THEORETICAL STUDY OF THE ELECTRON STRUCTURE AND PROPERTIES OF DITHIOCARBAMATES AND THEIR COMPLEXES WITH TRANSITION METALS

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The semiempirical CNDO/2 method was used to calculate the electron structure of derivatives of dithiocarbamates, R_2N-CS_2, as anions and radicals. We studied changes in the oxidation-reduction and bonding properties by changes of $R = H$, CH_2, C_2H_5, C_3H_5. Calculations were also carried out on model complexes of R_2N-CS_2 with metals Cu, Mn, Fe, Co, Ni. Differences in the electron structure of these complexes with various numbers of ligands, various states of oxidation and varying spin multiplicity of the central atoms were evaluated.

Dithiocarbamates (dtc) and especially their complexes with transition metals belong among compounds with broad application and use in analytical chemistry and also in various areas in industry and agriculture, *e.g.* as antioxidants, vulcanization accelerators, fungicides, *etc.*[1]. Consequently, a great deal of attention is paid to elucidation of the relationships between the structure and properties of these compounds[2]. Such knowledge can contribute both to understanding of the mechanism of their action and also to discovery of derivatives or complexes of dtc with required properties or biological action. Besides the experimental method of structural study, theoretical study of the electron structure of these compounds is becoming increasingly important. Quantum chemical calculations yield a detailed picture of the electron density distribution, strength of individual bonds, conformation, reactivity, *etc.* In this region, Keijzers and de Boer[3] employed the EHT method for interpretation of the parameters of the ESR spectra of some complexes of dtc. Semiempirical INDO calculations on the electronic structure of $(C_2H_5)_2NCS_2^-$ ligands have been published[4] as well as CNDO/2 study of the bonding properties in some complexes of dimethyl-dtc with transistion metals[5]. This work deals with complete calculations of the basic characteristics of the electron structure of free dtc ligands and also of selected complexes, which should yield basic information on the nature of the forces acting in these compounds.

Further works in this series will examine more closely the optimal geometrical arrangement in dtc complexes or ligands and also the effect of the medium (crystal lattice and solvent) on the properties of dtc complexes.

METHODS AND CALCULATIONS

The size of the studied systems excludes the use of the nonempirical *ab initio* method for the calculations. Thus the electron structure and properties of the studied compounds were calculated using the quantum chemical CNDO/2 method with standard parametrization, considering all the valence electrons[6]. For transition metals, the parametrization of Clack and coworkers[7] was used. The calculations were carried out using the MOSEMI (ref.[8]) and GEOMO (ref.[9]) programs on a M-4030 computer in the computer centre of the Slovak Technical University.

Calculations were carried out both for the free ligands $dtcR_2^-$ and $dtcR_2^\bullet$ and also for selected complexes.

In calculations on the studied system the experimental geometry[10-12], primarily bond lengths, bonding and dihedral angles were used for part of the complex (Scheme 1). Standard geometry was considered for the remainder of the ligand molecule, —R (—H, —CH_3, —C_2H_5, —C_3H_5) (ref.[13]). The same geometry was used for the $dtc^\bullet$ radical as for the dtc^- anion.

RESULTS AND DISCUSSION

The Electron Structure of the dtc Ligands

This part deals with calculations on the dtc ligands depicted in Scheme 1, where R is H, CH_3, C_2H_5 or allyl. These structures were considered either as anions with closed electron shells, *i.e.* $(S_2C{-}NR_2)^-$, as also as open shell systems with an unpaired electron, *i.e.* $(S_2C{-}NR_2)^\bullet$. Both types represent model systems for study of complexes.

SCHEME 1

Tables I and II list the energies of the molecular orbitals E_{HOMO} and E_{LUMO}, the atomic charges Q_S, Q_C, Q_N and also the Wiberg indices characterizing the bonding abilities, primarily for the S–C and C–N or N–C′ bonds. (C′ are carbons in the R fragment bonded directly to an N atom).

The results listed in Tables I and II can be used for rough estimate of the ability of various dtc ligands to form complexes. It is especially interesting to note the values of the various indices for the dtc ligands and the changes in these indices with a change in substituent R. Complex formation should depend, besides other factors, on the ability of the model dtc^- ligand to donate an electron. The energy of the highest occupied molecular orbital E_{HOMO} is a measure of this ability. The E_{HOMO} value for the $(S_2C{-}NR_2)^-$ ligands increases slightly in the order R = H, CH_3, C_2H_5, C_3H_5, indicating greater donor ability in this order. The E_{HOMO} value increases more markedly for the allyl substituents. It is, however, interesting that this value again decreases when the allyl group is twisted out of the ligand plane, at $\theta = 30°$ (Scheme 1).

