Metal Complexes of Dithiocarbazic Acids

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A number of metal complexes of dithiocarbazic acid and its 3-phenyl and 3,3-dimethyl derivatives have been prepared and characterized. Neutral complexes of the type ML$_2$ or ML$_3$ were obtained for each ligand and NS bonding was observed for complexes of dithiocarbazic acid while SS bonding was observed in its substituted analogues. The stereochemistry of these complexes is discussed in relation to changes in their infrared and electronic absorption spectra. Certain of the complexes of dithiocarbazic acid were reacted with base to give anionic species which have been isolated as their tetramethylammonium salts.

Introduction

It has been known for some time that mixture of a primary or secondary amine with CS$_2$ will result in a condensation to create a dithiocarbamate (I). A wide range of complexes can be readily formed from such ligands and coordination in most cases occurs solely through the two sulfur atoms. An analogous reaction occurs upon reacting a hydrazine and CS$_2$ and the product is called a dithiocarbazate (II).

R$_2$N–CS$_2^-$ R$_2$N–NH–CS$_2^-$

(I)   (II)
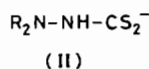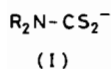
The dithiocarbazate ligands also would be expected to form a wide range of complexes but studies have not been as extensive as those for the dithiocarbamate analogues. In principle, bonding in dithiocarbazate complexes can occur either through the two sulfur atoms or through the terminal nitrogen and the thiol sulfur as shown in III and IV.

These different modes of bonding should produce marked changes in the properties of the complexes which are prepared and these are of significant

(III)

(IV)
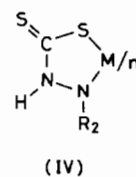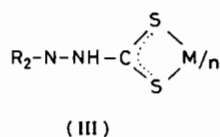
interest due to the current activity in the study of sulfur–nitrogen ligands [1, 2]. In this paper we wish to report our investigation of a number of complexes of dithiocarbazic acid and its 3-phenyl and 3,3-dimethyl derivatives.

Experimental

Ligand Preparation

Each of the dithiocarbazic acid ligands was prepared as the corresponding hydrazinium salt using methods similar to those reported in the literature [3]. The appropriate hydrazine and CS$_2$ were allowed to condense and the following species were isolated: NH$_2$NHCS$_2^-$·NH$_2$NH$_3^+$, C$_6$H$_5$NHNHCS$_2^-$·C$_6$H$_5$NHNH$_3^+$ and (CH$_3$)$_2$NNHCS$_2^-$·(CH$_3$)$_2$NNH$_3^+$.   Satisfactory analyses were obtained but the melting points were not distinct and decomposition appeared to occur upon melting.

The white solids could be stored in a vacuum desiccator for periods of at least two months without noticeable deterioration. However, over longer periods, gradual decomposition occurred with the production of a syrup-like mixture. Attempts to recrystallize this mixture gave very low yields of initial material and therefore fresh preparations of ligand were prepared as needed.

Complex Preparation

The neutral complexes ML$_n$ were prepared by the addition of a stoichiometric amount of the freshly

TABLE I. IR Data.

L = $H_2NNHCS_2^-$

	$\nu C-N$	$\nu CS_2(a)$	$\nu CS_2(s)$	$\nu M-N$	$\nu M-S$
Ligand	1518	970, 958	717	–	–
L_3Co	1465	990, 965	655	530	375
L_3Cr	1475	985	640	530	385
L_3Fe	1470	990, 970	655	530	370
L_2Ni	1510	986	672	535	345
L_2Pd	1504	980, 950	652	522	325
L_2Pt	1500	984	645	470	350
L_2Zn	1488	982, 955	654	520	370
L_2Cd	1480	955	645	495	380
L_2Hg	1490	940	645	480	310
L_2Sn	1475	935	640	478	345
L_2Pb	1465	930	635	478	335

L = $C_6H_5NHNHCS_2^-$

	$\nu C-N$	$\nu CS_2(a)$	$\nu CS_2(s)$		$\nu M-S$
Ligand	1570	990, 973	715		–
L_3Co	1505	988	677		339
L_3Cr	1505	985	695		360
L_3Fe	1505	995	688		352
L_2Ni	1526	985	686		368
L_2Pd	1542	980	680		320
L_2Pt	1510	980	680		315
L_2Zn	1500	975	680, 665		330
L_2Cd	1496	963	687		325
L_2Hg	1490	963	678		304
L_2Sn	1499	974	684		307
L_2Pb	1496	968	670		293

