RELATION BETWEEN THE INFRARED SPECTRA OF METAL DITHIOCARBAMATES AND THEIR CRYSTAL STRUCTURE AND ELECTRONIC EFFECTS OF SUBSTITUENTS

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Received April 9th, 1979

The IR spectra of dithiocarbamic acids alkali salts and Ni(II), Cu(II), and Zn(II) chelates are studied in the region of 3 800—200 cm^{-1}. The results are correlated with X-ray diffraction data. 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 ν(C—N), ν(C—S), and ν(M—S) band positions remaining unaltered.

Dithiocarbamates, general formula $M(R_2NCS_2)_2$, possess a lone electron pair at the nitrogen atom, which brings about conjugation with the CSS group; thus the electron density at the C—N, C—S, and M—S bonds can be affected by the hydrocarbon chains. The aim of the present work was to seek, how the changes of the electron density effected by both replacement of the alkyl substituents at the nitrogen atom and changes in the coordination sphere of the metal atom manifest themselves in the shifts of the principal absorption bands in the infrared spectra of the dithiocarbamates, particularly the band near 1 500 cm^{-1}, attributed to the ν(C—N) stretching vibration[1-4], the band in the 960 cm^{-1} range, belonging to the ν(C—S) stretching vibration[5-7], and the band in the region 400 – 350 cm^{-1}, due to the ν(M—S) stretching vibration[8-10].

EXPERIMENTAL

The infrared spectra of nickel, copper, and zinc bis(dithiocarbamate) chelates as well as of alkali dithiocarbamates were scanned in the region 3 800—400 cm^{-1} on a spectrophotometer UR 20 (Zeiss, Jena) in KBr disks, and in the region 600—200 cm^{-1} on an instrument Perkin-Elmer 225 in Nujol mulls.

RESULTS AND DISCUSSION

The positions of the ν(C—N) and ν(C—S) absorption bands of alkali dithiocarbamates are given in Table I, those of the ν(C—N), ν(C—S), and ν(M—S) bands of the dithiocarbamate chelates are listed in Table II. Table III presents data on the C—N, C—S, and M—S bond lengths found in literature.

The ν(C—N) band position is seen to be affected mainly by the nature of the central atom and the character of the group attached to the nitrogen atom. The structure of the coordination sphere does not affect appreciably the ν(C—N), ν(C—S), and ν(M—S) band positions despite the associated changes in the C—N and M—S bond lengths. These bonds are shortest in the Ni(II) and Cu(II) dithiocarbamates possessing planar structure. High differences in the C—N and M—S bond lengths are found between $Cu(Me_2DTC)_2$ and $Cu(Et_2DTC)_2$ (for the abbreviations used in the formulas see Table I footnote), the bonds being shorter in the former compounds. The difference in the M—S bond length can be related to the differences in the chelate structures, whereas the relatively smaller difference in the C—N bond length is probably associated with the electronic effects of the alkyl groups. While in $Cu(Me_2DTC)_2$ the CuS_4 coordination sphere is really planar and the molecules form chains only *via* weak interactions of Cu—S (319 pm), in $Cu(Et_2DTC)_2$ the Cu(II) atom is 26 pm tilted from the S_4 plane, the coordination can be looked upon as tetragonally pyramidal, and the substance exists in dimer form. This arrangement of the latter compound brings about a lengthening of the M—S bonds and thereby their weakening as compared with the corresponding bonds in $Cu(Me_2DTC)_2$. This concept is supported by the data on the M—S bond lengths in $Cu(PpDTC)_2$: the square planar coordination of CuS_4 is in this case obviously due to the presence of the bulky substituent, which sterically hinders formation of pyramidal configuration of the central atom. Since this complex does not involve any methyl group, the electron density at the C—N bond is not increased on account of hyperconjugation and thus the bond is not shortened; M—S bonds, on the other hand, are shortened owing to the more stable planar structure.

Comparing the data of Tables I and II we find that the lowering of the average M—S interatomic distances in $Cu(Me_2DTC)_2$ in comparison with the ethyl derivative is not adequately reflected by the shift of the ν(M—S) band to higher wavenumbers. Obviously, the axial bonds joining the CuS_4 chains do not have a substantial effect on the M—S stretching vibration; this is corroborated also by the good relation between the ν(M—S) wavenumbers and the average CuS_4 bond lengths in the substances $Cu(Me_2DTC)_2$, $Cu(Et_2DTC)_2$, $Cu(Pr_2DTC)_2$, and $Cu(PpDTC)_2$.

