

Molecular orbital study of M(sacacen) complexes

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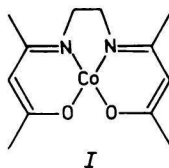
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The ground-state electronic structure of Co(sacacen), Ni(sacacen), and Cu(sacacen) complexes was studied by MO LCAO SCF calculations within the CNDO UHF approximation. The calculated one-electron energy levels were compared with known photoelectron spectra recorded by using He(I) and He(II) irradiation. For open shell systems the UHF and projected spin densities were calculated. The bonding situation is discussed in terms of Wiberg indices, atomic charges, and the energy partitioning.

Методом MO LCAO SCF расчета с приближением CNDO UHF было изучено основное электронное состояние комплексов Co(sacacen), Ni(sacacen) и Cu(sacacen). Рассчитанные одноэлектронные энергетические уровни были сравнены с известными фотоэлектронными спектрами, полученными с использованием излучения He(I) и He(II). Были рассчитаны UHF и проектированные плотности спина для систем с открытой оболочкой. Связь в этих комплексах обсуждается при помощи индексов Вайберга, атомных зарядов и распределения энергии.

Stimulated largely by the existence of important biochemical systems, a number of cobalt complexes with macrocyclic tetradentate Schiff-base type ligands were prepared and studied as models for natural oxygen carriers [1]. The reversible oxygenation of Co(salen) and its derivatives occurs in both, the solid state and in solution in the presence of certain organic bases. The efficiency of this process is such that this system was once taken into consideration for the production of oxygen from air [2].



A similar complex, *N,N'*-ethylenebis(acetylacetonate iminato) cobalt(II), Co(acacen), I, and its adducts with molecular oxygen were intensively studied

using experimental and theoretical methods. Some of the experimental data (mainly based on photoelectron spectroscopy and e.s.r. study) were compared with characteristics obtained by the MO LCAO SCF approach within the all-valence INDO UHF approximation [3, 4] or *ab initio* — RHF calculations [5—7] in the minimal basis set.

Many other transition metals, M, form complexes of the M(acacen) type with their properties rather similar to those of Co(acacen). In recent years analogous complexes M(sacacen), with the oxygen atoms in the acacen ligand replaced by sulfur atoms, were subject to intensive study [8—11].

To obtain preliminary information about the electronic structure of M(sacacen) complexes, the all-valence CNDO UHF molecular orbital calculations [12, 13] were performed for M = Co, Ni, Cu. The CNDO/2 parametrization used here for the first row transition metals is described elsewhere [14]. Actually, the UHF spin density matrix is not produced from an eigenfunction of the S^2 operator. Therefore, the single annihilation operator technique [15] was used to obtain the “projected” spin densities being not too far from the pure spin state value. Finally, the energy partitioning on the metal–ligand, E_{M-L} , ligand–ligand, E_{L-L} , and the one-centre part of the total energy, E_{mono} , was performed as in [16].

Results

The geometric structure of M(acacen) complexes is known from the X-ray experiments [17, 18] unlike to that of M(sacacen) complexes. In calculations it was estimated combining the X-ray data of analogous complexes, idealized replacing the methyl groups by hydrogens and keeping the C_{2v} symmetry. The numbering scheme of 23 atoms in the model structure is shown in Fig. 1. The cartesian coordinates used in the calculations are listed in Table 1. Thus

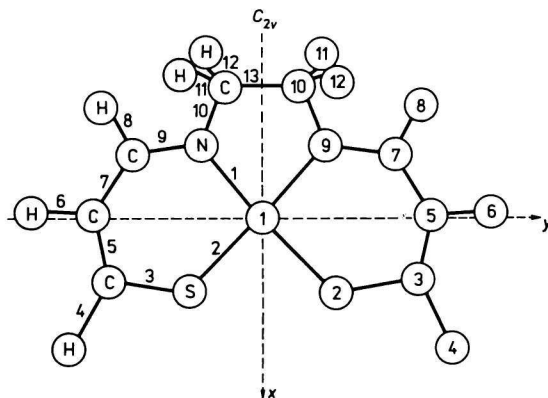


Fig. 1. Numbering system of atoms and bonds in M(sacacen) complexes.

