A study of the nature of coordination in metal monothiocarbamates based on infrared spectroscopy and the HSAB concept

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Abstract. The nature of coordination in metal monothiocarbamates is shown to depend on the hardness or softness of the metal ion. Thus, the monothiocarbamate ion acts as a monodentate ligand with metal-sulphur bonding when the metal ion is a soft acid while it acts as a bidentate ligand when the metal ion is a hard acid; it can exhibit either behaviour when the metal ion is a borderline acid. In dialkyltin and dialkylmonocholorotin complexes, the monothiocarbamate ion acts as a bidentate ligand with strong Sn–S bonding while in trialkyl-or triaryl-tin complexes it acts essentially as a monodentate ligand. Thus, $R_3Sn(I)$ seems to be a soft or borderline acid while $R_2Sn(II)$ is a hard acid.

Keywords. Monothiocarbamates; hard and soft acids; infrared spectra of monothiocarbamates; organotin monothiocarbamates.

1. Introduction

The monothiocarbamate (MTC) ligand is an interesting ambident anion where the metal ion can coordinate with sulphur or oxygen. Recent structural and infrared spectral studies of MTC complexes of metals have shown that the MTC ion can act as a monodentate ligand with metal-sulphur bonding or as a bidentate ligand with both oxygen and sulphur involved in the coordination. There appear to be some instances where the infrared spectra cannot unambiguously decide the nature of coordination. We thought that it should be possible to rationalise the infrared spectra and structures of these metal complexes based on considerations of the basicity of the ligand sites and the acidity of the metal ions. By virtue of the differences in the electronegativities of sulphur and oxygen, the basicities of the two sites are considerably different. In the Drago–Weyland (1965) scale the base parameter C_B will be much higher for sulphur than for oxygen, while E_B will be smaller

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P.(A)—1

for sulphur. We would, therefore, expect systematic variations in the nature of coordination of metal ions to the MTC ion. In this paper, we report the normal vibrations of the MTC anion and classify metal complexes based on systematics in the infrared spectra. We have shown that such a classification of metal ions is consistent with the hard and soft acids and bases (HSAB) concept (Pearson 1963). We have also analysed the infrared spectra of several types of organotin complexes of MTC and tentatively assigned their configurations.

2. Experimental

Infrared spectra were recorded on Perkin–Elmer 12A and 580 spectrometers. Methods of preparation of organotin monothiocarbamates are those described in the literature (Crosby *et al* 1979).

3. Normal vibrations of monothiocarbamate ion

In table 1, we have listed the important vibrational frequencies in the ir spectrum of the Me_2 MTC anion. The broad band around 1520 cm^{-1} shows the presence of a shoulder around 1570 cm^{-1}. In principle, we can consider the 1570 cm^{-1} band as due to C=O stretching and the 1520 cm^{-1} band as due to C⋯N stretching. However, normal vibrational analysis shows that both these bands have contributions

Table 1. Important normal vibrations of monothiocarbamate ion[a].

Band position, cm^{-1}	Assignment
1570 (sh)	ν (C=O) + ν (C–N)[b]
1520 (S)	ν (C=O) + ν (C–N)[b]
1030	ν_{asym} (CNC)
990	ν (CS)[c]
930	ν_{sym} (CNC)
825	ν (CNC)
700	γ (NCOS)
615	δ (NCO)
535	ν (CS) + δ (SCO)
415	δ (SCO)
300	ρ (SCO) + δ (CNC)

(*a*) Analysis is made of the bands of N,N-dimethyl monothiocarbamate.

(*b*) Both these bands are due to mixed vibrations and can be written as ν (C⋯O + C⋯N). In the 1570 cm^{-1} band, contribution of (C=O) is over 65% while in the 1520 cm^{-1} band the contribution is less than 50%.

(*c*) This is the stretching mode of the C⋯S bond of MTC.

from these two stretching modes with the 1570 cm⁻¹ band having a greater contribution from C=O stretching. We shall designate the 1570 cm⁻¹ band as due to v (C⋯O + C⋯N) mixed mode. It would, therefore, be appropriate to consider the relative position of the 1570 cm⁻¹ band due to v (C⋯O + C⋯N) as indicative of the nature of coordination in metal complexes. The other bands that may be affected by metal coordination are those at 990, 700, 615, 535 and 415 cm⁻¹ (table 1). However, shifts of these bands may not provide clear-cut information on the nature of coordination.

Normal vibration analysis of N,N-dimethylmonothiocarbamate ion, Me₂ MTC, was carried out by employing Urey–Bradley force field. The structural parameters for the ion could be obtained by comparison with related molecules and also from x-ray data of some of the metal complexes. The first set of force constants could be taken from related ions and amide type derivatives (Tantry and Shankaranarayana 1979). The final set of stretching force constants which gave reasonable agreement with observed frequencies is the following:

k (C⋯O)   8·7 mdyne/Å; k (C⋯N)   5·6 mdyne/Å

k (C—S)   3·4 mdyne/Å; k (C—N)   3·3 mdyne/Å.

