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^{13}C NMR Spectra of Dithiocarbamates. Chemical Shifts, Carbon–Nitrogen Stretching Vibration Frequencies, and π Bonding in the NCS$_2$ Fragment

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From the ^{13}C NMR spectra of 71 dithiocarbamates, the chemical shifts of the carbon atom of the NCS$_2$ moiety are correlated to the π bonding in the NCS$_2$ fragment. With the aid of pattern recognition techniques, the dithiocarbamates are divided into five classes: (i) the free ligands; (ii) "normal" oxidation state transition metal dtc's; (iii) "normal" coordination number main group dtc's and organic dtc's; (iv) "high" oxidation state transition metal dtc's; (v) "low" coordination number main group dtc's. Normal, high, and low refer to the fractional oxidation number (FON), a useful quantity, defined as the ratio between oxidation number and coordination number. "Normal" is FON = $^1/_2$. A high FON refers to a high oxidation state or a low coordination number and correlates with a high $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ and a low $\delta(\mathrm{N}^{13}\mathrm{CS}_2)$. As such, the FON is a characteristic property distinguishing classes ii and iii from classes iv and v. It is not the difference between transition metals and main group element but rather the difference between symmetric and asymmetric dithiocarbamate bonding that distinguishes classes ii and iv from classes iii and v. In a semiempirical way $\delta(\mathrm{N}^{13}\mathrm{CS}_2)$ could be expressed as a linear function of the sum of the CN, CS1, and CS2 π-bond orders, and $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ of the CN π-bond order. The sum of the π-bond orders is derived to be maximal for equal π bonds and to decrease with increasing inequality of the three π bonds. Therefore, the free ligands (class i), with nearly equal π bonds, are located at the upper limit of δ values; the compounds with high $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ (classes iv and v) have low CS and low total π-bond orders, thus low δ values; and the compounds with asymmetrically bonded dtc (classes iii and iv) have low total π-bond orders and low δ values. For the various classes estimates of mean CN and CS π-bond orders, calculated from $\delta(\mathrm{N}^{13}\mathrm{CS}_2)$ and $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ values, are given. Other effects, which influence $\delta(\mathrm{N}^{13}\mathrm{CS}_2)$, are the substituent on nitrogen and the period to which the central metal belongs.

Introduction

^{13}C NMR spectroscopy is a valuable analytical technique for the determination of the structures of organometallic and coordination compounds. As such it has been applied to transition metal dithiocarbamates in several cases. From our own results[2] and those of others[3-9] we observed that the chemical shift of the carbon atom in the NCS$_2$ fragment of the dithiocarbamate ligand varies with the coordinated atom and with changes in the molecular framework. Up to now, no attention was paid to the factors which influence these shift variations, and the information contained herein was not made explicit. In order to unravel the various influences, we have undertaken a systematic investigation of a large number of diamagnetic dithiocarbamates, covering nearly all features expected to play a possible role.

Application of pattern recognition techniques proved to be very helpful in classifying the measured compounds into distinct groups and in relating on empirical grounds the $\delta(\mathrm{N}^{13}\mathrm{CS}_2)$ with the bonding modes and with the carbon–nitrogen stretching vibration frequencies. This permitted an

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evaluation of these relations within the scope of a simple π-MO model in terms of $\mathrm{C}\overline{\cdot\,\cdot}\mathrm{N}$ and $\mathrm{C}\overline{\cdot\,\cdot}\mathrm{S}$ π-bond orders.

Experimental Section

Broad-band proton-decoupled, Fourier-transformed ^{13}C NMR spectra were recorded at 15.0–15.1 MHz on a Bruker WP-60 spectrometer. A pulse width of 2 μs (15° pulse) was employed. Ambient temperature was about 40 °C. $Ir(Et_2dtc)_3(C_8H_{12})$ was measured at −10 °C and $[Bu_4N][Bu_2dtc]$ at 0 °C. Chemical shifts are reported relative to tetramethylsilane, with the deuterated solvent carbon signal as internal reference. Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer in the solid state in CsI disks and in solution in $CHCl_3$ between NaCl plates.

Complexes. The complexes were synthesized following standard literature methods: $VO(Et_2dtc)_3$;[10] $[Bu_4N][NiPhHdtc)(mnt)]$ and $Au(mnt)(n\text{-}Bu_2dtc)$;[11] $Ir(Et_2dtc)(C_8H_{12})$ and $Ir(Et_2dtc)_3(C_8H_{12})$;[12] $M(R_2dtc)_2I_3$,[13] $MBr(R_2dtc)_2$,[14,15] and $MBr_2(R_2dtc)$[15,16] (M = As or Sb and R = *n*-Bu); $PhC(=O)CH_2(Et_2dtc)$;[17] and $[Et_2dtcCH_2-]_2$.[18]

$Sn(Et_2dtc)_3BPh_4$ was obtained as a white precipitate from the reaction of 1.0 mmol of $SnCl_4{\cdot}5H_2O$ and 1.1 mmol of $NaBPh_4$ with 3.0 mmol of $NaEt_2dtc{\cdot}3H_2O$ in methanol after stirring the solution during 2 h. The compound was recrystallized from a chloroform–diethyl ether mixture. Anal. Calcd for $SnC_{39}H_{50}N_3S_6B$: C, 53.07; H, 5.71; N, 4.76. Found: C, 52.81; H, 5.79; N, 4.96.

$MeAs(Et_2dtc)_2$ was prepared from $MeAsI_2$ (1 mmol) and $NaEt_2dtc{\cdot}3H_2O$ (2 mmol) in methanol. After the disappearance of the yellow color, the solvent was removed under reduced pressure, the residue was taken up in chloroform, and the solution was filtered. After removal of the chloroform under reduced pressure, a white product was obtained, which was used as such. Anal. Calcd for $AsC_{11}H_{23}N_2S_4$: C, 34.18; H, 5.97; N, 7.25. Found: C, 33.86; H, 5.97; N, 7.10.

$[n\text{-}Bu_4N]_2[M(S_2CNPh)_2]$ (M = Pd, Pt). These novel compounds were prepared as described for the nickel complex[19] by deprotonation of $M(PhHdtc)_2$ with NaOH in a warm ethanol solution. Anal. Calcd for $PdC_{46}H_{82}N_4S_4$: C, 59.68; H, 8.93; N, 6.06. Found: C, 59.50; H, 8.80; N, 5.96. Calcd for $PtC_{46}H_{82}N_4S_4$: C, 54.46; H, 8.15; N, 5.52. Found: C, 54.45; H, 8.39; N, 5.60.

$Me(Ph_2dtc)$ was prepared by adding an equivalent amount of MeI to $Na(Ph_2dtc){\cdot}2H_2O$ dissolved in methanol. After stirring of the mixture for 2 h, the product crystallized by adding water to the solution. Anal. Calcd for $C_{14}H_{15}NS_2$: C, 64.83; H, 5.05; N, 5.40. Found: C, 64.57; H, 5.01; N, 5.35.

Other compounds were prepared as described[20,21] or were available at the Inorganic Chemistry Department of this University.

Results

^{13}C NMR spectra of 71 dithiocarbamates[22] and a few dithiocarbonimidato complexes have been measured. All ^{13}C resonances, as expected from the molecular structures, have been observed and assigned. δ values are given in Tables I and II. The $N^{13}CS_2$ chemical shifts are found in the range 185–220 ppm downfield to Me_4Si.

The measured compounds, in which the coordinated elements cover an important part of the periodic table, include organic, main group, and transition metal dithiocarbamates. In addition, the dithiocarbonimidato complexes $M(S_2CNPh)_2^{2-}$ (M = Ni, Pd, Pt) have been measured. Normal and high oxidation state complexes as well as symmetrically and asymmetrically bonded dtc complexes are included. Coordination numbers range from 2 to 8.

As substituents on nitrogen, mostly ethyl and butyl and in some cases phenyl or others have been used. The influence on $\delta(N^{13}CS_2)$ of the substituent on nitrogen is small (not exceeding 1 ppm), when *N*,*N*-dialkyldithiocarbamates are compared (see, e.g., the series of Ni compounds). The presence of one proton substituent on nitrogen (irrespective of the second substituent) is accompanied by an upfield shift of about 3 ppm with respect to the dialkyl-substituted compounds (cf. the Ni compounds and the three PhHdtc complexes). The $N^{13}CS_2$ chemical shifts of the four *N*,*N*-diphenyldithiocarbamates are approximately 8 ppm more downfield than those of the corresponding *N*,*N*-dialkyldithiocarbamates. Clearly, the effect of the substituent on nitrogen is additive to the effect of the central atom.

The solvent effect has been measured for $Ni(n\text{-}Bu_2dtc)_2$ and has been found to be small, less than 1 ppm, except for Me_2SO, where coordination of solvent molecules may have influenced the shift.

In Figure 1 a chart of $\delta(N^{13}CS_2)$ values is presented. The compounds are divided into groups corresponding to the occurrence of the coordinated element in the periodic system and to its electronic configuration. Moreover, groups are made from the free ligands, the organic dtc's, the high oxidation state transition metals, and a series of As(III) and Sb(III) compounds with varying composition. The phenyl-substituted derivatives are placed on the left-hand side, and the alkyl-substituted derivatives on the right.

Except for the closed-shell d^0 and d^{10} complexes there is obviously a contribution to $\delta(N^{13}CS_2)$ related to the period number of the central atom: the heavier atom complexes have higher δ values than their lighter congeners.