L = $(CH_3)_2NNHCS_2^-$

	$\nu C-N$	$\nu CS_2(a)$	$\nu CS_2(s)$		$\nu M-S$
Ligand	1505	975, 960	710		–
L_3Co	1511	1008	670		380
L_3Cr	1510	1002	675		383
L_3Fe	1504	1004	680		367
L_2Ni	1528	998	687		370
L_2Pd	1548	998	685		340, 335
L_2Pt	1516	1000	673		325
L_2Zn	1505	1000, 974	680		335
L_2Cd	1495	1008	690		320
L_2Hg	1495	980	640		298
L_2Sn	1500	1000	680		312
L_2Pb	1494	980	660		297

recrystallized ligand to an aqueous solution of the metal halide ($\sim 0.25 M$). The mixtures were stirred for approximately five minutes (1 hr for Co(III) and Cr(III)) and the precipitated products were filtered, washed thoroughly with dilute HCl and vacuum dried. The Co(III) complexes were prepared from trans-[Co(en)$_2$Cl$_2$]Cl and dilute acid rather than from a simple salt.

All complexes except those of dithiocarbazic acid itself were recrystallized from hot methanol. Physical properties of the complexes are reported in Table I. Infrared spectra of the species were

recorded as Nujol mulls or KBr discs on a Perkin-Elmer 621 infrared spectrophotometer. Diffuse reflectance and electronic spectra of methanol solutions were recorded on a Cary 14 spectrophotometer.

The neutral complexes containing the dithiocarbazate ligand could be dissolved in ~6 M NaOH to create anionic species of the type ML_n^{x-}. These species were isolated by precipitation as the tetramethylammonium salt using tetramethylammonium chloride.

Analytical data for complexes are shown in Table IV (deposited). Metal analyses were performed using approved methods as outlined in standard texts [4, 5]. Other elements were analyzed by A. B. Gygli Microanalysis Laboratory, Toronto.

Results and Discussion

Dithiocarbazic Acid Complexes

A few complexes containing the dithiocarbazate ion as a ligand have been prepared previously [6–9]. However, with the exception of nickel(II) and zinc-(II) these complexes have been only partially characterized. Part of the difficulty in characterization is due to the very low solubility of the complexes in most common solvents. As a consequence, many of the complexes were formed with various amounts of free ligand or free hydrazine in the solid crystalline product. Thus most attempts at characterization were concerned with determining the mode of ligand bonding; complex purity and overall stereochemistry were not of prime importance. The complexes reported in this work all have simple stoichiometries of ligand to metal and they extend the list of complexes reported previously. Because of the low solubility, spectroscopic studies were necessarily restricted to infrared and diffuse reflectance measurements and indeed reflectance spectra were only of use for the nickel(II), chromium(III) and cobalt(III) species, all of which are colored and have visible absorption bands.

Characteristic infrared data for the complexes prepared in this work are given in Table I. For complexes containing the unsubstituted dithiocarbazate (dtcz) ligand, bands were observed at 470–535 cm^{-1}, corresponding to $\nu(M-N)$ frequencies while a further band at 310–385 cm^{-1} was assigned to $\nu(M-S)$. These bands were missing in the IR spectrum of the free ligand and showed an obvious dependence on the metal present. Hence NS bonding is indicated. Previous workers have tended to focus attention on the $\nu(C-N)$ band as an indication of bonding mode. This was done by making comparisons with dithiocarbamate complexes and assignments were largely empirical, depending on a range of values for $\nu(C-N)$. However, $\nu(C-N)$ is quite variable, depending on the degree of substitution on the ligand. Therefore, specifiying a range has very limited usefulness. A better basis would be to consider shifts relative to the parent ligand. For the dtcz complexes $\nu(C-N)$ was always shifted to lower frequencies but for the substituted dtcz complexes where SS bonding occurs both higher and lower values were observed (*vide infra*).

Similarly, the $\nu(C-S)$ asymmetric stretch has also been used in the past in trying to assign the mode of bonding. By comparison with dithiocarbamate complexes, splitting or band broadening was interpreted to be indicative of NS bonding. However, for the ligand dtcz and its substituted analogues, two bands were present in each case and on complex formation, it was found that these either persisted or gave rise to a broad band, regardless of the mode of bonding. Moreover, the direction of the shift in band position bore no relation to the mode of bonding and seemed to be more dependent on the actual metal involved. Thus this region of the spectrum also has limited value in assessing the bonding mode and identification of the $\nu(M-N)$ and $\nu(M-S)$ bands is essential even though they may be combined with other vibrational modes.