Table 1

Atomic coordinates [10^{-10} m] in the model structure of $M(\text{sacacen})^a$

Atom		Coordinate		
No.	Type	x	y	z
1	M	0.00	0.00	0.00
2	S	1.58	1.43	0.00
3	C	1.23	3.07	0.00
4	H	2.05	3.76	0.00
5	C	-0.06	3.33	0.00
6	H	-0.08	4.45	0.00
7	C	-1.26	2.55	0.00
8	H	-2.17	3.11	0.00
9	N	-1.37	1.28	0.00
10	C	-2.68	0.74	0.00
11	H	-3.12	1.13	0.89
12	H	-3.12	1.13	-0.89

a) Remaining atoms No. 13–23 have negative y coordinate (C_{2v} symmetry).

on the valence basis set of 63 atomic orbitals the molecular orbital arrangement was calculated for the lowest spin state, *i.e.* singlet for $M = \text{Ni}$ and doublet for $M = \text{Co}, \text{Cu}$.

The calculated molecular orbitals were classified within the irreducible representations of the C_{2v} point group of symmetry. The d metal and ligand orbital components of molecular orbitals are listed in Table 2. Fig. 2 shows the calculated one-electron energy levels above -17 eV. The levels below -21 eV are nearly the same for all complexes considered. Comparing the calculated energy levels with known photoelectron spectra (Fig. 3) it is obvious that the calculated levels are more diffuse and they are shifted towards lower (more negative) energies. From Fig. 2 the following conclusions can be drawn.

(i) The α and β levels in the given complex are approximately equivalent; only levels of the same symmetry as the highest occupied molecular orbital (HOMO) are splitted, namely the a_2 levels in the Co complex and b_2 levels in the Cu complex. The splitting is marked with dashed lines.

Table 2

List of irreducible representations of molecular orbitals and their components

Representation	Components
a_1	$d_{z^2}, d_{x^2-y^2}, \sigma_L$
a_2	d_{yz}, π_L
b_1	d_{xz}, π_L
b_2	d_{xy}, σ_L

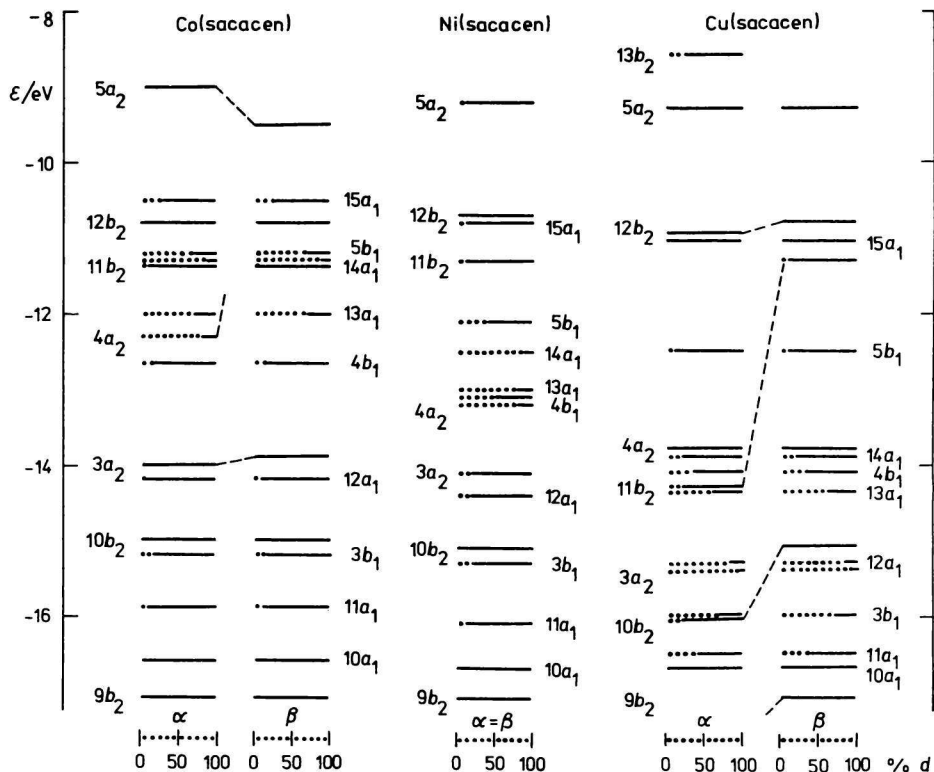


Fig. 2. Calculated one-electron energy levels of M(sacacen) complexes. *d* Character of molecular orbitals is shown by dotted lines: 5, 15, 25, etc. percent.

