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A Semiempirical Molecular Orbital Study of Transition Metals Maleonitriledithiolate Redox Series

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CNDO and iterative extended Hückel methods have been used for the study of the electronic structure of maleonitriledithiolate complexes of Co, Ni and Cu for various formal oxidation states of the central atom, the aim being to describe the changes in the energy of molecular orbitals and in their composition depending on the overall number of electrons. The electronic charge distribution and bond orders connected with the variation of the overall charge of these complexes were also evaluated. The results of both methods were compared and used for the interpretation of redox properties. The electronic charge distribution reflects qualitatively the reactivity of sulphur centers. Both methods indicate, in the case of the redox series Comnt$_2^{n-}$, remarkable orbital relaxation in accordance with experimental findings.

Introduction

The intensive study of transition metal complexes with maleonitriledithiolate ligands, Mmnt$_2^{n-}$, began by the first report of Gray *et al.* [1]. These complexes are characterized by their relatively high stability, and are noted for the formation of redox series, *i.e.* sets of complexes whose members differ only by the overall number of electrons. The one-electron transfer reactions which connect the different oxidation states of these complexes are reversible, with well defined half-wave potentials. Therefore the redox properties of Mmnt$_2^{n-}$ complexes have been intensively studied [2, 3]. The knowledge of the electronic structure of these complexes can contribute to a better understanding of their redox properties. The electronic structure of maleonitriledithiolate complexes was studied by semiempirical methods [4, 5] or was deduced from experimental measurements [18, 19]. The published calculations have used π-approximation in the ligand skeleton and they do not explicitly take into account the influence of the variation in overall number of electrons on the electronic structure.

Recently, the redox series of bis(maleonitriledithiolate) complexes of first row transition metals were completed [6–8], resulting in the requirement of all valence electrons calculations to cover the whole region of possible formal oxidation states. The interpretation ability of the individual semiempirical methods depends on the approximation and the proper parametrization, and therefore two different semiempirical methods were used in our calculations: the iterative extended Hückel method (IEHM)[9], and the CNDO method [10]. The use of these quantum chemical methods makes it possible to interpret structural phenomena connected with redox processes.

Calculation Methods

The electronic structure of Mmnt$_2^{n-}$ complexes was studied by CNDO and IEHM using the following approximations: Throughout IEHM the wave functions of Richardson [11, 12] and Clementi [13] were used. The charge dependent diagonal matrix elements of the effective Hamiltonian were approximated by valence orbital ionization potentials [14], the off-diagonal matrix elements by Wolfsberg–Helmholz expression [15].

CNDO calculations were based on the following parametrization: For elements C, N, and S the standard CNDO/2 parametrization of Pople *et al.* [10], and for the first row transition metal elements the parametrization according to Clack *et al.* [16] with Gouterman exponents was used. The open shell systems were calculated using the UHF approach.

The planar bis(maleonitriledithiolato) complexes of D_{2h} symmetry were located in the rectangular coordinate system in the following way: the metal atom coincided with the centre of the coordinate system and the plane formed by the ligand atoms was identified with the x, y plane (Fig. 1).

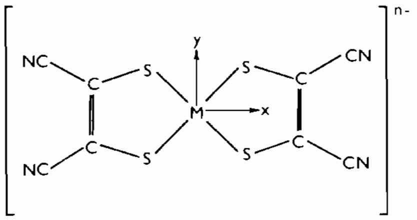

Fig. 1. The geometry and the coordinate system of Mmnt$_2^{n-}$ complexes.

Results and Discussion

By the semiempirical methods described above calculations of complexes Comnt$_2^{n-}$, Nimnt$_2^{n-}$, Cumnt$_2^{n-}$ (n = 1, 2, 3) were performed. The geometry of these complexes was taken from the experimental X-ray measurements [17]. Because of the lack of experimental data for all oxidation states calculated, the geometry of the individual complexes was not varied during the change of the formal oxidation state of the central atom using the geometry of Mmnt$_2^-$ complexes. Test calculations on the complexes Nimnt$_2^-$ and Nimnt$_2^{2-}$, the structure of which is known, showed that the rather small variation of the geometry accompanying the change in the overall number of electrons preserves *qualitatively* the sequence of orbital levels, charge densities and bond indices, so that the rigid geometry approximation was used throughout the calculations.

