Molecular orbital study of M(sacacen) complexes
II. Charged systems

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The electronic structure of eighteen models of N,N'-ethylenebis-(thioacetylacetoneiminato) M^{II+n} complexes, *viz.* M(sacacen)^n for M = Co, Ni, Cu and $n = +1, 0, -1$ was studied on the basis of MO LCAO SCF calculations using the CNDO UHF method. Ionization potentials of these Schiff-base complexes were estimated by Koopmans theorem and by ΔSCF approximation, and were compared with experimental data obtained from photoelectron spectra. Calculations show that the occupation of electronic levels in these complexes obeys a certain "Aufbau" principle. However, more detailed analyses show that for the Co(sacacen) complex the Koopmans theorem breaks down while for Cu(sacacen) it is qualitatively valid. Referring to the published papers for the analogous Cu(acacen) complex a different interpretation of photoelectron spectra is proposed.

Была изучена электронная структура 18-ти моделей комплексов N,N'-этиленбис(тиоацетилацетониминато)M^{II+n}, а именно M(sacacen)^n, где M = Co, Ni, Cu; $n = +1, 0, -1$, на основании расчетов MO LCAO SCF с использованием метода CNDO UHF. Потенциалы ионизации этих комплексов оснований Шиффа были определены из теоремы Купманса в ΔSCF приближении и затем были сравнены с экспериментальными данными, полученными из фотоэлектронных спектров. Расчеты показали, что заселение электронных уровней подчиняется определенному типу «застройки». Однако, более детальные анализы показали, что комплекс Co(sacacen) не входит в рамки теоремы Купманса, а Cu(sacacen) ей подчиняется. Предлагается, с учетом литературных данных по аналогичным комплексам Cu(acacen), отличное истолкование фотоэлектронных спектров.

At present a great number of complexes of transition metals with macrocyclic Schiff bases is known. To the unusual properties of these complexes belongs the ability to fix small molecules into axial positions, while the quasi-equatorial plane of the tetradental macrocyclic ligand remains practically unchanged. The bonded small molecule can be transferred together with the macrocycle parents or it can be selectively activated for a certain type of chemical reactions. Therefore the

investigation of these compounds is stimulated largely by models of important natural carriers (*e.g.* of dioxygen carriers such as myoglobin and hemoglobin) and also by problems of homogeneous catalysis.

M(acacen) complexes, *i.e.* N,N'-ethylenebis(acetylacetoneiminato) M^{II}, were studied in these connections. Both, experimental and theoretical investigations were carried out for these compounds. The structure was studied by X-ray analysis [1, 2] and the electronic structure by e.s.r. [3—5] and ultraviolet photoelectron spectroscopy (UPS) [6, 7]. Quantum chemical molecular orbital calculations were done on semiempirical [6—8] and *ab initio* [9—11] levels. However, only simplified model structures were considered in the calculations and the results concerning the ground-state electronic structure depend on the method used. Preliminary semiempirical INDO UHF calculations [7] for the Co complex were criticized by *Veillard* and coworkers [11] on the basis of their *ab initio* RHF calculations in the minimal basis set. On the other hand, some conclusions based on the preliminary *ab initio* calculations [9, 10] were criticized again by *Fantucci* and *Valenti* [8] at the same time and in the same journal.

In the recent years also the thio and seleno analogues of M(acacen) were experimentally studied [12—17] and they were marked as M(tacacen), M(sacac)₂en, M(S-acacen) or M(sacacen) and M(Se-acacen) complexes. Here the oxygen atoms in the ligand were substituted by sulfur or selene. Preliminary semiempirical molecular orbital calculations of the electronic structure of low-spin M(sacacen) complexes with M = Co, Ni, and Cu are presented in paper [18]. Also He(I) and He(II) photoelectron spectra of these complexes are known [14]. Therefore, a more detailed theoretical study of these complexes appears to be interesting especially for the following reasons.

(i) The paradoxical violation of Koopmans theorem for transition metal compounds is well documented [19—22]. That means not only its well known quantitative failure but also its qualitative breakdown taking place in many cases. Another alternative for the calculation of ionization potentials is the ΔSCF approximation. The effect of the electron correlation (the electrostatic correlation energy), however, is not considered in this approximation.

