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Extended Hückel Calculations on Diimine Substituted Oxalate Cobalt(III) Complexes*

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Tris(oxalato)cobaltate(III) is known as typical thermo- and photoreactive compound. Substitution of oxalate by α-diimines reduces the thermally induced redox decomposition. EHT calculations on diimine substituted Co(III) complexes with different aliphatic and aromatic diimine ligands have been carried out. It results in the EHT–LUMO energies being able to be used to estimate the thermodynamic redox stability of the mixed ligand complexes and are helpful for planned syntheses of photocatalytically interesting systems.

Introduction

The oxalate complexes of various transition metals (Mn(III), Fe(III), Co(III)) are interesting compounds concerning their photo- and thermochemical behaviour [1, 2]. In the course of photolytically as well as thermally induced reactions, reduced metal species and ligand radicals are formed [1]. In the case of the $[Co(ox)_3]^{3-}$ ion kinetic labile cobalt(II) complexes and oxalate radicals produced photolytically (1)

$$K_3[Co(ox)_3] \xrightarrow[kT]{h\nu} K_2[Co(ox)_2] + K^+ + C_2O_4^{\bar{\cdot}} \quad (1)$$

are of special interest on catalytical reasons [3].

Otherwise, the thermal instability of tris(oxalato)-cobaltate(III) is contradictory for the application of this compound as photocatalyst in unconventional photographic processes or in photopolymerization reactions [4]. However, from our experimental work it follows that oxalate substitution by heterocyclic ligands like 1,10-phenanthroline (phen) and 2,2′-bipyridine (bipy) as well as other π-acceptor ligands decreases the thermoreactivity of this class of coordination compounds without any essential influence on their light-sensitivity [5, 6]. Moreover, these ligands exert a stabilizing influence upon the reduced central metal ions. Thus, at room temperature mixed ligand complexes of the type $[Co(N\text{-}N)_2ox]X$ (N-N = phen, bipy; X = various acido ligands) exclusively undergo photolytic redox decompositions to give cobalt(II) complexes and reactive and in solid state long-living oxalate anion radicals (2):

$$2[Co(N\text{-}N)_2ox]X \xrightarrow[kT]{h\nu} [Co(N\text{-}N)_2ox] + [Co(N\text{-}N)_2X_2] + 2CO_2 \quad (2)$$

$$(T \geqslant 423\ K)$$

Our experimental and quantum chemical investigations [7, 8] have shown that aliphatic α-diimines (glyoxal and biacetyl derivatives) are much more effective π-acceptor ligands than the heteroatomic compounds phen and bipy, respectively. In this paper we discuss the influence of substitution by both aromatic and aliphatic diimines on the electronic structure of the oxalate cobalt(III) system to explain their different thermoreactivity and for synthetic reasons to predict thermally stable but photoactive mixed ligand complexes.

Calculational Method

The common EHT method [9] has been applied to calculate the following systems: $[Co(ox)_3]^{3-}$; $[Co(N\text{-}N)(ox)_2]^-$ with N-N = bipy, glyoxalbismethylimine (gmi); $[Co(N\text{-}N)_2ox]^+$ with N-N = phen, bipy, biacetylbismethylimine (bmi), gmi and $[Co(N\text{-}N)_3]^{3+}$ with bipy and gmi.

Because of the large dimension and the low symmetry (mixed ligand complexes are of C_2 symmetry) of the systems the use of iterative procedures cannot be accepted. Therefore, we employed an EHT version without charge iteration (CDC 1604 A). The largest system calculated in this study was the $[Co(bipy)_3]^{3+}$ cation (177 atomic orbitals).

The diagonal matrix elements H_{ii} for the main group elements were taken from Basch *et al.* [10] and the orbital exponents from Clementi and

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TABLE I. EHT Parameters Used for the Calculation.

Atom	H_{ii} (ns) (eV)	H_{ii} (np) (eV)	ζ_s	ζ_p
H	−13.61	–	1.0	–
C	−19.42	−10.64	1.608	1.568
N	−25.57	−13.19	1.924	1.917
O	−32.34	−15.80	2.246	2.227

TABLE II. Geometrical Data.

Complex	Bond lengths (nm)		Bond Angles (°)		
Co–diimine[a]	Co–N	0.198	N–Co–N	82	[20, 21]
Co–ox	Co–O	0.192	O–Co–O	84	[22]
	O–C	0.129	Co–O–C	114	
	C–C	0.152	O–C–O	123	
	C–O	0.123	O–C–C	114	

[a] For the geometry of the diimine ligands see ref. [7].