Molecular Orbitals

In the sequence of molecular orbitals of isoelectronic d^8 Mmnt$_2^{n-}$ systems, given by IEHM, the orbital 4b$_{2g}$ is identified as the highest occupied molecular orbital (HOMO). This orbital of b$_{2g}$ symmetry is composed of the d$_{xz}$ orbital of the central atom and the appropriate symmetric combination of π-orbitals of ligands. The orbital 4b$_{2g}$ is composed from 75% d$_{xz}$ orbital of the central atom in the case of the complex Comnt$_2^{3-}$. When going along the isoelectronic series the contribution of the central atom orbital to the HOMO is strongly reduced as shown in Fig. 2. The lowest unoccupied orbitals (LUMO) of these d^8 systems are essentially the ligand localized molecular orbitals.

In connection with the variation of the overall charge of complexes the orbital energies are shifted and the composition of the individual orbitals is changed, but no crossing of molecular orbital levels is observed. Changes which accompany the redox process are most significant in the case of Comnt$_2^{n-}$ series. The shift of molecular orbitals caused by the addition of one electron into the system Comnt$_2^{2-}$ is shown in Fig. 3. Fig. 2 illustrates the variation of the composition of the redox orbital, 4b$_{2g}$, during the successive transition from Comnt$_2^-$ to Comnt$_2^{3-}$. For

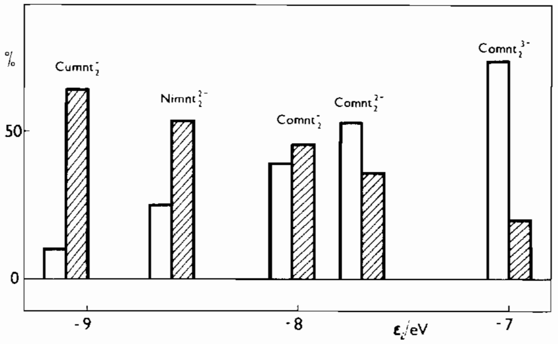

Fig. 2. The composition and the relative position of 4b$_{2g}$ molecular orbitals of Mmnt$_2^{n-}$ complexes. IEHM results. The white area is the contribution of the metal d$_{xz}$ orbital, the shaded area is the contribution of the ligand π system.

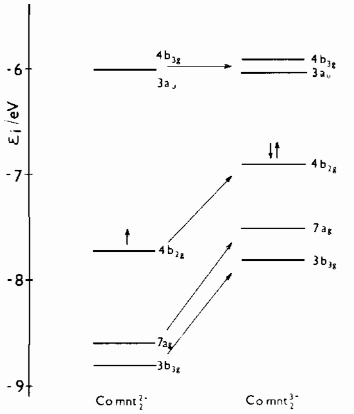

Fig. 3. The change of the molecular orbital scheme of Comnt$_2^{2-}$ caused by the addition of one electron—IEHM.

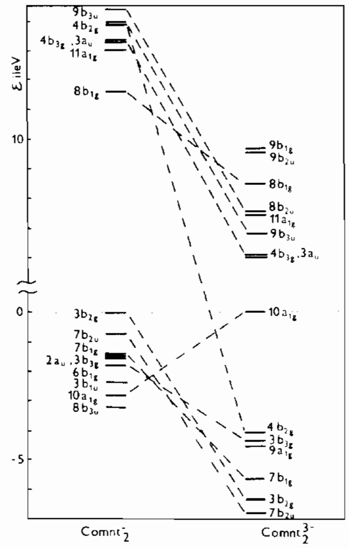

Fig. 4. The comparison of CNDO molecular orbital schemes of closed shell systems Comnt$_2^-$ and Comnt$_2^{3-}$. For clarity the energy of HOMO is identified with the zero of the energy scale in both cases.

complexes Nimnt$_2^{n-}$ the changes accompanying the redox process are not so apparent and the electronic structure of complexes Cumnt$_2^{n-}$ is not practically influenced by the variation of the formal oxidation state of the central atom. The gap between HOMO and LUMO lowers when going from Cumnt$_2^{n-}$ to Comnt$_2^{n-}$ series, in qualitative agreement with the observed spectra. Within a given series a substantial change is observed only in the case of cobalt complexes.

