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Effect of the Bridging Mode of the Thiocyanate Group in Compounds on Infrared Spectra

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The bonding mode of the thiocyanate group in coordination compounds can be determined with the aid of diagnostic rules for the ν(CN) or ν(CS) stretching frequencies in infrared spectra [1]. It seems that these rules can be simply used in the case of terminal bonded NCS groups in analogous compounds. However, more complicated conditions appear when NCS groups are present as bridges. Although in the case of a bridging NCS group it is possible to expect [2] a higher ν(CN) frequency value than for the terminal group, there are examples of some compounds with known crystal structure indicating deviations from this assumption. This situation is pointed out [3] by Bailey *et al.* who on the basis of several literature data [4] demonstrate the variability range of the ν(CN) frequency in various groups of thiocyanate complexes.

In Table I are given our measurements of the NCS stretching frequencies in three thiocyanate compounds of copper, which by X-ray analysis exhibit a different bridging mode of NCS groups as well as some internuclear distances in these compounds. From this survey it can be seen that the frequency ν(CN) increases markedly, whereas ν(CS) decreases with an increasing number of copper atoms bonded with one NCS group.

This finding is not reasonably explainable just on the basis of increasing number of coordination σ-bonds formed by sulphur atom, where one would expect rather opposite shifts of stretching frequencies. It is therefore necessary to take into consideration the effect of back-donating π-bonds Cu ⟶ S or Cu ⟶ N on the reorganization of electron density inside NCS groups.

In the case of CuNCS we may anticipate strong π-bond interactions Cu ⟶ S made possible by the overlap of occupied $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals of copper(I) atoms with similar vacant $3d_\pi$ orbitals of sulphur atoms of NCS group. It can be expected that these π-interactions prevail over Cu ⟶ N π-interactions and consequently there occurs a shift of electron density from the internuclear space C–S to space C–N (Figure 1a).

In $Cu(NCS)_2(NH_3)_2$ the back π-transfer to the sulphur atom is also possible as a result of overlap of

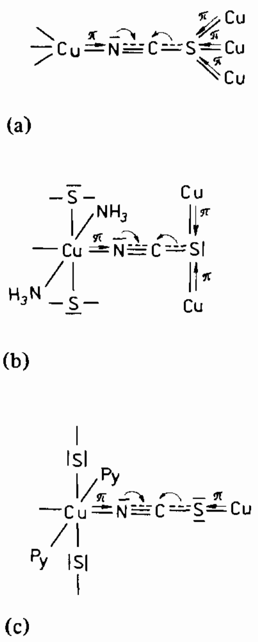

Figure 1. Schematic representation of the supposed electron shift in the NCS group as conditioned by the mode of bridging.

TABLE I. Infrared and Structural Data for Three Selected Thiocyanate Compounds of Copper.[a]

Compound	ν(CN) (cm^{-1})	ν(CS) (cm^{-1})	Internuclear Distance (Å)		Mode of Bridging	Ref.
			Cu–NCS	Cu–SCN		
$Cu(NCS)_2(py)_2$[a]	2072	824		3.00	-NCS–	5
$Cu(NCS)_2(NH_3)_2$	2096 2116	796 807	1.96	3.02[b]	-NCS<	6
CuNCS	2173	723 748	1.93	2.36[b]	-NCS≤	7

[a] py = pyridine. [b] In the respective compounds there are a few slightly different Cu–SCN distances and the values given are their averages.

$3d_{xz}$ and $3d_{yz}$ orbitals of copper(II) and sulphur atoms. This transfer is necessarily weaker than in the preceding case, not only in consequence of the bidentate sulphur atom but also due to a weaker overlap caused by a longer internuclear distance Cu–S (Figure 1b). Still weaker is naturally the considered π-transfer in the case of $Cu(NCS)_2(py)_2$ (Figure 1c) with the unidentate sulphur atom. It is possible, therefore, to expect that the influence of $Cu \longrightarrow S$ π-bonds on the shifts of electron density in NCS groups will less and less compete with the influence of $Cu \longrightarrow N$ π-bonds, which as a final consequence can lead to the shifts of frequencies ν(CN) and ν(CS) observed.

Thus, it is evident that the stretching frequency values of bridging NCS groups can occur in a relatively wide range depending on the number and character of coordination bonds of these groups. Naturally, it would be desirable to correlate the ν(CN) frequencies with the bonding mode of NCS groups for a greater number of compounds, but only rarely are both the crystal structure and infrared data for a certain compound known.

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