Raimondi [11] (Table I). The off-diagonal terms H_{ij} have been approximated by the Wolfsberg–Helmholz relation [12] $H_{ij} = 0.5\ K\ S_{ij}\ (H_{ii} + H_{jj})$ with K = 1.75. The VOIPs for the d, s and p-orbitals of cobalt were estimated regarding their sensitive charge and configuration dependence from calculations carried out for similar cobalt(III) complex compounds [13, 14]: d = −12.5 eV, s = −10.2 eV, p = −6.0 eV (*set A*). Additionally, a cobalt VOIP set from Lohr and Lipscomb [15] has been taken: d = −11.0 eV, s = −10.0 eV, p = −8.0 eV (*set B*). The metal orbital exponents used are the optimized values for the Co–N distance of 0.198 nm supplied by Zerner and Gouterman [16].

TABLE IV. EHT Results for Gmi–Oxalate Co(III) Systems.

Complex		Net Charges			LUMO Energy (eV)
		Co	N	O	
$[Cogmi(ox)_2]^-$	A	1.58	−0.48	−1.22	−10.60
	B	1.95	−0.64	−1.20	−9.74
$[Co(gmi)_2ox]^+$	A	1.18	−0.53	−1.21	−10.23
	B	1.68	−0.69	−1.20	−9.72
$[Co(gmi)_3]^{3+}$	A	0.91	−0.57	−1.20	−9.78
	B	1.47	−0.72	−1.20	−9.61

A non-distorted D_3 symmetry for the tris complexes $[Co(N\text{-}N)_3]^{3+}$ and a C_2 symmetry for the mixed ligand complexes have been assumed. The bond distances and bond angles of the calculated complexes are given in Table II.

Results and Discussion

Successive oxalate substitution by 2,2′-bipyridine in the series $[Co(ox)_3]^{3-}$, $[Co(bipy)(ox)_2]^-$, $[Co(bipy)_2ox]^+$ and $[Co(bipy)_3]^{3+}$ leads to a stepwise decrease of the cobalt net charge combined with an increasing negative charge of the diimine nitrogen (Table III). Furthermore, in agreement with the redox behaviour of these systems a destabilization of the lowest unoccupied MOs results. The correlation between the EHT–LUMO energies and the available reduction potentials of the bipyridine substituted oxalate complexes is given in Fig. 1. Substitution by an aliphatic diimine ligand, *e.g.* gmi, gives smaller changes of the metal charge and of the LUMO energy (Table IV). Figure 2 shows the LUMO energies of the diimine–oxalate mixed ligand complexes

TABLE III. EHT Results and Reduction Potentials for the Bipy Substituted Oxalate Co(III) Complexes.

Complex		Net Charges				LUMO Energy (eV)	$E_{1/2}$ (eV)
		Co	N	C	O		
$[Co(ox)_3]^{3-}$	A	2.18	–	–	−1.18	−10.83	0.57 [23]
	B	2.24			−1.20	−9.63	
$[Cobipy(ox)_2]^-$	A	1.21	−0.49	0.49	−1.22	−10.50	–
	B	1.78	−0.64	0.46	−1.20	−9.60	
$[Co(bipy)_2ox]^+$	A	0.84	−0.57	0.46	−1.22	−10.05	0.06[a]
	B	1.39	−0.65	0.45	−1.20	−9.57	
$[Co(bipy)_3]^{3+}$	A	0.61	−0.61	0.45		−9.58	−0.03[a]
	B	1.06	−0.66	0.45		−8.94	

[a] Half-wave potentials of the reduction in 0.05 N NO_3^-/H_2O soln., dropping Hg-electrode *vs.* SCE at 293 K. Compounds have been used: $[Co(bipy)_2ox]SCN \cdot 4H_2O$, $[Co(bipy)_3](ClO_4)_3$.

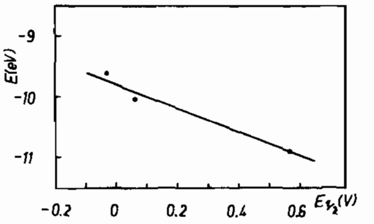

Fig. 1. Correlation between EHT–LUMO energies of bipy substituted oxalate Co(III) compounds and their reduction potentials (see Table III).

