Contribution from the Istituto di Chimica dell'Università di Trieste, 34127, Trieste, Italy

MO Studies for Transition Metal Complexes with Polydentate Ligands. I. Investigation of Parameter Variations in the Case of Diammine-Fe^{II} -Bisdimethylglyoximato Complex

G. De Alti, V. Galasso and A. Bigotto

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The electronic structure of $Fe^{II}(Dmg)_2(NH_3)_2$ has been investigated by the SCCC–MO method. The influence of parameter variations, like the choice of atomic orbitals, the charge dependence of the diagonal terms in the Hamiltonian matrix, the weight given to the off-diagonal terms and the method of evaluating the atomic charges, both on the ground-state properties and the electronic spectra have been examined and discussed.

Introduction

This is the first paper in a series devoted to a study of the electronic structure, related properties and spectra of transition metal chelate complexes by means of the Wolfsberg-Helmholz semiempirical molecular orbital method as developed by Ballhausen and Gray.[1]. Here attention is confined to a theoretical investigation on some critical assumptions required in the SCCC–MO method. These are the choice of atomic orbitals, the dependence of one-electron Hamiltonian diagonal matrix element of ligand atomic functions upon the computed charge on atom, the method used to calculate the atomic charge and the K-parameter. The scrutinization of all these parameters has been carried out through a comparative analysis of the results obtained for metal electronic configuration, atomic charges, energy diagram, electronic spectrum and quadrupole splitting of Mössbauer spectrum of the $Fe^{II}(Dmg)_2(NH_3)_2$ complex, (Dmg = dimethylglyoximato monoanion).

Method of calculation. Molecular orbital calculations have been carried out by the semiempirical MO–LCAO method in the modified version proposed by Ballhausen and Gray,[1] known as the self-consistent charge and configuration method. Twenty-seven atomic orbitals have been considered as basis functions: nine metal orbitals, (3d, 4s, and 4p), one $2p\sigma$ orbital for each nitrogen and one $2p\pi$ orbital for each nitrogen, carbon and oxygen. No hybridization effect has been taken into account. Three sets of atomic orbitals have been considered: 1) The atomic orbitals are single Slater functions with Zerner and Gouterman[2] exponents for metal and with Clementi and Raimondi[3] exponents for ligand atoms. This set has been denoted by 1.

2) The metal orbitals are linear combinations of Slater functions with the exponents and coefficients proposed by Richardson *et al.*,[4] (the 3d and 4p functions have been taken from set II relative to Fe^+ in the d^7 and d^6p configurations, respectively; the 4s function has been assumed to be neutral atom function, the only one available). The ligand atomic orbitals are the same as in the first set. This second set has ben designated by 2.

3) The metal orbitals are the same as in the second set . The ligand atomic orbitals are linear combinations of Slater functions, corresponding to SCF 2p function of nitrogen in ^4S state and of carbon and oxygen in ^3P state, proposed by Clementi, Roothaan and Yoshimine.[5] This third set has been labelled by 3.

The diagonal matrix element H_{ii} of one-electron Hamiltonian has been estimated as the negative of the valence state ionization energy (VSIE) of the i-th orbital. The charge dependence of VSIE of the i-th orbital has been approximated by the following quadratic relation:

$$(VSIE)_i = aq^2+bq+c$$

where a, b, and c parameters are obtained from spectroscopic data on free atoms and ions, and q is the net charge on the atom. The parameters of metal orbitals have been taken from Basch, Viste and Gray.[6] On the other hand, as regards the ligand orbitals two possibilities have been examined: 1) The a and b parameters have been set equal to zero. Thus, the VSIE is charge-independent and equal to c parameter, which has been taken from spectral data on appropriate valence states of neutral atoms.[2,7] This scheme has been designated by I.

(1) C. J. Ballhausen and H. B. Gray, « Molecular Orbital Theory », W. A. Benjamin Inc., New York, 1964.