From a cursory examination of Table I it would appear that for each ligand the complexes could be grouped into three categories; viz., complexes in the (III) oxidation state, square planar transition metal complexes and non-transition metal complexes. The 3+ metal complexes are considered to be octahedral on the basis of their diffuse reflectance

TABLE II. IR Data for Anionic Complexes of dtcz.

Complex	νC–N	νCS$_{2_a}$	νCS$_{2_s}$	νM–N	νM–S
[(CH$_3$)$_4$N]$_2$NiL$_2$	1485	946	630	520	370
[(CH$_3$)$_4$N]$_2$PdL$_2$	1485	950	650	502	350
[(CH$_3$)$_4$N]$_2$PtL$_2$	1484	946	652	445	340
[(CH$_3$)$_4$N]$_3$CoL$_3$	1486	951	655	530	365
[(CH$_3$)$_4$N]$_3$CrL$_3$	1475	948	658	530	370

spectra. Calculated β values in Table II are consistent with this interpretation and with NS bonding by the ligand. The β values are intermediate between those for MS_6 and MN_6 species of the corresponding metal ion. For these tris complexes the possibility of *cis–trans* (or *fac–mer*) isomerism exists and it is quite likely that the product obtained is a mixture of the two isomers. Unfortunately the solids are sufficiently insoluble that a thin layer chromatogram can not be made to see if this is the case. However, the color of the cobalt(III) complex would suggest that this is correct. For the analogous thiosemicarbazide complexes where *cis* and *trans* isomers have been separated [10], the colors are red-violet and green respectively. The observed brown color for the dtcz cobalt(III) complex would thus be consistent with a mixture of the two isomers.

The IR data for the M(III) complexes all form a pattern. The values for $\nu(M-N)$ and $\nu(M-S)$ are all at higher values relative to the M(II) complexes but do not show significant variations from metal to metal. The high value for these bands is consistent with the greater interaction anticipated due to the higher charge of the metal. The $\nu(C-N)$ bands for these complexes fall in the range 1465–1475 cm^{-1} and represented the largest decrease relative to the free ligand for the complexes studied. This would suggest a decrease in the relative importance of canonical structure 3 below,
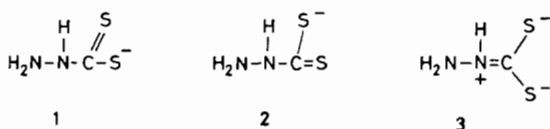
Since NS bonding is indicated, this decrease is not surprising since it would tend to favor electron donation to the metal via one sulfur atom only and the greater interaction for M(III) complexes should give rise to the greatest decrease.

The Ni(II), Pd(II) and Pt(II) complexes have the highest values for $\nu(C-N)$. The charge/size ratio of Ni^{2+} is less than that for M^{3+} and hence it would not be expected that the metal–ligand interaction would be as extensive. Hence the $\nu(C-N)$ bands would be expected to be at higher frequencies than the M(III) counterparts. The geometry of these complexes is almost certainly square planar. Electronic absorption spectra for the nickel(II) complex (Table II) are consistent with this interpretation and both Pd(II) and Pt(II) would be unlikely to show other arrangements with ligands such as these where steric hindrance is not a problem. Once again the question of isomerism is a possibility. However, these complexes again are too insoluble to detect the presence of more than one isomer and regions of the IR spectrum where *cis–trans* identification is often

possible are sufficiently poorly defined to be used for these complexes.

The remaining complexes involve non-transition metals which are known to form complexes with a variety of geometries. An examination of the $\nu(C-N)$ bands for these complexes shows that a significant lowering occurs relative to the free ligand anion and in many cases it approaches the values of the M(III) complexes. Thus it is rather unlikely that a planar arrangement of the ligands is present in these species but rather one in which the arrangement of the ligands is significantly different. Tetrahedral complexes are often formed with these metal ions since no extra ligand field stabilization is possible. This structure exists as a strong possibility since $\nu(C-N)$ is markedly decreased relative to the square planar complexes and as indicated above this is consistent with a strong interaction. Since only s and p orbitals are available on the metal for complex formation, a tetrahedral arrangement would provide a better arrangement than square planar. Indeed this situation has even been proposed in the case of a distorted six-coordinate complex of Sn(II) [11]. Support for a different geometry also is given by the markedly lower values for the asymmetric $\nu(C-S)$ stretch for these same complexes. While the tetrahedral geometry is not proven on the basis of the above observations, a planar arrangement would certainly appear to be unlikely.