The main group dtc's (below 202 ppm) are well separated from the normal valence state transition metal dtc's (above 202 ppm). The high oxidation state transition metal dtc's, however, have a low $\delta(N^{13}CS_2)$ value and are also found quite below 202 ppm. This latter observation suggests a correlation between $\delta(N^{13}CS_2)$ and the carbon–nitrogen stretching vibration in the infrared spectra: $\nu(\mathrm{C}\overline{\cdot\,\cdot}\mathrm{N})$ is found around 1500 cm^{-1} for *N*,*N*-dialkyldithiocarbamates and around 1350 cm^{-1} for phenyl-substituted dithiocarbamates and is lower for normal oxidation state complexes but higher for high oxidation state complexes. $\nu(\mathrm{C}\overline{\cdot\,\cdot}\mathrm{N})$ values, measured in the solid state as well as in solution, are given in Table I. Usually, no large differences between the two values have been observed. The solution IR values are plotted against the $\delta(N^{13}CS_2)$ values, in Figure 2 for *N*,*N*-dialkyldithiocarbamates and in Figure 3 for aryldithiocarbamates. Although no straightforward correlation exists between $\delta(N^{13}CS_2)$ and $\nu(\mathrm{C}\overline{\cdot\,\cdot}\mathrm{N})$, generally higher $\nu(\mathrm{C}\overline{\cdot\,\cdot}\mathrm{N})$ values correlate with lower $\delta(N^{13}CS_2)$ values for the d-block metals on the one hand and for the main group elements on the other. Remarkable in this respect are the dithiocarbonimidato complexes, which can be prepared by the deprotonation of the bis(*N*-phenyldithiocarbamato) compounds. This deprotonation leads to a high $\mathrm{C}\overline{\cdot\,\cdot}\mathrm{N}$ π-bond order, a high value for $\nu(\mathrm{C}\overline{\cdot\,\cdot}\mathrm{N})$, and, following the trend of the dtc compounds, a low $\delta(N^{13}CS_2)$ value.

Other noticeable features of some spectra are the coupling constants of the $N^{13}CS_2$ carbon with some other nuclei and the α-$^{13}CH_2$ chemical shifts of the nitrogen substituents.

The coupling constants ^2J(Pt–C) in $Pt(n\text{-}Bu_2dtc)_2$ (125.0 Hz) and $Pt(Et_2dtc)_3ClO_4$ (70.9 Hz) and ^2J(P–C) in $P(Et_2dtc)_3$ (21.1 Hz) are large. The ^2J(Pt–C) values are comparable with the recently reported 125 Hz for $Pt(i\text{-}Bu_2dtc)_2$.[6] These high values can be attributed to the chelate bonding, which effectuates a double through bond coupling mechanism, and to a short metal-to-carbon distance in the four-membered ring. The ^2J(Rh–C) in $Rh(n\text{-}Bu_2dtc)_3$ is also observed and is 4.5 Hz, in agreement with 3.8 Hz reported recently for $Rh(C_5Me_5)(Me_2dtc)_2$ and 4.0 Hz for $Rh(C_5Me_5)(NCBPh_3)(Me_2dtc)$.[8]

For a specific alkyl group a rather large variation is observed in α-$^{13}CH_2$ chemical shifts: for ethyl, from 55.0 to 42.2 ppm; for *n*-butyl, from 57.3 to 48.0 ppm. The position of $\delta(\alpha\text{-}^{13}CH_2)$ seems to be determined largely by the position of the central metal within a group of the periodic table: differences within a group are small compared to differences between these various groups.

Classification of Compounds

In order to evaluate the importance of the influence of various factors on the $\delta(N^{13}CS_2)$ values and to improve the classification of the dithiocarbamates, we applied several nu-

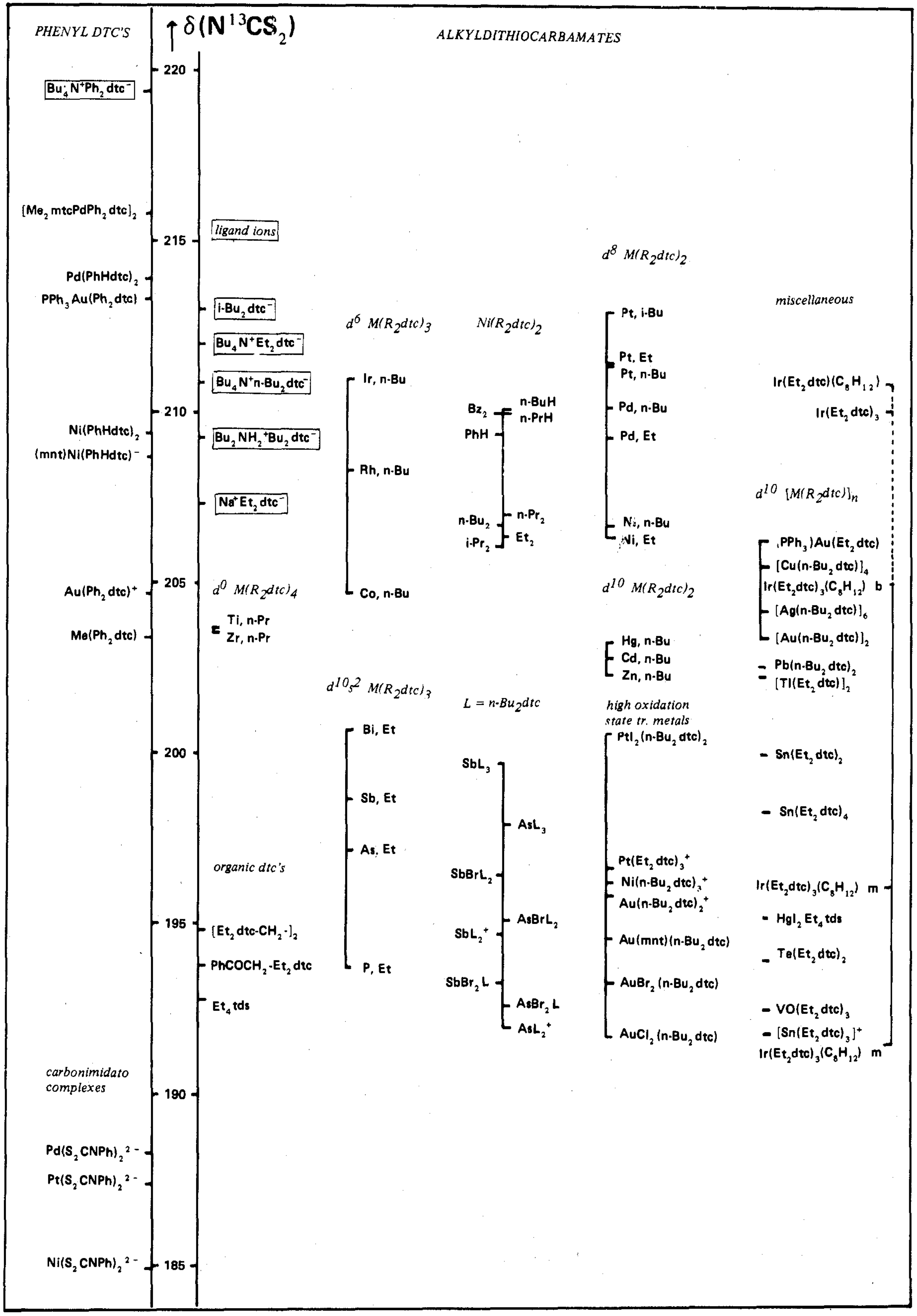


Figure 1. Chart of δ($N^{13}CS_2$) values.

merical pattern recognition techniques[23] by use of the computing program ARTHUR.[24] Three features turned out to be sufficient for the classification of the compounds: two measured quantities, i.e., ν(C⋯N) in solution and δ($N^{13}CS_2$); one parameterization, the "atom number". The atom numbers are given as follows: 3, 4, 5, or 6 to the d^6, d^8, and $d^{10}s^2$ metals belonging to periods 3, 4, 5, and 6; 3 to all other compounds.

Three clusters resulted from the calculations: (i) the free ligands, (ii) the compounds with both a high ν(C⋯N) and a low δ($N^{13}CS_2$) value, (iii) all others. The second cluster con-

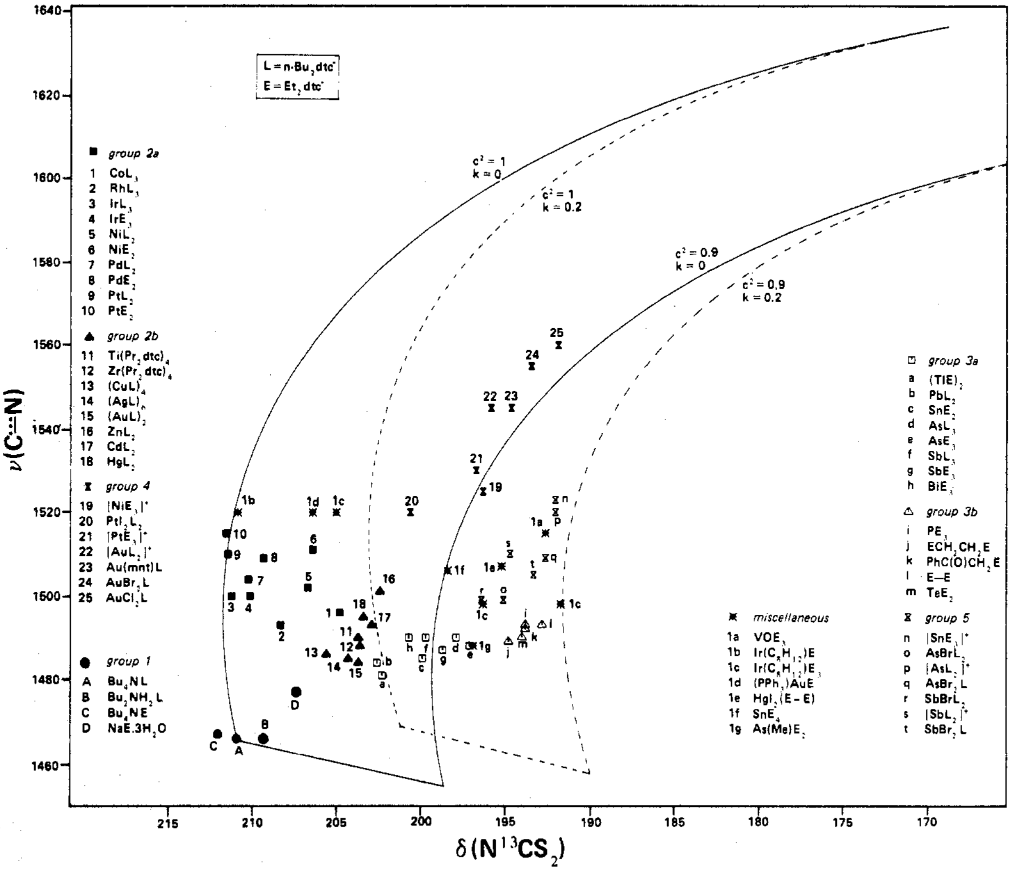


Figure 2. ν(C⃛N) vs. $\delta(N^{13}CS_2)$ of *N*,*N*-dialkyldithiocarbamates: (—) asymmetry parameter $k = 0$, (- - -) asymmetry parameter $k = 0.2$.