(2) M. Zerner and M. Gouterman, *Theoret. Chim. Acta*, *4*, 44 (1966).
(3) E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, *38*, 2686 (1963).
(4) J. W. Richardson, W. C. Nieuwpoort, R. R. Powell and W. F. Edgell, *J. Chem. Phys.*, *36*, 1057 (1962); J. W. Richardson, R. R. Powell and W. C. Nieuwpoort, *ibid.*, *38*, 796 (1963).
(5) E. Clementi, C. C. J. Roothaan and M. Yoshimine, *Phys. Rev.*, *127*, 1618 (1962).
(6) H. Basch, A. Viste and H. B. Gray, *Theoret. Chim. Acta*, *3*, 458 (1965); *J. Chem. Phys.*, *44*, 10 (1966).
(7) M. Zerner and M. Gouterman, *Inorg. Chem.*, *5*, 1699 (1966).

2) The a, b and c parameters have been taken from Zerner and Gouterman.[2,7] This charge-dependent scheme has been denoted by II.

The VSIE of axial ligand orbital has always been assumed to be charge-independent and set equal to 84.7 kK, *i.e.* the ionization potential of ammonia.[8]

The off-diagonal matrix element H_{ij} has been evaluated by means of the Wolfsberg-Helmholz approximation:

$$H_{ij} = KS_{ij}(H_{ii}+H_{jj})/2$$

where K parameter has been given the value 2.

In accord with the proposal by Ingraham,[9] the hydrogen atoms in hydrogen-bridge between the two oxygen atoms have been assumed to neutralize ½ negative charge on each oxygen so that the four oxygens are considerd neutral with a total of six electrons.

In all calculations an initial zero net charge has been assumed for all atoms. Then, after each cycle, the new net atomic charge has been computed by means of the Mulliken[10] population analysis, but using only a fraction of the predicted change in charge in order to assure the convergence of the iterative process. This has been achieved when all adjusted and computed net charges agreed to 0.01 units.

Further calculations have been performed either assigning different sets of values to K parameter or using the Löwdin[11] population analysis. They are fully discussed in the last sections.

The σ-type MO's span the irreducible representations a_g, b_{1g}, b_{2u} and b_{3u}. The π-type MO's span a_u, b_{1u}, b_{2g} and b_{3g}.

The oscillator strengths of the one-electron transitions have been calculated by taking into account only the diagonal elements of the transition moment matrix between atomic orbitals.

The quadrupole splitting in the ^{57}Fe Mössbauer resonance spectrum has been estimated following the approximate treatment fully described in the following.

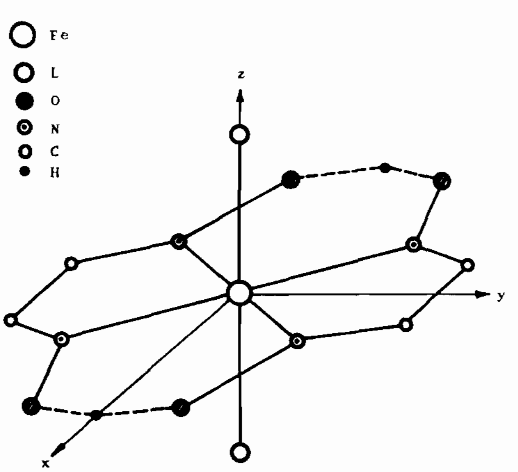

Figure 1. Structure of the complex $Fe^{II}(Dmg)_2L_2$

(8) J. D. Morrison, A. J. C. Nicholson, *J. Chem. Phys.*, *20*, 1021 (1952).
(9) L. L. Ingraham, *Acta Chem. Scand.*, *20*, 283 (1966).
(10) R. S. Mulliken, *J. Chem. Phys.*, *23*, 1833, 1841, 2338, 2343 (1955).
(11) P. O. Löwdin, *J. Chem. Phys.*, *19*, 1570 (1951).