(ii) In transition metal complexes the orbital energy of half-filled $3d$ orbitals is often lower (more negative) than that of doubly occupied ligand orbitals [19].

(iii) A substitution on the macrocycle ligand skeleton affects the ionization potentials [23]. This was experimentally proved for β-diketonates and their thioanalogues [24].

(iv) The inclusion of sulfur $3d$ atomic orbitals into the basis set for molecular orbital calculations can affect the values of ionization potentials.

(v) The values of the first ionization potentials of M(sacacen) complexes (M = Co, Ni, Cu) are very close. Actually, the UPS spectra of Co and Ni complexes are very similar but different from UPS spectrum of the Cu complex [14]. Likewise

the UPS spectra of Co(acacen) and Ni(acacen) are similar [6, 7], the first ionization of Cu(acacen), however, was distinguished at a much higher energy [6]. It is not certain whether the UPS spectrum of Cu(acacen) was sufficiently resolved and correctly interpreted.

Results

For molecular orbital calculations the MO LCAO SCF method of the semiempirical all-valence type was applied within the CNDO UHF approximation [25—27]. The used basis set consists of valence atomic orbitals (AO) including $4p$-AO's of the metal atom. Also the sulfur $3d$-AO's were included in the basis set for selected systems. *Slater* AO's [28] were used with exponents for metals according to *Zerner* and *Gouterman* [29] and with a hydrogen exponent equal to 1.2. The electronic levels were occupied in the usual way: the lowest eigenvalues were regarded as occupied levels in each iteration of the SCF procedure.

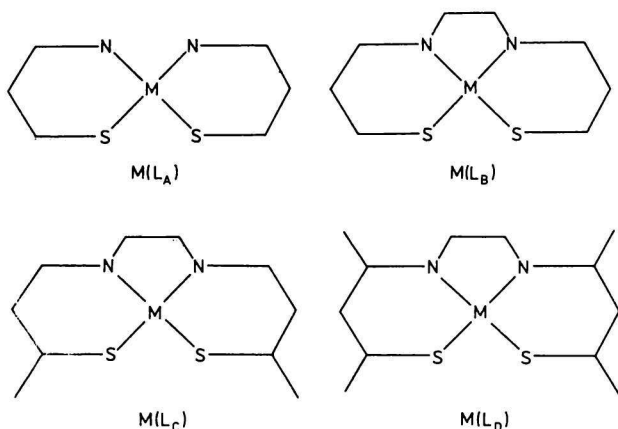The macrocyclic ligand was considered in three simplified models (Fig. 1).

Fig. 1. Model structures of the M(sacacen) complex: $M(L_A)$, $M(L_B)$, and $M(L_C)$. $M(L_D)$ is the real structure. Only heavy atoms (M, C, N, S) are shown.

(i) In the ligand L_A the ethylene bridge and four methyl groups are substituted by hydrogens, i.e. only 19 atoms are considered in the model complex $M(L_A) = MC_6H_8N_2S_2$. The valence basis set consists of 57 AO's. A similar ligand (on substituting of sulfur atoms by oxygens) was considered in the *ab initio* calculations by *Veillard* and coworkers [9—11].

(ii) In the ligand L_B four methyl groups are substituted by hydrogens, i.e. 23 atoms are considered in the model complex $M(L_B) = MC_8H_{10}N_2S_2$ and the basis set consists of 67 valence AO's. A similar ligand was considered in semiempirical CNDO and INDO UHF calculations [6—8] of M(acacen) complexes. The extended basis set includes sulfur $3d$-AO's, i.e. the size of the basis set is 77 AO's and the complex is marked as $M(L_{B'})$.

(iii) In the ligand L_C only two methyl groups (the neighbours of the ethylene bridge) are substituted by hydrogens, *i.e.* 29 atoms are considered in the model complex $M(L_C)$ = $MC_{10}H_{14}N_2S_2$ and the basis set covers 79 valence AO's. The real M(sacacen) complex, *i.e.* $MC_{12}H_{18}N_2S_2$ contains 35 atoms and it is marked as $M(L_D)$.