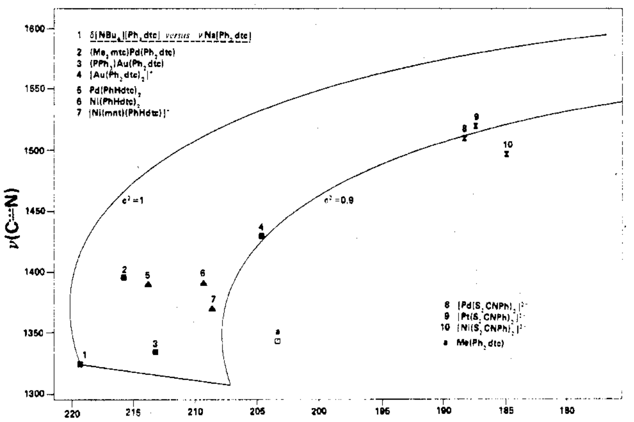


Figure 3. ν(C⃛N) vs. $\delta(N^{13}CS_2)$ of phenyldithiocarbamates and phenyldithiocarbonimidato complexes. Asymmetry parameter $k = 0$.

tained two well-separated groups: one of high oxidation state transition metals, i.e., Ni(IV), Pt(IV), and Au(III) complexes, and another which we call interpretatively as *low coordination number main group dtc's*, M(dtc)$_2$Br, M(dtc)Br$_2$, and M(dtc)$_2^+$ (M = As, Sb) and Sn(dtc)$_3^+$. The third cluster contained four groups: (i) d^8 and d^6 normal valence state transition metal complexes, M(dtc)$_3$ (M = Co, Rh, Ir) and M(dtc)$_2$ (M = Ni, Pd, Pt); (ii) d^0 and d^{10} normal valence state transition metal complexes, M(dtc)$_4$ (M = Ti, Zr), M(dtc)$_2$ (M = Zn, Cd, Hg), and [M(dtc)]$_m$ (M = Cu, Ag, Au); (iii) normal coordination number main group dtc's, [Tl(dtc)]$_2$, M(dtc)$_2$ (M = Sn, Pb), and M(dtc)$_3$ (M = As, Sb, Bi); (iv) organic dtc's including P(dtc)$_3$ and Te(dtc)$_2$.

The groups are summarized with their classifying feature values in Table III. The various groups are indicated with distinct symbols in the ν(C⃛N) vs. $\delta(N^{13}CS_2)$ plot, Figure 2.

A test set has been composed of seven compounds, which were classified in the groups, defined by the training set VO(Et$_2$dtc)$_3$, (PPh$_3$)Au(Et$_2$dtc), AsMe(Et$_2$dtc)$_2$, Ir(C$_8$H$_{12}$)(Et$_2$dtc), and Ir(C$_8$H$_{12}$)(Et$_2$dtc)$_3$, because of the presence of ligands other than halides or sulfur, HgI$_2$(Et$_4$tds) because the two sulfur atoms of the dtc fragment are bonded to two different atoms, and Sn(Et$_2$dtc)$_4$ because it is fluxional, containing two monodentate and two bidentate dithiocarbamate ligands;[25] Ir(C$_8$H$_{12}$)(Et$_2$dtc)$_3$ also contains one bidentate and two monodentate dtc ligands, but these show distinct resonances in both the ^{1}H and ^{13}C NMR spectra, excluding fluxionality on the NMR time scale.

The results of the test set place HgI$_2$(tds), VO(dtc)$_3$, and Sn(dtc)$_4$ in group 5; (PPh$_3$)Au(dtc), Ir(C$_8$H$_{12}$)(dtc), and the dtc ligand of Ir(C$_8$H$_{12}$)(dtc)$_3$, assigned as bidentate, have been placed in group 2; and As(Me)(dtc)$_2$ and the two dtc ligands of Ir(C$_8$H$_{12}$)(dtc)$_3$, assigned as monodentate, have been placed in group 4.

A detailed description of the pattern recognition calculations will be given elsewhere.[26]

Discussion

Influence of the Period. It is noted that within groups of isostructural compounds, e.g., M(dtc)$_4$, M(dtc)$_3$, and M(dtc)$_2$, there is an increased paramagnetic contribution of the central metal to the total shielding, an increased downfield shift. This is possibly explained by the decrease in the mean excitation energy (d–d transitions and charge-transfer transitions) going down a group.[27] This effect of periodicity seems to be small, less than 1 ppm, for d^0 and d^{10} configurations, e.g., Ti $\simeq$ Zr and Zn $\lesssim$ Cd $\lesssim$ Hg. The oligomeric d^{10} complexes of Cu, Ag, and Au are not isostructural, and for these compounds comparison is less appropriate. Apparently this influence is larger, when partly filled d shells are present (see the downfield shift

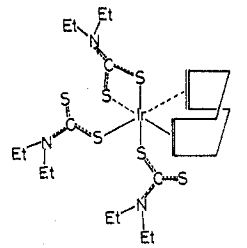


Figure 4. Proposed structure of Ir(Et$_2$dtc)$_3$(C$_8$H$_{12}$).

of 6.4 ppm going from Co to Ir (d^6 configuration) and of 5.1 ppm going from Ni to Pt (d^8 configuration)) and also when lone pairs and readily accessible outer d orbitals are present, because there is a shift increase of 6.9 ppm going from P to Bi (d^{10}s^2 main group complexes).

Transition Metals vs. Main Group Elements; Symmetrical vs. Asymmetrical Bonding. That the δ(N^{13}CS$_2$) values of the main group and organic dtc's are found well below the values of the normal valence state transition metal dtc's can, at least partly, be attributed to the increasing asymmetry in the MS$_2$C moiety of the former classes of compounds. The organic dtc's indeed have the largest asymmetry and are found at the low extreme of δ values. Because the asymmetry involves different C$\overset{\cdots}{-}$S π bonds, the main contribution from the asymmetry to the lowering of δ(N^{13}CS$_2$) may be a bond order effect, although an effect of changing excitation energies cannot be ruled out. In this respect, Ir(C$_8$H$_{12}$)(Et$_2$dtc)$_3$ is remarkable, it contains one bidentate and two monodentate dtc ligands. Its probable structure is given in Figure 4. In agreement with this structure, three N^{13}CS$_2$ resonances are found, one at 205 ppm, attributed to the bidentate dtc ligand, and two below 197 ppm, attributed to the monodentate, asymmetrical dtc ligands.[28] So, it is not the difference between transition metals and main group elements but rather the difference between symmetrical and asymmetrical bonding which determines the difference between class 2 and class 3 and between class 4 and class 5.

Other compounds from the test set, which need comment, are HgI$_2$(Et$_4$tds), (PPh$_3$)Au(Et$_2$dtc), and VO(Et$_2$dtc)$_3$. HgI$_2$(tds) has asymmetrical dtc fragments and is classified as such; (PPh$_3$)Au(dtc) is asymmetric in the solid state; however, previous ^{1}H NMR results indicated symmetric bonding in solution.[29] This symmetric bonding finds confirmation in the δ(N^{13}CS$_2$) value of 206.4 ppm and in its classification in group 2. The position of VO(dtc)$_3$ in group 5 is not well understood on the basis of the dtc bonding mode but may be explained by an important contribution of the diamagnetic anisotropy of the axial V═O fragment, similar to the shift effect found in the ^{1}H NMR spectra of uranyl derivatives (UO$_2$)$^{2+}$.[30] In the square-planar d^8 compounds too, the δ values may contain a significant contribution of the magnetic anisotropy. By comparison with the d^6 systems, this contribution seems to be a few parts per million downfield.

High Oxidation States and Low Coordination Numbers; the Fractional Oxidation Number. The high oxidation state transition metal dtc's and the low coordination number main group dtc's are characterized by low δ(N^{13}CS$_2$) values and high ν(C$\overset{\cdots}{-}$N) values. They form a cluster, well separated from the "normal" oxidation state transition metal dtc's and the "normal" coordination number main group dtc's. It is the merit of the pattern recognition calculations to have revealed the group of hitherto unnoticed "low coordination number main group dtc's" and to have associated this group with the high oxidation state transition metal dtc's.

We have searched for an explanation, common to both groups, for the low δ and high ν. The fractional oxidation number (FON), defined as the ratio between oxidation number and coordination number, appears to be adequate, provided that the coordinating atoms have comparable donor properties. The FON can be seen as the mean charge on the metal to be compensated for by one ligating atom, in order to achieve near electroneutrality.