For the examined complex has been assumed the geometry of $Co^{III}(Dmg)_2(NH_3)_2NO_3$ as investigated by Viswanathan and Kunchur.[12] By referring to the molecular structure reported in Figure 1, the group L is indicated as « axial ligand » and the chelating group Dmg as « planar or in-plane ligand ».

Results and Discussion

Electronic Structure. The net charge on the atoms and the electronic configuration of iron are reported in Table I. By comparing the results obtained by means of the three considered orbital sets, the following features are apparent. Within the Scheme I the electronic population of the 3d and 4s metal orbitals and the net charge of the nitrogen, oxygen and axial ligand atoms do not undergo significant alterations, while the electronic population of the 4p metal orbital and the net charge of iron and carbon atoms show moderate variations. On the other hand, in the framework of the Scheme II, only the electronic population of the 4p orbital and the net charge of the iron atom display pronounced changes. Moreover it must be emphasized that among the results obtained from the same orbital set with either of the I and II Schemes, only the net charge of the carbon and oxygen atoms turns out to be strongly affected. A final observation of interest is that in all considered cases the net charge carried by iron is comparatively small and lies between +0.10 and +0.18. This evidently means that the electronic charge donated by the axial ligands does not remain on the metal atom but is widespread all over the molecule.

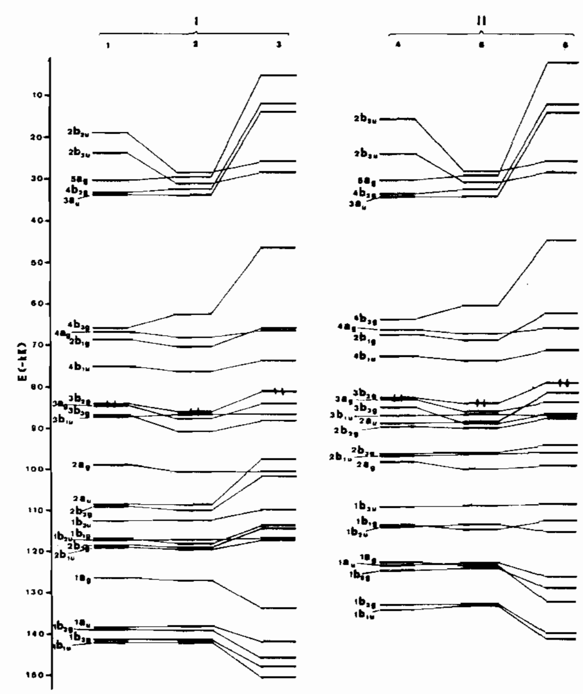

Figure 2. MO energy levels of the $Fe^{II}(Dmg)_2L_2$ complex. (For the meaning of the symbols I, II, 1, 2, and 3 see text).

(12) K. S. Viswanathan and N. R. Kunchur, *Acta Crystall.*, *14*, 675 (1961).

Table I. Electronic Population of Metal Orbitals and Net Atomic Charges

Scheme	I			II		
Orbital Set	1	2	3	1	2	3
3d	6.9546	6.9658	6.9907	6.9771	6.9918	7.0114
4s	0.5006	0.5247	0.5221	0.5104	0.5364	0.5261
4p	0.4283	0.3367	0.3506	0.4107	0.3143	0.3300
Fe	0.1165	0.1728	0.1366	0.1018	0.1575	0.1325
N	−0.0710	−0.0672	0.0065	−0.0397	−0.0416	−0.0200
C	0.1674	0.1399	0.0725	0.0174	0.0067	−0.0039
O	−0.4370	−0.4386	−0.4127	−0.2885	−0.2952	−0.2892
L [a]	0.6239	0.6454	0.5993	0.5706	0.5814	0.5599

[a] L stands for axial ligand atom.

Energy diagrams. The energy levels are depicted in Figure 2, where the highest level $5b_{1u}$, which is mainly metal $4p_z$ in character, is not reported.