Although the structure of the coordination sphere does not affect appreciably the positions of the absorption bands pursued, it influences the band shape in the region of 440–350 cm^{-1}. The ν(M—S) absorption bands comprise vibrations of all M—S bonds and are also affected by vibrations of the remaining parts of the molecule. The different energies of these bonds bring about band splitting (if the bond

TABLE I

Wavenumbers (cm^{-1}) of the ν(C—N) and ν(C—S) Vibrations of Dithiocarbamic Acids Alkali Salts

Compound[a]	ν(C—N)	ν(C—S)
$NaMe_2DTC$	1 490	989
$NaEt_2DTC$	1 480	990
KPr_2DTC	1 470	980
KPpDTC	1 475	980
KMoDTC	1 450	1 000
$NaiPr_2DTC$	1 440	945
$NaiBu_2DTC$	1 470	980
KMe,iPrDTC	1 485	975

[a] Symbols used: DTC dithiocarbamate, Me methyl. Et ethyl, Pr propyl, iPr isopropyl, Bu butyl, Pe pentyl, Hp heptyl, Oc octyl, Pp 1-piperidyl, Mo 4-morpholinyl.

TABLE II

Wavenumbers (cm^{-1}) of Vibrations of the C—N, C—S, and M—S Bonds in Ni(II), Cu(II), and Zn(II) Dithiocarbamates of the Type ML_2

L[a]	NiL_2			CuL_2			ZnL_2		
	ν(C—N)	ν(C—S)	ν(M—S)	ν(C—N)	ν(C—S)	ν(M—S)	ν(C—N)	ν(C—S)	ν(M—S)
$(Me_2DTC)^-$	1 532	974	384	1 528	976	352	1 525	975	379
$(Et_2DTC)^-$	1 522	993	387	1 508	995	356	1 505	995	380 400
$(Pr_2DTC)^-$	1 516	976	385	1 505	985	354	1 501	976	375 385
$(Bu_2DTC)^-$	1 511	972	—	1 506	965	—	1 504	965	—
$(Pe_2DTC)^-$	1 516	974	—	1 506	976	—	1 507	963	—
$(He_2DTC)^-$	1 515	977	—	1 503	980	—	1 500	973	—
$(Hp_2DTC)^-$	1 510	977	—	[b]	[b]	[b]	[b]	[b]	[b]
$(Oc_2DTC^-)^-$	1 506	976	—	[b]	[b]	[b]	[b]	[b]	[b]
$(iPr_2DTC)^-$	1 503	945	402	1 495	943	376	1 485	945	395 410
$(iBu_2DTC)^-$	1 508	985	—	1505	985	—	1 485	987	—
$(PpDTC)^-$	1 518	1 000	388	1 505	995	352	1 490	985	—
$(MoDTC)^-$	1 501	1 015 1 025	—	1 485	1 015 1 025	—	1 466	1 118 1 126	—

[a] For symbols see footnote to Table I; [b] the compound has not been prepared.

TABLE III

Interatomic Distances (pm) of the Bonds C—N, C—S, and M—S in Some Ni(II), Cu(II), and Zn(II) Dithiocarbamates