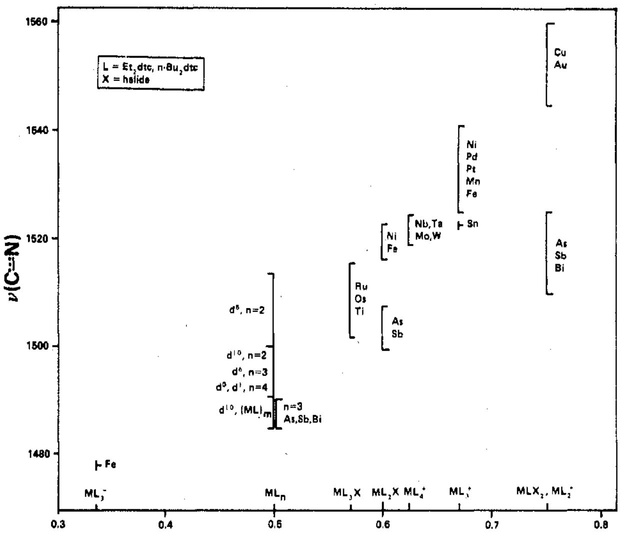


Figure 5. ν(C$\overset{\cdots}{-}$N) vs. FON = oxidation number/coordination number for *N,N*-dialkyldithiocarbamates.

Normal oxidation state metals and normal coordination number metals can then be defined as having a FON equal to 0.5. Normal oxidation state complexes involve M^{IV}(dtc)$_4$ (M = Ti, Zr, V, Nb, Mo), M^{III}(dtc)$_3$ (M = V, Cr, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, P, As, Sb, Bi) and M^{II}(dtc)$_2$ (M = Ni, Pd, Pt, Zn, Cd, Hg, Sn, Pb). All these complexes show a 1:2 ratio between oxidation number and coordination number.

For the transition metal compounds M^{V}(dtc)$_4^+$ (M = Nb, Ta, Mo, W), M^{IV}(dtc)$_3^+$ (M = Mn, Fe, Ni, Pt), M^{III}(dtc)$_2^+$ (M = Cu, Au) and Pt^{IV}I$_2$(dtc)$_2$, M^{III}X(dtc)$_2$ (M = Fe, Ni), and M^{III}X$_2$(dtc) (M = Cu, Au) and for the main group dtc's Sn^{IV}(dtc)$_3^+$, M^{III}(dtc)$_2^+$, M^{III}X$_2$(dtc), and M^{III}X(dtc)$_2$ (M = As, Sb; X = halide) this ratio exceeds 0.5, indicating that the central metal possesses excess positive charge. This results in an upfield shift contribution in the order 4–15 ppm, and an increase in ν(C$\overset{\cdots}{-}$N) of about 20–80 cm^{-1}.[19-21] Thus in FON are reflected changes in C$\overset{\cdots}{-}$N and C$\overset{\cdots}{-}$S π-bond orders which affect changes in δ(N^{13}CS$_2$). In this way not only ν(C$\overset{\cdots}{-}$N) but also δ(N^{13}CS$_2$) correlate with FON. Because of the other factors influencing δ(N^{13}CS$_2$), among which are excitation energy variations, there is no simple relationship between δ(N^{13}CS$_2$) and FON; however, ν(C$\overset{\cdots}{-}$N) and FON correlate well over a large range for a great number of dtc compounds. This correlation is visualized in Figure 5. It is seen in Figure 5 that square-planar d^8 complexes have quite high ν(C$\overset{\cdots}{-}$N) values. This is a well-known phenomenon, which is not yet fully understood. The low ν(C$\overset{\cdots}{-}$N) values of the oligomeric [M(dtc)]$_m$ complexes of the coinage elements reflect that these complexes have a less well-defined coordination number, which is not 2 but somewhat higher by secondary metal–metal and metal–bridging ligand interactions.

For the symmetrical dtc compounds of transition metals, the slope of ν/FON is aproximately 180 cm^{-1}, for the asymmetrical dtc compounds of group 5B this slope is approximately 120 cm^{-1}. This means that for the latter category of compounds the C$\overset{\cdots}{-}$N π bond and probably also the C$\overset{\cdots}{-}$S π bonds respond less to changes in M–S bonds. This reflects that main group elements are less apt for π interaction with the ligands than transition metals.

In compounds with mixed ligands, the FON is directly adequate for cases where the other ligands have net donor

Table I. Carbon-13 Chemical Shifts and Carbon–Nitrogen Stretching Frequencies of Dithiocarbamates and Carbonimidato Complexes

	^{13}C chemical shifts[a]					$\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ str freq[b]	
	-NCS$_2$	α-CH$_2$	β-CH$_2$	γ-CH$_2$	CH$_3$	solid state (CsI)	solution (CHCl$_3$)
			Dithiocarbamates				
[*n*-Bu$_4$N]Et$_2$dtc	212.0	46.7			12.1	1485	1467
Na(Et$_2$dtc)[c]	207.3	48.0			12.7	1477	
[*n*-Bu$_2$NH$_2$]-*n*-Bu$_2$dtc	209.3	53.2	29.0	19.9	13.5		1466
[*n*-Bu$_4$N]-*n*-Bu$_2$dtc	210.9	52.5	28.5	19.7	13.5		1466
[*n*-Bu$_4$N]Ph$_2$dtc	219.4						
Na(Ph$_2$dtc)						1325	
Ti(*n*-Pr$_2$dtc)$_4$[d]	203.7	53.4	21.3		11.9	1490[e]	
Zr(*n*-Pr$_2$dtc)$_4$[d]	203.6	52.3	21.3		12.1	1488[e]	
VO(Et$_2$dtc)$_3$	192.6	42.9			12.4	1515	
Co(*n*-Bu$_2$dtc)$_3$	204.8	48.0	28.9	19.8	13.4	1490	1496
Rh(*n*-Bu$_2$dtc)$_3$	208.3[f]	48.6	28.9	19.9	13.5	1493	1496
Ir(*n*-Bu$_2$dtc)$_3$	211.2	48.2	29.0	20.0	13.5	1500	1500
Ir(Et$_2$dtc)$_3$	210.1	42.3			12.1	1490	1500
Ir(Et$_2$dtc)(C$_8$H$_{12}$)	210.8	44.6			12.3	1516	1520
Ir(Et$_2$dtc)$_3$(C$_8$H$_{12}$)	205.0[g]	47.3			12.0		1520[g]
	196.3[h]	43.3			13.1	1494	1498[h]
	191.7[h]	42.2			11.4		
Ni(Et$_2$dtc)$_2$	206.4	43.6			12.2	1510	1511
Ni(*n*-Pr$_2$dtc)$_2$	207.0	50.6	20.3		10.8	1508	1517
Ni(*n*-PrHdtc)$_2$	210.0	45.3	21.8		11.0	1525	
Ni(*i*-Pr$_2$dtc)$_2$	206.1	50.7			19.5	1495	1496
Ni(*n*-Bu$_2$dtc)$_2$	206.7	48.8	29.0	19.8	13.4	1505	1502
Ni(*n*-Bu$_2$dtc)$_2$[i]	207.5	48.8	29.3	20.0	13.7		
Ni(*n*-Bu$_2$dtc)$_2$[j]	206.6	49.3	29.4	20.2	13.5		
Ni(*n*-Bu$_2$dtc)$_2$[k]	203.7	48.1	27.9	18.6	12.6		
Ni(*n*-BuHdtc)$_2$	210.1	43.4	30.6	19.8	13.0	1533	1516
Ni(Bz$_2$dtc)$_2$	210.0	50.6				1495	1497
Ni(PhHdtc)$_2$[j]	209.4					1391	1423
[*n*-Bu$_4$N]Ni(PhHdtc)(mnt)[j]	208.7					1370	
Ni(*n*-Bu$_2$dtc)$_3$ClO$_4$	196.3	49.9	29.1	19.9	13.5	1510	1525
Pd(Et$_2$dtc)$_2$	209.3	43.8			12.2	1518	1509
Pd(*n*-Bu$_2$dtc)$_2$	210.2	49.2	29.0	19.9	13.5	1504	1504
Pd(PhHdtc)$_2$[j]	213.9					1390	1409
[(Me$_2$mtc)Pd(Ph$_2$dtc)]	215.9					1410	1396
Pt(Et$_2$dtc)$_2$	211.5[l]	44.0			12.3	1520	1515
Pt(*n*-Bu$_2$dtc)$_2$	211.4[m]	49.2	29.0	19.8	13.5	1510	1510
Pt(*i*-Bu$_2$dtc)$_2$[n]	213.0[o]	56.4	26.9		20.1		
Pt(Et$_2$dtc)$_3$ClO$_4$	196.7[p]	44.8			12.0	1540	1530
PtI$_2$(*n*-Bu$_2$dtc)$_2$	200.6[q]	49.4[r]	29.0	19.8	13.4	1523	1520
		48.1[r]					
[Cu(Et$_2$dtc)]$_4$[i]	203.9	50.2			12.0	1486	1490
[Cu(*n*-Bu$_2$dtc)]$_4$[i]	205.6	55.9	29.2	20.3	13.8	1485	1486
[Ag(*n*-Pr$_2$dtc)]$_6$	204.5	58.7	20.2		11.2	1482	1482
[Ag(*n*-Bu$_2$dtc)]$_6$	204.3	56.9	28.9	20.1	13.6	1480	1485
[Au(*n*-Bu$_2$dtc)]$_2$	203.7	57.3	28.6	20.0	13.5	1488	1484
Ph$_3$PAu(Et$_2$dtc)	206.4	49.2			12.1		1520
Ph$_3$PAu(Ph$_2$dtc)	213.3					1340	1335
Au(*n*-Bu$_2$dtc)$_2$AuBr$_2$	195.8	52.1	29.1	19.9	13.4	1550	1545
Au(Ph$_2$dtc)$_2$ClO$_4$[k]	204.7						1430
AuCl$_2$(*n*-Bu$_2$dtc)	191.8	51.7	28.8	19.8	13.3	1575	1560
AuBr$_2$(*n*-Bu$_2$dtc)	193.4	51.3	28.9	19.9	13.4	1565	1555
Au(mnt)(*n*-Bu$_2$dtc)	194.6	51.4	28.8	19.8	13.2	1555	1545
(CH$_3$)$_2$Au(Me$_2$dtc)	207.9				40.2	1553	
Zn(*n*-Bu$_2$dtc)$_2$	202.4	54.3	28.7	19.7	13.4	1493	1501
Cd(*n*-Bu$_2$dtc)$_2$	202.9	56.4	28.7	19.9	13.5	1495	1493
Hg(*n*-Bu$_2$dtc)$_2$	203.4	56.7	28.7	19.8	13.5	1492	1495
[Tl(Et$_2$dtc)]$_2$	202.3	47.6			12.6	1483	1481
Sn(Et$_2$dtc)$_2$	199.9	47.2			12.1	1485	
Sn(Et$_2$dtc)$_3$BPh$_4$	192.0	52.6			11.7	1528	1523
Sn(Et$_2$dtc)$_4$	198.4	49.6			11.9	1505	1506
Pb(*n*-Bu$_2$dtc)$_2$	202.6	52.7	28.9	20.1	13.6	1480	1484
P(Et$_2$dtc)$_3$	193.8[s]	47.4			11.9	1487	1493
As(Et$_2$dtc)$_3$[t]	197.1	47.5			12.0	1494	1488
As(*n*-Bu$_2$dtc)$_3$[t]	197.9	53.1	28.8	19.8	13.4	1480	1490
AsBr(*n*-Bu$_2$dtc)$_2$[t]	195.1	53.6	28.7	19.7	13.3	1505/1515	1499
AsBr$_2$(*n*-Bu$_2$dtc)[t]	192.6	53.6	28.9	19.8	13.4	1522	1509
As(*n*-Bu$_2$dtc)$_2$I$_3$[t]	192.0	54.4	28.9	19.9	13.5	1529	1520
CH$_3$As(Et$_2$dtc)$_2$	196.9	48.1			12.0	1486	1488
Sb(Et$_2$dtc)$_3$[t]	198.7	47.8			11.8	1492	1487
Sb(*n*-Bu$_2$dtc)$_3$[t]	199.7	53.6	28.8	19.9	13.5	1482[u]	1490
SbBr(*n*-Bu$_2$dtc)$_2$[t]	196.4	54.1	28.7	19.8	13.3	1499	1499
Sb(*n*-Bu$_2$dtc)$_2$I$_3$[t]	194.7	54.7	28.9	19.9	13.5	1513[u]	1510
SbBr$_2$(*n*-Bu$_2$dtc)[t]	193.3	54.4	28.9	19.9	13.4	1517	1505

