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Detecting the Bonding Type of Dithiocarbamate Ligands in Their Complexes as Inferred from the Asymmetric CS Mode

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The IR spectra of a number of dithiocarbamate (dtc) complexes ($M(R_2dtc)_n$, *n* = 2, *M = Ni, Cu, Zn, Cd, Pb, Hg, Se, Te; n = 3, M = Cr, Fe, Co, As, Sb, Bi, R = Et,* Pr^n, Pr^i, Bu^n, Bu^i*), as well as the laser Raman spectra of a few colourless compounds* ($M(Et_2dtc)_2$ *M = Zn, Cd, Pb, Hg), have been recorded and discussed as to the validity of the Bonati–Ugo (BU) criterion for discerning the dtc bonding type from its* $\nu_{as}(CS)$ *band (*ca. *1000* cm^{-1}*). By comparing these bands for dtc complexes containing different N-substituted ligands, their splittings can be proved to be due to interligand coupling of the CS ligand modes. Further comparison with X-ray diffraction data shows that the dtc ligands, irrespective of the host complex or the ligand bonding type, are at sites of* C_1 *symmetry, thus ruling out the possibility to detect the ligand bonding type from the solid state vibrational spectra. New evidence is presented that the R–N modes are present in the 1000* cm^{-1} *region, thus making it unsuitable for the determination of the ligand bonding type.*

Introduction

There are at present several physical methods of discerning the bonding type of the dithiocarbamate ligands ($R_2NC(S)S^-$, R_2dtc^-) in their complexes [1–3]. The earliest is the Bonati–Ugo (BU) method [1], based on ligand IR spectra. Electronic spectra ($\pi \rightarrow \pi^*$ intraligand transitions [2]) and ^1H NMR *vs.* $\nu(CN)$ correlations [3] have also been used.

The BU method, however, is by far the most popular one. It consists of tracing the 950–1050 cm^{-1} spectral region where the $\nu_{as}(CS)$ mode is thought to appear. A single symmetrical band suggests the presence of symmetrically-bonded (two equivalent CS bonds) ligands, while a split 1000 cm^{-1} band indicates asymmetrically bonded (two inequivalent CS bonds) ligands (unidentate or bidentate asymmetric).

The BU method has been checked by Brown *et al.* [4] employing normal coordinate analysis in Urey–Bradley force-field calculations of $Cr(R_2dtc)_3$ treated in a 1:1 model as $Cr-R_2dtc$. Splittings larger than 20 cm^{-1} were taken to indicate unidentate bonding while those of less than 20 cm^{-1} suggest asymmetrically bidentate ligands, or in the limit of no splitting, symmetrical bidentate ligands. Moreover, $\nu(R-N)$ was found to mix extensively with $\nu_{as}(CS)$ and thus to affect profoundly the spectral envelope in the 1000 cm^{-1} region. These findings substantiate earlier results about the effect of N-substituents [5], and are in agreement with previous normal coordinate calculations [4, 6–9].

The BU criterion is known to have failed in certain cases discussed in detail elsewhere [4], though the reasons behind this were not fully examined. In this paper we have tried to prove that the ligand skeleton vibrational spectra cannot be used to discern the bonding type of the dtc ligands.

The present study is restricted to the 950–1050 cm^{-1} region and the crystal and solution spectra are treated at three levels: (a) ligand ν_{as}(CS) and ν_s(CS) modes; (b) interligand, [intramolecular] coupling of the ν(CS) modes; (c) site and correlation (dynamic) effects in the solid state spectra.

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TABLE I. Crystallographic Data on $M(Et_2dtc)_n$ Compiled from [11].

Space group	Factor group	Z	Z^B	Site of dtc	Complexes of
Bis-dtc					
$P2_1/c$ $P2_1/a$	C_{2h}	2	2	C_1	Ni(sym) Hg(asym)
$P2_1/m$	C_{2h}	4	4	C_1	Cu, Cr, Mn, Fe(sym) Zn, Cd, Te(asym)
$P2_12_12_1$	D_2	4	4	C_1	Se(asym)
Cc	C_s	4	2	C_1	Pb(asym)
Tris-dtc					
$P2_1/c$ $P2_1/a$ $P2_1/m$	C_{2h}	4	4	C_1	Cr, Mn, Fe hs(sym) As, Sb, Bi(asym) Ru, Rh, Tl(sym)
$C2/c$ $C2/m$	C_{2h}	4	2	C_1	Co, Ir, Fe ls(sym)
$A2/a$	C_{2h}	4	2	C_1	Ga(asym), In(sym)

Z is the number of molecules in the crystallographic unit cell. Z^B is the number of molecules in the Bravais space cell. (sym) and (asym) denote two equivalent or inequivalent (by two standard deviations) CS bonds in the ligands, respectively.

