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A STUDY OF THE ELECTRONIC STRUCTURE OF THE THIOCYANATE ION

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1. INTRODUCTION

The behaviour of the thiocyanate ion is unusual from some points of view. In particular it is capable of forming chemical bonds through either the nitrogen atom or the sulphur atom. Such behaviour is common to organic and inorganic compounds.

Recently studies on transition metal compounds where the thiocyanate group often occurs as a ligand, have indicated that the preference towards sulphur or nitrogen bonding depends upon the nature of the central metal ion, and upon the nature of the other ligands[1,2].

Structural investigations[3–6] show that whilst the ion itself is always linear, the metal–ligand bond angle is different in the two cases. With nitrogen bonding, the metal–ligand bond angle is around 180°, whilst with sulphur, the metal–ligand bond angle is about 100°. It is clear from the angles involved, that with sulphur bonding, the orbitals of the ion which participate are essentially those of the π type in the free ion, whilst with nitrogen bonding the principal orbitals involved are those which are σ in the free ion. It is evident that the bidentate nature of the ion results in a competition between the σ and π orbitals to be involved in the chemical bond.

Another interesting characteristic of the thiocyanate ion occurs in its transition metal complexes. In such complexes an absorption hand occurs near 30,000 to 38,000 cm^{-1}. Such a band does not occur in the free ion, and is independent of the mode in which the ligand is hound.

These bands are definitely charge transfer in nature since they are independent of the central metal ion and its oxidation state[7]. It is very likely that the bands derive from a transition which is forbidden in the free ion, but becomes allowed when the ion is bonded. We feel that a study of the electronic structure of the free ion will he useful in explaining both the spectral properties, and the bidentate nature of the ion.

This is the aim of the present work, in which we conduct a semi-empirical quantum mechanical calculation.

2. METHOD OF CALCULATION

We have used the S.C.F.–L.C.A.O. molecular orbital theory[8,9] and have taken into account both σ and π molecular orbitals.

The approximations introduced are almost the same as those used by Pariser and Parr in their study of unsaturated hydrocarbons[10,11], namely:

a) All integrals of the type

$$\chi_p(1)\chi_q(1)\,d\tau_1 \tag{1}$$

where χ_p and χ_q are atomic orbitals on different atoms, have been put equal to zero ("differential overlap approximation").

b) In place of the integrals:

$$\begin{aligned} U_p &= \int \chi_p^*(1)[-\tfrac{1}{2}\nabla^2 + U_A]\chi_p(1)\,d\tau_1 \\ g_{pp} &= \int \chi_p^*(1)\chi_p^*(2)\frac{1}{r_{12}}\chi_p(1)\chi_p(2)\,d\tau_1\,d\tau_2 \\ g_{pq} &= \int \chi_p^*(1)\chi_q^*(2)\frac{1}{r_{12}}\chi_p(1)\chi_q(2)\,d\tau_1\,d\tau_2 - \\ &\qquad \tfrac{1}{2}\int \chi_p^*(1)\,\chi_q^*(2)\frac{1}{r_{12}}\chi_q(1)\chi_p(2)\,d\tau_1\,d\tau_2 \end{aligned} \tag{2}$$

we have used semi-empirical quantities which correctly give the energies of the various valence states[12] for each atom.

c) We associate with each *s* orbital a uniformly charged sphere, and to each *p* orbital, two tangential uniformly charged spheres. From a calculation of the resultant electrostatic repulsion energy, we have estimated the values of the two centre Coulomb integrals. The radii of the spheres have been so chosen that the values of the Coulomb integrals calculated therefrom are the same as the semi-empirical values of the one centre g_{pp} integrals when R, the distance between the two centres, approaches zero.

d) Integrals of the type

$$H_{pq} = \int \chi_p^*(1)H_{core}(1)\chi_q(1)\,d\tau_1 = \beta_{pq} \tag{3}$$

(χ_p and χ_q are atomic orbitals on different atoms) are evaluated according to the following expression:[13]

$$\beta_{pq} = \tfrac{1}{2}(I_p + I_q)S_{pq} \tag{4}$$

in which I_p and I_q are the χ_p and χ_q ionisation potentials respectively, when the atoms are in the valence state; S_{pq} is the overlap integral.