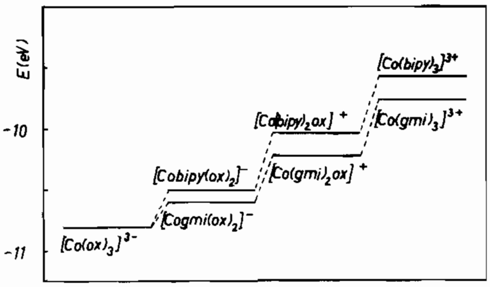

Fig. 2. EHT–LUMO energies of different diimine/oxalate cobalt(III) complexes.

of Co(III). It follows that gmi–oxalate compounds are more reactive concerning the thermodynamic ease of their reduction. This is in agreement with experimental results on mixed ligand oxalate cobalt(III) complexes with glyoxal and biacetyl derivatives [17] which are very sensitive to thermal redox decomposition. The calculated energy changes are independent of the metal VOIP set used.

It has been concluded that the EHT–LUMO energies of the systems under study are a suitable measure for estimating the redox behaviour.

The better π-acceptor ability of the aliphatic diimines reflected by lower-lying antibonding π-orbitals compared to bipy and phen [7] was confirmed by higher net charges of the central metal of analogous Co(III) complex systems ($[Co(gmi)_3]^{3+}$ = 0.91; $[Co(bipy)_3]^{3+}$ = 0.61). These circumstances indicate a stronger π-back donation from the metal to the aliphatic diimine ligands. The LUMO's of the corresponding metal complexes are also decreased. In the mixed ligand complexes described the metal d-orbitals are split in the following order of increasing energy:

$$3\,d_{yz} < 3\,d_{xz} < 3\,d_{x^2-y^2} < 3\,d_{z^2} < 3\,d_{xy},$$

whereas for the tris complexes of the type $[Co(N\text{-}N)_3]^{3+}$ the following order results:

$$3\,d_{xz}\,(a_1) < 3\,d_{x^2-y^2}, 3\,d_{yz}\,(e) < 3\,d_{z^2}, 3\,d_{xy}\,(e).$$

The energy separation between filled and empty 'd-MOs' in the series $[Co(gmi)_3]^{3+}$, $[Co(gmi)_2ox]^+$, $[Co(gmi)(ox)_2]^-$ and $[Co(ox)_3]^{3-}$ supports the 'average-environment' rule [18]:

$$Dq([MA_nB_{6-n}]) = n/6\,Dq([MA_6]) + (6-n)/6\,Dq([MB_6])$$

Assuming a pseudooctahedral arrangement of the ligands the differences between the mean values of the energies of the three bonding MOs (t_{2g}) and the two antibonding MOs (e_g) are considered to be Δ = 10 Dq. For the series of gmi substituted complexes given above the following values have been obtained: 19700 cm^{-1}, 18000 cm^{-1}, 14900 cm^{-1} and 12000 cm^{-1}. These results are closely related to the experimental values.

Some reflections on the reactivity of the oxalato–bis(diimine) cobalt(III) complexes should be discussed. Among the series of substituted oxalate complexes the oxalato–bis(diimine) cobalt(III) complexes have a favoured position concerning their thermal redox stability, whereas the bis(oxalato)–monodiimine systems still essentially show a reactivity comparable to the unsubstituted species $[Co(ox)_3]^{3-}$.

TABLE V. EHT Results for Different Bis(diimine)–Oxalate Co(III) Complexes.

Complex		Net Charges				LUMO Energy (eV)
		Co	N	C	O	
$[Co(gmi)_2ox]^+$	A	1.19	−0.54	0.57	−1.21	−10.23
	B	1.68	−0.63	0.55	−1.20	−9.72
$[Co(bmi)_2ox]^+$	A	0.97	−0.64	0.68	−1.22	−10.12
	B	1.48	−0.71	0.67	−1.20	−9.56
$[Co(bipy)_2ox]^+$	A	0.84	−0.57	0.46	−1.22	−10.05
	B	1.39	−0.65	0.45	−1.20	−9.55
$[Co(phen)_2ox]^+$	A	0.78	−0.57	0.41	−1.22	−10.02
	B	1.37	−0.66	0.40	−1.20	−9.53

Therefore, the problem is to vary the kind of other ligands in the monooxalato system in such a manner that the mixed ligand complexes obtained are stable towards thermal decomposition but sufficiently photosensitive.

In comparison with the heteroaromatic α-diimine ligands bipy and phen, respectively, the aliphatic representatives gmi and bmi cause a reduced thermal redox stability indicated by a lowering of the calculated EHT–LUMO energies. This is also reflected in the change of the cobalt charge in the different bis(diimine) complexes (Table V). Otherwise, the aliphatic diimine ligands in the mixed ligand complexes considered show bathochromic shifted CT bands from MLCT type, which are of special importance concerning the spectral sensitization of the oxalate cobalt(III) systems in the visible spectral region [19].

The results obtained give some new insights for preparing oxalate cobalt(III) mixed ligand complexes with special thermal and photochemical behaviour.

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