Experimental

The IR (400–3600 cm^{-1}) spectra of the following complexes have been recorded: $M(R_2dtc)_n$, n = 2, M = Ni, Cu, Zn, Cd, Hg, Pb, Se, Te; n = 3, Cr, Fe, Co, As, Sb, Bi; R = Et, Pr^n, Pr^i, Bu^n, Bu^i. The laser Raman spectra for some of the colourless compounds, $M(Et_2dtc)_2$, M = Zn, Cd, Hg, Pb, have also been recorded. The compounds were prepared and characterized as described elsewhere [10]. The IR spectra were recorded on an IRS 113V Bruker spectrometer with ±1 cm^{-1} resolution (or better), or a Perkin Elmer 180 with ±2 cm^{-1} resolution (or better). The Raman spectra were recorded on a GDM 1000 Zeiss Laser Raman spectrometer with Ar laser excitation.

Survey of Structural Data

The crystal structures of the dtc complexes have been reviewed in detail elsewhere [11].

The bis-dtc complexes are predominantly $P2_1/c$ or $C2/c$ with very few exceptions, those relevant to our study being $Se(Et_2dtc)_2$ of $P2_12_12_1$ (D_2^4) symmetry [12], $Pb(Et_2dtc)_2$ of Cc symmetry [13], and $Cu(Pr_2^idtc)$ of $P\bar{1}$ (C_i^1) symmetry [14].

The tris-dtc complexes listed in the experimental part are of $P2_1/c$ or $C2/c$ symmetry (see [11]).

The crystal structure data are most abundant for the di-Et-dtc complexes, and for this reason they are used here to illustrate the problem. As displayed by Table I, the site symmetry of the ligands in these complexes is invariably C_1, regardless of the space group and ligand type of bonding. In this case the bonding type is denoted as inferred from available crystallographic data by comparing the CS bond lengths [11–14].

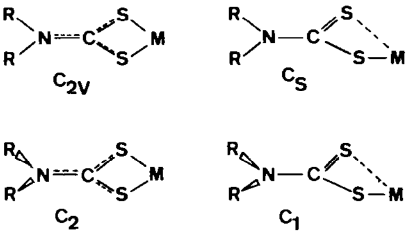

Fig. 1. Different bonding types of the dithiocarbamate ligand.

Results and Discussion

Effect of Ligand Site Symmetry

The group theoretical treatment (see, for example [15]) of the dtc ligand skeleton mode (R regarded as united atom) in various possible site symmetries of the M–dtc unit produced the results given in Table II.

The ligand skeleton geometries in the various bonding types are illustrated in Fig. 1. Since the ligand in the highest possible symmetry has no

TABLE II. Ligand Skeleton Modes for the R_2NCS_2–M Unit.

Ligand Site[§] Symmetry	Bonding Type	Modes	Activity IR	Activity R	Activity C	ν_{as}(CS) (pol)	ν_s(CS) (pol)
C_{2v}	sym	$5A_1, A_2^*, 4B_1, 2B_2$	11	12	11	B_1 (x)	A_1 (z)
C_2	sym	6A, 6B	12	12	12	B (x,y)	A (z)
C_s	asym	9A′, 3A″	12	12	12	A′ (x,y)	A′ (x,y)
C_1	asym	12A	12	12	12	A (x,y,z)	A (x,y,z)

[§] See Fig. 1. *IR inactive; (pol) polarization.

TABLE III. Compatibility Schemes between the Ligand Site, Molecular Symmetry and Ligand Bonding Type.

Ligand Site	Molecular Symmetry	Bonding Type	Ligand Site	Molecular Symmetry	Bonding Type
Bis-dtc			Tris-dtc		
C_{2v}	D_{2h}, D_{2d}	sym	C_{2v}	D_{3h}	sym
C_2	D_2	sym	C_2	D_3	sym
C_s	C_{2v}	sym	C_1	C_3	asym
	C_{2h}, C_{2v}	asym			
C_1	S_4, C_2, C_s	asym			

degenerate vibrational modes, going down to C_1 in the series C_{2v}–C_2–C_s–C_1 would not give rise to band splittings. Hence such splittings (used in the BU procedure) have to come up from the different selection rules defined by interligand or intermolecular couplings.