(ii) In the Ni complex the levels $4a_2$ and $3a_2$ are shifted towards lower energies with respect to the Co complex. Similarly, adding an electron to the Ni complex (thus forming a Cu complex) the b_2 levels for α electrons ($12b_2 - 7b_2$) are shifted towards lower energies.

(iii) The first ionization potential of Co(sacacen) and Ni(sacacen) corresponds, according to the Koopmans theorem, to the $5a_2$ level and that involves a pseudoaromatic π_L electronic system of the ligand (mainly π orbitals of the sulfur atoms). In the Cu(sacacen) this level corresponds to the second ionization since new $13b_2$ HOMO is formed involving both, the d_{xy} (20%) and the σ_L orbitals. The observed trend of the first ionization potentials is reproduced by calculations, namely

$$I_p[\text{Cu(sacacen)}] < I_p[\text{Co(sacacen)}] < I_p[\text{Ni(sacacen)}]$$

(iv) In the series of complexes with $M = \text{Co, Ni, Cu}$ the cluster of d levels moves in direction of lower energies. The d character of molecular orbitals is marked in Fig. 2 by dotted lines.

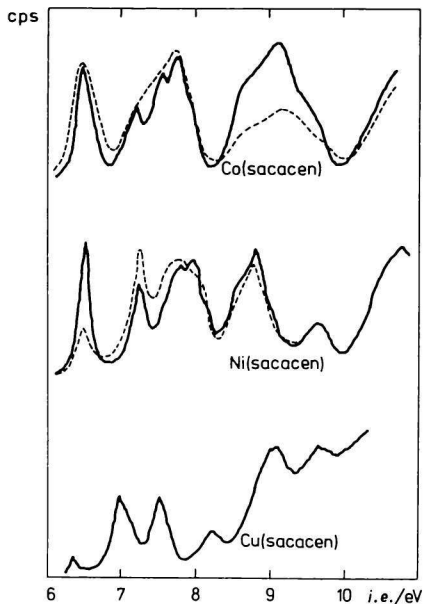


Fig. 3. Experimental He(I) (—) and He(II) (---) photoelectron spectra of $M(\text{sacacen})$ complexes. Spectra are taken over from Ref. [10].

An analysis of the spin density distribution shows its high localization on the metal atom (Table 3). The highest contribution to the atomic spin density $\rho(M)$ comes from the d_{yz} orbital of the Co atom and/or the d_{xy} orbital of the Cu atom. The high spin density on the d_{yz} orbital of the Co atom is due to the open levels of the a_2 symmetry which mainly consist of the d_{yz} orbital. In the Cu complex these levels are closed. Then the high spin density on the d_{xy} orbital of the Cu atom arises from the new open levels of the b_2 symmetry. Thus, the following relations were established for the Co complex

$$\rho(d_{yz}) \gg \rho(d_{xz}) \sim \rho(d_{xy}) \sim 0$$

and

$$\rho(d_{xy}) \gg \rho(d_{xz}) \sim \rho(d_{yz}) \sim 0$$

for the Cu complex. These results can be explained on the basis of known e.s.r. data for

Table 3
Projected spin densities

		M	
		Co	Cu
Atomic:	$\rho(M)$	0.984	0.873
Orbital:	$\rho(d_{yz})$	0.985	0.000
	$\rho(d_{xy})$	0.000	0.880

$$\rho(d_x^2) \sim \rho(d_x^2 - y^2) \sim \rho(d_{xz}) \sim 0.0$$

Co(acacen) [19] and Co(sacacen) [11]: $g_{xx} > g_{yy} \sim g_{zz}$, $A_{xx} > A_{yy} \sim A_{zz}$. For Cu(acacen) the following relations were determined [20]: $g_{xx} \sim g_{yy} < g_{zz}$, $A_{xx} \sim A_{yy} < A_{zz}$.

