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Molecular Orbital Study of Coordinated Dioxygen. II. Dioxygen Activation on Co(II) Complexes

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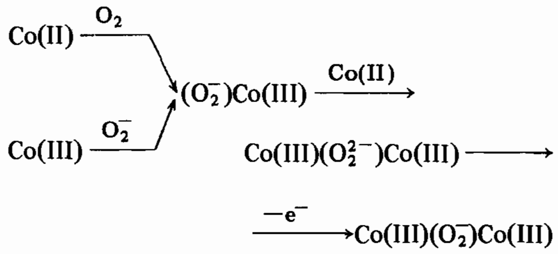
Introduction

Many transition metals give the following reactions with molecular oxygen [1]:

$$L_nM + O_2 \underset{(1)}{\rightleftarrows} L_nMO_2 \underset{(2)}{\overset{ML_n}{\rightleftarrows}} L_nMO_2ML_n$$

$$\underset{(3)}{\rightleftarrows} 2L_nMO \underset{(4)}{\overset{2ML_n}{\rightleftarrows}} 2L_nMOML_n$$

Depending on the concrete transition metal M and the nature of ligands L, this general reaction scheme can be stopped at step (1) or (2). For example, for cobalt complexes it was postulated [2]:



The discussion about the formal oxidation state of coordinated dioxygen has a long history. For example, the mononuclear superoxo form has been proposed [3] on the grounds of an interpretation of ESR spectra. However, a different interpretation of ESR spectra gives a different answer to the question whether the coordinated dioxygen is a singlet or an activated doublet [4–7]. Products of reactions (1) and (2) often occur in various oxidation reactions as effective catalysts. Therefore, it is also interesting to study their geometry and electronic structure by quantum chemical computational methods especially if experimental data are not available.

The present study concerns the model system of dioxygen fixation; Co(II) complexes have been studied by the MO–LCAO–SCF method on the CNDO/2 level of Hamiltonian approximation [8, 9]. In complexes of $O_2CoCl_4L^{2-}$ type, by L = none, NH_3, imidazole (Im) and pyridine (Py), the electronic structure and the nature of bonding have been investigated. They are studied in terms of spin densities, one-electron energy levels, energy partitioning [10, 11], Wiberg indices [12], atomic charges, the equilibrium O–O distance and the stretching harmonic force constant.

Results and Discussion

The geometry of $O_2CoCl_4L^{2-}$ complexes has been fixed as shown in Fig. 1. Experimental geometries of axial ligands have been chosen [13, 14] while the geometry of $Co-O_2$ group has been taken near to the calculated optimum values for the $O_2CoCl_4^{2-}$ ion [15]. The orientation of imidazole, Im, and pyridine, Py, ligands has been fixed for their planes to be parallel with the $Co-O_2$ plane (C_s symmetry) and/or perpendicular – Im′, Py′.

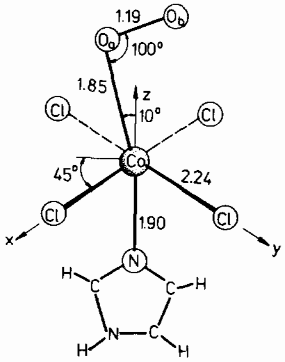


Fig. 1. Used geometry of $O_2CoCl_4L^{2-}$ (example: L = Im).

Calculated characteristics of the free dioxygen, free superoxide ion and the coordinated dioxygen are listed in Table I. The calculated O–O distance r_1 = 1.19 Å is the same as for the free superoxide ion; it is somewhat longer than that in the free dioxygen: r_1 = 1.13 Å. The harmonic force constant and the Wiberg index of the O–O bond decrease after the coordination of dioxygen. The bicentric part of energy E(O–O) also decreases after coordination of dioxygen and corresponds to the value for the free superoxide ion. The data presented in Table I support the conclusion that the coordinated dioxygen is activated in such a way, or softened, with respect to the free dioxygen. The properties of an activated dioxygen are the same

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TABLE I. Calculated Characteristics of Free and Coordinated Dioxygen.

	Free		L					
	O_2^{a}	O_2^-^{a}	none^a	NH_3^{b}	Im^b	Im′^{b}	Py^b	Py′^{b}
Equilibrium distance O–O, Å	1.13	1.19	1.19	1.19				
Harmonic force constant, N cm^{-1}	55.8	45.2	44.1	40.1				
Bicentric part of energy, eV	–46.4	–34.4	–34.6	–34.7	–34.6	–34.6	–34.6	–34.7
Wiberg index	1.500	1.250	1.178	1.176	1.173	1.173	1.172	1.174
O_2 *spin density*	2.000	1.000	1.000	1.000	1.000	1.000	0.999	0.999
O_2 *charge*	0	–1.0	–0.452	–0.441	–0.445	–0.444	–0.438	–0.439

^{a}For the optimum geometry [15]. ^{b}For the estimated geometry (Fig. 1).

TABLE II. Calculated Properties of $O_2CoCl_4L^{2-}$.