Table II shows convincingly that the change in symmetry and bonding type of the ligand in the 1:1 model is ineffective in producing CS band splittings or the appearance of new bands. The only change in the number of ligand skeleton bands on going down from C_{2v} to C_2 (loss of two symmetry planes, see Fig. 1) is expected when the A_2 IR-inactive mode becomes IR-active. This mode is, however, an out-of-plane wagging mode of the ligand, which should appear at much lower frequencies than the ν(CS) modes under consideration here.

A survey of Table I, as well as available structural data on other N-substituted dtc complexes [11], shows that in the solid state irrespective of the bonding type and host complex the dtc ligands are always on sites of C_1 symmetry. This finding rules out any chances of detecting differences in the ligand bonding type from solid state IR or Raman spectra in the CS stretch region, since such differences are lost at the lowest symmetry site.

The symmetry governing the selection rules for the solution spectra is the molecular symmetry of the complex. Do the possible molecular symmetries of the bis- and tris-dtc complexes admit detection of the ligand bonding type?

Table III lists the compatibility schemes for these complexes. The results have been obtained by examining the sites that are compatible with the molecular point symmetry group in published Tables [15]. Table III is valid for any bis- and tris-bidentate complexes with bonding types similar to those of dtc. As seen from Table III, the various ligand bonding types may be discerned if they show a different number of bands in the studied range. This is not the case with the dtc ligands (see Table II) and this explains why the 400–1600 cm^{-1} regions of the dtc complexes, having the same N-substituent, look similar. In other words, despite the different compatibility schemes, the dtc ligand bonding type cannot be detected from the vibrational pattern of the CS region, even in solution.

TABLE IV. Intramolecular Coupling of the ν(CS) Modes and the Resultant Selection Rules for the Bis-dtc Complexes.

Symmetry adapted combination	Molecular symmetry				
	D_{2h}	D_2	C_{2h}	C_{2v}	C_s
$\nu_s' + \nu_s''$	A_g R	A R	A_g R	A_1 R + IR	A′ R + IR
$\nu_s' - \nu_s''$	B_{2u} IR	B_2 R + IR	B_u IR	B_1 R + IR	A″ R + IR
$\nu_{as}' + \nu_{as}''$	B_{3u} IR	B_3 R + IR	B_u IR	B_2 R + IR	A′ R + IR
$\nu_{as}' - \nu_{as}''$	B_{1g} R	B_1 R + IR	A_g R	A_2 R	A″ R + IR

′ and ″ denote the two dtc ligands in the bis-complex.

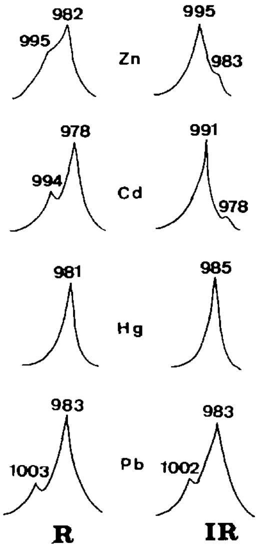

Fig. 2. Raman (left) and Infrared (right) bands (cm^{-1}) in the 950–1050 cm^{-1} region of the solid state spectra for some di-Et dtc complexes.

TABLE V. Intramolecular coupling of the ν(CS) modes and the resultant selection rules for the tris-dtc complexes.

Symmetry adapted combination	Molecular symmetry		
	D_{3d}	D_3	D_{3h}
$\nu_s' + \nu_s'' + \nu_s'''$	A_{1g} R	A_1 R	A_1' R
$2\nu_s' - \nu_s'' - \nu_s'''$ $\nu_s'' - \nu_s'''$	E_g R	E R + IR	E′ R + IR
$\nu_{as}' + \nu_{as}'' + \nu_{as}'''$	A_{2u} IR	A_2 IR	A_2'' R + IR
$2\nu_{as}' + \nu_{as}'' - \nu_{as}'''$ $\nu_{as}'' - \nu_{as}'''$	E_u IR	E R + IR	E″ R

This assertion would not hold for complexes of bidentate ligands that have higher symmetry, admitting degenerate modes.

Coupling of Ligand Modes

Consider the various possible schemes of inter-ligand couplings of the ν(CS) modes as a possible source of band splitting in the ν_{as}(CS) region.