The geometry of complexes was estimated by the analogy with similar Schiff-base complexes. Further it was idealized keeping the macrocyclic ligand to be strictly planar, so that C_{2v} symmetry of the complex was fixed (in the case of $M(L_C)$ the symmetry was C_s). The used Cartesian coordinates of the model structure $M(L_B)$ are presented in paper [18]. For series of M = Co, Ni, Cu the same geometry of complexes was considered.

MO LCAO SCF calculations were performed for fifteen low-spin and three high-spin complexes. Actually, low-spin complexes are of the $Co(L_X)$ and $Co(L_X)^+$ type for X = A, B', C and further $Co(L_B)^n$, $Ni(L_B)^n$, and $Cu(L_B)^n$ for $n = +1, 0, -1$. The complexes $Co(L_A)^+$, $Co(L_B)^+$, and $Cu(L_B)^+$ were considered to be high-spin, too.

Table 1

Number of occupied molecular orbitals within individual representations of the C_{2v} symmetry point group in $M(L_X)^n$ complexes

$M(L_X)^n$			Spin multiplicity	Representation*								Valence electrons
L_X		M^n		a_1		a_2		b_1		b_2		
L_A	Co^-		3	13	12	4	3	4	4	11	11	62
	Co^+		1	13	13	3	3	4	4	11	11	62
	Co		2	13	13	4	3	4	4	11	11	63
L_B	Co^+		3	15	14	5	4	5	5	12	12	72
	Co^+		1	15	15	4	4	5	5	12	12	72
	Co	Ni^+	2	15	15	5	4	5	5	12	12	73
	Co^-	Ni Cu^+	1	15	15	5	5	5	5	12	12	74
		Cu^+	3	15	15	5	4	5	5	13	12	74
	Ni^-	Cu	2	15	15	5	5	5	5	13	12	75
		Cu^-	1	15	15	5	5	5	5	13	13	76
$L_{B'}$	Co^+		1	15	15	4	4	5	5	12	12	72
	Co		2	15	15	5	4	5	5	12	12	73
L_C	Co^+		1	16	16	5	5	7	7	14	14	84
	Co		2	16	16	6	5	7	7	14	14	85
Components:				σ_L		π_L		π_L		σ_L		
				d_{z^2}		d_{yz}		d_{xz}		d_{xy}		
				$d_{x^2-y^2}$								

* The number of α-MO's is listed in the first column, β-MO's in the second column for a given representation.

The occupied molecular orbitals were classified in terms of irreducible representations of the C_{2v} symmetry point group. The results of the symmetry analysis are listed in Table 1, together with the components of the irreducible representations, *i.e.* with $3d$-AO's of the metal and ligand σ or π orbitals.

The first ionization potentials I_p^1 of M(sacacen) complexes were estimated in two ways:

(i) using the Koopmans theorem, namely

$$I_p^1 \sim -\varepsilon_i \tag{1}$$

where ε_i is the orbital energy of the highest occupied molecular orbital (HOMO);

(ii) by the ΔSCF approximation, *viz.*

$$I_p^1 \sim \Delta SCF = E(X^+) - E(X) \tag{2}$$

where $E(X)$ and $E(X^+)$ are the total SCF energies of the neutral and the positively charged complex, respectively.

The point (i) must be commented as follows. In the diagrammatic many-body perturbation theory the ionization potential is expressed in the form of a convergent series. The first (zeroth-order) term is simply represented by the $-\varepsilon_i$ value. This is the statement of the Koopmans theorem. The second (first-order) term vanishes for closed shell systems as well as for open-shell systems within the unrestricted Hartree—Fock approach. In the restricted Hartree—Fock approach this correction becomes significant as it covers coulomb (J) and exchange (K) integrals over molecular orbitals. The third (second-order) term includes a part of the correlation and relaxation energy. Therefore, the possible failure of the Koopmans theorem (this is one particular problem under study) can be examined using the ΔSCF approach where the last (relaxation) term is taken into account.