In all the considered cases the MO's which have the largest contribution of metal 3d atomic orbitals are:

$3b_{3g} \sim 3d_{yz}$; $3a_g \sim 3d_{x^2-y^2}$; $3b_{2g} \sim 3d_{xz}$; $2b_{1g} \sim 3d_{xy}$; $4a_g \sim 3d_{z^2}$

It must be however underlined that the participation of the $3d_{xz}$ metal orbital to the $3b_{2g}$ MO is rather limited ($\sim 50\%$) in the case of the orbital set 3 within the Scheme II, so that this MO must be regarded in this case as a « d » MO only with particular caution. In this connection it is also worth pointing out that the $3a_g$ MO is always essentially a pure $3d_{x^2-y^2}$ metal orbital. Moreover between the « d » MO's the $2b_{1g}$ and $4a_g$ are antibonding in nature. With respect to the ordering of the energies two slightly different situations are observed:

$$3b_{3g} < 3a_g < 3b_{2g} \ll 2b_{1g} < 4a_g$$

for orbital sets 1 and 2; and

$$3b_{3g} < 3a_g < 3b_{2g} \ll 4a_g < 2b_{1g}$$

for orbital set 3.

In all these d-orbital splitting patterns the $3d_{yz}$, $3d_{x^2-y^2}$, and $3d_{xz}$ lie relatively close together as well as the $3d_{xy}$ and $3d_{z^2}$ do, these latter being some 15 kK higher in energy.

The axial ligand atomic orbitals participate only to the MO's belonging to the symmetry species a_g and b_{1u}. The most important contributions are for the $2a_g$, $4a_g$, and $3b_{1u}$ MO's. The $3b_{1u}$ bonding MO, which consists predominantly of the axial ligand orbitals, picks up an energy closely corresponding to the VSIE assumed for the axial ligand orbital, *i.e.* the ionization potential of ammonia (84.7 kK). The remainder MO's are essentially built out from the orbitals of Dmg in-plane ligand and in particular the a_u MO's are completely formed by the π-type atomic orbitals of Dmg. The bonding MO's of Dmg character lie in the region −110-140 kK.

The principal features of the energy diagram, especially in the frontier region, are maintained for each of the three orbital sets in both the Schemes I and II. In particular the $3b_{2g}$ and $4b_{1u}$ MO's always are the top occupied and the lowest empty MO respectively; moreover, their energy spacing is always about 7-10 kK, the largest separation being observed in the case of the orbital set 2. The $4b_{3g}$ antibonding MO undergoes the most substantial displacement in energy on passing from one to another orbital set. Generally speaking, within a given charge-dependence scheme the two orbital sets 1 and 2 yield closely parallel results. As far as the « d » MO's are concerned, their energy values are lower with the orbital set 2 in both the schemes. Nevertheless the Scheme I yields « d » MO's a bit more stable (*i.e.* lower in energy) and, generally, with a slightly more marked metal character.

Electronic Spectra. The simple theoretical approach used herein is known to be not very reliable in discussing electronic spectra because the interelectronic repulsions are not taken into account explicitly. Nevertheless, we try give some qualitative considerations about the electronic absorption spectra from the results of the present calculations. So far Table II collects the symmetry-allowed one-electron transitions up to 50 kK, whose oscillator strengths are comparatively large. A glance at Table II reveals that the transitions $3b_{1u} \rightarrow 4b_{3g}$ and $2a_u \rightarrow 4b_{3g}$ are the most sensitive to the type of orbital set while the transitions $2b_{2g} \rightarrow 4b_{1u}$, $2a_u \rightarrow 4b_{3g}$, and $2b_{3g} \rightarrow 4b_{1u}$ are strongly affected by the charge-dependence scheme. At any rate, if one wishes to compare the theoretical transitions to the experimental spectrum, each of the observed bands must be considered as formed by several near-lying transitions of different nature.

