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MO Studies for Transition Metal Complexes with Polydentate Ligands. V. On the Influence of the Nature and Arrangement of the Donor Atoms in Ni^{II} Planar Complexes

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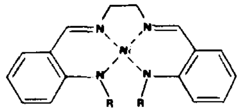
A theoretical insight on the role exerted both by the nature and configuration of the set of donor atoms in transition metal complexes is given in terms of MO's, as derived from SCCC–MO theory, with the description of the bonding in tetra-coordinate Ni^{II} chromophores having nitrogen and/or oxygen atoms as donors. The electron distribution around the metal atom (atomic charges and bond overlap populations), and the energy level diagrams anticipate the trend: $NiN_4 > NiN_2O_2$ (cis) $\simeq$ NiN_2O_2 (trans) $>$ NiO_4 *chromophore, for the stability of the complexes and for their reluctance to modify stereochemistry and magnetism, in accord with experimental findings.*

Introduction

In the previous paper of this series[1] we have reported a theoretical investigation on the electronic structure of cobalt(III) complezes with tetradentate Schiff-bases like bae, salen, and saloph performed in order to obtain an insight on the role played by the extension of π-conjugation through the enlargement of the equatorial macrocycle surrounding the metal. The extended Wolfsberg-Helmholz MO calculations do not predict significantly different bonding situations around the central metal atom.

Now we proceed to describe the results of a theoretical analysis on another important factor, presumably more critical in determining the electronic structure and properties of transition metal complexes, *i.e.* the nature and arrangement of the set of donor atoms. To go on dealing with complexes formed with polydentate ligands, we have considered four different cases of tetracoordination involving electronegative donor atoms (nitrogens and/or oxygens) in square-planar (or nearly so) arrangements. It is reasonable to expect the conclusions achieved for these planar arrangements to be valid also for other different symmetries, in view of the fact that it is the nature rather than the configuration of the set of donor atoms that controls primarily the electronic distribution around the metal atom. Of course, the main significance of results is in the *trends* that are provided and not in the absolute results for any one molecule.

Complexes of Ni^{II} have been investigated because the rather usual square-planar stereochemistry and the known structural lability and isomerism of some Ni^{II} complexes[2] make these more appropriate for the present study. In particular, the following compounds have been analysed: Ni^{II} (amben) (1), Ni^{II} (salen) (2), Ni^{II} (salim) (3), and Ni^{II} (salal) (4).*



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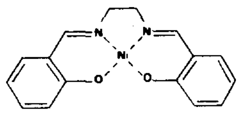

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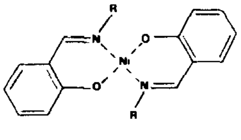

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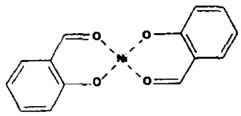

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Structural formulae

These compounds contain respectively an «N_4», «N_2O_2» *cis*, «N_2O_2» *trans*, and «O_4» system of atoms coordinated with the central metal atom.

The synthesis and properties of the amben («N_4») derivative have been reported very recently in the literature.[3] The other complexes are instead known

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[1] Part IV, G. De Alti, V. Galasso and A. Bigotto, *Inorg. Chim. Acta*, *6*, 129 (1972).

[2] L. Sacconi, in « Transition Metal Chemistry », ed R.L. Carlin, M. Dekker, Inc., New York, 1968, vol. 4, p. 199.

* Amben = NN'-bis-(*o*-amino-benzylidene)-1,3-diaminoethanato dianion; salen = NN'-ethylenebis(salicylideneiminato)dianion; salm = bis-salicylaldiminato dianion; salal = bis-salicylaldehydato dianion.

[3] M. Green and P.A. Tasker, *J. Chem. Soc.* (A), *1970*, 2531.

[4] J.V. Dubsky and A. Sokol, *Coll. Czech. Chem. Comm*, 3, 548 (1931); P. Pfeiffer, E. Breith, E. Lubbe and T. Tsumaki, *Annalen*, *503*, 84 (1933).

[5] P. Pfeiffer, H. Buchholz and O. Bauer, *J. prakt. Chem.*, *129*, 170 (1931) W. Klemm and K.H. Raddatz, *Z. anorg. Chem.*, *250*, 207 (1942).