The results of calculations are collected in Table 2.

Table 2

Calculated and experimental values of the first ionization potentials of M(sacacen) and M(acacen) complexes

Model structure $M(L_x)^n$	M(sacacen)			M(acacen)	
	CNDO[a]		Exp.[b] I_p^1	Calc.[c,d]	Exp.[c,d] I_p^1
	$-\varepsilon_i^{HOMO}$	ΔSCF		$-\varepsilon_i^{HOMO}$	
Co(L_A)	9.22	7.7			
Co(L_B)	9.03	7.5	6.49	8.23	6.67
Co(L_C)	8.94	7.2			
Co(L_B')	8.47	7.7			
Ni(L_B)	9.19	8.2	6.53	8.09	6.80
Cu(L_B)	8.61	7.7	6.36	7.41	7.00

a) This paper; *b*) Ref. [14]; *c*) Ref. [6]: CNDO calculations; *d*) Ref. [7]: INDO calculations.

Discussion

The assignment of the ground-state electronic configuration of the Co(acacen) complex was not unequivocal [8, 11]. On the basis of the e.s.r. experiment in the nematic phase [5] the configuration $(d)^6(d_{z^2})^1$ was accepted as the ground state. It was also in agreement with the *ab initio* RHF calculations [9—11] of the model structure $Co(L_A) = CoC_6H_8O_2N_2$ according to which the configuration $(d)^6(d_{z^2})^1$ was more stable than $(d)^6(d_{yz})^1$ by 0.57 eV [11]. On the other hand, it follows from the semiempirical INDO UHF calculations of $Co(L_B) = CoC_8H_{10}O_2N_2$ that the ground-state electronic configuration of Co(acacen) is $(d)^6(d_{yz})^1$, however, in an axially coordinated system of Co(acacen)NH₃ the ground-state configuration is $(d)^6(d_{z^2})^1$. Finally, it was shown that in cobalt complexes with a Schiff-base macrocyclic ligand the energy separation between $(d)^6(d_{z^2})^1$ and $(d)^6(d_{yz})^1$ configurations decreases as the strength of the axial bond decreases. In very weakly coordinating solvents such as toluene it is not possible definitely to decide which is the ground state [30]. A single crystal e.s.r. experiment shows that the $(d)^6(d_{yz})^1$ configuration is the ground state of Co(acacen) [17].

The CNDO UHF calculations presented here show that the ground-state electronic configuration of Co(sacacen) is $(d)^6(d_{yz})^1$. This follows from the simplified molecular orbital diagram presented in Fig. 2: the levels of a_1, b_1, and b_2 symmetry are doubly occupied and the unpaired electron lies on the level of a_2 symmetry. In the model structure of $Co(L_B)$ there are five a_2 levels occupied with α electrons and four a_2 levels occupied with β electrons. The $1a_2$, $2a_2$, and $3a_2$ levels exhibit nearly the same orbital energies and composition for α and β electrons. An unusual picture is shown by the higher a_2 levels. The level $4a_2^\alpha$ is practically a neat d_{yz} orbital while the last occupied β level — $4a_2^\beta$ is predominantly of the ligand character. Thus the d_{yz} orbital is absent within the occupied β levels, so the level $4a_2^\alpha$ is to be regarded as an open one. The unusual result is that seven doubly occupied levels ($13a_1$, $11b_2$, $14a_1$, $5b_1$, $12b_2$, $15a_1$, $5a_2$) have a higher (less negative) energy than the open level $4a_2^\alpha$. A similar result was obtained previously by INDO UHF calculations of the Co(acacen) complex [8]. The basic question to this point is, which level is preferentially ionized. Does the first ionization potential correspond to the highest occupied MO $5a_2^\alpha$ or to the less negative open level $4a_2^\alpha$? In a word, is the Koopmans theorem for this compound qualitatively valid or does its breakdown take place? According to *Bacon* and *Zerner* [31], ionizations of d levels are often accompanied by 10—20 eV of relaxation energy, while the ligand orbitals exhibit relaxation energy typically less than 1 eV. It leads to the situation where open (singly occupied) d levels in a complex can be preferentially ionized despite the fact that they are often "buried" below a set of doubly occupied ligand MO's.

