

Comparative study on the IR spectra of some transition metal dithiocarbamates

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(Received: October 01, 2008; Accepted: November 04, 2008)

ABSTRACT

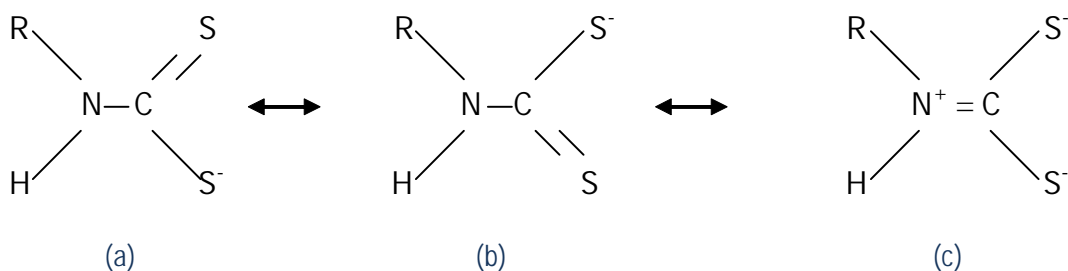
This study explores how the changes of the electron density due to the substitution of the various substituents on the nitrogen atom of the various amines manifest themselves in the shifts of principal absorption bands attributed to the $\nu(\text{C-N})$, $\nu(\text{C-S})$ and $\nu(\text{M-S})$ stretching vibrations.

Key words: IR spectra, transition metal dithiocarbamates.

INTRODUCTION

Extensive studies have been reported on the mode of bonding of dithiocarbamate ligands to

the metal¹⁻³. The different resonating structures of the dithiocarbamate moiety can be represented as:



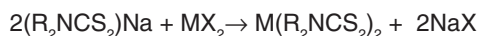
The extent to which these resonance forms contribute to the other structure and this effect on the physical and chemical properties have been extensively studied. It was suggested that the resonance form (c) contributes to the structure to a considerable extent, but resonance forms (a) and (b) too contributing equally to the structure provided dipole moment studies were also taken into consideration⁴. It was also pointed out that the contribution of the resonance form (c) is greater than that of the others to the total structure of dithiocarbamate complexes and it increases appreciably in n-alkyl derivatives⁵.

Extending our work^{6,7} on transition metal dithiocarbamates, we are reporting here the comparative study on the IR spectra of some transition metal dithiocarbamates.

EXPERIMENTAL

All amines viz. dimethylamine, diethylamine, dipropylamine, diisopropylamine, diisobutylamine, piperidine; carbon disulphide, sodium hydroxide, salts of nickel, copper and zinc (all E. Merck) were used as such. Solvents (all BDH) were purified by standard methods⁸ before use.

In the present work, the replacement reaction method⁹ was adopted for the synthesis of all the complexes studied. This method involves replacement reaction using the sodium salt of the dithiocarbamate with metal salt.



The infrared spectra of the prepared sodium dithiocarbamates as well as metal dithiocarbamates were scanned by Nujol technique in the region 4000-200 cm^{-1} on Perkin Elmer Model 1620 Fourier-Transform Infrared (FT-IR) spectrophotometer by Jamia Millia Islamia University, New Delhi, India.

RESULTS AND DISCUSSION

The major interest in the preparation of these transition metal dithiocarbamates was to study the effect of the attachment of dithiocarbamate

ligand to 3d-transition metal in presence of different organic substituents (R). Dithiocarbamates, general formula $M(R_2NCS_2)_2$, possess a lone electron pair at the nitrogen atom, that brings about conjugation with CSS group. Thus the electron density at the C-N, C-S and M-S bonds can be affected by the replacement of hydrocarbon chains.

The Tables 1 and 2 present the IR spectral

Table 1: IR Spectral data of sodium dithiocarbamates

Compound	$\nu(C-N)$	$\nu(C-S)$
Na[Me ₂ dtc]	1490	989
Na[Et ₂ dtc]	1480	990
Na[Pr ₂ dtc]	1470	980
Na[iPr ₂ dtc]	1440	945
Na[iBu ₂ dtc]	1470	980
Na[Pip dtc]	1475	980

Table 2: IR Spectral data of Ni(II),Cu(II) and Zn(II) dithiocarbamates of the type ML₂

L	NiL ₂			CuL ₂			ZnL ₂		
	$\nu(C-N)$	$\nu(C-S)$	$\nu(M-S)$	$\nu(C-N)$	$\nu(C-S)$	$\nu(M-S)$	$\nu(C-N)$	$\nu(C-S)$	$\nu(M-S)$
[Me ₂ dtc] ⁻	1532	974	384	1528	976	352	1525	975	379
[Et ₂ dtc] ⁻	1522	993	387	1508	995	356	1505	995	380,400
[Pr ₂ dtc] ⁻	1516	976	385	1505	985	354	1501	976	375,385
[iPr ₂ dtc] ⁻	1503	945	402	1495	943	376	1485	945	395, 410
[iBu ₂ dtc] ⁻	1508	985	391	1505	985	386	1485	987	390
[Pip dtc] ⁻	1518	1000	388	1505	996	398	1490	985	399

Table 3: Average bond lengths (pm) of C-N, C-S and M-S bonds in some Ni(II), Cu(II) and Zn(II) dithiocarbamates