[6] G.N. Tyson, Jr., and S.C. Adams, *J. Amer. Chem. Soc.*, *62*, 1228 (1940).

since several years.[4-6] For compounds (1)-(3) the experimental evidence[3,7,8] supports diamagnetic and planar (or nearly so) tetracoordinate form, while the salal («O_4») complex is characterised by paramagnetism and, very presumably, by non-planar configuration.[6,9] However, in order to get a comparative analysis of the theoretical findings for closely related structures, also the symmetry of the latter complex has been assumed to be fully-planar.

Computational Details and Results

The electronic structures have been determined by the extended Wolfsberg-Helmholz MO method in the Ballhausen-Gray version. The Ni and N/O atoms have been considered σ- and π-bonded while only π bonding within the ligands has been taken into account. Thus the following AO basis set has been adopted: the 3d, 4s, and 4p of Ni, the $2p\sigma$ and $2p\pi$ of N and O, the $2p\pi$ of the C atoms entering into the π interaction. The multi-exponential functions of Richardson *et al.*[10] have been used for Ni^+ and those of Clementi and Raimondi[11] for the other atoms. The appropriate valence-orbital-ionization-potentials have been derived from the collection by Basch *et al.*[12]

A symmetrical and fully-planar geometry has been used for (3) and (4), taking the structural parameters from X-ray studies.[13,14] In view of the close analogy, the salim geometry has been transferred also to the salen derivative. Finally, in analogy with the diaquosalal derivative in which the four oxygens make a square-planar arrangement,[14] the amben structure has been postulated to have an «N_4» square-planar environment with Ni–N bonds of 1.90 Å, N–C of 1.30 Å, N=C of 1.24 Å, C–C of 1.44 Å and with all the benzenic C–C bonds of 1.39 Å. The ligand is assumed to lie in the xy plane, with the x axis bisecting the N–Ni–N angle in (1) and (2), the interligand O–Ni–N angle in (3) and the interligand O–Ni–O angle in (4).

The atomic charges and the metal orbital configurations are collected in Table I. The interatomic overlap populations are listed in Table II. Finally, in Figure 1 are presented the one-electron energy level schemes.

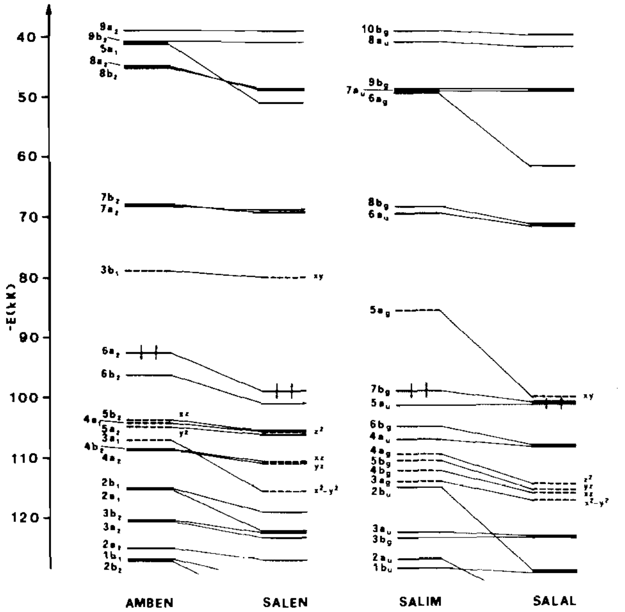
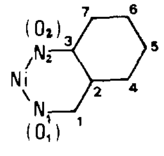


Figure 1. One-electron energy level diagram for Ni^{II} planar complexes.

Table I. Electronic population of metal orbitals and atomic net charges[a].

Complex	"N_4"	"N_2O_2"(*cis*)	"N_2O_2"(*trans*)	"O_4"
3d	8.854	8.854	8.840	8.710
4s	0.583	0.571	0.563	0.497
4p	0.348	0.278	0.294	0.260
Ni	+0.215	+0.297	+0.303	+0.533
N_1	−0.100	+0.037	−0.027	
O_1				−0.336
N_2	−0.249			
O_2		−0.566	−0.508	−0.492
C_1	+0.281	+0.321	+0.323	+0.437
C_2	−0.080	−0.042	−0.041	−0.045
C_3	+0.176	+0.153	+0.153	+0.183
C_4	+0.037	+0.042	+0.042	+0.064
C_5	−0.098	−0.060	−0.060	−0.062
C_6	+0.041	+0.046	+0.046	+0.068
C_7	−0.116	−0.079	−0.079	−0.082

[a] Atom numbering is assumed as follows:



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(8) H.C. Clark and A.L. Odell, *J. Chem. Soc.*, *1995*, 3431, 3435.