Table I (*Continued*)

	^{13}C chemical shifts^a					$C\overset{\ldots}{-}N$ str freq^b	
	-NCS$_2$	α-CH$_2$	β-CH$_2$	γ-CH$_2$	CH$_3$	solid state (CsI)	solution (CHCl$_3$)
$Bi(Et_2dtc)_3$	200.7	48.2			12.1	1490	1490
$Te(Et_2dtc)_2$	194.0	47.2			11.8	1490	1490
Et_4tds	192.8	49.2			12.0	1496	1493
HgI_2Et_4tds	195.2	55.0^r			14.6^r	1511	1507
		49.3^r			11.8^r		
$[Et_2dtcCH_2-]_2$	194.8	49.2^r			12.9^r	1483	1489
		46.6			12.1		
$PhC(=O)CH_2(Et_2dtc)$	193.8	49.8^r			13.1^r	1489	1492
		47.3^r			12.1^r		
$Me(Ph_2dtc)$	203.4					1353	1344
		carbonimidato Complexes					
$[n\text{-}Bu_4N]_2Ni(S_2CNPh)_2$	184.9					1480	1497
$[n\text{-}Bu_4N]_2Pd(S_2CNPh)_2$	188.3					1503	1510
$[n\text{-}Bu_4N]_2Pt(S_2CNPh)_2$	187.4					1510	1520

[a] In CDCl$_3$, if not indicated otherwise; in parts per million relative to tetramethylsilane. [b] In cm^{-1}. [c] In D$_2$O. [d] Data taken from ref 2, with corrections. [e] Data taken from D. C. Bradley and M. H. Gitlitz, *J. Chem. Soc. A*, 1152 (1969). [f] ^2J(Rh–C) = 4.5 Hz. [g] Bidentate bonded dtc. [h] Monodentate bonded dtc. [i] In C$_6$D$_6$. [j] In acetone-d_6. [k] In Me$_2$SO-d_6. [l] No Pt–C coupling observed due to the low solubility of the compound. [m] Pseudo triplet, ^2J(Pt–C) = 125 Hz. [n] Data taken from ref 6. [o] ^2J(Pt–C) = 125 Hz. [p] Pseudo triplet, ^2J(Pt–C) = 70.9 Hz. [q] Pseudo triplet, ^2J(Pt–C) = 70.1 Hz. [r] Two resonances due to restricted rotation around the $C\overset{\ldots}{-}N$ bond; see, e.g., A. M. Grotens and F. W. Pijpers, *Recl. Trav. Chim. Pays-Bas.* **92**, 619 (1973). [s] ^2J(P–C) = 21.2 Hz. [t] See also ref 15. [u] See also ref 13.

Table II. Remaining Carbon-13 Chemical Shifts^a

	$C_{aromatic}$				n-Bu$_4$N$^+$ or n-Bu$_2$NH$_2$$^+$				
	C_{ar}–N	C_{ortho}	C_{meta}	C_{para}	α-CH$_2$	β-CH$_2$	γ-CH$_2$	CH$_3$	others
$[n\text{-}Bu_4N]Et_2dtc$					58.5	23.7	19.3	13.2	
$[n\text{-}Bu_2NH_2]\text{-}n\text{-}Bu_2dtc$					45.8	27.0	19.9	13.2	
$[n\text{-}Bu_4N]\text{-}n\text{-}Bu_2dtc$					57.9	23.4	19.1	13.5	
$[n\text{-}Bu_4N]Ph_2dtc$	149.7	128.6	128.0	124.9	58.6	23.8	19.4	13.3	
$[Et_2dtc\text{-}CH_2-]_2$									35.5 (CH$_2$S)
$(Ph_2dtc)Me$	145.3	129.5	127.9	128.3					20.7 (CH$_3$)
$(Et_2dtc)CH_2C(O)Ph$	136.0^h	128.4	128.4	133.1					193.2 (C=O), 44.7 (CH$_2$)
$Ir(Et_2dtc)(C_8H_{12})$									66.4 (-C=C-), 32.2 (-C–C-)
$Ir(Et_2dtc)_3(C_8H_{12})$									88.8, 67.0, 58.4, and 51.4 (-C=C-); 27.8, 24.5, and 23.9 (-C–C-)
$Ni(Bz_2dtc)_2$	144.9^h	129.0	128.4	134.0					
$Ni(PhHdtc)_2$^{b}	137.6	123.2	129.4	127.2					
$[n\text{-}Bu_4N]Ni(PhHdtc)(mnt)$^{b}	137.6	122.2	129.3	126.4	59.0	24.0	19.7	13.3	125.3 (mnt), 117.8 (mnt)
$[n\text{-}Bu_4N]_2Ni(S_2CNPh)_2$	149.5	122.8	127.4	120.8	58.8	23.9	19.3	13.3	
$Pd(PhHdtc)$^{b}	137.0	123.4	129.4	127.2					
$[Me_2mtcPdPh_2dtc]_2$	140.5	127.2	129.4	128.2					167.2 (NCOS), 40.8 and 36.9 (CH$_3$)
$[n\text{-}Bu_4N]_2Pd(S_2CNPh)_2$	149.3	123.0	127.5	120.9	59.1	24.3	19.5	13.6	
$Pt(PhHdtc)_2$	137.6	130.0	127.4	123.1					
$[n\text{-}Bu_4N]_2Pt(S_2CNPh)_2$	148.1	122.9	127.6	121.1	58.8	24.2	19.5	13.5	
$Ph_3PAu(Et_2dtc)$^{c}	131.7^f	134.1	128.8	131.1					
$Ph_3PAu(Ph_2dtc)$	147.2								
$Au(Ph_2dtc)_2ClO_4$^{d}	138.9	131.4	127.0	130.7					
$(CH_3)_2Au(Me_2dtc)$									5.3 (CH$_3$-Au)
$Au(n\text{-}Bu_2dtc)(mnt)$									122.0 and 114.6 (mnt)
$Sn(Et_2dtc)_3BPh_4$^{e}	164.1^g	136.0	125.3	121.5					
$(CH_3)As(Et_2dtc)_2$									24.6 (CH$_3$-As)

[a] In CDCl$_3$, if not indicated otherwise; in ppm relative to tetramethylsilane. [b] In acetone-d_6. [c] ^1J(P–C) = 18 Hz.; ^2J(P-C$_o$) = 15 Hz; ^3J(P–C$_m$) = 12 Hz; ^4J(P–C$_p$) = 3 Hz; see, e.g., O. A. Gansow and B. Y. Kimura, *Chem. Commun.*, 1621 (1970). [d] In Me$_2$SO-d_6. [e] ^1J(^{11}B–^{13}C) = 50 Hz; the o, m, and p signals were broadened due to ^{11}B–^{13}C coupling; see J. D. Odom, L. W. Hall, and P. D. Ellis, *Org. Magn. Reson.*, 6, 360 (1974). [f] C_{ar}–P. [g] C_{ar}–B [h] C_{ar}–C.

properties comparable to dtc. Otherwise, compensations for donor differences have to be introduced. This is well demonstrated by the series of Au(III) compounds AuL$_2$(dtc) (L$_2$ = Cl$_2$, Br$_2$, mnt, dtc). More strongly donating ligands cause somewhat lower ν and more downfield δ values. This is also true for PtI$_2$(dtc)$_2$ with respect to Pt(dtc)$_3$$^+$. Regarding compounds of the test set, the positions of Ir(C$_8$H$_{12}$)(dtc), (PPh$_3$)Au(dtc), and AsMe(dtc)$_2$ are well understandable on the basis of the presence of the strongly electron-accepting C$_8$H$_{12}$ and PPh$_3$ ligands and the strongly electron-donating methyl ligand, respectively.