It follows from Table 1 that starting from the Co(sacacen)⁺ ion and going to the Co(sacacen) or Ni(sacacen)⁺ a new level of a_2 symmetry is filled. In Ni(sacacen) or

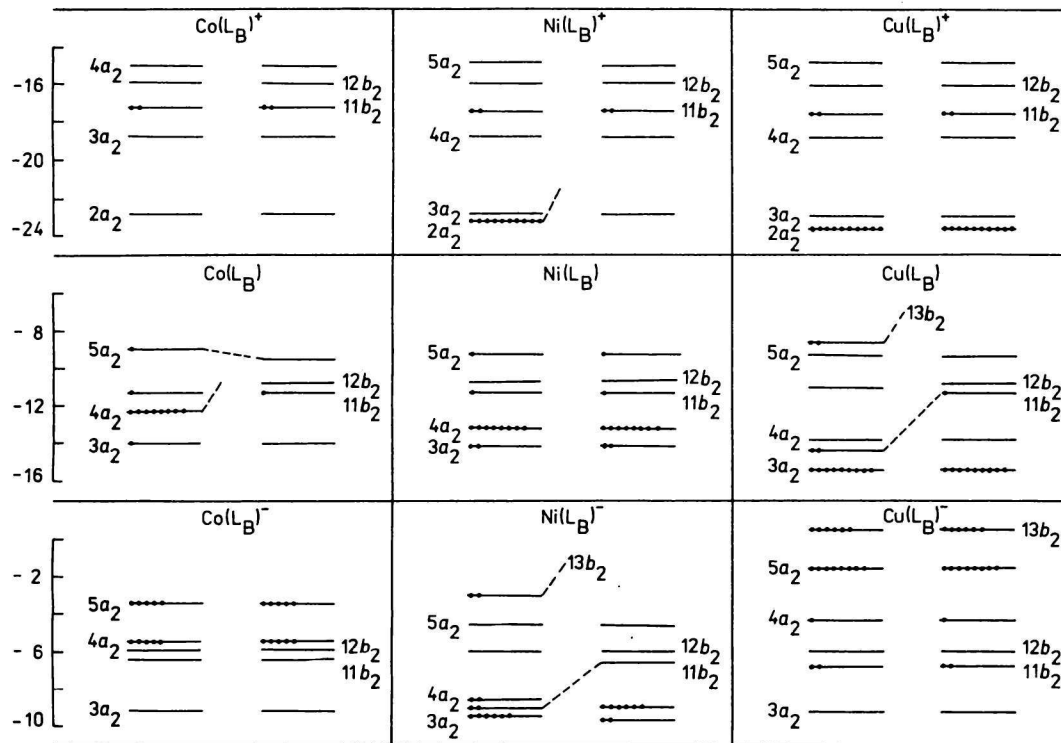*Fig. 2.* The one-electron energy levels (eV) in models M(L_B)^n of M(sacacen) complexes. Only the levels of a_2 and b_2 representations within HOMO's are shown. Dotted lines represent the *d* character of MO's (5, 15, 25, etc. percent of a *d*-AO in the MO). Left levels belong to α electrons, right to β.

Cu(sacacen)$^+$ complexes this level is closed (occupied by two electrons). Since the level a_2 consists only of d_{yz} AO of the metal and ligand π orbitals, an electron on the level a_2 is localized outside of the σ plane of the complex. However, a great increase of the relative intensity of the first band in the He(II) UPS spectrum of Co(sacacen) indicates [14] that the first ionization corresponds to a level predominantly involving the d-metal orbital. It seems that the open level $4a_2^\alpha$ is preferentially ionized and that in Co(sacacen) a breakdown of the Koopmans theorem takes place. This point was cleared up by direct MO LCAO SCF calculations of the Co(sacacen)$^+$ system. These calculations show that the d_{yz} AO is absent within occupied molecular orbitals of Co(sacacen)$^+$ and thus not the HOMO — the level $5a_2^\alpha$ but the open level $4a_2^\alpha$ is ionized (the numbering of levels is valid for the Co(L$_B$) model).