4. Classification of metal complexes based on infrared spectra

As mentioned earlier, literature reports on MTC complexes of metals indicate the presence of either metal-sulphur coordination where the MTC acts as a monodentate ligand or both metal-sulphur and metal-oxygen coordination where the MTC ion acts as a bidentate ligand. It appears that of the three important resonance structures of MTC ion (I to III), only the first two appear to be of significance in explaining the coordination in metal complexes. The resonance form I would favour

$$\mathrm{I} \qquad\qquad \mathrm{II} \qquad\qquad \mathrm{III}$$
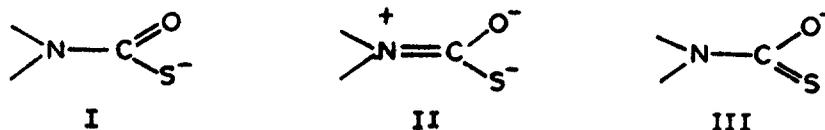
metal-sulphur bonding (monodentate ligand) while II would favour a bidentate ligand. If MTC ion acts as a monodentate ligand, we would expect a higher C=S stretching vibrational frequency than when the MTC ion acts as a bidentate ligand. Accordingly, a few workers have suggested that the appearance of a band above 1545 cm⁻¹ (C⋯O + C⋯N stretching) would indicate that the MTC ion is present as a monodentate ligand bonded through sulphur; conversely, an ir band below 1545 cm⁻¹ due to C⋯O + C⋯N stretching is considered to be characteristic of a bidentate ion (Krankovits *et al* 1971; Pijpers *et al* 1974). Although such a generalisation has been criticised due to the observation of a band around 1565 cm⁻¹ in a cobalt complex with a chelated MTC ligand (involving a Co–O bond of 2·16 Å), it is our considered view that this criterion (based on the position of the C⋯O + C⋯N stretching band) would serve a useful purpose in classifying metal monothiocarbamates.

In table 2 we have listed the position of the C⋯O + C⋯N stretching band in a number of MTC complexes. We can clearly see two distinct ranges of C⋯O + C⋯N stretching frequencies, 1550–1590 and 1510–1550 cm⁻¹, of which the former

can be considered to be characteristic of monodentate MTC complexes and the latter as due to bidentate complexes. In the case of Zn(II) and Fe(II), we see evidence for both monodentate and bidentate complexes; the same is the case with the Mn(I) complex. We shall discuss these complexes later in the light of the HSAB concept.

Vibrational frequencies of MTC other than the $C\text{---}O + C\text{---}N$ stretching frequency are also affected in the complexes. Thus, we see that the v $(C\text{---}S)$ mode around 990 cm⁻¹ in the ligand is shifted to lower frequencies in all other complexes (generally in the range 900–950 cm⁻¹). The Hg(II) complex where the MTC acts as a monodentate ligand shows this at 900 cm⁻¹ while the Re complex shows this around 920 cm⁻¹. Complexes of Ni, Ti and Zr where MTC is a bidentate ligand show this in the range of 932–940 cm⁻¹. While we are tempted to suggest that the lowering of the v $(C\text{---}S)$ frequency is much more when MTC acts as a monodentate ligand, more systematic studies are necessary to confirm this observation. We find that the γ (NCOS), δ (NCO) and δ (SCO) modes do not show any discernible systematics in the complexes probably because of the presence of extensive coupling.

5. Application of the HSAB concept

It is most interesting that in metal complexes where MTC acts as a monodentate ligand (table 2), the metal ions are all soft acids (class *b*) whereas in all those com-

Table 2. Positions of $C\text{---}O + C\text{---}N$ stretching bands in monothiocarbamate complexes[a].

Monodentate	Bidentate
Hg(II) 1570 (S) (McCormick and Greene 1972)	Ti(IV) 1550 (H) (Chisholm and Extine 1977)
Ag(I) 1580 (S) (Araki *et al* 1976)	Zr(IV) 1546 (H) (Chisholm and Extine 1977)
Au(I) 1590 (S) (Pijpers *et al* 1974)	Th(IV) 1515–1540 (H) (Bagnal and Yanir 1974)
Pd(II) 1570–1590 (S) (Krankovits *et al* 1973; Springsteen *et al* 1977)	U(IV) 1515–1520 (H) (Bagnal and Yanir 1974)
Pt(II) 1590 (S) (Springsteen *et al* 1977)	Ni(II) 1525–1566 (HS) (McCormick and Stormer 1972)
Rh(I) 1565 (S?) (Pijpers *et al* 1974)	Cd(II) 1510–1550 (HS?) (McCormick and Greene 1972)
Re(III) 1590 (HS?) (Annuar 1979)[b]	