Table IV presents the results of coupling two ν_{as}(CS) and two ν_s(CS) in a bis-dtc complex. Table V lists the results for the tris-dtc complexes. The results in both Tables have been obtained by projection operator techniques [16].

Consider first Table IV in conjunction with Table I. As seen for the C_{2h} factor group (solid state spectra), the two ν_{as}(CS) from the two ligands in a molecule are expected to give rise to one IR active (B_u) and one R active (A_g) ν_{as}(CS) combination. Figure 2 displays the 950–1050 cm^{-1} region for some representative (colourless or weakly coloured) bis di-Et–dtc complexes. The di-Et–dtc complexes were chosen to represent the bis-dtc class since their spectra are simplest and the structural data most abundant.

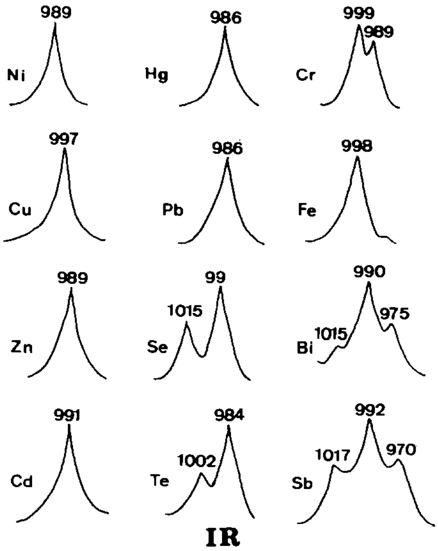

Fig. 3. Infrared bands in the solution spectra of some bis and tris di-Et dtc complexes in the 950–1050 cm^{-1} region. Solvent CH_2Cl_2.

Despite the presence of highly asymmetric dtc ligands in the Zn, Cd and Hg complexes, a single ν_{as}(CS) band is observed in the IR spectrum, in full accord with Table IV. The corresponding Raman spectra show a non-coincident high-intensity peak, again in compliance with the selection rules in Table IV. For the Zn and Cd complexes, however, where asymmetric bridging ligands are known to exist [11], additional features appear in both the IR and Raman spectra: weak shoulders in the Raman spectra coincident with the IR band and *vice versa*. There is no such shoulder for $Hg(dtc)_2$, which is almost linear [11]. These shoulders may be tentatively attributed to scrambled R–N and C–S modes (*vide infra*) due to which the inversion centre is lost and the exclusion rule becomes inoperative.

Further illustration of the intramolecular coupling of the CS modes comes up from the di-Et–dtc Pb complex. In accord with the selection rules for C_s (Table IV) its Raman and IR spectra show two coincident CS bands at 983 and 1003 cm^{-1}.

The above examples clearly demonstrate that the splittings in the 950–1050 cm^{-1} spectral region of solid bis-dtc complexes may be due to interligand coupling of the CS modes for the molecule. The same refers also to the solution spectra if the symmetries enumerated represent the effective molecular geometry.