The spectrum of $Fe^{II}(Dmg)_2(NH_3)_2$, reported by Császár and Fügedi,[13] consists essentially of two bands and one shoulder. The nature of the band centred at about 19 kK has been thoroughly investigated by Jillot and Williams[14] and identified as a charge-transfer (CT) band of metal-to-ligand (M→L) character on the basis of the observation that it moves to shorter frequencies as the strength of the axial ligand base increases. The band recorded at about 44 kK has been assigned[13] to a transition $\pi \rightarrow \pi^*$ of Dmg ligand, because such a band also occurs in the same range of frequency in free Dmg.

On the basis of the present calculation the following interpretation of the electronic spectrum can be afforded. The $3b_{3g} \rightarrow 4b_{1u}$ and $3b_{1u} \rightarrow 4a_g$ low-lying transitions have the nature of a CT between metal and ligand, «d_{xz}»→L and L′→«d_{z^2}» respecti-

(13) J. Császár and K. Fügedi, *Acta Chem. Hung.*, 32, 451 (1962).
(14) B. A. Jillot and R. J. P. Williams, *J. Chem. Soc.*, 1958, 462.

Table II. Electronic Transitions

Scheme	I						II					
Orbital Set	1		2		3		1		2		3	
Transition	E	f										
$3b_{3g}\rightarrow 4b_{1u}$	11.6	0.09	14.3	0.14	14.4	0.10	12.1	0.06	14.6	0.08	15.0	0.06
$3b_{1u}\rightarrow 4a_g$	20.2	0.24	18.5	0.24	20.5	0.24	20.8	0.25	19.2	0.25	20.7	0.25
$3b_{1u}\rightarrow 4b_{3g}$	21.3	0.09	24.0	0.06	40.3	0.09	23.2	0.02	26.1	0.02	41.9	0.04
$2a_g\rightarrow 4b_{1u}$	23.6	0.06	24.1	0.06	26.6	0.07	25.4	0.05	26.1	0.04	28.7	0.06
$2b_{2g}\rightarrow 4b_{1u}$	34.2	0.20	33.6	0.18	28.0	0.14	16.6	0.26	16.1	0.22	16.1	0.15
$2a_u\rightarrow 4b_{3g}$	42.7	0.38	46.0	0.41	51.1	0.66	25.0	0.39	27.7	0.39	36.5	0.67
$2b_{3g}\rightarrow 4b_{1u}$	43.6	0.05	42.5	0.04	41.2	0.05	23.3	0.03	22.0	0.04	22.6	0.03
$1b_{3u}\rightarrow 2b_{1g}$	43.9	0.37	42.4	0.40	46.8	0.56	41.7	0.37	39.8	0.39	45.9	0.55
$1b_{3u}\rightarrow 4a_g$	45.8	0.08	44.2	0.04	43.5	0.07	43.0	0.07	41.3	0.08	42.5	0.07
$1b_{2u}\rightarrow 2b_{1g}$	48.7	0.25	46.8	0.28	53.7	0.40	46.3	0.25	44.4	0.27	52.8	0.39
$1b_{2u}\rightarrow 4a_g$	50.5	0.13	48.9	0.14	50.4	0.12	47.6	0.12	45.9	0.14	49.3	0.12
$2b_{1u}\rightarrow 4b_{3g}$							32.8	0.08	35.4	0.09	51.2	0.14

vely, (where L can be essentially regarded as the in-plane ligand and L′ as the axial ligand). Thus both of these transitions may be considered as contributing to the band recorded at about 19 kK. The position of these transitions is not significantly influenced by the type orbital set nor by the charge-dependence scheme.

