCl_2$	35.7[7]

In this table, our data are concerned with the value at room temperature, and they should have about 1 megacycle/sec. added to them to compare with those of the compounds at 77°K. As seen from the table, there is a close relation between the valence state of the central atom, e.g., sulfur and the resonance frequency of the chlorine attached to it.

It would be difficult to explain the difference between the frequencies of sulfur and carbon compounds cited above in view of electronegativities of the composed atoms, because both sulfur and carbon atoms have the same negativity 2.5, according to Pauling. Of course, it is more difficult to interpret the slight frequency shifts between the ring compounds and the corresponding oxychlorides.

However, the frequency decrease of phosgene in comparison with cyanuric chloride might be attributed to its resonance structure $\dot{O}\equiv CC\bar{l}Cl$ which may be deduced from the shorter distance 1.18A[8] between the carbon and oxygen than the normal double bond length 1.21A. The corresponding triple bond structure would hardly contribute anything to cyanuric chloride, and this may be the case also in both trithiazyl trichloride and thionyl chloride which is low pyramid structure[9].

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