There are no Raman spectra for the tris-dtc complexes and thus comparison is

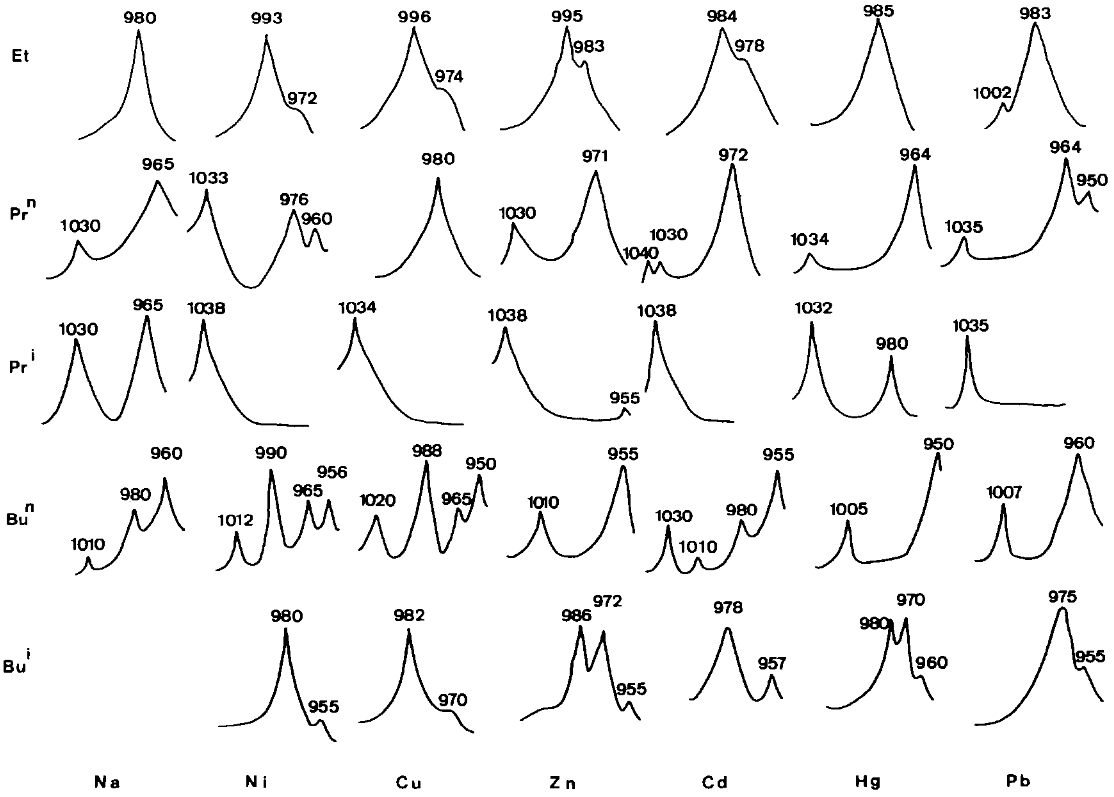

Fig. 4. Solid state IR spectra of bis-dtc complexes with different N-substituents in the 950–1050 cm^{-1} region.

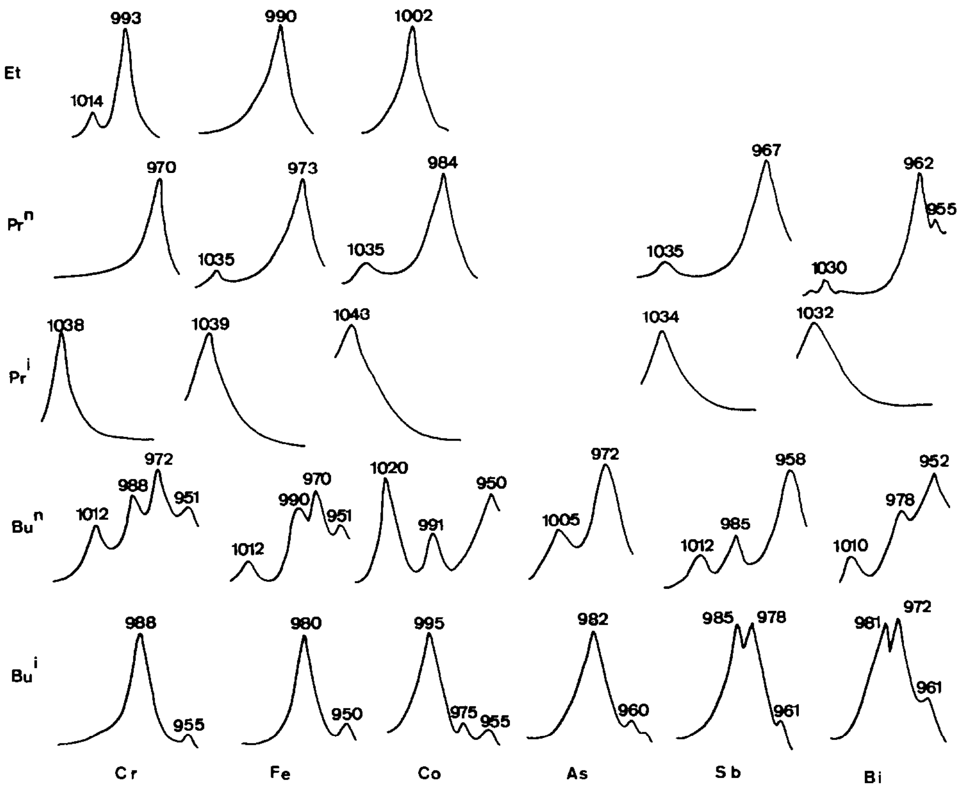

Fig. 5. Solid state IR spectra of tris dtc complexes with different N-substituents in the 950–1050 cm^{-1} region.

impossible. The solution spectra are discussed below.