e) The penetration integrals

$$(\mathrm{B}: \chi_{p_A}{}^{*}\chi_{p_A}) = \int \chi_{p_A}{}^{*}(1)\mathrm{U_B}{}^{*}\chi_{p_A}(1)\,\mathrm{d}v_1 \tag{5}$$

(which represent the potential energy of the orbital χ_p on atom A, in the field $U_B{}^*$ of the neutral atom B) are evaluated in such a manner that they correctly reproduce the dissociation energies of the molecules CS and CN. The following atomic orbitals are used as a basis to construct the molecular orbitals (the orbitals $\chi_S(3p_\sigma)$, $\chi_C(2p_\sigma)$, $\chi_N(2p_\sigma)$ have the same orientation along the z axis. This axis passes through the S, C and N atoms, the nitrogen atom being on the positive side):

$$\begin{aligned}
&\text{Sulphur:}\quad \chi_S(3s),\ \chi_S(3p_\sigma),\ \chi_S(3p_\pi{}^{+}),\ \chi_S(3p_\pi{}^{-})\\
&\text{Carbon:}\quad \chi_C(2s),\ \chi_C(2p_\sigma),\ \chi_C(2p_\pi{}^{+}),\ \chi_C(2p_\pi{}^{-})\\
&\text{Nitrogen:}\quad \chi_N(2s),\ \chi_N(2p_\sigma),\ \chi_N(2p_\pi{}^{+}),\ \chi_N(2p_\pi{}^{-})
\end{aligned} \tag{6}$$

Assuming axial symmetry for the ion ($C_{\infty v}$), we have the following molecular orbitals:

a) six A_1 orbitals

$$\phi_{\sigma_1},\ \phi_{\sigma_2},\ \phi_{\sigma_3},\ \phi_{\sigma_4},\ \phi_{\sigma_5},\ \phi_{\sigma_6} \tag{7}$$

formed by the linear combination of the following atomic orbitals:

$$\chi_S(3s),\ \chi_S(3p_\sigma),\ \chi_C(2s),\ \chi_C(2p_\sigma),\ \chi_N(2s),\ \chi_N(2p_\sigma)\,. \tag{8}$$

b) six E_1 orbitals

$$\phi_{\pi_1}{}^{+},\ \phi_{\pi_1}{}^{-},\ \phi_{\pi_2}{}^{+},\ \phi_{\pi_2}{}^{-},\ \phi_{\pi_3}{}^{+},\ \phi_{\pi_3}{}^{-} \tag{9}$$

formed by the linear combination of the following atomic orbitals:

$$\chi_S(3p_\pi{}^{+}),\ \chi_C(2p_\pi{}^{+}),\ \chi_N(2p_\pi{}^{+}) \text{ and } \chi_S(3p_\pi{}^{-}),\ \chi_C(2p_\pi{}^{-}),\ \chi_N(2p_\pi{}^{-}) \tag{10}$$

The ground state wave function is

$$\Psi_\sigma({}^1\Sigma^{+}) = \mathrm{A}[(\phi_{\sigma_1})^2(\phi_{\sigma_2})^2(\phi_{\sigma_3})^2(\phi_{\sigma_4})^2(\phi_{\pi_1}{}^{+})^2(\phi_{\pi_2}{}^{+})^2\,(\phi_{\pi_1}{}^{-})^2\,(\phi_{\pi_2}{}^{-})^2] \tag{11}$$

in which A denotes an anti-symmetric product.

3. RESULTS AND CONCLUSIONS

We report in Fig.1 the energies of the various molecular levels as given by the roots of the secular equation.