The $2a_u\rightarrow 4b_{3g}$ transition turns out to be a $\pi\rightarrow\pi^*$ transition of Dmg ligand because the a_u MO's are due only to the Dmg orbitals and the contribution of d metal orbital to the $4b_{3g}$ MO is very small. This transition should be the principal responsible for the intense, broad band measured at about 44 kK, to which even the other transitions calculated in the range 40-50 kK are expected to contribute to some extent. As above mentioned, the energy of this transition is substantially altered by the type of orbital set and by the charge-dependence scheme. However, it must be underlined the fact that the more satisfactory agreement with the experimental spectral datum is achieved by using either of the orbital sets 1 and 2 in the framework of the Scheme I.

The shoulder measured at about 35 kK may be attributed to the $2b_{2g}\rightarrow 4b_{1u}$ transition, L→L in character, for all the cases in the Scheme I. On the other side, the assignment of this shoulder is more problematic within the Scheme II.

Finally, all d→d parity-forbidden transitions are evaluated in the range between 15 and 28 kK. Thus the d→d type bands may fall under the CT intense band centred at 19 kK.

Mössbauer Spectra. On the basis of the calculated electronic structure, in an attempt to gather some information about one of the most important parameters of Fe^{57} Mössbauer resonance spectra of Fe^{II}-$(Dmg)_2(NH_3)_2$, the quadrupole splitting has been evaluated through an approximate treatment. The quadrupole splitting, which is dependent on the electric-field gradient (EFG) and is sensitive to the symmetry of the nuclear environment, is given by:[15]

$$\Delta = \frac{1}{2}e^2Q(q^2+\eta^2q^2/3)^{1/2}$$

where Q represents the nuclear quadrupole moment of the 14.4 Kev state in Fe^{57}, q the EFG at the nucleus and η the asymmetry parameter. If one assumes two separate contributions to q, a valence contribution, q_v, coming from the charge distribution of the nonspherical 3d « valence » electrons of the Fe^{II} ion in the crystal field, and a lattice contribution, q_l, coming from the assumed distribution of the ligand around the Fe^{II} ion, then the EFG is given by:

$$q = (1-R)q_v+(1-\gamma_\infty)q_l$$

where $(1-R)$ and $(1-\gamma_\infty)$ are the so-called Sternheimer antishielding factors, which correct for the polarization of the ferric-like core by the EFG of the valence and lattice charge distribution. In a similar manner the asymmetry parameter η is defined by:

$$q\eta = (1-R)q_v\eta_v+(1-\gamma_\infty)q_l\eta_l$$

In the MO framework, q_v and $q_v\eta_v$ can be written in the form of the sum of the expectation values of the EFG operators for all the 3d « valence » electrons:

$$q_v = 2\sum_{i,k} c_{ik}^2\left<\frac{V_{zz}}{e}\right>_k = 2\sum_{i,k} c_{ik}^2A_k\left<r^{-3}\right>$$

and

$$q_v\eta_v = 2\sum_{i,k} c_{ik}^2\left<\frac{V_{xx}-V_{yy}}{e}\right>_k = 2\sum_{i,k} c_{ik}^2A_k'\left<r^{-3}\right>$$

in which the index k refers to the 3d orbitals, the index i runs over all the occupied MO's, c_{ik} is the coefficient of the k-th 3d orbital in the i-th MO, $\left<r^{-3}\right>$ is the expectation value of r^{-3} for an iron 3d orbital, and A_k and A_k' are the angular contributions to the EFG.

An approximate estimate of the contributions from the ligands can be obtained by using a point-charge model, then:

$$q_l = \sum_i\left<\frac{V_{zz}}{e}\right>_i = \sum_i q_i\,\frac{3\cos^2\theta_i-1}{r_i^3}$$

and

$$q_l\eta_l = \sum_i\left<\frac{V_{xx}-V_{yy}}{e}\right>_i = \sum_i q_i\,\frac{3\sin^2\theta_i\cos2\varphi_i}{r_i^3}$$

(15) R. Ingalls, *Phys. Rev.*, *133A*, 787 (1964).

in which q_i represents the net charge on the i-th ligand and (r_i, ϑ_i, φ_i) are the position polar coordinates.