Compound^a	C—N bond	C—S bond	M—S bond	Ref.
Ni((Et$_2$)DTC)$_2$	C—N 133	C—S$_1$ 171·3 C—S$_2$ 170·0 average 170·7	M—S$_1$ 219·5 M—S$_2$ 220·7 average 220·1	13
Ni(Pr$_2$DTC)$_2$	C—N 133	C—S$_1$ 172·2 C—S$_2$ 169·3 average 170·8	M—S$_1$ 219·7 M—S$_2$ 220·9 average 220·3	14
Ni(iPr$_2$DTC)$_2$	C—N 133	C—S$_1$ 172 C—S$_2$ 169 average 170·5	M—S$_1$ 218·0 M—S$_2$ 218·2 average 218·1	15
Ni(PpDTC)$_2$	C—N 132	C—S$_1$ 171·8 C—S$_2$ 163·7 average 167·8	M—S$_1$ 220·1 M—S$_2$ 221·1 average 220·6	16
Cu(Me$_2$DTC)$_2$	C—N 131	C—S$_1$ 172·6 C—S$_2$ 171·6 average 172·1	M—S$_1$ 230·2 M—S$_2$ 231·9 average 231·05	17
Cu(Et$_2$DTC)$_2$	C$_1$—N 133 C$_2$—N 135 average 134	C$_1$—S$_1$ 171·3 C$_1$—S$_2$ 170·8 C$_2$—S$_3$ 171·1 C$_2$—S$_4$ 173·6 average 171·7	M—S$_1$ 230·1 M—S$_2$ 229·7 M—S$_3$ 231·7 M—S$_4$ 233·9 M—S$'_4$ 285·1 average 242·1	18
Cu(Pr$_2$DTC)$_2$	C$_1$—N 132 C$_2$—N 134 average 133	C$_1$—S$_1$ 172·4 C$_1$—S$_2$ 171·5 C$_2$—S$_3$ 171·1 C$_2$—S$_4$ 173·5 average 172·2	M—S$_1$ 232·3 M—S$_2$ 232·4 M—S$_3$ 232·2 M—S$_4$ 233·2 M—S$'_4$ 274·1 average 242·8	19
Cu(PpDTC)$_2$	C—N 133	C—S$_1$ 173·6 C—S$_2$ 171·4 average 172·5	M—S$_1$ 228·6 M—S$_2$ 230·3 average 229·5	20
Zn(Me$_2$DTC)$_2$	C$_1$—N 132·5 C$_2$—N 136·8 average 134·7	C—S$_1$ 169·9 C—S$_2$ 173·9 C—S$_3$ 174·8 C—S$_4$ 170·0 average 172·1	M—S$_1$ 231·2 M—S$_2$ 242·9 M—S$_3$ 233·3 M—S$'_4$ 237·3 M—S$_4$ 282 average 245·3	21

TABLE III
(*Continued*)

Compound[a]	C—N bond	C—S bond	M—S bond	Ref.
$Zn(Et_2DTC)_2$	C_1—N 134 C_2—N 137·3 average 135·7	C—S_1 173·7 C—S_2 172·3 C—S_3 172·5 C—S_4 172·2 average 172·7	M—S_1 235·5 M—S_2 244·3 M—S_3 233·1 M—S'_4 238·3 M—S_4 281·5 average 246·5	13

[a] For symbols see footnote to Table I.

lengths differ more than 50 pm) or at least asymmetry in the band shape and occurrence of shoulders (if the bond length differences are smaller); only if the bond lengths differ less than 2 pm, the symmetry of the bands remains intact. The IR spectra of roughly symmetrical coordination formations, where the bond lengths are approximately equal (planar nickel chelates), are therefore simpler, whereas those of deformed formations (most of the copper and zinc chelates) are more complex. The complexity of the spectrum and splitting of the bands in the case of $Ni(Me_2DTC)_2$ along with the high melting point of the substance (>340°C) indicate that the compound occurs in dimer or polymer form, in which the coordination is not strictly square planar. The analogous splitting of the ν(M—S) bands and complexity of spectra of the zinc chelates point to the occurrence of dimers.

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 can be best investigated on the nickel bis(dithiocarbamate) chelates, where the inner coordination sphere is the same in all cases, *viz.* planar (the nickel atom lies in the centre of symmetry of the basic cell).

If a methyl group is substituted for hydrogen at the nitrogen atom, the wavenumber of the ν(C—N) band increases substantially[1,2,6,11], obviously on account of the hyperconjugation effect of the methyl group. As can be seen from Table II, lengthening of the alkyl chain is accompanied by a decrease of the ν(C—N) band wavenumber; the lowest values are found for $Ni(Bu_2DTC)_2$, $Cu(Pr_2DTC)_2$, and $Zn(Pr_2DTC)_2$, further lengthening of the chain does not lead to appreciable changes. Taking into account that the lengthening of the alkyl chain on going from $Ni(Et_2DTC)_2$ to $Ni(Pr_2DTC)_2$ is not accompanied by a change in the C—N bond length, the gradual lowering of the ν(C—N) vibrational frequency with lengthening alkyl chain, occurring in spite of the increasing inductive effect of the alkyl groups, can be ascribed to the growing mass of the latter. This is in accordance with the findings[12] concerning the proportions of influence of the kinematic and electronic factors on the vibrations of bonds in dithiocarbamates. The lowest ν(C—N) frequenceis pertain to 4-morpholine carbodithioic acid chelates and potassium salt, which can be explained in terms of the lowering of electron density at the C—N bond brought about by the highly electronegative oxygen atom in the ring. In agreement with this concept, the chelates derived from piperidine do not exhibit such anomaly, their frequencies and C—N interatomic distances being comparable with the values for the derivatives with alkyl groups possessing the same number of carbon atoms.