L =	NH_3	Im	Im′	Py	Py′
Total energy (eV):	–3765.8	–4681.8	–4681.8	–4773.6	–4773.6
Bicentric part of energy (eV):					
–E(O_a–O_b)	34.7	34.6	34.6	34.6	34.7
–E(Co–O_a)	21.4	21.4	21.4	21.4	21.4
–E(Co–O_b)	6.7	6.6	6.6	6.6	6.6
–E(Co–Cl)	18.1	18.1	18.1	18.0	18.0
–E(Co–N)	20.5	20.3	20.3	19.2	19.1
Wiberg index:					
W(O_a–O_b)	1.18	1.17	1.17	1.17	1.17
W(Co–O_a)	0.75	0.74	0.74	0.75	0.75
W(Co–O_b)	0.14	0.13	0.13	0.13	0.14
W(Co–Cl)	0.61	0.60	0.60	0.60	0.60
W(Co–N)	0.51	0.51	0.51	0.49	0.49
Atomic charge (e):					
Q(O_b)	–0.21	–0.23	–0.23	–0.23	–0.23
Q(O_a)	–0.23	–0.21	–0.22	–0.21	–0.21
Q(Co)	+0.53	+0.55	+0.55	+0.54	+0.54
Q(Cl)	–0.61	–0.61	–0.61	–0.61	–0.61
Q(N)	–0.09	–0.004	–0.004	+0.04	+0.04
Orbital energy of HOMO (eV):					
$\epsilon(n_\alpha)$	–0.42	–0.33	–0.32	–0.55	–0.54
$\epsilon(n_\beta)$	–0.42	–0.33	–0.32	–0.55	–0.54
$\epsilon(n_\alpha - 1)$	–0.74	–0.63	–0.63	–0.87	–0.86

as the properties of the free superoxide ion. The exception from this rule is only a charge transfer onto O_2 which is not complete. This is in harmony with suggestions of Tovrog *et al.* [7] based on ESR spectra analysis.

A more detailed picture about the effect of an axial ligand on dioxygen activation follows from Table II. On the ground of these results we can see that there are no significant changes in properties of $O_2CoCl_4L^{2-}$ going from the ammonia to imidazole or

TABLE III. Projected Spin Densities[a].

L =	NH_3	Im	Im′	Py	Py′
Atomic:					
O_b	0.6801	0.6886	0.6895	0.6913	0.6854
O_a	0.3195	0.3110	0.3101	0.3083	0.3141
Co	−0.0008	−0.0007	−0.0007	−0.0008	−0.0007
4Cl	0.0010	0.0010	0.0011	0.0010	0.0012
N	0.0000	0.0000	0.0000	0.0000	0.0000
Orbital[b]*:*					
$O_b(p_x)$	0.3401	0.3443	0.3444	0.3457	0.3443
$O_b(p_y)$	0.3401	0.3443	0.3451	0.3457	0.3443
$O_a(p_x)$	0.1597	0.1555	0.1549	0.1541	0.1571
$O_a(p_y)$	0.1597	0.1555	0.1552	0.1541	0.1571
$Co(d_{xz})$, $Co(d_{yz})$	0.0005	0.0004	0.0004	0.0004	0.0005
$Co(d_{x^2-y^2})$	−0.0003	−0.0002	−0.0002	−0.0002	−0.0003
$Co(p_x)$, $Co(p_y)$	−0.0007	−0.0007	−0.0006	−0.0006	−0.0007

[a] Single annihilation procedure according to [16]. [b] $O_b(s) = O_b(p_z) = O_a(s) = O_a(pz) = Co(d_{z^2}) = Co(d_{xy}) = Co(s) = Co(p_z) = 0.0000$.

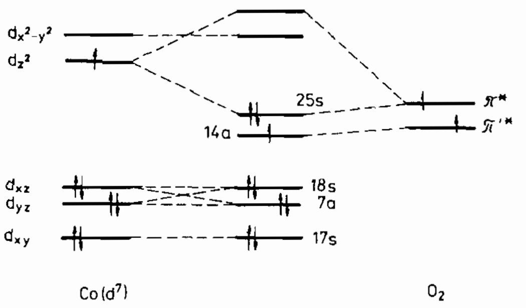

Fig. 2. Simplified MO diagram of $O_2CoCl_4Im^{2-}$.

pyridine as axial ligands. The dioxygen activation is only slightly supported. The simplified MO diagram (Fig. 2) shows that the spin-pairing of an electron on cobalt d_{z^2} orbital with one of the π^* electrons of dioxygen occurs. However, this HOMO (the highest occupied molecular orbital) is made up predominantly by π^* orbital of the dioxygen, so that for the ground-state electron configuration of the complex we can write $\pi'^*(1)\ \pi^*(2)$. Then the unpaired electron is localized on oxygen atoms in the plane perpendicular to the Co–O–O plane. Calculated spin densities are listed in Table III. A rotation of imidazole or pyridine (*e.g.* L = Im′ or L = Py′) does not change the properties of the complex.

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