COMMUNICATIONS TO THE EDITOR

The Electronic Structure of
Co(N-[2-((2-aiminoethyl)thio)ethyl]-2-aminoacetamide)(NO$_2$)$_2$Complex

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Studies on cobalt complexes containing flexible tetradentate ligands in recent years have shown that it is useful to relate the structure and bonding of transition metal complexes to those of the Co(III) through the geometry, their reactions, and the stereochemistry of the reaction products.[1-4]

In this work we set out to investigate the binding of metal to ligand in Co(gee)(NO$_2$)$_2$ complex. Our approach is to use the EHT-SPD molecular orbital method.[5] A cobalt metal employes the 3d, 4s, and 4p atomic orbitals in coordination bonding. The best orbitals available are the multiexponential orbitals.[6,7] These orbitals were obtained by expressing the 3d, 4s, 4p and 4d atomic orbitals as a linear combination of 82 Slatertype atomic orbitals and adjusting the free parameters in order to obtain maximum overlap with atomic self consistent field wave functions for the appropriate maximum overlap.

The experimental preparations are known for a Co(III) complexes which contain linear tetradentate ligands having an NSNN donor atom set consisting of terminal amin or pyridine groups and internal amide and thioether donors, which were designed to adopt the cis-β geometry.[8-10]

The ligands are by design unsymmetrical, and it is therefore even more difficult to assign a stereochemistry to the complexes by spectroscopic methods although ^{13}C NMR spectroscopy strongly points to the formation of only one isomer.[11]

The geometries of Co(gee)(NO$_2$)$_2$ were constructed from the probable bond angles, bond lengths, and dihedral angles.[12] The calculation of atomic cartesian coordinates of the molecular system was carried out with the aid of modified version of Hildebrandt program.[13] The numbering scheme of Co(gee)(NO$_2$)$_2$ are shown in Figure 1.

The results of calculation for the nonhydrogen atoms of the Co(gee)(NO$_2$)$_2$ complex are shown in Table 1. In Table I we list the coefficients of the cobalt atomic orbitals in the molecular system. The lowest molecular orbital is primarily composed of the d$_{x^2-y^2}$ atomic orbitals on the complexes and is strongly bonding.

The lowest orbital combines the p atomic orbitals of the coordination site atoms with the same algebraic sign and is a dπ-pπ bonding type complex orbital. The calculated frontier orbital energies for the lowest unoccupied molecular orbital energy in -11.899 eV and highest occupied molecular

orbital energy is shown to be -12.045 eV. According to these calculations, the complex configuration is the most stable for a variety of six coordination site atom NNNNNS and this provides a rationale for the formulation as Co(gee)(NO$_2$)$_2$ coordination compound.

Three dimensional coordinates of Co(gee)(NO$_2$)$_2$ complex are shown in Table 2. For the interpretation of structural preference of cobalt complex in Table 2, we have considered molecular orbital factors controlling the dihedral angle. And also, we can predict the coordination ability to bonding formation atomic charges. The stability of ligand which is shown by atomic charge of coordination site atom was in the order of N$_{15}$>N$_{12}$>N$_{13}$>N$_9$>N$_5$>S$_1$ and it can be seen in Figure 1.

Figure 1 shows the valence electron for the nonhydrogen atom skeleton of the Co(gee)(NO$_2$)$_2$.

The model shows the expected migration of electron density maxima at coordination towards the center of cobalt and distinct electron density maxima at coordination sites predicted on the basis of hybridization of coordination atoms. In case of nitrogen N(9), the lone pairs are stabilized by a strong bond in the same plane.

The visible spectra of the dinitro, diazido, and oxalato complexes are similar to those for analogous cobalt complexes of NNNN[14] and NSSN[15,16] donor sets. The assignment of the gross stereochemistry about the metal is not possible, however, since often there is very little difference(<10 nm) between the λ max values for cis-α and cis-β isomers. It means
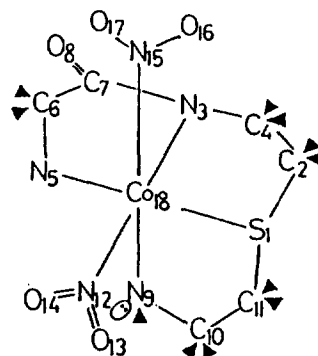

Figure 1. The numbering scheme of Co(gee)(NO$_2$)$_2$ complex.

Table 1. **Molecular orbitals for Cobalt in Co(gee)(NO₂)₂**

AO \ MO	34	35	36	37
s	0.0314	−0.0536	−0.1043	0.0265
P_x	0.0404	−0.0250	−0.0227	0.0418
P_y	0.0668	0.0565	−0.1028	0.0180
P_z	−0.0172	0.0644	−0.0209	−0.0350
$d_{x^2-y^2}$	−0.1270	−0.1816	−0.1736	0.0460
d_{z^2}	−0.0342	0.0295	0.1670	−0.0385
d_{xy}	−0.1528	0.0369	−0.1288	−0.1327
d_{xz}	−0.0750	0.0993	−0.1299	−0.2584
d_{yz}	0.0111	−0.0757	−0.0340	−0.2058

Table 2. **Three dimensional coordinates and Net Charges in Co(gee)(NO₂)₂**

Atom	X	Y	Z	Net charge
S(1)	2.2330	0.0000	0.0000	−0.1808
N(3)	0.0730	1.9006	0.0000	−1.1710
N(5)	−1.9408	0.2510	0.0000	−1.0553
N(9)	−0.0006	−0.0160	−1.9939	−1.1034
N(12)	−0.1509	−1.9141	0.0000	−1.2362
N(15)	−0.0488	0.0000	1.9404	−1.2499
Co(18)	0.0000	0.0000	0.0000	1.1428

that the charge transition in their region, resulting in charge transfer from ligand to a metal orbital.

These results show that no tetragonal splitting of the ¹T₁ state was observed in the absorption spectra. The Co(gee)(NO₂)₂ establishes the geometry of this complex as that expected from cis-β mode.[17] The conversion of this complex to the other derivative and its reconversion to the same dinitro compound suggest that the cis-β geometry is preserved in the other gee containing complexes.

Thus EHT-SPD calculation provides many meaningful chemical informations such as stereochemistry as well as charge transfer interactions between cobalt metal and a coor-dination site atoms.

Abbreviation used: geeH, (N-[2-((2-aminoethyl)thio)ethyl]-2-aminoacetamide)

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