Both mono- and bi-dentate

Zn(II) 1565–1575 (HS) (Krankovits *et al* 1973); 1512–1540 (HS) (McCormick and Greene 1972)

Fe(II) 1570 (HS) (Springsteen *et al* 1977); Fe(II, III) 1520–1545; Fe(II) (HS), Fe(III) (H) (Nakajima *et al* 1976)

Co(II) 1565 (HS) (Pierpont *et al* 1974)

Mn(I) 1600; 1540 (HS?) (Tanaka *et al* 1975)

(a) In brackets we have shown the classification of the metal ions according to HSAB concept: S, soft; H, hard and HS, borderline (hard or soft).

(b) With dimethyl MTC as ligand.

plexes where MTC acts as a bidentate ligand they are generally hard (class *a*) or borderline acids. Thus in complexes of Th(IV), U(IV), Zr(IV) and Hf(IV) which are hard acids MTC acts as a bidentate ligand while in complexes of Ag(I) and Hg(II) which are soft acids, it acts as a monodentate ligand. In Zn(II) complexes we see both monodentate and bidentate behaviour because Zn(II) is a borderline acid. In the case of iron complexes, only with Fe(II) which is a borderline acid does MTC show monodentate behaviour; bidentate behaviour is shown in some instances in Fe(II) complexes, but always in Fe(III) complexes since Fe(III) is a hard acid. It is interesting that in the Co(II) complex where MTC shows bidentate behaviour, the metal ion is a borderline acid. We believe that Cd(II) which shows bidentate behaviour should probably be classified as a borderline acid (instead of as a soft acid). Accordingly, the σ_A parameter of Ahrland (1968) varies as Zn(II) $<$ Cu(II) $<$ Cd(II) $<$ Ag(I); here Zn(II) and Cu(II) are definitely borderline acids, while Ag(I) is a soft acid on Pearson's scale. In the case of Mn, it appears that Mn(I) complexes show both monodentate and bidentate behaviour. It is likely that Mn(I) is a borderline acid; Rh(I) is probably a soft or borderline acid. In rhenium(III) complexes which show the C$\doteq$O + C$\doteq$N stretching band in the region 1550–1590 cm^{-1} (Annuar, 1979), Re(III) may be acting as a soft or borderline acid. The only real anomalous case we have found in this study is that of the Tl(I) complex of MTC (Magee and O'Connor 1971) which shows bidentate behaviour of the ligand (C$\doteq$O + C$\doteq$N stretching frequency, 1525–1538 cm^{-1}) although Tl(I) is a soft acid. In spite of such minor exceptions, it is gratifying that HSAB concept provides a useful classification of thiocarbamate complexes based on which we can carry out further investigations of this interesting system. It may be noted that the infrared spectra of metal monothiobenzoates are also consistent with the predictions of the HSAB concept (Savant *et al* 1970). In the monothiobenzoates also, Cd(II) behaves anomalously as in the present study.

6. Infrared spectra of organotin monothiocarbamate complexes

Of the different types of organotin monothiocarbamates we have studied, the complexes of the general formulae R_2Sn $(R_2'MTC)_2$ and R_2Sn $(R_2'MTC)Cl$ show the C$\doteq$O + C$\doteq$N stretching frequency in the range 1555–1585 cm^{-1}. The complexes of the general formula R_3Sn $(R_2'MTC)$ show this frequency in the range 1595–1620 cm^{-1} (table 3). The high C$\doteq$O + C$\doteq$N stretching frequency in R_3Sn $(R_2'MTC)$ complexes suggests the coordination in these complexes to be distinctly different from the other two types of tin complexes. It is also interesting that the C$\cdots$S stretching mode of the R_3Sn $(R_2'MTC)$ complexes is considerably lower than in the other complexes. By analogy with selenium complexes (Tanaka *et al* 1973), we feel that in the R_3Sn $(R_2'$ MTC) complexes MTC effectively acts as a monodentate ligand with strong Sn–S bonding. The Sn–S stretching frequencies in these compounds are found in the range 390–400 cm^{-1}. The structure of the tetra-coordinated tin complexes may be similar to those reported by Sheldrick and Sheldrick (1970) in the case of analogous tin dithiocarbamates, by Dalton and Jones (1970) in the case of trimethyltin MTC and Tanaka *et al* (1973) in the case of selenocarbamates. In conjunction with the NMR results (Crosby *et al* 1979), we feel that the configuration may be a highly distorted trigonal bipyramid with a long Sn...O distance and a short Sn–S bond.