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(10) 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).

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(12) H. Basch, A. Viste and H.B. Gray, *Theoret. Chim. Acta*, *3*, 458 (1965).

(13) E. Frasson, C. Panattoni and L. Sacconi, *J. Phys. Chem.* *63*, 1908 (1959).

(14) J.M. Stewart, E.C. Lingafelter and J.D. Breazeale, *Acta Cryst.*, *14*, 888 (1961).

Table II. Bond overlap populations [a]

		"N_4"	"N_2O_2"(*cis*)	"N_2O_2"(*trans*)	"O_4"
Ni—N_1	σ	0.527	0.582	0.548	
	π	0.080	0.076	0.079	
Ni—O_1	σ				0.411
	π				0.038
Ni—N_2	σ	0.527			
	π	0.088			
Ni—O_2	σ		0.356	0.406	0.411
	π		0.055	0.052	0.043
N_1—C_1		0.531	0.560	0.559	
O_1—C_1					0.412
N_2—C_3		0.381			
O_2—C_3			0.161	0.161	0.174
C_1—C_2		0.339	0.290	0.291	0.338
C_2—C_3		0.355	0.418	0.417	0.397
C_3—C_4		0.434	0.441	0.441	0.419
C_4—C_5		0.555	0.534	0.544	0.555
C_5—C_6		0.453	0.484	0.483	0.474
C_6—C_7		0.565	0.528	0.527	0.532
C_5—C_7		0.405	0.481	0.481	0.476

[a] For atom numbering see below Table I.

Discussion

An inspection of the results assembled in Table I reveals the following intrinsic features of the electronic structures on going along the systems «N_4», «N_2O_2» *cis*, «N_2O_2» *trans* and «O_4»: The 3d and 4s orbital populations remain sensibly constant for the first three systems, undergoing a moderate lowering on passing to «O_4» system. On the other hand, the electron density on the 4p orbital is largest in the «N_4» case, takes up a slightly lower value for the «N_2O_2» *cis* and *trans* systems and is even smaller for «O_4». Consequently, the following trend operates for the net positive charge on the Ni atom:

$$"N_4" < "N_2O_2"(cis) \cong "N_2O_2"(trans) \ll "O_4"$$

By assuming an inverse correspondence between the metal charge (and hence the ionic character of the metal-ligand bond) and the stability of the complex, as was found to be the case for metal porphyrins,[15] the reverse order is then predicted for the *relative* stability of the present complexes.

Keeping in mind that the «N_4» and «O_4» systems are formed by two pairs of equivalent atoms which carry rather different atomic charges, the following situations can be distinguished as far the charges on the donor atoms are considered. The iminic nitrogen bears a negative charge of *ca.* 0.1 a.u. in the «N_4» system and approaches the neutrality in the «N_2O_2» systems. On the aminic nitrogens present in the «N_4» set is predicted a much more negative charge. The phenolic oxygen displays a singular behaviour. Indeed its negative charge remains virtually unaffected on passing from «O_4» to «N_2O_2» system, (both being of *trans* type), while undergoes a net increase when going to the «N_2O_2» *cis* system. A lower negative charge is found for the ketonic oxygen atom of the «O_4» system. Out of all the carbon atoms the more significant charge alterations occur for those directly linked to the donor atoms.

In every case the interatomic overlap populations (Table II) of the nickel-to-nitrogen bond is significantly greater than for the corresponding nickel-to-oxygen bond. Both in these bonds however the π contribution is always remarkably less important than the σ. Despite of the apparently large π-acceptor capacity of the highly-conjugated polydentate ligands, the nickel-to-donor atom bonds have thus a large amount of σ character and a rather scarse of π. Looking now at the *total* (σ+π) overlap population of all the nickel-donor atom interactions as an approximate measure of the bonding capacity of the metal atom, from the observed order:

$$"N_4" > "N_2O_2"(cis) \simeq "N_2O_2"(trans) > "O_4"$$

one may infer an inverse disposability of the nickel atom to coordinate with further ligands, (*ie.* to increase its coordination number), or to change stereochemistry. This would be consistent with experimental findings. Indeed, the «N_4» system shows a strong tendency to remain planar, tetracoordinate and diamagnetic.[3] As a solid the «N_2O_2» *cis* system is diamagnetic and hence planar; in pyridine solution it displays a tendency to form five- and six-coordinate diamagnetic complexes.[3,8] The «N_2O_2» *trans* system has a certain tendency to modify the molecular arrangement:[2] six-coordinate, paramagnetic compounds are formed in donor solvents[15] and recently the five-coordinate, paramagnetic monoadduct with pyridine has also been isolated.[16,17,*] Finally, the «O_4» system readily coordinates with two water or pyridine molecules forming octahedral complexes in which the solvent molecules occupy apical positions[6,7,14] or assumes