Using CNDO, the molecular orbital $4b_{2g}$ emerges again as HOMO for closed shell isoelectronic d^8 systems Nimnt$_2^{2-}$ and Cumnt$_2^-$ and has mainly ligand character with contribution of 9.8% and 1% d_{xz} orbital of the central atom, respectively. For the closed shell d^8 system Comnt$_2^{3-}$ CNDO method results in the $10a_{1g}$ (51.4% $d_{x^2-y^2}$) as HOMO, the $4b_{2g}$ orbital (73.3% d_{xz}) being energetically stabilized in this case (Fig. 4). The comparison of the composition of the orbital $4b_{2g}$ with the nature of the central atom shows that the contribution of d_{xz} orbital of the central atom is reduced in the direction from Comnt$_2^{3-}$ (73.3%) to Cumnt$_2^-$ (1%), in general agreement with IEHM results. The LUMO of these d^8 systems is the mainly ligand localized MO $4b_{3g}$ for Comnt$_2^{3-}$, Nimnt$_2^{2-}$ and the metal localized $8b_{1g}$ orbital (58.8% d_{xy}) for Cumnt$_2^-$ (see Table I for results). Results in Table I show that with increasing negative charge on the complex all energy levels are shifted to more positive values (compare the orbital energy of the $3a_u$, nonbonding ligand localized orbital, for Cu, Ni and Co complex). This shift of energy levels is due to the electrostatic influence of the increasing overall negative charge.

Because of different α and β spin-parts in the open shell UHF calculations, the localization of the unpaired electron density in paramagnetic Mmnt$_2^{n-}$ complexes was deduced by the analysis of UHF spin density matrices, rather than from one-electron molecular orbitals. Such analysis shows that the unpaired electron is localized either in the orbital of b_{2g} symmetry in the case of complexes Comnt$_2^{2-}$, Nimnt$_2^-$ or in the orbital of b_{1g} symmetry in the complex Cumnt$_2^{2-}$. These results indicate that the metal localization of the unpaired spin density falls down in the sequence Comnt$_2^{2-}$ > Nimnt$_2^-$ > Cumnt$_2^-$, consistent with the EPR measurements [18–20]. Along the redox series Nimnt$_2^{n-}$, Cumnt$_2^{n-}$ the sequence of molecular orbital is preserved independently of n. However, the orbital relaxation is observed in the Comnt$_2^{n-}$ series. As shown in Fig. 4 HOMO of Comnt$_2^-$ is of $3b_{2g}$ symmetry; the increase in the overall number of electrons in the system induces a strong orbital relaxation: the orbital $4b_{2g}$ is shifted down into the region of occupied orbitals, whereas the $10a_{1g}$ orbital (predominantly metal localized orbital) is relatively destabilized and becomes HOMO.

The CNDO and IEH methods give a qualitatively similar description of the electronic structure of Mmnt$_2^{n-}$ complexes. Trends of individual characteristics are in both cases analogous. The localization of HOMO and LUMO orbitals of isoelectronic d^8 Mmnt$_2^{n-}$ complexes differs in the case of Cumnt$_2^-$, where CNDO indicates as LUMO the metal localized $8b_{1g}$ orbital in accordance with experimental findings (in contrast with the ligand localized molecular orbital calculated by IEHM). The change of the energy of molecular orbitals with the variation of the overall charge of the complex differs remarkably in the case of the redox series of complexes Comnt$_2^{n-}$, because of the considerable orbital relaxation which IEHM is not able to describe to a full extent.

Redox Properties and Charge Distribution

During the reduction of the closed shell system Cumnt$_2^-$, the LUMO (*i.e.* $8b_{1g}$) of this complex is filled up stepwise. The UHF CNDO calculation

TABLE I. Selected Molecular Orbitals of Closed Shell d^8 Maleonitriledithiolate Complexes—CNDO Method[a]. Energies in eV.

Comnt$_2^{3-}$			Nimnt$_2^{2-}$			Cumnt$_2^-$		
Orbital	Energy	Character	Orbital	Energy	Character	Orbital	Energy	Character
$7b_{1g}$	3.610	σ_L	$7b_{2u}$	−3.211	p_y, σ_L	$3b_{3g}$	−8.443	d_{yz}, π_L
$9a_{1g}$	4.735	d_{z^2}, π_L	$2a_u$	−3.001	π_L	$7b_{2u}$	−8.373	p_y, σ_L
$3b_{3g}$	4.938	d_{yz}, π_L	$3b_{3g}$	−2.490	d_{yz}, π_L	$2a_u$	−8.258	π_L
$4b_{2g}$	5.196	d_{xz}, π_L	$7b_{1g}$	−1.305	d_{xy}, σ_L	$7b_{1g}$	−7.877	d_{xy}, σ_L
$10a_{1g}$[b]	9.285	$d_{x^2-y^2}, \sigma_L$	$4b_{2g}$[b]	−0.978	d_{xz}, π_L	$4b_{2g}$[b]	−6.155	d_{xz}, π_L
$4b_{3g}$[c]	15.264	π_L	$4b_{3g}$[c]	10.741	π_L	$8b_{1g}$[c]	4.168	d_{xy}, σ_L
$3a_u$	15.268	π_L	$3a_u$	10.752	π_L	$4b_{3g}$	6.776	π_L
$9b_{3u}$	16.079	σ_L	$10a_{1g}$	11.474	d, σ_L	$3a_u$	6.788	π_L
$8b_{2u}$	16.702	p_y, σ_L	$9b_{3u}$	12.329	p_x, σ_L	$11a_{1g}$	6.890	d, π_L