The electron density distribution in dtc^- ligands is characterized by the charge values Q_S, Q_C and Q_N. The whole negative charge of the ligand is practically localized on the sulphur atoms. Carbon, C even has a positive charge between 0·21 and 0·16, in dependence on R. There is a small negative charge on nitrogen. As the CNDO/2 mehod was used, these values must be considered approximate.

Small differences between the ligand properties also follow from the Wiberg index values, which approximately characterize the bond order. The very similar character of the S–C and C–N bonds should be noted. The N–C′ bond is a single

TABLE I

Calculated indices of the electron structure[a] of the $(dtc)^-$ ligand

System	Q_S	Q_C	Q_N	$W.I._{S-C}$	$W.I._{C-N}$	$W.I._{N-C'}$	E_{HOMO}
$[S_2C{-}NH_2]^-$	−0·587	0·183	−0·154	1·263	1·228	—	−0·100
$[S_2C{-}N(CH_3)_2]^-$	−0·590	0·170	−0·174	1·279	1·184	1·007	−0·100
$[S_2C{-}N(C_2H_5)_2]^-$	−0·596	0·171	−0·096	1·275	1·193	0·981	−0·098
$[S_2C{-}N(C_3H_5)_2]^-$	−0·679	0·1837	−0·107	1·267	1·200	0·986	−0·057
$[S_2C{-}N(C_3H_5)_2]^-$ [b]	−0·603	0·168	−0·103	1·274	1·196	0·682	−0·095

[a] E_{HOMO} Values in atomic units; [b] allyl groups twisted out of the plane of the complex by an angle of $\theta = 30°$.

TABLE II

Indices of the electron structure[a] of the $(dtc)^{\cdot}$ ligand

System	Q_S	Q_C	Q_N	$W.I._{S-C}$	$W.I._{C-N}$	$W.I._{N-C'}$	E_{SMO}
$[S_2C{-}NH_2]^{\cdot}$	0·219	0·216	−0·080	1·199	1·465	—	−0·002
$[S_2C{-}N(CH_3)_2]^{\cdot}$	0·194	0·169	−0·055	1·164	1·515	0·954	−0·007
$[S_2C{-}N(C_2H_5)_2]^{\cdot}$	0·143	0·163	−0·059	1·160	1·523	0·962	−0·009
$[S_2C{-}N(C_3H_5)_2]^{\cdot}$	0·138	0·155	−0·063	1·160	1·533	0·95	−0·011

[a,b] See Table I.

one and its bond order does not change even by a change in the ligand substituent R for allyl.

Similar conclusions can be drawn from calculations on the (dtc)• ligand, which differs from the above system in the lack of one electron. This is thus a simple model of the situation where the electron in the complex moves completely to the central atom, but does not consider their mutual interactions.

The results of calculations of the indices of the electron structure are given in Table II. Similar conclusions can be drawn from these indices as from the values for $(\mathrm{dtc})^-$. The energy of the singly occupied molecular orbital E_{SMO} gradually decreases for R from H to allyl, indicating a tendency for the ligand $(\mathrm{dtc})^{\bullet}$ to share an electron from the central atom. However, differences in E_{SMO} are very small. A further interesting factor is the marked change in the charge on the sulphur atoms (positive in $\mathrm{dtc}^{\bullet}$) and the marked increase in the Wiberg indices for the C=N bond. In dtc• it has marked double character, in contrast to dtc^-. Considering that the experimental observations for the IR spectra of the dtc complexes[14] indicate that the C=N bond is double in these systems, it can be expected that the ligand in dtc complexes has $\mathrm{dtc}^{\bullet}$ character to the same degree as dtc^- character. This is also confirmed by calculations for the complexes in the subsequent section.

The Electron Structure of dtc *Complexes with Various Metals*

This part deals with obtaining the basic characteristics of the electron structure of model complexes of dtc with metals Me = Fe, Co, Ni, Cu, Mn, in order to evaluate changes in the electron structure of these complexes during a change in the central atom and during a change in the number of ligands and oxidation state of the central atom. For simplicity we always considered (S_2C–NH_2) as the ligand, with the geometry given for bis-complexes in Scheme 1, where the whole system was planar. This geometry represents the average of the experimental geometries of a number of complexes[11,12].