Analogically, the Koopmans theorem breaks down also for Ni(sacacen), as the d_{yz} AO is absent within occupied β MO's of Ni(sacacen)$^+$. Therefore not the $5a_2^\beta$ level (the HOMO) but the $4a_2^\beta$ level is preferentially ionized.

A new level of the b_2 symmetry is filled when passing from Ni(sacacen) to Cu(sacacen) or Ni(sacacen)$^-$ complexes. This level is closed in Cu(sacacen)$^-$ and probably also in Zn(sacacen). It can consist only of d_{xy} AO of the metal and ligand σ orbitals and according to the calculations it is to 20% of the d_{xy} character in Cu(sacacen). Thus the electron on the b_2 level is localized in the σ plane of the complex, on the CuN$_2$S$_2$ chromophore. Its effective photon cross section is very small and the corresponding peak in the UPS spectrum is low. This peak was not recorded by preliminary measurements [32] as it was overlapped by the intensive peak of the second ionization.

The presented results indicate that for M(sacacen) complex the occupation of the electronic levels obeys an "Aufbau" principle. The Koopmans theorem is qualitatively valid for the first level of Cu(sacacen) but it fails for Co(sacacen) and Ni(sacacen). The band assignment of UPS spectra was done as follows

$$I_p^1(M = Cu, b_2) < I_p^1(M = Co, a_2) < I_p^1(M = Ni, a_2) < I_p^2(M = Cu, a_2)$$
$$\quad 6.36 \qquad\qquad 6.49 \qquad\qquad 6.53 \qquad\qquad 6.99$$

(The values of ionization potentials are in eV.)

Analogous M(acacen) complexes with M = Co, Ni, Cu were studied using CNDO and INDO UHF methods [6, 7] and the He(I) UPS spectra of these complexes are also known. The results of calculations are qualitatively similar to those presented in this paper: the HOMO in Co(acacen) is of a_2 symmetry, while in Cu(acacen) it is of b_2 symmetry. The first ionizations in UPS spectra were assigned as

$$I_p^1(M = Co, a_2) < I_p^1(M = Ni, a_2) < I_p^1(M = Cu, b_2)$$
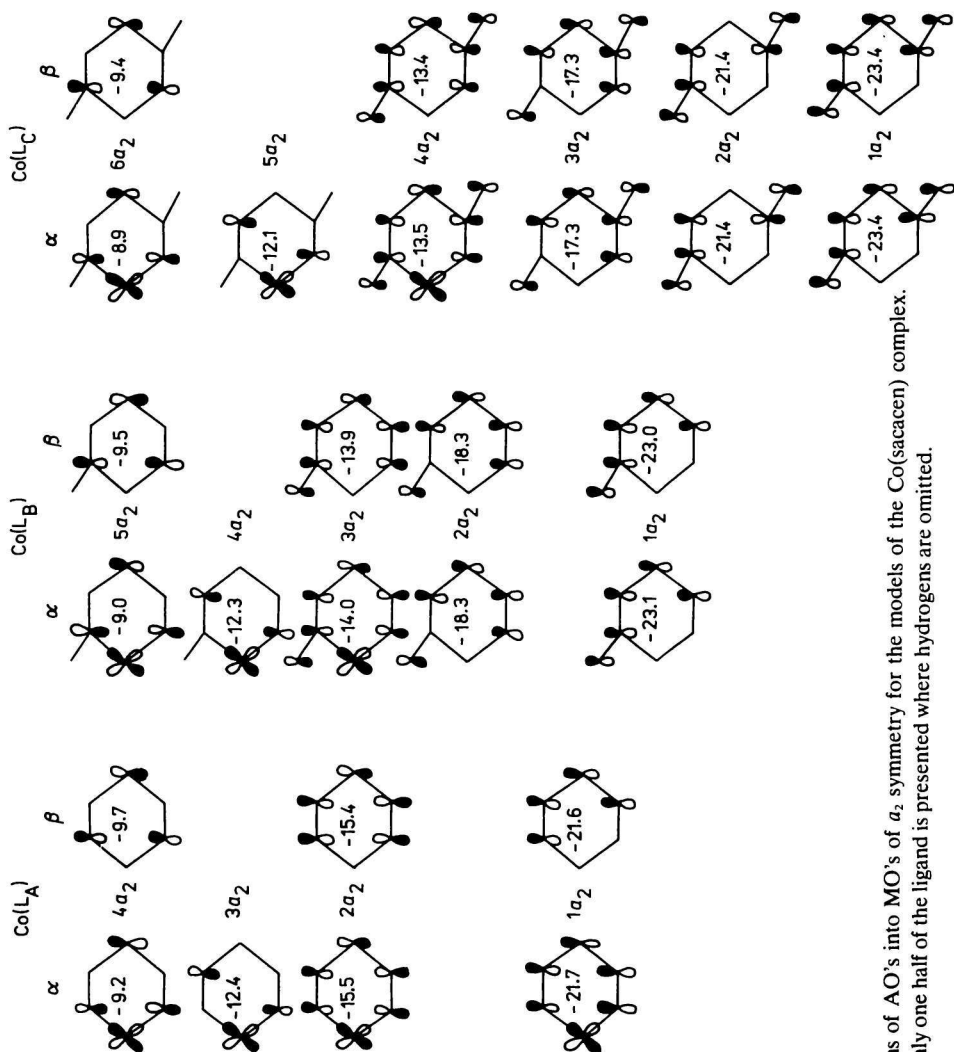$$\quad 6.67 \qquad\qquad 6.80 \qquad\qquad 7.00$$