One exception to the above conclusions may occur in the case of Zn(II). The relative values of $\nu(C-N)$ are more consistent with those of the square planar entities, as are the $\nu(C-S)$ bands. Thus for this species a planar arrangement may be present. Both the symmetric and asymmetric $\nu(C-S)$ bands are quite broad for the Zn(II) complex and it is possible that a type of interaction similar to that shown in Fig. 1 takes place [12]. X-ray structural data revealed that for the dithiocarbamate complex of Zn(II), a five-coordinate structure existed with bridging between a zinc atom and a sulfur atom of another complex unit. Such an interaction has also been observed for the Zn(II) complex of carbazic acid where a pyramidal arrangement around the zinc was also found [14]. Hence the zinc(II) complex of dtcz may be basically a pyramidal structure with the two ligands in an approximately planar arrangement.

Thus a comparison of the overall IR spectra would tend to indicate that changes in geometry can be detected in these complexes and hence could potentially be useful in the characterization of related complexes.

Phenyldithiocarbazic Acid Complexes

Although the preparation of the anion of this acid has been reported previously, few complexes have been prepared or characterized. The nickel(II) and zinc(II) species have been reported and some

IR data were presented [8, 13]. However, little was said about the complexes except that SS bonding was indicated. Consequently the data presented here are largely for new species. The key difference which is to be noted from Table I is the fact that there is no band which can be readily assigned to the ν(M–N) frequency while the ν(M–S) band is readily observed at approximately 360–293 cm^{-1}. The trend in ν(M–S) values is in the direction predicted by increasing mass of the metal and decreasing bond strength. These complexes thus apparently have SS bonding; and the possibility of geometric isomerism is not a consideration. Certain features should also be pointed out relative to the parent unsubstituted dtcz ligand. First the ν(C–N) band of the ligand anion is moved to higher frequencies which would suggest a greater contribution of C=N character to the bond. For this ligand, π-delocalization is possible over the entire molecule and thus the C–N bond order should be increased. Secondly it should be noted that the ν(C–N) frequencies of the complexes formed are again lower than that for the parent anion. This is in contrast to reports by early workers that NS and SS bonding could be distinguished by changes in this band. Both the unsubstituted and phenyl substituted complexes show a decrease in the frequency of this band upon complexation. However, NS bonding occurred in one case and SS bonding in the other.

As before three sub-groups can be identified for this series of complexes. The M(III) complexes have ν(C–N) all at the same value and it is lowered relative to the free ligand anion.

However, in contrast to the complexes of dtcz, these values are not the lowest of the complexes studied. SS bonding is indicated for the phenyl substituted species by both the absence of a ν(M–N) band in the IR spectra and the β values shown in Table II for the Cr(III) and Co(III) species. The decrease in ν(C–N) for these complexes is consistent with flow of electron density from the ligand to the metal. However, it is unusual that the ions with a +3 oxidation state are not the lowest of the group.

The square planar Ni(II), Pd(II) and Pt(II) complexes all have values higher than the octahedral complexes, as for dtcz but follow the trend, Pd > Ni > Pt. The non-transition metals have the lowest values of the three groups, and do not have as large a variation as for the dtcz complexes. The Zn(II) complex has the highest value of ν(C–N) and this may suggest a structural difference as with the dtcz ligand. However, the differences are small among the five species and this higher value is within experimental error. Thus these non-transitional metal complexes, where tetrahedral geometry is favored, all show the greatest lowering of ν(C–N), as found to be the case for the dtcz complexes. Thus this region

cannot be used to distinguish between NS and SS bonding.

As mentioned earlier, the ν(C–S)(asymmetric) values are lowest for the non-transitional metals and fall approximately in the same range. Similarly the values for the square planar and octahedral complexes fall within a range for their grouping. This is suggestive that there are similarities in overall structure within a group but again disproves any relationship to the mode of bonding.

N,N-Dimethyldithiocarbazic Acid Complexes

As was observed for the phenyl-substituted complexes, no band corresponding to ν(M–N) was found for the complexes of this ligand. A band corresponding to ν(M–S) appeared in all cases and as shown in Table I, followed a range of values which would be predicted from increasing mass of the metal ion and decreasing bond strength. These complexes thus may be considered to have SS bonding and the β values given in Table II for the Co(III) and Cr(III) complexes support this fact.