The bonding situation in M(sacacen) complexes was interpreted in terms of *Wiberg* indices [21] (Table 4), atomic charges (Table 5), and the energy partitioning (Table 6). The *Wiberg* indices show that all bonds are of the single type except the N–C bond (between atoms 9 and 7) and the C–C bond (between atoms 5 and 3) which rather appear to be of the double type. Thus, the classical chemical formula of these chelates, *I*, may be regarded as

Table 4
Wiberg indices

Bond		M		
No.	Type	Co	Ni	Cu
1	M–N	0.67	0.68	0.62
2	M–S	0.87	0.88	0.81
3	S–C	1.08	1.09	1.08
4	C–H	0.96	0.96	0.96
5	C–C	1.75	1.75	1.74
6	C–H	0.93	0.93	0.93
7	C–C	1.19	1.19	1.19
8	C–H	0.95	0.95	0.95
9	C–N	1.62	1.63	1.62
10	N–C	0.96	0.96	0.96
11	C–H	0.96	0.96	0.96
13	C–C	1.01	1.01	1.01

Table 5
Atomic charges [e]

Atom		M		
No.	Type	Co	Ni	Cu
1	M	-0.17	-0.22	-0.17
2	S	-0.17	-0.16	-0.17
3	C	+0.11	+0.11	+0.12
4	H	0.00	0.00	0.00
5	C	-0.09	-0.09	-0.09
6	H	-0.02	-0.02	-0.02
7	C	+0.22	+0.22	+0.23
8	H	-0.03	-0.03	-0.03
9	N	-0.04	-0.03	-0.05
10	C	+0.10	+0.10	+0.11
11	H	0.00	0.00	0.00

Table 6
Total energy terms [eV]^a

M	$-E_T$	$-E_{\text{mono}}$	$-E_{\text{bi}}$	$-E_{\text{M-L}}$	$-E_{\text{L-L}}$
Co	3597.6	2940.1	657.6	114.7	542.9
Ni	3799.9	3133.6	666.3	123.0	543.3
Cu	4031.0	3360.1	670.9	128.3	542.6

$$a) E_T = E_{\text{mono}} + E_{\text{bi}} = E_{\text{mono}} + E_{\text{M-L}} + E_{\text{L-L}}$$

a good approximation degree describing their bonding situation. Atomic charges exhibit charge alternation typical for CNDO/2 calculations [12]. The magnitude of atomic charges indicates, however, only slightly polar bonds; the negative charge is concentrated rather in the region of the donor atoms N and S. In the complex series with M=Co, Ni, Cu both, the Wiberg indices and the atomic charges are changed very little. Thus the bonding in this series does not significantly change. The energy partitioning (Table 6) in this complex series shows that the ligand–ligand interaction energy is rather constant while the metal–ligand stabilization energy slightly increases.

Discussion

Opening the discussion it has to be pointed out that the above presented calculations mainly depend on three factors:

(i) the model structures of complexes considered here are with respect to the reality rather idealized;

(ii) the method used is of the semiempirical all-valence type;

(iii) the ionization potentials were estimated on the basis of the *Koopmans* theorem [22], where the “thawing” energy accompanying the ionization and the effects of the electron correlation (the electrostatic correlation energy) are not included. Thus, a better agreement between the calculated one-electron energy levels and the known photoelectron spectra can hardly be expected. On the other hand, a more sophisticated interpretation and band assignment of the photoelectron spectra are possible. The main conclusions are that the first ionization potentials of Co and Ni complexes cover the pseudoaromatic π_L electronic system of the ligand ($5a_2$), while the ionizations involving d metal orbitals are at much higher energies. The observed fact that the photoelectron spectra of Co and Ni complexes are very similar can be understood as an effect of the filling of the same a_2 level. In Cu(sacacen) a new σ type HOMO of the b_2 symmetry is formed involving both, the d_{xy} and σ_L orbitals. Thus the differences in the photoelectron spectra of Ni and Cu complexes will be significant. However, the great increase of the relative intensity of the first band in the He(II) spectrum of Co(sacacen)

indicates that the first ionization corresponds to a level predominantly involving the *d* metal orbital. It seems that the open level $4a_2$ is preferentially ionized in the Co(sacacen) and Koopmans theorem fails. This point is to be cleared up using Δ SCF approximation [23].

The localization of the spin density is high on the central atom, namely outside the complex plane in Co(sacacen) unlike to Cu(sacacen) where the spin density is localized in the plane of the complex. This predicts the different types of spin anisotropy in Co(sacacen) and Cu(sacacen).

The bonding situation in the studied complexes is quite similar; Wiberg indices indicate that their bonding is by the classical chemical formula well represented.

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