Fig. 3. Combinations of AO's into MO's of a_2 symmetry for the models of the Co(sacacen) complex. Only one half of the ligand is presented where hydrogens are omitted.

However, the first band for Cu(acacen) is very broad and strong intense. It seems that the first low peak which is of b_2 symmetry is overlapped by the second intensive peak of the a_2 symmetry. On the basis of the above arguments it may be assumed that the UPS spectrum of Cu(acacen) presented in [6] is poorly resolved and erroneously interpreted. The band assignment of the first ionizations in UPS spectra in the present paper is

$$I_p^1(M = Cu, b_2) < I_p^1(M = Co, a_2) < I_p^1(M = Ni, a_2) < I_p^2(M = Cu, a_2)$$
$$\quad ? \qquad\qquad\quad 6.67 \qquad\qquad\quad 6.80 \qquad\qquad\quad 7.00$$

Preliminary INDO UHF calculations of Co(acacen) complex [7] were criticized by *Dedieu et al.* [11]. The calculations by *Fantucci* and coworkers [7] yield four doubly occupied MO's and one singly occupied MO within the a_2 irreducible representation. According to *Dedieu et al.*: "Since this representation includes only the $3d_{yz}$ orbital of Co and the $(\pi_i - \pi_i')$ orbitals of the acacen ligand (of which only three are doubly occupied for the free ligand) there should be at most four
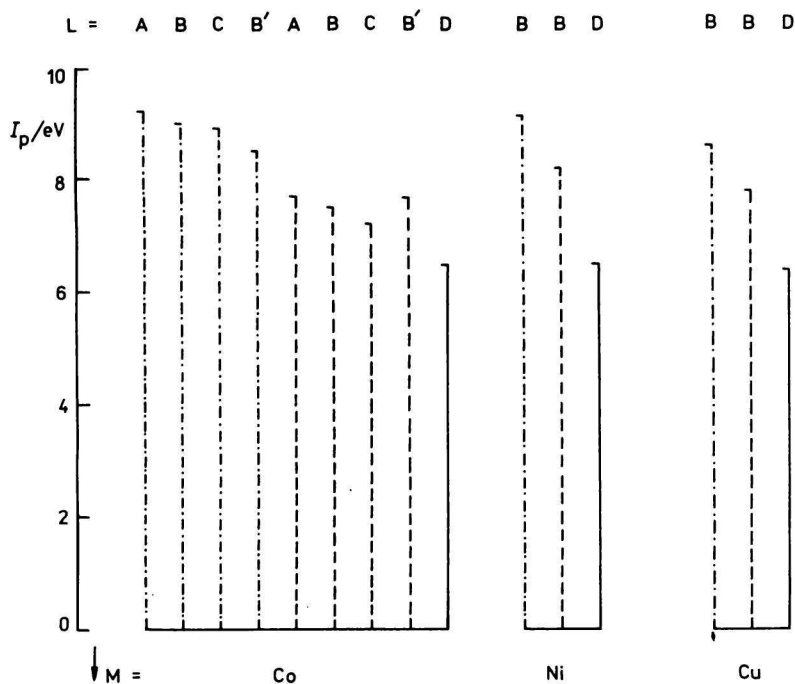