The orbitals obtained are the following:

$$
\begin{aligned}
\phi_{\sigma_1} &= 0{,}243\chi_S(3s)+0{,}179\chi_S(3p_\sigma)+0{,}653\chi_C(2s)+0{,}168\chi_C(2p_\sigma)\\
&\quad + 0{,}637\chi_N(2s)-0{,}221\chi_N(2p_\sigma)\\
\phi_{\sigma_2} &= -0{,}598\chi_S(3s)-0{,}217\chi_S(3p_\sigma)-0{,}280\chi_C(2s)+0{,}555\chi_C(2p_\sigma)\\
&\quad + 0{,}452\chi_N(2s)+0{,}067\chi_N(2p_\sigma)\\
\phi_{\sigma_3} &= 0{,}478\chi_S(3s)-0{,}297\chi_S(3p_\sigma)-0{,}247\chi_C(2s)-0{,}144\chi_C(2p_\sigma)\\
&\quad + 0{,}418\chi_N(2s)+0{,}653\chi_N(2p_\sigma)\\
\phi_{\sigma_4} &= -0{,}444\chi_S(3s)+0{,}646\chi_S(3p_\sigma)+0{,}084\chi_C(2s)-0{,}370\chi_C(2p_\sigma)\\
&\quad + 0{,}161\chi_N(2s)+0{,}465\chi_N(2p_\sigma)\\
\phi_{\sigma_5} &= 0{,}379\chi_S(3s)-0{,}631\chi_S(3p_\sigma)+0{,}557\chi_C(2s)-0{,}319\chi_C(2p_\sigma)\\
&\quad - 0{,}097\chi_N(2s)+0{,}193\chi_N(2p_\sigma)\\
\phi_{\sigma_6} &= 0{,}118\chi_S(3s)+0{,}134\chi_S(3p_\sigma)+0{,}344\chi_C(2s)+0{,}635\chi_C(2p_\sigma)\\
&\quad - 0{,}424\chi_N(2s)+0{,}516\chi_N(2p_\sigma)\\
\phi_{\pi_1}{}^{+} &= 0{,}386\chi_S(3p_\pi{}^{+})+0{,}683\chi_C(2p_\pi{}^{+})+0{,}620\chi_N(2p_\pi{}^{+})\\
\phi_{\pi_1}{}^{-} &= 0{,}386\chi_S(3p_\pi{}^{-})+0{,}683\chi_C(2p_\pi{}^{-})+0{,}620\chi_N(2p_\pi{}^{-})\\
\phi_{\pi_2}{}^{+} &= -0{,}870\chi_S(3p^{+})+0{,}046\chi_C(2p^{+})+0{,}491\chi_N(2p^{+})\\
\phi_{\pi_2}{}^{-} &= -0{,}870\chi_S(3p^{-})+0{,}046\chi_C(2p^{-})+0{,}491\chi_N(2p^{-})\\
\phi_{\pi_3}{}^{+} &= -0{,}307\chi_S(3p^{+})+0{,}729\chi_C(2p^{+})-0{,}612\chi_N(2p^{+})\\
\phi_{\pi_3}{}^{-} &= -0{,}307\chi_S(3p^{-})+0{,}729\chi_C(2p^{-})-0{,}612\chi_N(2p^{-})
\end{aligned}
\tag{12}
$$

From these molecular orbitals we have calculated the charge distribution in the ion:

$$q_S = 0.48 \qquad q_C = 0.01 \qquad q_N = 0.51 \tag{13}$$

in good agreement with the values obtained from the resonance structures given by Llewellyn H. Jones[14] (obtained from an infrared study of KSCN)

$$q_S = 0.54 \qquad q_C = 0 \qquad q_N = 0.46 \tag{14}$$

The charge is almost equally distributed over the terminal atoms thus explaining the bidentate nature of the ion. It is not possible to draw any conclusion about the molecular orbitals in the chemical bond; it appears evident in fact, from these results, that the alternatives of forming a chemical bond to nitrogen or to sulphur, depends principally on the rearrangement of the electron distribution which accompanies the formation of the bond.