Free Ligands and Proton Bonding. For the free ligands there is no charge compensation on sulfur by coordinated atoms. This results in extremely low ν($C\overset{\ldots}{-}N$) values. They have also δ(N^{13}CS$_2$) values at the higher limit of the observed value range. This turns out from the theory to be somewhat accidental.

For Na(Et$_2$dtc)·3H$_2$O and (Bu$_2$NH$_2$)(Bu$_2$dtc) higher ν and lower δ values are found with respect to the anhydrous ions. This we explain by hydrogen bridging between water or the Bu$_2$NH$_2$ ion and the sulfur atoms. The proton bonding weakens the $C\overset{\ldots}{-}S$ bonds at the profit of the $C\overset{\ldots}{-}N$ bonds, which results in a small increase of ν(C–N). Furthermore, proton bonding may introduce a slight inequivalence in the two $C\overset{\ldots}{-}S$ bonds. Both these effects may contribute to the observed lowering of the δ(N^{13}CS$_2$) value.

Theoretical Considerations

We have searched for an explanation for the empirical correlation between δ and ν, shown in Figure 2. With a simple

Table III. Classification of Dithiocarbamates According to $\nu(\mathrm{C}\overset{..}{-}\mathrm{N})$, $\delta(\mathrm{N^{13}CS_2})$, and "Atom Number"

group	$\nu(\mathrm{C}\overset{..}{-}\mathrm{N})$	$\delta(\mathrm{N^{13}CS_2})$	atom no.[a]
1. free ligands	1466–1477	207–212	3
2. normal valence state transition metal dtc's	1480–1520	202–212	3–4–5–6
2A d^6 and d^8 complexes	1490–1520	205–212	4–5–6
2B d^0 and d^{10} complexes	1480–1501	202–206	3
3. normal coordination number main group and organic dtc's	1480–1496	193–203	3–4–5–6
3A main group dtc's	1480–1494	197–203	4–5–6
3B organic dtc's, $\mathrm{PE_3}$ and $\mathrm{TeE_2}$[b]	1483–1496	193–195	3–5
4. high oxidation state transition metal dtc's	1520–1555	193–201	4–6
5. low coordination number main group dtc's	1499–1529	192–196	4–5

[a] For explanation, see text. [b] $\mathrm{E = Et_2dtc}$.

molecular orbital model, applied to the $\mathrm{NCS_2}$ fragment of the dithiocarbamate ligand, we will evaluate in this section ν and δ as a function of the $\mathrm{C}\overset{..}{-}\mathrm{N}$ and $\mathrm{C}\overset{..}{-}\mathrm{S}$ π-bond orders.

The $\mathrm{C}\overset{..}{-}\mathrm{N}$ Stretching Vibration Frequency. The carbon–nitrogen stretching vibration frequency, $\nu(\mathrm{C}\overset{..}{-}\mathrm{N})$, or more precisely, ν^2, is a measure for the total $\mathrm{C}\overset{..}{-}\mathrm{N}$ bond order. Within a series of dithiocarbamates, changes in $\mathrm{C}\overset{..}{-}\mathrm{N}$ bond order can be measured by $\Delta(\nu^2) = \nu^2 - \nu_{\mathrm{ref}}^2$. We attribute these changes mainly to changes in the $\mathrm{C}\overset{..}{-}\mathrm{N}$ π-bond order, P_{CN}. For a small range of frequency values $\Delta(\nu^2) \approx \Delta\nu$. In MO theory, this results in the equation[31]

$$\Delta\nu = a(\Delta P_{\mathrm{CN}}) \tag{1}$$

The proportionality constant a can be determined with the formula

$$a = [\nu(\mathrm{CN})_i - \nu(\mathrm{CN})_j]/(P_{\mathrm{CN}_i} - P_{\mathrm{CN}_j}) \tag{2}$$

where i and j represent two standard $\mathrm{C}\overset{..}{-}\mathrm{N}$ bonds. Standard $\mathrm{C}\overset{..}{-}\mathrm{N}$ π-bond orders can be estimated with MO theory, while the corresponding $\mathrm{C}\overset{..}{-}\mathrm{N}$ frequencies can be taken from experimental data. Kinematic coupling with the lower frequency vibrations, present in the compounds, does not affect the validity of the linear interpolation.

The Paramagnetic Shielding Contribution. It is generally accepted that the paramagnetic shielding is dominantly responsible for changes in $\delta(^{13}\mathrm{C})$. For the paramagnetic shielding of a sp^2-hybridized carbon, theoretical formulas are derived in ref 32 and 33. The following type of expression for chemical shift differences, $\Delta\delta(^{13}\mathrm{C})$, has been obtained by Alger et al.[33]

$$\Delta\delta(^{13}\mathrm{C}) = (1/\Delta E)(-A_\pi(\Delta Q_\pi) - B_\sigma(\Delta Q_\sigma) + C_\pi(\Delta P_\pi)) \tag{3}$$

In this expression, ΔE is the average excitation energy, Q_π is the π charge on carbon and Q_σ the σ charge on carbon, P_π is the total π-bond order, $P_\pi = P_{\mathrm{CN}} + P_{\mathrm{CS1}} + P_{\mathrm{CS2}}$, with P_{CX} as the CX π-bond order (X = N, S1, S2), and A_π, B_σ, and C_π are semiempirical proportionality constants.

Alger et al. use $\Delta E = 8$ eV. For dtc derivatives in C_{2v} symmetry, the most important contributions to ΔE come from the $\mathrm{B_1}$, $\mathrm{A_1} \rightarrow \mathrm{B_2}$, $\sigma \rightarrow \pi^*$ type transitions. Four such transitions are found in the range 7–10 eV, and we assume that $\Delta E = 8$ eV is a reasonable estimate for the dtc compounds.

Alger et al. give estimates for the other quantities "pending the availability of better values" and they ultimately arrive at the equation

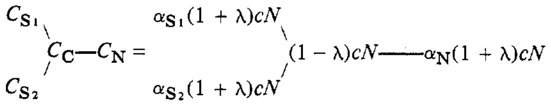
$$\Delta\delta(^{13}\mathrm{C}) = -100(\Delta Q_\pi) - 67(\Delta Q_\sigma) + 76(\Delta P_\pi) \tag{4}$$

which is suitable for a discussion of general trends.

π-MO Theory of the $\mathrm{NCS_2}$ Fragment. In MO theory the π-bond order, P_{CX}, and the π-charge on carbon, Q_{C}, are given by

$$P_{\mathrm{CX}} = \sum_i 2C_{\mathrm{C}}^iC_{\mathrm{X}}^i \qquad Q_{\mathrm{C}} = \sum_i 2(C_{\mathrm{C}}^i)^2 \tag{5}$$

where the summations run over all filled MO's. C_{X}^i is the coefficient of p$_z$ of atom X in the ith MO. The contribution of the various π-MO's to the π-bond order and to the π charge may be collected in one single MO of the form A. Proof for this is given in the Appendix, where also some symbols are explained.



A

Because of the larger electronegativity of nitrogen and sulfur compared to carbon, the polarization factor λ is in the range $0 \le \lambda < +0.2$. c^2 is a covalency factor, which contains information about the degree of mixing of the $\mathrm{NCS_2}$ MO with the orbitals of the metal and of the substituents on nitrogen. In this orbital, $\alpha_{\mathrm{S1}}^2 + \alpha_{\mathrm{S2}}^2 + \alpha_{\mathrm{N}}^2 = 1$, with a maximum value of $\alpha_{\mathrm{S1}} + \alpha_{\mathrm{S2}} + \alpha_{\mathrm{N}} = 3^{1/2}$. It is useful to introduce the algebraic substitution $\alpha_{\mathrm{N}} = \cos y$, such that $\alpha_{\mathrm{S1}}^2 + \alpha_{\mathrm{S2}}^2 = \sin^2 y$, with a maximum value of $\alpha_{\mathrm{S1}} + \alpha_{\mathrm{S2}} = 2^{1/2}\sin y$. The difference between symmetric and asymmetric bonding in the dtc ligand can now be expressed mathematically. For symmetrically bonded dtc, $\alpha_{\mathrm{S1}} = \alpha_{\mathrm{S2}}$ and the maximum of $2^{1/2}\sin y$ is obtained for $\alpha_{\mathrm{S1}} + \alpha_{\mathrm{S2}}$. For asymmetrically bonded dtc, $\alpha_{\mathrm{S1}} \neq \alpha_{\mathrm{S2}}$ and $\sin y \le \alpha_{\mathrm{S1}} + \alpha_{\mathrm{S2}} < 2^{1/2}\sin y$. We introduce an asymmetry parameter k ($0 \le k \le -1 + 2^{1/2}$), so that $\alpha_{\mathrm{S1}} + \alpha_{\mathrm{S2}} = (-k + 2^{1/2})\sin y$. So, a larger asymmetry implies a larger k.