So far the quadrupole splitting has been tacitly assumed to be independent of temperature. However, as a first approximation, the Boltzmann factors may be neglected when the « d » orbital splitting energies are much larger than thermal energies. This has ben considered to be the present case. On the other side, even the contribution of the 4p electrons to the EFG has been neglected, owing to the fact that the value of $<r^{-3}>_{3d}$ is about twice that of $<r^{-3}>_{4p}$ and the electronic populations of 4p are much smaller than those of 3d.

Then using the values given by Ingalls:[15] $Q = 0.29\times10^{-24}$ cm^2, $(1-R) = 0.68$, $(1-\gamma_\infty) = 12$, and $<r^{-3}> = 4.8$ *a.u.*, and considering only the ligand contributions from the nitrogen atoms, the estimates of quadrupole splitting are:

Scheme	I			II		
Orbital Set	1	2	3	1	2	3
Δ (cm/sec)	0.120	0.160	0.178	0.140	0.147	0.168

Thus the evaluated quadrupole splitting turns out to be moderately dependent upon the type of orbital set and the charge-dependence scheme. However in all cases the order of magnitude of the calculated quadrupole splitting appears fairly well compatible with those experimentally found by Ablov *et al.*[16] on $Fe^{II}(Dmg)_2Py_2$ (0.18 cm/sec) and by Dale *et. al.*[17] on the structurally similar Fe^{II}bis(nioxime)$(NH_3)_2$ complex (0.17 cm/sec). A direct comparison cannot be made because in the former complex the pyridine-like nitrogen axial ligand displays σ-donor as well as π-acceptor properties. Finally, it must be noticed that recently Burger *et. al.*[18] reported the Mössbauer spectra of some iron Dmg complexes. Unfortunately their data cannot be compared with the present estimates because the spectra were recorded on complexes without axial ligands and having two kinds of Fe^{II} differring in their bonding.

Variation of the K Parameter. Two further calculations have been performed by assigning different values to the K parameter in the Wolfsberg-Helmholz formula of extra-diagonal matrix element. In particular, the following sets of values have been investigated: 1.8 for σ-type and 2.0 for π-type interactions, and 1.8 for both σ- and π-type interactions; in the above reported calculations $K_\sigma = K_\pi = 2.0$. With respect to the previous results, the electronic structure of the complex does not appear to be very sensitive to a given choice of K parameter values and displays the same behaviour on going over from the I to the II Scheme. As an example, Table III summarizes the metal orbital populations and the net atomic charges estimated from all the considered sets of K. As far as the energy diagram is concerned, the principal features, in particular the « d » MO's ordering and character, are maintained; only the position of a few levels, which are very close each to other in the case $K_\sigma = K_\pi = 2.0$, is inverted. However, the largest splitting between the top filled MO and the lowest virtual one is observed in the case of $K = 2.0$. Owing to the fact that the energy levels lie at slightly different positions, the electronic spectral patterns calculated from the various sets of K look somewhat different as far as the position of the transitions is concerned. It must be however underlined that the value of the $\pi\rightarrow\pi^*$ transition ($2a_u\rightarrow4b_{3g}$) more consistent with the experimental datum is estimated by adopting $K_\pi = 2.0$ within the Scheme I.

Population Analysis. In order to test to what extent different methods of evaluating the charges on atoms can affect the energy levels and molecular properties, further computations have been carried out on the examined complex by making use of the approximation proposed by Löwdin[11] within both the Schemes I and II. The results, in general, look very like to those previously obtained with Mulliken[10] population analysis. It can be underlined only the fact that the iron electronic configurations differ slightly from the previous ones. Taking, as an example, the case of orbital set 2 in the framework of the Scheme II, the iron configuration is $d^{6.99}s^{0.54}p^{0.31}$ with the Mulliken method and $d^{7.13}s^{0.43}p^{0.16}$ with the Löwdin method. The corresponding metal net charges are +0.16 and +0.28. Finally, from the present results can be drawn the conclusion that, at least for this complex, no substantial differences turn out from using these two methods of evaluating the atomic charges. The discrepancies do not seem to be so dramatic as those found by Cusachs and Politzer[19] on organoboron compounds, where the choice of one of these two approximations plays a critical role especially when the 2p orbital of hydrogen atom is taken into account.