[a] The molecular orbitals are characterized by the dominant contributions of the individual orbitals. π_L: ligand π orbitals; σ_L: ligand σ orbitals. [b] HOMO. [c] LUMO.

indicates for Cumnt$_2^{2-}$ a doublet ground state $^2B_{1g}$, in agreement with EPR study. The totally reduced species, Cumnt$_2^{3-}$, has a ground state $^1A_{1g}$ with fully occupied orbital $8b_{1g}$.

The ground state of the complex Nimnt$_2^{2-}$ is the $^1A_{1g}$ state with the fully occupied $4b_{2g}$ orbital. Both methods show that during the one-electron oxidation the electron is removed from molecular orbital $4b_{2g}$ and the complex Nimnt$_2^{-}$ with the doublet ground state, $^2B_{2g}$, is formed. The unpaired spin density of Nimnt$_2^{-}$ is considerably localized on d_{xz} orbital of the central atom, consistent with the conclusion of EPR study [18]. Further oxidation would result in the removal of the electron from the same orbital $4b_{2g}$. The IEHM places the extra electron in the process Nimnt$_2^{2-}$ → Nimnt$_2^{3-}$ into the $4b_{3g}$, a ligand localized orbital. The UHF–CNDO method, on the other hand, indicates the formation of the $^2A_{1g}$ state with the spin density localized predominantly on the metal, using $(d_{x^2-y^2} + d_{z^2})$ orbital. This description is in accordance with the analysis of experimental results which point to the Nimnt$_2^{3-}$ as a complex of univalent nickel [6, 7].

A more complicated situation arises in the case of redox series Comnt$_2^{n-}$. Here, both methods show that a strong orbital relaxation accompanies the redox change. For the open shell system Comnt$_2^{2-}$, IEHM and CNDO methods give identical doublet ground state, $^2B_{2g}$, again in full agreement with EPR measurements. When compared with Nimnt$_2^{-}$ and Cumnt$_2^{2-}$, the spin density in Comnt$_2^{2-}$ is to a greater extent localized on the central atom. The addition of one electron to the Comnt$_2^{-}$, forming Comnt$_2^{2-}$, results in an increase of the electron density in the $4b_{2g}$ orbital. The addition of the next electron, *i.e.* the formation of Comnt$_2^{3-}$, causes in the CNDO picture a relative stabilization of $4b_{2g}$ orbital with respect to other orbitals (however, it has to be kept in mind that the increase of the overall charge results in an absolute increase of the energy of all orbitals). The orbital $10a_{1g}$ is shifted, at the same time, to higher energies and becomes HOMO in Comnt$_2^{3-}$. This orbital relaxation thus localizes the redox change on the metal atom. This leads to the conclusion that the concept of rigid redox orbital is not valid in the present and other systems with strong electronic relaxation. One-electron approximation cannot be used for these systems.

IEHM would describe the removal of an electron from Comnt$_2^{2-}$ as resulting in a closed shell configuration. On the other hand, UHF–CNDO calculation points to a stabilization of a triplet state of Comnt$_2^{-}$. This result agrees with the EPR measurement as well as with the general chemical properties of Comnt$_2^{-}$ [8].

The individual members of redox series discussed are connected by one-electron reversible steps studied electrochemically [3–8], and the semiempirical methods used describe reasonably redox transfer within these series. However, the correlation of reversible half-wave potentials with quantum chemical data requires further discussion and will be published elsewhere [21].