The dependence of the ν(C—S) vibrational frequency on the length of the alkyl chain at the nitrogen atom is rather complex. The C—S bond lengths in derivatives involving different alkyl substituents and the same central atom, whose inner coordination sphere is the same, are nearly equal; it can be therefore assumed that electronic effects practically do not influence the ν(C—S) vibrations. It is thus reasonable to attribute the lowering of the ν(C—S) frequencies with the lengthening alkyl chain to the growing mass of the alkyl group, the irregularities in the wavenumbers being associated with their spatial arrangement.

As mentioned above, the C—N and C—S bond lengths of the nickel chelates practically remain constant with changing alkyl substituent at the nitrogen atom (Table III), which implies that the +I inductive effect of the alkyl groups practically does not appear at these bonds. However, in $Ni(iPr_2DTC)_2$ the electron density at the M—S bond is enhanced and the bond is appreciably shortened, which can 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 is supported also by the ν(M—S) vibrational wavenumbers of $Ni(iPr_2DTC)_2$, $Cu(iPr_2DTC)_2$, and $Zn(iPr_2.DTC)_2$, which are 17, 22, and 20 cm^{-1}, respectively, higher than those of the respective *n*-derivatives.

In the alkali salts, the electronic effects are affected by the presence of the lone electron pairs at the sulphur atom, which prevent delocalization of the nitrogen electrons towards the —CS_2 group, because the negative charge at the sulphur atom acts against the electron donor effect of the alkyl groups. The hyperconjugation effect and the kinematic factors affect the ν(C—N) frequencies similarly as in the dithiocarbamate chelates, but the ν(C—N) bands lie at lower wavenumbers because of the lower π-share in the C—N bond. The mutually close positions of the ν(C—S) bands of the dithiocarbamic alkali salts and metal chelates imply that the effect of the M—S bond on the ν(C—S) vibrational frequencies is not very marked.

REFERENCES

1. Chatt J., Duncanson L. A., Venasi L. M.: Nature (London) *177*, 1042 (1956).
2. Pilipenko A. T., Melnikova N. V.: Ukr. Khim. Zh. *36*, 671 (1970).
3. Vigee C. S., Watkins C. L.: J. Inorg. Nucl. Chem. *34*, 3936 (1972).
4. Marcotrigiano G., Pallacini G. C., Preti C.: J. Inorg. Nucl. Chem. *36*, 3709 (1974).
5. Pilipenko A. T., Melnikova N. V.: Zh. Neorg. Khim. *14*, 462 (1969).
6. Melnikova N. V.: Zh. Prikl. Spektrosk. *12*, 1041 (1970).
7. Jensen K. A., Dahl B. M., Nielsen P. H., Borch G.: Acta Chem. Scand. *25*, 2029 (1971).
8. Durgaprasad G., Sathianarayana D. N., Patel C. C.: Can. J. Chem. *47*, 631 (1969).
9. Kellner R.: Anal. Chim. Acta *63*, 277 (1973).
10. Kellner R.: Anal. Chim. Acta *86*, 203 (1976).
11. Melnikova N. V., Pilipenko A. T.: Ukr. Khim. Zh. *35*, 951 (1969).
12. Brown D. A., Glass W. K., Burke M. A.: Spectrochim. Acta *A32*, 137 (1975).
13. Bonamico M., Dessy G., Mariani C., Vaciago A., Zambonelli L.: Acta Crystallogr. *19*, 619, 886, 898 (1965).
14. Peyronel G., Pignedoli A., Antolini L.: Acta Crystallogr. *B28*, 3596 (1972).
15. Newman P. W. C., White A. N.: J. Chem. Soc., Dalton Trans. *1972*, 2238
16. Kettman V., Garaj J., Kúdela Š.: This Journal *43*, 1204 (1978).
17. Field J. S., Einstein F. W. B.: Acta Crystallogr. *B30*, 2928 (1974).
18. Willa J. F., Hatfield W. E.: Inorg. Chem. *10*, 2038 (1971).
19. Peyronel G., Pignedoli A.: Acta Crystallogr. *23*, 398 (1967).
20. Kettman V., Garaj J., Kúdela Š.: This Journal *42*, 402 (1977).
21. Klug H. P.: Acta Crystallogr. *21*, 536 (1966).

Translated by P. Adámek.