A significant difference in the ν(C–N) frequency changes was found for the complexes of this ligand. Once again the square planar complexes showed the highest values for ν(C–N). Both the octahedral (3+) metal complexes and the square planar grouping showed values for ν(C–N) which were higher than the free ligand value. The group of non-transition metal complexes, however, had values which were lower. The Zn complex was unchanged from the ligand value. These findings again show that changes in ν(C–N) are unreliable in determining the mode of bonding for the ligands.

Summary

On the basis of the above data the following conclusions are drawn.

(1) The free unsubstituted ligand dtcz forms bidentate complexes with NS bonding while the dimethyl and phenyl ligands all exhibit SS bonding.

(2) The tris complexes have octahedral geometry while the bis complexes are either square planar or tetrahedral. The square planar geometry can be readily noted for all complexes by higher ν(C–N) values. In the NS bonded complexes, all C–N stretches are lower than the parent ligand while for the substituted complexes the pattern is not consistent.

(3) The (C–S) asymmetric stretch increases for all the complexes relative to the free ligand and the ranges of values are consistent with the geometric changes noted for ν(C–N). However, the differences among groupings are too small to be a diagnostic means by themselves.

(4) The use of ν(C–N) can be potentially useful for identifying other geometries by examining the

TABLE III. Diffuse Reflectance Spectral Data for Complexes.

	λ_{max}	λ_{max}	10 Dq	B	β
$(H_2NNHCS_2)_3Cr$	500	420	17,200	653	0.71
$(C_6H_5NHNHCS_2)_3Cr$	640	490	15,625	420	0.49
$((CH_3)_2NNHCS_2)_3Cr$	645	500	15,500	418	0.47
$(H_2NNHCS_2)_3Co(III)$	560	390	19,800	487	0.44
$(C_6H_5NHNHCS_2)_2Co(III)$	640	480	14,321	326	0.30
$((CH_3)_2NNHCS_2)Co(III)$	625	460	14,564	359	0.32
$(H_2NNHCS_2)_2Ni$	500				
$(C_6H_5NHNHCS_2)_2Ni$	625				
$((CH_3)_2NNHCS_2)_2Ni$	625				

relative positions of the band compared to the free ligand; obviously this would be useful for characterization of further complexes.

Anionic Complexes

The free dithiocarbazic acid ligand forms complexes of the type mentioned above. However, these complexes will convert to an anionic form on the addition of base. This is presumably due to the loss of the acidic proton from nitrogen atom 2. Upon complexation, it would be anticipated that electron density would be withdrawn from this nitrogen and hence an enhancement of the acidity of the proton would be predicted. The complexes which are formed maintain their NS bonding and can readily be converted back to the neutral complexes described earlier. This observation has been noted by other workers but the isolation of actual complexes has only been reported for nickel(II).

In this work anionic complexes have been isolated as solids by precipitation as the tetramethyl-ammonium salts. Only five complexes could be isolated as stable solids, however. The other complexes described in Table II were treated with base in the same manner but the solid obtained either showed evidence of decomposition or gave inconsistent analyses.

Spectral data for the anionic complexes are given in Table III and the major changes relative to the corresponding neutral complexes are noted below. The visible spectra of the Ni(II), Cr(III) and Co(III) complexes all bear striking resemblances·to the parent neutral complexes whose diffuse reflectance spectra were measured. Thus it would appear that electronic energy levels in the two types of complexes are not significantly changed. There was a distinct lowering of the $\nu(M-N)$ for the square planar complexes while the Cr(III) and Co(III) remained unchanged. The

square planar complexes also showed a distinct lowering of the $\nu(C-N)$; all had essentially same values. The asymmetric $\nu(C-S)$ was also lowered significantly and varied only slightly from compound to compound. The $\nu(C-S)_s$ was also lowered but showed only slight variation. The changes thus suggest that the ligand has undergone a definite redistribution of electron density and that this is relatively unaffected by the actual metal ion which becomes attached. The downward trend in $\nu(C-N)$ values is consistent with electron flow towards the coordinating nitrogen from the two lone pairs which are now present on the N_2 atom. Presence of these two lone pairs also would suggest that sp^3 hybridization would be present at this N atom and hence would decrease the amount of double bond character in the CN region. Consistent with such a decrease, a decrease would be predicted in the CS bands. Since they are less connected through the π system to the rest of the molecule they should move more independently and hence move to lower frequencies.

Acknowledgement

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