The charges on the individual centers calculated by semiempirical methods reflect the reactivity of these centers. Both methods give the negative charge on the sulphur atoms, which points to a nucleophilic reactivity of these atoms. In connection with the lowering of the formal oxidation state of the central atom, the calculated electron density on the sulphur atom rises in accordance with the observed trends in nucleophilic reactivity. An interesting result follows from the comparison of the reactivity of isoelectronic couples of complexes Comnt$_2^{2-}$–Nimnt$_2^{-}$ and Nimnt$_2^{2-}$–Cumnt$_2^{-}$. Complexes Comnt$_2^{2-}$ and Nimnt$_2^{2-}$ can be methylated on sulphur atoms whereas the corresponding isoelectronic complexes do not undergo this reaction [27]. The quantum chemical study (Table II) agrees with the experimental evidence. A lower electron density is localized on sulphur atoms of monoanions of isoelectronic couples of complexes Mmnt$_2^{n-}$ and the nucleophilic reactivity decreases at the same time. Both methods show that the charge on the central atom is influenced by the variation of the overall charge of complexes in a similar manner. Although the absolute value of the charge on the central atom calculated by IEHM agrees better with the one deduced from X-ray photoelectron spectroscopy, (the charge of 0.25 is deduced for nickel in the case of Nimnt$_2^{2-,1-}$) [22], it seems that CNDO, though giving unrealistic negative charges on the central atom, adequately describes the *trends* of changes of charges on the individual atoms caused by the variation of the overall number of electrons, as well as by the nature of the metal atom in maleonitriledithiolate complexes. The reduction of com-

TABLE II. Net Charges on the Metal and Sulphur Centers of Mmnt$_2^{n-}$ Complexes Computed by CNDO and IEH Methods.

Complex	CNDO		IEHM	
	M	S	M	S
Comnt$_2^{-}$	−0.196	−0.123	0.153	−0.088
Comnt$_2^{2-}$	−0.414	−0.218	0.125	−0.267
Comnt$_2^{3-}$	−0.590	−0.299	0.077	−0.310
Nimnt$_2^{-}$	−0.261	−0.098	0.143	−0.078
Nimnt$_2^{2-}$	−0.439	−0.211	0.119	−0.256
Nimnt$_2^{3-}$	−0.453	−0.340	0.114	−0.413
Cumnt$_2^{-}$	−0.324	−0.089	0.247	−0.067
Cumnt$_2^{2-}$	−0.454	−0.215	0.245	−0.131
Cumnt$_2^{3-}$	−0.768	−0.267	0.244	−0.164

TABLE III. Wiberg Indices of Neighbouring Atoms of Mmnt$_2^{n-}$ Complexes Calculated by CNDO Method.

Complex	Bond				
	M–S	S–C	C–C^a	C–C^b	C–N
Comnt$_2^-$	1.064	0.925	1.784	1.084	2.841
Comnt$_2^{2-}$	0.868	0.917	1.760	1.086	2.819
Comnt$_2^{3-}$	0.964	0.773	1.758	1.088	2.772
Nimnt$_2^-$	1.044	0.933	1.743	1.096	2.837
Nimnt$_2^{2-}$	0.851	0.917	1.757	1.097	2.817
Nimnt$_2^{3-}$	0.807	0.746	1.761	1.109	2.751
Cumnt$_2^-$	1.052	0.929	1.756	1.079	2.839
Cumnt$_2^{2-}$	0.807	0.926	1.730	1.081	2.816
Cumnt$_2^{3-}$	0.871	0.826	1.713	1.084	2.773

^{a}C=C bond in the chelate ring. ^{b}C$_{ring}$–C of the CN group.

plexes is accompanied by the lowering of the positive charge of the central atom. For the same charge type the electron density on the central atom when going from Comnt$_2^{n-}$ to Cumnt$_2^{n-}$ (Table II).

For the characterization of the strength of individual bonds of Mmnt$_2^{n-}$ complexes, and its change caused by the variation of the central atoms and of the overall charge of complexes, Wiberg bond indices [23] were used in the frame of CNDO method. Table III summarises Wiberg indices for neighbouring atoms of Mmnt$_2^{n-}$ complexes. The calculated Wiberg indices point to near single metal–sulphur and sulphur–carbon bonds in the chelate ring. The reduction of monoanions causes Wiberg indices for M–S, S–C bonds to decrease. W(C=C) increases in the case of Nimnt$_2^-$ and decreases in the case of Comnt$_2^-$ and Cumnt$_2^-$. Similar trends follow from the IEHM picture but this method indicates the increase of C=C bond order of Mmnt$_2^{n-}$ complexes induced by the reduction. The changes in calculated bonding indices can be correlated with the variation of stretching force constants. IR spectra of these redox series were described for n = –1, –2 [24–26] and the careful assignment of the individual vibrational frequencies for Ni series enables the comparison with calculated indices. The corresponding bonding indices vary qualitatively in the same manner as stretching force constants but the change of W(C=C) is too small to make this correlation conclusive. A greater change of W(C=C) would be expected from experimental results. The calculation is obviously influenced by the rigid geometry approximation used.

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