Solution Spectra

The solution spectra of both the bis and tris di-Et dtc complexes in the 950–1050 cm^{-1} region are illustrated in Fig. 3 by several examples. As seen from this Figure, Ni to Hg bis di-Et dtc complexes invariably show one band which is consistent with D_{2h} or C_{2h} symmetry. This is regardless of the fact that some of the complexes contain highly asymmetric ligands (Hg and Pb, for example) which probably also persist in solution. The Se^{II} and Te^{II} di-Et dtc complexes, due to the presence of an in-plane lone pair, are trapezoidal (C_{2v} or lower [11, 12]) and their spectra exhibit a split 1000 cm^{-1} band (compare with Table IV, C_s symmetry).

The transition metal tris-dtc complexes are invariably of D_3 molecular symmetry [11c]. The As, Sb and Bi di-Et dtc complexes, due to the stereochemically active lone pair, all have symmetry lower than D_3. Table V shows that the D_3 complexes should exhibit two ν_{as}(CS) bands (A_2 + E). The E mode should split in lower symmetries to produce a 3-band pattern in the ν_{as}(CS) range. In fact this is exactly the case, as evidenced by Fig. 3 where a few illustrative examples are given.

The above treatment provides the basis for claiming that at least for the di-Et dtc complexes (both bis and tris) the observed splittings in the 1000 cm^{-1} frequency range are due to intramolecular coupling of the ligands' ν_{as}(CS) modes and the resulting selection rules for the respective factor (or molecular) group. However, as shown below, the N-substituents affect this range and may blur the pattern for complexes other than the di-Et dtc's.

In the presence of intramolecular couplings, the splittings produced by the correlation field are weak and cannot be separated from the static effects in the solid state spectra [15]. Hence this dynamic effect will be ignored here and we will proceed to consider the effect of N-substituents' modes on the spectral pattern in the 1000 cm^{-1} range.

Effect of N-Substituents on the Spectral Pattern at 1000 cm^{-1}

The choice of the di-Et dtc compounds to illustrate the problem of symmetry was not accidental: the 1000 cm^{-1} region is most uncomplicated for these complexes (see Fig. 4).

The presence of R–N modes in the 1000 cm^{-1} region was suspected [5] and subsequently substantiated by normal coordinate calculations [4]. However, the use of the BU criterion to discern the dtc

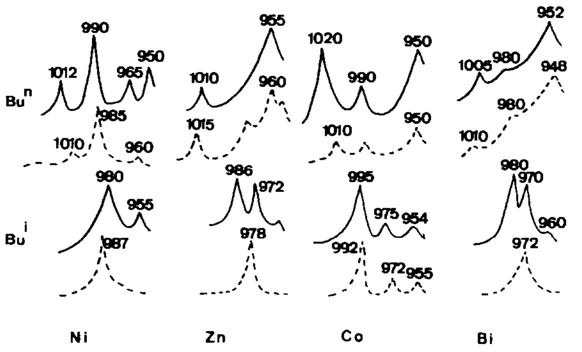

Fig. 6. IR spectra of solids and solutions of some bis and tris dtc complexes in the 950–1050 cm^{-1} region. Solid state spectra in Nujol suspensions and solution spectra in $CHCl_3$.

bonding type has continued with no attention being paid to the effect of substituents (see ref. [11] as a source; further evidence of recent origin [17–19]).

Figures 4–6 clearly demonstrate the fallibility of the BU criterion when more complicated N-substituents are present in the ligand. As seen from these Figures, a number of bands and shoulders appear in the studied spectral range. Since the N-substituents are known to have little or no effect on the crystal and molecular symmetry (for example, $(R_2dtc)_2Ni$, R = H, Me, Et, Pr^i, Me_5, Me_6 are all of $P2_1/m$ symmetry [11]), obviously the additional features in this range are due to R–N modes.

Conclusions

By comparing the 950–1050 cm^{-1} region with group theoretical predictions we have demonstrated that the splittings assigned thus far to different dtc bonding types should be attributed to intramolecular $\nu_{as}(CS)$ couplings.

The comparison of spectra for compounds with different N-substituents has revealed the large substituent effect on the number and positions of the bands in the 1000 cm^{-1} range, due to mixing of CS with RN modes, as suggested previously [4, 5].

These findings suggest that the attempts to detect the dtc bonding type from the 1000 cm^{-1} region are bound to produce misleading results and therefore should be viewed with caution.

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