For the tris-complex $\mathrm{Co(dtc)_3}$ the geometry of the dtc ligand was also considered as in Scheme 1. The spatial orientation of the ligands around the central atom was selected according to ref.[15]. The general formula of the complexes considered can be given as $^{K}[\mathrm{Me(L)}_x]^{q}$, where K is the spin multiplicity, x is the number of ligands and q is the total charge on the complex. The results of calculations on the complexes considered are given in Tables III and IV. Table III gives the Wiberg indices, yielding basic information on the bond strength as well as the charge on the individual atoms of the complexes. Table IV gives the orbital energies E_{HOMO} and E_{LUMO} and also the occupational coefficients of these orbitals for the individual atoms.

It follows from the charge values on the individual atoms in the complex that complex formation is accompanied by considerable charge transfer from the ligand to the central atom. Although the CNDO method over-evaluates this transfer, the q value indicates that the central atom has only a fractional positive charge in the complex. This transfer is largest for the copper complex Cu(dtc). For neutral complexes q_{Me} varies from 0·03 to 0·329 (for $Co(dtc)_3$), positively charged systems have a value of $q = 0{\cdot}556$ for $[Co(dtc)_2]^+$ and only 0·219 for $[Cu(dtc)_2]^+$. Thus the positive charge is also delocalized on the ligands. The degree of charge transfer also affects the stability constant β. The stability constants for various dtc complexes[16] were measured experimentally. Comparison of the $\log \beta_2$ values for the Me(dtc). complexes reveals that these values increase in the order Fe < Co < Ni < Cu, The charge on the central atom q_{Me} decreases in the same order (Table III).

Comparison of the Wiberg indices for the ligand bonds in complexes with hypothetical structures (dtc)• and $(dtc)^-$ reveals that the ligands have almost (dtc)• character in the complex. After complex formation the C—S bond is weaker and the C—N bond assumes double character. This corresponds to the experimentally measured IR spectra of these complexes[14]. The relatively high values of the Wiberg indices for the Me...S bonds reflect the covalent character of these bonds. It is interesting that the index for the S...Cu bond in the Cu(dtc) complex is even larger than that for the S–C bond. The Wiberg index decreases with an increasing number of ligands in the complex. Nonetheless, even for $Co(dtc)_3$ this index is still close to the values for other complexes $Me(dtc)_2$, indicating retention of covalency of the Me...S bond.

The studied complexes can be divided into several types in dependence on the HOMO and LUMO distribution on the individual atoms. The bis-complexes $Me(dtc)_2$ have the highest occupied molecular orbital localized primarly on the

TABLE III

Charge values on the atoms and Wiberg indices for the $^K[Me(dtc)_x]^q$ complexes[a]

Complex	Charge				Wiberg index		
	q_S	q_C	q_N	$q_M{}^c$	C—S	N—C	S—Me
$^1[Co(dtc)_2]^{1+}$	−0·153	0·291	−0·127	0·556	1·052	1·523	0·821
$^2[Co(dtc)_2]^0$	−0·223	0·280	−0·153	0·068	1·067	1·441	0·668
$^1[Co(dtc)_3]^0$	−0·258	0·279	−0·154	0·329	1·096	1·428	0·627
$^1[Fe(dtc)_2]^0$	−0·237	0·279	−0·153	0·127	1·066	1·440	0·658
$^1[Ni(dtc)_2]^0$	−0·215	0·281	−0·152	0·032	1·067	1·442	0·675
$^1[Cu(dtc)_1]^0$	−0·152	0·226	−0·150	−0·053	0·848	1·456	1·245
$^1[Cu(dtc)_2]^{1+}$	−0·069	0·290	−0·128	0·219	1·046	1·524	0·876
$^2[Cu(dtc)_2]^0$	−0·212	0·283	−0·152	0·016	1·064	1·443	0·654
$^2[Mn(dtc)_2]^0$	−0·262	0·276	−0·153	0·237	1·070	1·430	0·635

[a] In the $^K[Me(dtc)_x]^q$ complex, x is the number of ligands, K is the spin multiplicity and q is the complex charge.

sulphur atoms with small participation of the *d*-orbitals of the central atom. An exception is Mn(dtc)$_2$, where HOMO is localized almost completely on the *d*-orbitals of Mn. The lowest unoccupied MO in this group is again delocalized over the ligand chain, primarily on the C–N bond.