Fig. 4. The first ionization potentials of M(sacacen) complexes.
Calculated values: *a*) by Koopmans theorem (−·−·−); *b*) by ΔSCF approximation (- - - - -); experimental values (———).

doubly occupied orbitals within this representation (or three doubly occupied and one singly occupied)." This criticism is not justified, as the number of representations within occupied MO's depends on the concrete type of the model structure. Actually, applying ligand L_A the maximum numerousness of a_2 representation within the occupied MO's is equal to four. This is the case of the calculations performed by Dedieu and coworkers. In the calculations of Fantucci *et al.* the L_B ligand was used and thus the maximum size of a_2 representation within the occupied MO's is equal to five. This is explicitly shown in Fig. 3 which is based on the present CNDO UHF calculations of the individual models of Co(sacacen) for ligands L_A, L_B, and L_C. The combinations of AO's entered into the MO's are presented only if the LCAO coefficient is greater than 0.1 (*i.e.* the contribution of a given AO into MO is greater than one percent).

In comparing the calculated values of ionization potentials of M(sacacen) complexes with those obtained experimentally (Table 2) it is necessary to take into account the following factors.

(i) The geometry of the considered complexes was only estimated and it is rather idealized with respect to reality. Moreover, the complete sacacen ligand, *viz.* the M(L_D) complex was not considered.

(ii) The molecular orbital method used here is of the semiempirical all-valence type where only the valence AO's are included into the basis set.

(iii) The first ionization potentials are only estimated since the following relation is valid in general

$$I_p < \Delta SCF < -\varepsilon_i \qquad (3)$$

The values of ΔSCF include the relaxation energy accompanying the ionization process but the effects of the electron correlation are not covered in this approximation. The corrected ionization potentials for the electrostatic correlation energy can be evaluated applying the diagrammatic many-body perturbation theory [33] but for great basis sets such calculations are rather limited.

Opening the discussion of the quantitative results (Fig. 4) it may be concluded that relation (3) is in the performed calculations well fulfilled, *i.e.* the values of ΔSCF are better estimates of the first ionization potentials than the $-\varepsilon_i$ values of HOMO's according to Koopmans theorem. Secondly, the effect of the methyl groups in the series of ligands L_A, L_B, L_C is of the right order, *i.e.* the ionization potentials move to the experimental values. The effect of the basis set seems to be significant: the inclusion of the sulfur $3d$ AO's into the basis set (the model Co($L_{B'}$)) affects the calculated values of the first ionization potential.

Finally, it must be pointed out that the ionization of the open-shell system can produce systems in the singlet, as well as in the triplet spin state. Therefore MO LCAO SCF calculations were also carried out for the high-spin (triplet) complexes. The energy separation between the high-spin and low-spin complex cation Co(L_A)$^+$

is very small ($\Delta E < 0.02$ eV). The same result was obtained for the model structure $Co(L_B)^+$. Therefore the first band in the UPS spectrum of Co(sacacen) involves the ionization process yielding the singlet, as well as the triplet product. On the other hand, the $Cu(L_B)^+$ complex is more stable in the singlet spin state referring to the triplet one by 0.67 eV. Therefore it must be assumed that in the UPS spectrum of Cu(sacacen) the singlet and triplet ionization potentials may be well distinguished.

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