Now, the various quantities N, P_{CN}, P_{CS1}, P_{CS2}, P_π, and $Q_\pi = Q_{\mathrm{C}}$ can be expressed as functions of α_{X}, λ, and c, or as functions of y, k, λ, and c.

$$N^{-2} = (1+\lambda)^2 + (1-\lambda)^2 + 2S(1+\lambda)(1-\lambda)\sum_{\mathrm{X}}\alpha_{\mathrm{X}} = 2 + 2S\sum_{\mathrm{X}}\alpha_{\mathrm{X}} = 2 + 2S[\cos y + (-k + 2^{1/2})\sin y] \tag{6}$$

$$P_{\mathrm{CX}} = 2c^2N^2(1+\lambda)(1-\lambda)\alpha_{\mathrm{X}} = 2c^2N^2\alpha_{\mathrm{X}} \tag{7}$$

$$Q_{\mathrm{C}} = 2c^2N^2(1-\lambda)^2 \tag{8}$$

$$P_\pi = 2c^2N^2\sum_{\mathrm{X}}\alpha_{\mathrm{X}} = 2c^2N^2[\cos y + (-k + 2^{1/2})\sin y] \tag{9}$$

Only Q_{C} depends significantly on the bond polarization parameter λ. From extended Hückel calculations[34] it follows that the average overlap, S, is 0.20. Preservation of electrons requires that changes in bond charges, $2S(\Delta P_\pi)$, and changes in atomic π charges, Q_{C} and Q_{X}, cancel each other.

$$\Delta Q_{\mathrm{C}} + \sum_{\mathrm{X}}\Delta Q_{\mathrm{X}} + 2S(\Delta P_\pi) = 0$$

For a small value of λ in good approximation can be written $\Delta Q_{\mathrm{C}} = \sum_{\mathrm{X}}\Delta Q_{\mathrm{X}}$; therefore $\Delta Q_{\mathrm{C}} = -S(\Delta P_\pi) = -0.20(\Delta P_\pi)$. Substitution of this result in eq 4 gives

$$\Delta\delta(^{13}\mathrm{C}) = -100(\Delta Q_{\mathrm{C}}) - 67(\Delta Q_\sigma) + 76(\Delta P_\pi) = 96(\Delta P_\pi) - 67(\Delta Q_\sigma) \tag{10}$$

With the assumptions that changes in Q_σ are small and that in a good approximation they are linearly related to changes in P_π, the term $-67(\Delta Q_\sigma)$ represents an additional uncertainty in the numerical value of the coefficient of ΔP_π in the remaining simplified expression:

$$\Delta\delta(^{13}\mathrm{C}) = 96(\Delta P_\pi) \tag{11}$$

Table IV. Mean $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ and $\mathrm{C}\overset{\cdots}{-}\mathrm{S}$ π-Bond Orders As Calculated from $\delta(\mathrm{N^{13}CS_2})$ and $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ Values and Mean Crystallographic $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ and $\mathrm{C}\overset{\cdots}{-}\mathrm{S}$ Bond Distances for Groups of Compounds

group		$\Delta\delta$	$\Delta\nu$	P_π	P_{CN}	P_{CS}	r_{CN}, Å	r_{CS}, Å
1	free ligands	0	0	1.24[b]	0.33[b]	0.45[b]	1.34[c]	1.72[c]
2A,B	normal oxidation state transition metal dtc's	−5	31	1.19	0.42	0.38	1.33[d]	1.72[d]
3A	normal coordination number main group dtc's	−11	21	1.12	0.39	0.57	1.33[d,e]	1.67[d,e]
						0.16		1.77
3B	organic dtc's	−17	23	1.06	0.40	0.62	1.34[f]	1.64[f]
						0.04		1.81
4	high oxidation state transition metal dtc's	−16	75	1.07	0.55	0.26	1.30[g]	1.74[g]
5	low coordination number main group dtc's	−17	48	1.06	0.47	0.47	1.33[h]	1.69[h]
						0.13		1.75
6	dithiocarbonimidato complexes	−32	112[a]	0.91	0.65	0.13	1.28[i]	1.75[i]

[a] For comparison with alkyl-substituted dtc's the observed $\Delta\nu = 175$ cm^{-1} has been multiplied by 350/550. [b] From extended Hückel calculations.[34] [c] Reference 38. [d] Reference 39. [e] Reference 36. [f] Reference 35. [g] Reference 40. [h] Reference 41. [i] Reference 42.

$\delta(\mathrm{N^{13}CS_2})$, $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$, Asymmetry, and π-Bond Orders in the $\mathrm{NCS_2}$ Fragment. A localized double $>\mathrm{C{=}NR}$ bond has $\nu(\mathrm{C{=}N})$ at approximately 1640 cm^{-1} for R = alkyl and at approximately 1600 cm^{-1} for R = aryl, and $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ of free $\mathrm{R_2dtc^-}$ is 1466 cm^{-1} for R = *n*-butyl and 1325 cm^{-1} for R = phenyl. Extended Hückel calculations[34] resulted in a P_{CN} of free dtc of 0.334. P_{CN} of a localized double bond is $2/(2 + 2S) = 0.833$, assuming negligible polarization and an overlap $S = 0.20$. Hence, according to eq 1 and 2, for alkyldithiocarbamates

$$\Delta\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N}) = (1640 - 1466)\Delta P_{\mathrm{CN}}/(0.833 - 0.334) = 350(\Delta P_{\mathrm{CN}}) \quad (12a)$$

and for aryldithiocarbamates

$$\Delta\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N}) = (1600 - 1325)\Delta P_{\mathrm{CN}}/(0.833 - 0.334) = 550(\Delta P_{\mathrm{CN}}) \quad (12b)$$

Substitution of the various quantities from eq 6–9 in eq 11 and in eq 12 results in

$$\Delta\delta(\mathrm{N^{13}CS_2}) = 2c^2N^2(96[\cos y + (-k + 2^{1/2}) \sin y]) \quad (13)$$

$$\Delta\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N}) = 2c^2N^2(350 \cos y) \quad \text{(alkyl dtc's)} \quad (14a)$$

$$\Delta\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N}) = 2c^2N^2(550 \cos y) \quad \text{(aryl dtc's)} \quad (14b)$$

The contribution of asymmetry to the chemical shift is derived from formula 13 to be

$$\Delta\delta(\mathrm{N^{13}CS_2})_{\mathrm{asym}} = -2c^2N^2(96k \sin y) \quad (15)$$

which represents an upfield shift contribution. In Figures 2 and 3 the asymmetric dtc's (group 3) are indeed situated at significantly lower δ values for similar ν values than the symmetric dtc's (group 2). It can be seen that group 3B complexes are expected to have a larger asymmetry in the dtc fragment than group 3A complexes. This is in agreement with X-ray crystal structure data of thiuram disulfide[35] and As(dtc)$_3$.[36]

In Figures 2 and 3, graphs of $\Delta\delta(\mathrm{N^{13}CS_2})$ vs. $\Delta\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ are plotted, according to eq 13 and 14, as functions of c^2 and k, with the free dithiocarbamates as the references. As values for c^2 were chosen its maximum value of 1 and an arbitrary value of 0.9. These values of c^2 result in a band of calculated (δ,ν) points for each value of k: one band with $k = 0$, for symmetrically bonded dithiocarbamates; another one for which such a value of k has been chosen ($k = 0.2$) that this band contains all asymmetrically bonded dithiocarbamates.

The curvature of the bands expresses the calculated δ vs. ν relationship and implicitly the δ vs. FON relationship. On consideration of all the other factors involved, the high oxidation state transition metals (group 4) follow clearly this relationship (Figure 2). The trend is less obvious for the low coordination number main group complexes (group 5) but is still present. The calculated curve finds further support in the position of the dithiocarbonimidato complexes (Figure 3).

The curve shows also that the position of the free ligands near the upper limit of the range of observed δ values agrees with the developed model. This results from the nearly equal CN and CS π-bond orders, present in the free dithiocarbamate, in such a way that the maximum value of $3^{1/2}$ is approached for $\alpha_{\mathrm{S1}} + \alpha_{\mathrm{S2}} + \alpha_{\mathrm{N}}$. In this respect, dtc resembles trimethylenemethane, $\mathrm{(CH_2)_3C}$. It is this resemblance which made the dithiocarbamato ligand suitable for the study of π-bond order effects on the $\delta(^{13}\mathrm{C})$ of the central carbon atom. Changes in π-bond orders cover a maximum range for trimethylenemethane derivatives but are much smaller for, e.g., allyl derivatives: according to eq 9, the maximum ΔP_π going from a delocalized $\mathrm{(CH_2)_3C}$ to a localized $\mathrm{(CH_2X)_2C{=}CH_2}$ is about 0.44, corresponding to a maximum range of δ values of about 42 ppm, but going from a delocalized $\mathrm{(CH_2)_2CH}$ to a localized $\mathrm{(CH_2X)HC{=}CH_2}$ it is about 0.24, corresponding to a maximum range of δ values of about 23 ppm. The influence of π-bond order changes apparently is manifest only when a large range of dtc derivatives is considered, but for a small range of $\delta(\mathrm{N^{13}CS_2})$ values, or for allyl-like systems, contributions from changes in ΔE and in other quantities may be of the same order of magnitude.

Other coordination compounds appropriate for the study of bond order effects on chemical shifts involve dithiocarbonates and xanthates, as well as trithiocarbonates and thioxanthates. However, for these compounds no direct information from IR data about one of the π bonds can be obtained. Insofar, carbamate derivatives appear to be quite unique (see, e.g., ref 37).

The measured $\Delta\delta(\mathrm{N^{13}CS_2})$ and $\Delta\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ values can give only an indication of the values of the CN and CS π-bond orders. Approximate order-of-magnitude calculations for the $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ and $\mathrm{C}\overset{\cdots}{-}\mathrm{S}$ π bonds for groups of compounds from the $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ and $\delta(\mathrm{N^{13}CS_2})$ values are given in Table IV. For comparison, mean $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ and $\mathrm{C}\overset{\cdots}{-}\mathrm{S}$ bond distances for these groups are also given.