Table 3. Important frequencies in organotin monothiocarbamate complexes (cm^{-1}).

	ν (C$\cdots$O + C$\cdots$N)	ν (C$\cdots$S)
$Me_2Sn(Me_2MTC)_2$	1585	935
$Me_2Sn(Et_2MTC)_2$	1578	950
$Et_2Sn(Me_2MTC)_2$	1580	959
$Et_2Sn(Et_2MTC)_2$	1570	944
$Ph_2Sn(Me_2MTC)_2$	1585	940
$Ph_2Sn(Et_2MTC)_2$	1569	950
$Me_2Sn(i\text{-}Pr_2MTC)_2$	1555	..
$Ph_2Sn(Me_2MTC)$ Cl	1585	960, 920[a]
$Ph_2Sn(Et_2MTC)$ Cl	1580	945, 927[a]
$Me_3Sn(Me_2MTC)$	1620	910
$Ph_3Sn(Me_2MTC)$	1600	914
$Ph_3Sn(Et_2 MTC)$	1595	912

(a) Either of these bands can be assigned to this mode.

Complexes of the formula $R_2Sn\,(R'_2MTC)_2$ have probably a distorted octahedral structure wherein MTC acts as a bidentate ligand with strong metal–sulphur bonding and very weak metal–oxygen bonding. Accordingly, we have not been able to assign any bands to the Sn...O stretching mode. In doing so, we propose that the relatively lower frequency range for ν (C$\cdots$O + C$\cdots$N) found in the case of dialkyltin complexes within the related series of complexes (table 3) can be taken as indicative of the bidentate nature of the ligand. This assignment is in conformity with the structure proposed for the corresponding selenium analogues by Tanaka *et al* (1973). Accordingly, the C$\cdots$S stretching frequency is higher in these complexes compared to that in $R_3Sn\,(R'_2MTC)$.

The frequency range of the (C$\cdots$O + C$\cdots$N) stretching mode is higher in $R_2Sn\,(R'_2MTC)_2$ complexes (table 3) as compared to other metal complexes where MTC acts as a bidentate ligand (table 2) partly because of the nature of the Sn–S bonding. The Sn–S stretching bands in these complexes are in the range 340–380 cm^{-1}, somewhat lower than in $R_3Sn\,(R'_2MTC)$ complexes.

The Sn–C stretching modes of $R_2Sn\,(R'_2MTC)_2$ complexes throw some light on the stereochemistry of these complexes. Thus, the asymmetric and symmetric C–Sn–C stretching modes are around 570 and 520 cm^{-1} respectively in these compounds when R_2 and R'_2 are alkyl groups (Me, Et or i-Pr). The intensity ratio $I(Sn\text{–}C)_{sym}/I(Sn\text{–}C)_{asym}$ is less than 0·4 in these complexes and is close to the value found in dithio- (Honda *et al* 1968), diseleno- (Kamitani *et al* 1970) and thioselenocarbamates (Kamitani and Tanaka 1970). This would suggest a distorted *trans*-octahedral configuration for the dialkyltin monothiocarbamates.

The ν(C$\cdots$O + C$\cdots$N) and ν(C$\cdots$S) frequency ranges in $R_2Sn\,(R'_2MTC)$ Cl complexes are similar to those in $R_2Sn\,(R'_2MTC)_2$ complexes (table 3). It is likely that MTC acts as a bidentate ligand with strong Sn–S bonding and very weak Sn–O bonding. The Sn–Cl stretching frequencies in these chloro complexes are in the range 280–300 cm^{-1}. The configuration of these diphenylchlorotin complexes

would be similar to those of the analogous dimethylchlorotin complexes of seleno-carbamates (Tanaka *et al* 1973) which seem to possess a distorted trigonal bipyramidal configuration.

The phenyl substituted tin compounds exhibit characteristic Sn-phenyl stretching vibrations in the range 450–570 cm^{-1}. In this region we also find the deformation frequencies of the monosubstituted benzene ring as well. We have, therefore, not attempted to analyse this region in detail.

We can understand the nature of coordination in organotin monothiocarbamates in the light of HSAB concept. According to Pearson (1963) Sn(IV) and Me_2Sn(II) are hard acids. We should, therefore, expect them to form complexes where MTC is a bidentate ligand as indeed found in the present study in the case of R_2Sn ($R'_2MTC)_2$ and $R_2Sn(R'_2MTC)$ Cl complexes. R_3Sn(I), on the other hand, would be expected to be a soft acid or at least a borderline acid. It is interesting that we find high $\nu(C \cdots O + C \cdots N)$ characteristics of the monodentate ligand in R_3Sn ($R'_2 MTC$) complexes.

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