The basic oxidation reduction characteristics of the model complexes can be estimated from the values of the energies of the highest occupied molecular orbital (E_{HOMO}) and lowest unoccupied molecular orbital (E_{LUMO}). The ease of oxidation should increase in the order Co(dtc)$_3$ < Fe(dtc)$_2$ < Co(dtc)$_2$ < Ni(dtc)$_2$ < Mn(dtc)$_2$ < < Cu(dtc)$_2$ < Cu(dtc). Complexes with nonzero overall charge have not been included here. Of this series, three complexes were also studied experimentally[16], Co(dtc)$_3$ ($E_{1/2}$ = 0·53 V), Ni(dtc)$_2$ ($E_{1/2}$ = 0·345 V) and Cu(dtc)$_2$ ($E_{1/2}$ = 0·11 V). The experimental trend in the oxidation potentials of these complexes is in agreement with the calculated values. On the other hand the comparison with photoelectron spectra[17] is not so simple. The reduction properties of the studied com-

TABLE IV

Energies of the molecular orbitals E_{HOMO} and E_{LUMO} (eV) and coefficients of occupation[a] of these MO's on the individual atoms

Complex	E_{HOMO} E_{LUMO}	Me	S	C	N
^{1}[Co(dtc)$_2$]$^{1+}$	−16·172	3·9^p	19·3^p	8·1^p	0·3^p
	− 5·269	64·0	8·8^p	0·4^p	0
^{2}[Co(dtc)$_2$]^0	− 9·816	4·9^d	22·5^p	2·1^p	0
	3·231	0·5^p	4·0^p	36·0^p	8·0^p
^{1}[Co(dtc)$_3$]^0	−10·191	1·9^p	14·0^p	3·2^p	1·3^p
	2·077	80·7^d	5·8^p	0·2^p	0
^{1}[Fe(dtc)$_2$]^0	− 9·937	5·2^d	22·5^p	2·3^p	0
	3·266	0·4^p	3·0^p	36·0^p	8·0^p
^{1}[Ni(dtc)$_2$]^0	9·682	4·3^d	22·9^p	2·0^p	0
	3·207	0·5	2·9^p	36·0^p	8·0^p
^{1}[Cu(dtc)$_1$]^0	− 3·617	75·2^d	6·3^p	10·8^s	1·1^{s,p}
	1·735	79·8^{s,p,d}	4·2^{p,s}	9·1^s	1·9^s
^{1}[Cu(dtc)$_2$]$^{1+}$	−16·307	4·0^p	18·8^p	8·7^p	0·3^p
	− 6·208	56·4^d	10·7^p	0·5^p	0
^{2}[Cu(dtc)$_2$]^0	− 8·506	9·9^d	21·9^p	1·2^p	0
	3·187	0·5^p	2·8^p	36·0^p	8·0^p
^{2}[Mn(dtc)$_2$]^0	− 9·258	96·5^d	0·6^p	0·3^s	0
	3·324	0·4^p	3·0^p	36·0^p	8·0^p

[a] Coefficients of occupation of the MO's on the individual atoms are expressed in percent. The index next to the number indicates the dominant type of atomic orbital (*s*, *p* or *d*).

plexes can be estimated from the E_{LUMO} values. The following order of increasing tendency to be reduced was found for complexes with overall zero charge: Mn(dtc)$_2$ < Fe(dtc)$_2$ < Co(dtc)$_2$ < Ni(dtc)$_2$ < Cu(dtc)$_2$ $\ll$ Co(dtc)$_3$. The differences between the E_{LUMO} values are relatively small for all the bis-complexes. A greater change occurs only for the Co(dtc)$_3$ complex. Thus it is not surprising that some changes in the determined trend can be expected on the basis of chemical experience (*e.g.* poorer reducibility of the Cu complex compared to the Fe, Co and Ni complexes). It is, however, clear that this trend yields only basic information on the energies of the molecular orbitals involved in oxidation-reduction processes. The oxidation-reduction properties are affected by a number of other factors (kinetic, thermodynamic, effect of medium, *etc.*), that must be considered in more detailed evaluations.

A further simplification in this work involved is employing the same geometry of the bis-complexes for various central atoms. It has been found, however, that the effect of optimization of the geometry of the complexes does not basically affect the individual calculated indices. This effect and the effect of the medium will be considered in greater detail in subsequent works in this series.

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