With regard to the spectral properties of the SCN group we consider now only those electronic states of the SCN^- ion derived from the excitation $\phi_{\pi_2}{}^{\pm} \rightarrow \phi_{\pi_3}{}^{\pm}$. One can, in such a case, construct four wave functions. We have

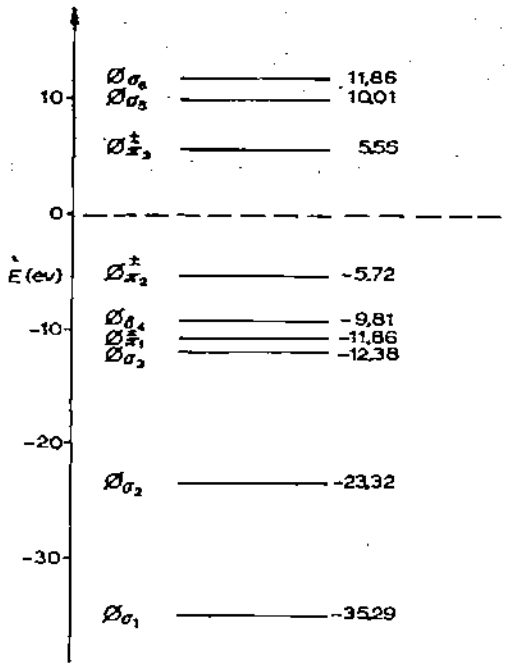

Fig. 1. Molecular orbital energy levels for the thiocyanate ion.

not included in these, the part due to the orbitals ϕ_σ and $\phi_{\pi_1}{}^{\pm}$ in as much as the electron distribution for these orbitals is equal to that of the ground state. The four wave functions are:

$$\Psi_1(^1\Sigma^+) = \frac{1}{\sqrt{2}}\left[\mathbf{A}[(\phi_{\pi_2}{}^+)^1(\phi_{\pi_2}{}^-)^2(\phi_{\pi_3}{}^+)^1] + \mathbf{A}[(\phi_{\pi_2}{}^+)^2(\phi_{\pi_2}{}^-)\ (\phi_{\pi_3}{}^-)^1]\right]$$

$$\Psi_2(^1\Sigma^-) = \frac{1}{\sqrt{2}}\left[\mathbf{A}[(\phi_{\pi_2}{}^+)^1(\phi_{\pi_2}{}^-)^2(\phi_{\pi_3}{}^+)^1] - \mathbf{A}[(\phi_{\pi_2}{}^+)^2(\phi_{\pi_2}{}^-)^1(\phi_{\pi_3}{}^-)^1]\right]$$

$$\Psi_3(^1\Delta) = \mathbf{A}[(\phi_{\pi_2}{}^+)^2(\phi_{\pi_2}{}^-)^1(\phi_{\pi_3}{}^+)^1]$$

$$\Psi_4(^1\Delta) = \mathbf{A}[(\phi_{\pi_2}{}^+)^1(\phi_{\pi_2}{}^-)^2(\phi_{\pi_3}{}^-)^1] \qquad (15)$$

in which the states described by the functions $\Psi_3(^1\Delta)$ and $\Psi_4(^1\Delta)$ are degenerate, and **A** denotes a singlet antisymmetrical product.

From the four possible transitions:

$$\Psi_0(^1\Sigma^+) \rightarrow \Psi_1(^1\Sigma^+)$$
$$\Psi_0(^1\Sigma^+) \rightarrow \Psi_2(^1\Sigma^-)$$
$$\Psi_0(^1\Sigma^+) \rightarrow \Psi_3(^1\Delta)$$
$$\Psi_0(^1\Sigma^+) \rightarrow \Psi_4(^1\Delta) \qquad (16)$$

only the first is allowed.

The calculated energy for the allowed transition is 8.07 eV, equivalent to 65,100 cm^{-1}. This result is in good agreement with the experimental data in that the absorption band of KNCS, in aqueous solution occurs above 50,000 cm^{-1}, and in the solid occurs[7] at 55,000 cm^{-1}.

Of the three forbidden transitions, we consider only $\psi_0(^1\Sigma^+) \rightarrow \psi_2(^1\Sigma^-)$, the calculated energy is 4.56 eV (36,800 cm^{-1}). From the above discussion it is evident that this transition, though forbidden in the free ion may become allowed when the thiocyanate ion is bonded to a metal, and may be responsible for the band observed in this region in transition metal thiocyanates.

The interactions between the various excited configurations, and the allowed transitions when the group is bonded to a metal atom, will be the subject of future investigations.

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