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[*] A calculation performed on the hypothetical tetrahedral form of the «N_2O_2» system yields a high energy barrier for the conversion from planar to tetrahedral structure. Thus the planar configuration appears to be strikingly favoured. This result is in contrast with the hypothesis advanced by Willis and Mellor[7] in order to explain the paramagnetism observed for pyridine solution. However, the very small energy gap found between the highest occupied MO and the lowest empty MO (only 0.6 kK) of the tetrahedral form would be diagnostic of possible spin-unpairing.

(15) M. Zerner and M. Gouterman, *Theoret. Chim. Acta*, *4*, 44 (1966).

(16) S. Yamada, E. Ohno, Y. Kuge, A. Takeuchi, K. Yamanouchi and K. Iwasaki, *Coord. Chem. Rev.*, *3*, 247 (1968).

(17) G.N. LaMar, *Inorg. Chim. Acta*, *3*, 183 (1969).

(18) D.A. Bone, E.D. McKenzie and K. Rowan, *Chem. Comm.*, 1970, 420.

a polymeric structure in which the oxygen atoms are presumed to act as bridging ligands.[9]

As expected, the interatomic overlap populations of the C—N (aminic) and C—O (phenolic) bonds are sensibly less than those for the C—N (iminic) and C—O (ketonic) bonds in the «N_4» and «O_4» sets respectively. A virtual constancy of values is found for the C—N, C—O, and C—C bonds both of the «N_2O_2» systems. On passing from the «N_2O_2» systems either to «N_4» or «O_4» system only a slight alteration takes place in the quoted bonds.

Consider now the one-electron energy level diagrams (Figure 1). In all cases the first virtual MO level has predominantly «$d_{x^2-y^2}$» metal character, the highest occupied MO's bear π ligand nature and under these lie the other levels of «d» metal character relatively close each to other. As regards the «d» orbital order the present calculations lead to the following results:

$d_{x^2-y^2} < d_{yz} \simeq d_{z^2} \simeq d_{xz} \ll d_{xy}$ for the "N_4" set,

$d_{x^2-y^2} < d_{yz} \simeq d_{xz} < d_{z^2} \ll d_{xy}$ for the "N_2O_2" *cis* set,

$d_{x^2-y^2} < d_{yz} < d_{xz} < d_{z^2} \ll d_{xy}$ for the "N_2O_2" *trans* set, and

$d_{x^2-y^2} < d_{xz} \simeq d_{yz} \simeq d_{z^2} \ll d_{xy}$ for the "O_4" set.

The observed level inversions must be probably attributed to the different geometrical parameters used for the various molecules. However, owing to the inherent deficiencies of the theoretical approach and of the closeness of the four lower «d» levels, no particular significance must be attached to these orderings. To note that for all systems the «d_{z^2}» level is predicted to be less stabilized than the «$_{x^2-y^2}$. This is consistent with the suggestion made for the «N_4» set by Green and Tasker.[3] One further point is worthy of note. The very little energy gap between the highest filled and the first virtual MO's in the «O_4» system strongly suggests a triplet ground state in agreement with the paramagnetism of Ni^{II} (salal). A high tendency to coordinate further groups is also inferred in agreement with the existence of the octahedral diagno-derivate[6,14], Generally speaking, the energy diagram shifts toward lower energies passing from « N_4 » to « O_4 » system.

As a final remark, it is worthwhile noting that calculations performed assuming for all the four complexes in turn the geometrical parameters of each of the complexes do not lead to substantially different results from those above presented. In particular, essentially the same metal charge and configuration are obtained, while only slight alterations in the donor atom charges and quite similar charge distribution in the remaining atoms are found. The « d » level orderings are also preserved; instead the energy gap between the highest occupied and the first virtual MO's' decreases on passing from « N_2O_2 » to « N_4 » geometrical parameters and from « N_4 » to « O_4 » geometrical parameters. Then it can be concluded that the electronic structure and related properties of the investigated complexes depend almost exclusively on the nature of the donor atoms.