Compound	C-N Bond	C-S Bond	M-S bond
Ni[Et ₂ dtc] ₂	133	170.7	2201
Ni[Pr ₂ dtc] ₂	133	170.8	220.3
Ni[iPr ₂ dtc] ₂	133	170.5	218.1
Ni[Pip dtc] ₂	132	167.8	220.6
Cu[Me ₂ dtc] ₂	131	172.1	231.05
Cu[Et ₂ dtc] ₂	134	171.7	242.1
Cu[Pr ₂ dtc] ₂	133	172.2	242.8
Cu[Pip dtc] ₂	133	172.5	229.5
Zn[Me ₂ dtc] ₂	134.7	172.1	245.3
Zn[Et ₂ dtc] ₂	135.7	172.7	246.5

data of sodium dithiocarbamates and dithiocarbamate chelates respectively. Table 3 presents data on the C-N, C-S and M-S average bond lengths found in literature.¹⁰⁻¹⁸

The $\nu(\text{C-N})$ band position was seen to be affected mainly by the nature of central atom and the character of the group attached to the nitrogen atom. On the other hand the structure of the coordination sphere did not affect appreciably the positions of the absorption bands pursued, it influenced the band shape in the region 440-350 cm^{-1} . The $\nu(\text{M-S})$ absorption bands comprised vibrations of all M-S bonds and were also affected by vibrations of the remaining parts of the molecule. The effect of the substituents bonded at the nitrogen atom on the electron density distribution at the C-N, C-S and M-S bonds could be best studied on the nickel bis(dithiocarbamate) chelates, where the inner coordination sphere was the same in all cases, viz. planar (the nickel atom was in the centre of symmetry of the basic cell).

If a methyl group is substituted for hydrogen at the nitrogen atom, the wave number of the $\nu(\text{C-N})$ band increases substantially,^{4,19-21} due to the hyperconjugation effect of the methyl group. As seen from the Table 2, lengthening of the alkyl chain was accompanied by a decrease of the $\nu(\text{C-N})$ band wave number; the lowest values were observed for $\text{Ni}(\text{Bu}_2 \text{ dtc})_2$, $\text{Cu}(\text{Pr}_2 \text{ dtc})_2$ and $\text{Zn}(\text{Pr}_2 \text{ dtc})_2$; further lengthening of the chain did not lead to appreciable changes. Taking into account that the lengthening of the alkyl chain on from $\text{Ni}(\text{Et}_2 \text{ dtc})_2$ to $\text{Ni}(\text{Pr}_2 \text{ dtc})_2$ was not accompanied by a change in the C-N bond length, the gradual lowering of the $\nu(\text{C-N})$ vibrational frequency with lengthening alkyl chain, occurring in spite of the increasing inductive effect of the alkyl groups, could be attributed to the growing mass of the latter. This was in accordance with the observations²² concerning the proportions of influence of the kinematic and electronic factors on the vibrations of bonds in dithiocarbamates. The frequencies of the chelates derived from piperidine and their C-N interatomic distances were comparable with alkyl groups possessing the same number of carbon atoms.

The dependence of the $\nu(\text{C-S})$ vibrational frequency on the length of the alkyl chain at the

nitrogen atom was somewhat complex. The lowering of the $\nu(\text{C-S})$ frequencies with the lengthening alkyl chain was ascribed to the growing mass of the alkyl group. The irregularities in the wave numbers were associated with their spatial arrangement.

As evident from the Table 3, the C-N and C-S bond lengths of the nickel chelates practically remained constant with changing alkyl substituent at the nitrogen atom, which indicates that the +I effect of the alkyl groups practically did not appear at these bonds. However in $\text{Ni}(\text{iPr}_2 \text{ dtc})_2$ the electron density at the M-S bond was enhanced and the bond was appreciably shortened, which could be explained by combination of the hyperconjugation and inductive effects of the isopropyl groups and conjugation of the electronic system of the substance, enabling charge transfer from the alkyl groups as far as the M-S bonds. This view was also supported by the $\nu(\text{M-S})$ vibrational wave numbers of $\text{Ni}(\text{iPr}_2 \text{ dtc})_2$, $\text{Cu}(\text{iPr}_2 \text{ dtc})_2$ and $\text{Zn}(\text{iPr}_2 \text{ dtc})_2$, which were 17, 22 and 20 cm^{-1} respectively, higher than those of the respective n-derivatives.

In the case of sodium dithiocarbamates, the electronic effects were affected by the presence of the lone electron pairs at the sulphur atom, which prevented delocalization of the nitrogen electrons towards the $-\text{CS}_2$ group, because the negative charge at the sulphur atom acted against the electron donor tendency of the alkyl groups. The hyperconjugation effect and the kinematic factors affected the $\nu(\text{C-N})$ frequencies similarly as in the dithiocarbamate chelates, but the $\nu(\text{C-N})$ bands appeared at lower wave numbers because of the lower π -share in the C-N bond. The mutually close positions of the $\nu(\text{C-S})$ bands of the sodium dithiocarbamates and metal dithiocarbamates implied that the effect of the M-S bond on the $\nu(\text{C-S})$ vibrational frequencies was not very marked.

CONCLUSION

With respect to all these experimental facts we could conclude that the position of the absorption bands of the dithiocarbamates is affected mainly by the nature of the central atom and the character of the group bonded to the nitrogen atom, influencing the charge density distribution at the C-N and M-S

bonds. The structure of the coordination sphere affects the M-S and C-N bonds which however manifests itself only in the IR band shape, the $\nu(\text{C-N})$, $\nu(\text{C-S})$ and $\nu(\text{M-S})$ band positions remaining unchanged.

ACKNOWLEDGEMENTS

We are grateful to the Principal and the Chairman, Department of Chemistry, G.F.(P.G.) College, Shahjahanpur(UP), India for providing the necessary infrastructure for this work.

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