Concluding Remarks. From a comparative analysis of the results obtained following both the Schemes I and II as far as the atomic charges, metal configuration, energy diagram, « d » orbital ordering and quadrupole splitting of Mössbauer spectrum are concerned, not too different numerical values are observed for all the three considered orbital sets. Moreover, substantially similar results are reached by assuming different sets of values of K parameter for σ- and π-type interactions as well as by computing the net atomic charges by means of Löwdin's instead of Mulliken's population analysis. The present results suggest that the ground-state molecular properties are described with the same degree of accuracy by all the considered procedures. On the other side, owing to the inherent deficiencies of the theoretical approach, the results for the spectral pattern must be treated with caution. Nevertheless, it can be inferred that the more satisfactory agreement with the observed spectrum is provided by the orbital sets 1 and 2 in the framework of the charge-dependence Scheme I and with $K_\sigma = K_\pi = 2.0$.

(16) A. V. Ablov, V. I. Gol'danskii, R. A. Stukan and E. F. Makarov, *Dokl. Akad. Nauk SSSR, 170,* 128 (1966).
(17) B. W. Dale, R. J. P. Williams, P. R. Edwards and C. E. Johnson, *Trans. Far. Soc., 64,* 620 (1968).
(18) K. Burger, L. Korecz, I. B. A. Manuaba and P. May, *J. Inorg. Nucl. Chem., 28,* 1673 (1966).
(19) L. C. Cusachs and P. Politzer, *Chem. Phys. Lett., 1,* 529 (1968).

Table III. Electronic Population of Metal Orbitals and Net Atomic Charges for Orbital Set 2.

K	$K_\sigma = 2.0, K_\pi = 2.0$		$K_\sigma = 1.8, K_\pi = 2.0$		$K_\sigma = 1.8, K_\pi = 1.8$	
Scheme	I	II	I	II	I	II
3d	6.9658	6.9918	7.0224	7.0516	7.0109	7.0625
4s	0.5247	0.5364	0.4482	0.4702	0.4554	0.4867
4p	0.3367	0.3143	0.3039	0.2717	0.2903	0.2234
Fe	0.1728	0.1575	0.2255	0.2065	0.2434	0.2274
N	−0.0672	−0.0416	−0.1089	−0.0576	−0.1839	−0.0735
C	0.1399	0.0067	0.1425	0.0007	0.1714	0.0049
C	−0.4386	−0.2952	−0.4384	−0.2972	−0.4514	−0.2853
L [a]	0.6454	0.5814	0.6969	0.6048	0.8062	0.5941

[a] L refers to the axial nitrogen atom.

In summary, for the ligand atoms the use of sophisticated atomic functions as well as the extension of the charge-dependence to the VSIE of their orbitals seem not to be strictly necessary. Thus in the future investigations on the electronic structure and properties of transition metal complexes with polydentate ligands we will generally make use of a simple basis of atomic orbitals and of the charge-dependence of VSIE restricted to metal orbitals.

A final observation of interest is that the latter conclusion is in agreement with that reached by Jørgensen *et al.*[20] on the basis of Wolfsberg-Helmholz calculations incorporating the Madelung interaction coulomb energy to the ligand energy. These corrections indeed make the ligand energy nearly invariant with charge.

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(20) C. K. Jørgensen, S. M. Horner, W. E. Hatfield and S. Y. Tyree, *Int. J. Quant. Chem.*, *1*, 191 (1967).