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Appendix

The π-bond orders, P_{CX}, and π charges, Q_{C}, in which the central sp^2-hybridized carbon atom is involved, can be collected in one single MO. For this operation, we start with the following set of π-MO's:

$$\phi_k = C_{\mathrm{C}}{}^k p_{\mathrm{C}} + \sum_{\mathrm{X}} C_{\mathrm{X}}{}^k p_{\mathrm{X}} + \phi_{\mathrm{res}}{}^k$$
$$\mathrm{X = S1, S2, N}$$

$\phi_{\text{res}}{}^k$ is the residual part of the MO, involving orbitals of the central metal and of the substituents on nitrogen. p_{X} is the p_π orbital of atom X and C_{X} its coefficient. The MO's are taken to be orthonormal: $\langle\phi_k|\phi_l\rangle = \delta_{kl}$. Now, $P_{\text{CX}} = 2\sum_k C_{\text{C}}{}^k C_{\text{X}}{}^k$ and $Q_{\text{C}} = 2\sum_k (C_{\text{C}}{}^k)^2$, where the summation runs over the filled MO's. Two filled orbitals ϕ_{a} and ϕ_{b} are combined into two new orbitals ψ_1 and ψ_2, with the requirement that in one orbital the carbon coefficient is zero: $\psi_1 = \lambda\phi_{\text{a}} + \mu\phi_{\text{b}}$ and $\psi_2 = \mu\phi_{\text{a}} - \lambda\phi_{\text{b}}$, with $\lambda^2 + \mu^2 = 1$. $\langle\psi_i|\psi_j\rangle = \delta_{ij}$. The coefficient of carbon in ψ_2 is $\mu C_{\text{C}}{}^a - \lambda C_{\text{C}}{}^b = 0$; hence $\mu C_{\text{C}}{}^a = \lambda C_{\text{C}}{}^b$. With this condition fulfilled, the contributions of ψ_1 to P_{CX} and Q_{C} are

$$P_{\text{CC}}(1) = 2(\lambda C_{\text{C}}{}^a + \mu C_{\text{C}}{}^b)(\lambda C_{\text{X}}{}^a + \mu C_{\text{X}}{}^b) = 2(C_{\text{C}}{}^a C_{\text{X}}{}^a + C_{\text{C}}{}^b C_{\text{X}}{}^b)$$

and similar for Q_{C}. This means that the contributions of ϕ_{a} and ϕ_{b} to P_{CX} and Q_{C} are collected in ψ_1. By combination of the next filled ϕ_k with ψ_1, a new orbital is obtained, which again contains all information on P_{CX} and Q_{C}. Repeating the procedure results in one final MO of the form

$$\psi' = N'(C_{\text{C}}p_{\text{C}} + \sum_{\text{X}} C_{\text{X}}p_{\text{X}} + \psi_{\text{res}})$$

where N' is the normalization constant. We truncate this MO to functions of the NCS_2 fragment only: $\psi = cN(C_{\text{C}}p_{\text{C}} + \sum_{\text{X}} C_{\text{X}}p_{\text{X}})$, where $\langle\psi|\psi\rangle = c^2$. In this expression, c^2 is a covalency factor, expected to be close to 1.

The coefficients C_{C} and C_{X} may be rewritten as functions of a polarization term λ, defined by the equation $\sum_{\text{X}} C_{\text{X}}{}^2/C_{\text{C}}{}^2 = (1 + \lambda)^2/(1 - \lambda)^2$. With $C_{\text{C}} = 1 - \lambda$ and $\alpha_{\text{X}} = C_{\text{X}}/(1 + \lambda)$ we obtain $\sum_{\text{X}} \alpha_{\text{X}}{}^2 = \alpha_{\text{S1}}{}^2 + \alpha_{\text{S2}}{}^2 + \alpha_{\text{N}}{}^2 = 1$ and $\psi = cN[(1 - \lambda)p_{\text{C}} + \sum_{\text{X}}(1 + \lambda)\alpha_{\text{X}}p_{\text{X}}]$.

Registry No. [*n*-Bu$_4$N]Et$_2$dtc, 71195-45-4; Na(Et$_2$dtc), 148-18-5; [*n*-Bu$_2$NH$_2$]-*n*-Bu$_2$dtc, 2391-80-2; [*n*-Bu$_4$N]-*n*-Bu$_2$dtc, 71195-46-5; [*n*-Bu$_4$N]Ph$_2$dtc, 71215-00-4; Na(Ph$_2$dtc), 2801-05-0; Ti(*n*-Pr$_2$dtc)$_4$, 40678-69-1; Zr(*n*-Pr$_2$dtc)$_4$, 40788-52-1; VO(Et$_2$dtc)$_3$, 36464-03-6; Co(*n*-Bu$_2$dtc)$_3$, 28090-32-6; Rh(*n*-Bu$_2$dtc)$_3$, 71215-01-5; Ir(*n*-Bu$_2$dtc)$_3$, 41278-33-5; Ir(Et$_2$dtc)$_3$, 41278-30-2; Ir(Et$_2$dtc)(C$_8$H$_{12}$), 55046-26-9; Ir(Et$_2$dtc)$_3$(C$_8$H$_{12}$), 55046-28-1; Ni(Et$_2$dtc)$_2$, 14267-17-5; Ni(*n*-Pr$_2$dtc)$_2$, 14516-30-4; Ni(*n*-PrHdtc)$_2$, 71215-02-6; Ni(*i*-Pr$_2$dtc)$_2$, 15694-55-0; Ni(*n*-Bu$_2$dtc)$_2$, 13927-77-0; Ni(*n*-BuHdtc)$_2$, 23648-25-1; Ni(Bz$_2$dtc)$_2$, 38542-61-9; Ni(PhHdtc)$_2$, 15553-44-3; [*n*-Bu$_4$N]Ni(PhHdtc)(mnt), 71215-04-8; Ni(*n*-Bu$_2$dtc)$_3$ClO$_4$, 71215-05-9; Pd(Et$_2$dtc)$_2$, 15170-78-2; Pd(*n*-Bu$_2$dtc)$_2$, 17501-12-1; Pd(PhHdtc)$_2$, 52613-86-2; [(Me$_2$mtc)Pd(Ph$_2$dtc)]$_2$, 65123-41-3; Pt(Et$_2$dtc)$_2$, 15730-38-8; Pt(*n*-Bu$_2$dtc)$_2$, 69629-89-6; Pt(Et$_2$dtc)$_3$ClO$_4$, 71215-08-2; PtI$_2$(*n*-Bu$_2$dtc)$_2$, 71242-57-4; [Cu(Et$_2$dtc)]$_4$, 52133-93-4; [Cu(*n*-Bu$_2$dtc)]$_4$, 52487-34-0; [Ag(*n*-Pr$_2$dtc)]$_6$, 24651-16-9; [Ag(*n*-Bu$_2$dtc)], 17501-10-9; [Au(*n*-Bu$_2$dtc)]$_2$, 59306-90-0; Ph$_3$PAu(Et$_2$dtc), 38331-55-4; Ph$_3$PAu(Ph$_2$dtc), 54412-86-1; Au(*n*-Bu$_2$dtc)$_2$AuBr$_2$, 21151-11-1; Au(Ph$_2$dtc)$_2$ClO$_4$, 71215-06-0; AuCl$_2$(*n*-Bu$_2$dtc), 60886-25-1; AuBr$_2$(*n*-Bu$_2$dtc), 21069-35-2; Au(mnt)(*n*-Bu$_2$dtc), 33517-42-9; (CH$_3$)$_2$Au(Me$_2$dtc), 23908-41-0; Zn(*n*-Bu$_2$dtc)$_2$, 136-23-2; Cd(*n*-Bu$_2$dtc)$_2$, 14566-86-0; Hg(*n*-Bu$_2$dtc)$_2$, 21439-58-7; [Tl(Et$_2$dtc)]$_2$, 35163-31-6; Sn(Et$_2$dtc)$_2$, 16248-90-1; Sn(Et$_2$dtc)$_3$BPh$_4$, 71215-10-6; Sn(Et$_2$dtc)$_4$, 33790-72-6; Pb(*n*-Bu$_2$dtc)$_2$, 27803-77-6; P(Et$_2$dtc)$_3$, 69267-80-7; As(Et$_2$dtc)$_3$, 17767-20-3; As(*n*-Bu$_2$dtc)$_3$, 14907-95-0; AsBr(*n*-Bu$_2$dtc)$_2$, 71195-47-6; AsBr$_2$(*n*-Bu$_2$dtc), 71195-48-7; As(*n*-Bu$_2$dtc)$_2$I$_3$, 71195-49-8; CH$_3$As(Et$_2$dtc)$_2$, 71215-24-2; Sb(Et$_2$dtc)$_3$, 22914-73-4; Sb(*n*-Bu$_2$dtc)$_3$, 14907-93-8; SbBr(*n*-Bu$_2$dtc)$_2$, 71215-23-1; Sb(*n*-Bu$_2$dtc)$_2$I$_3$, 71195-50-1; SbBr$_2$(*n*-Bu$_2$dtc), 71195-51-2; Bi(Et$_2$dtc)$_3$, 20673-31-8; Te(Et$_2$dtc)$_2$, 15080-52-1; Et$_4$tds, 97-77-8; HgI$_2$Et$_4$tds, 27821-89-2; [Et$_2$dtcCH$_2$–]$_2$, 15351-61-8; PhC(=O)CH$_2$(Et$_2$dtc), 61998-04-7; Me(Ph$_2$dtc), 71195-52-3; [*n*-Bu$_4$N]$_2$Ni(S$_2$CNPh)$_2$, 19743-56-7; [*n*-Bu$_4$N]$_2$Pd(S$_2$CNPh)$_2$, 71215-12-8; [*n*-Bu$_4$N]$_2$Pt(S$_2$CNPh)$_2$, 71215-14-0; Pt(PhHdtc)$_2$, 71215-15-1.

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(22) Abbreviations used in this paper: R$_2$dtc, *N,N*-dialkyl(aryl)dithiocarbamate; R$_2$mtc, *N,N*-dialkyl(aryl)thiocarbamate; R$_4$tds, *N,N,N′,N′*-tetraalkylthiuram disulfide; R, the normally used abbreviations; mnt, maleonitriledithiolate, S$_2$C$_2$(CN)$_2{}^{2-}$.

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