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Kinetics of Axial Substitution in (Ligand)bis(*o*-benzosemiquinonediiminato)-cobalt(III) Complexes

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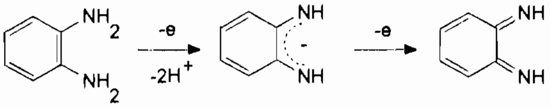
Although the chemistry of transition metal *o*-quinone and semiquinone complexes has attracted considerable attention,[1] much less information is available on the related *o*-quinoneimine and semiquinonenimine complexes. The bidentate ligand *o*-benzosemiquinonediiminato(1−) (s-BQDI), derived from the 1-electron oxidation of o-phenylenediamine (OPD), is unstable in the free state[2] but can be stabilized by complex formation.[3] It is converted to unstable *o*-benzoquinonediimine (BQDI) upon removal of a second electron (eq 1). BQDI can also be stabilized by complexation.[4]



(1)

(OPD) (s-BQDI) (BQDI)

When Co(II) salts and OPD dissolved in MeOH are exposed to O_2, the catalytic formation of 2,3-diaminophenazine takes place via a series of oxidative dehydrogenation steps.[5−7] Cobalt complexes of *s*-BQDI and BQDI are involved as intermediates in this multistep reaction, because if OPD is oxidized in the presence of L (Ph_3P, Ph_3As or Ph_3Sb), oxidation stops at the s-BQDI stage. This ligand is stabilized by the metal and complexes $[LCo^{III}(s\text{-}BQDI)_2]ClO_4$ are formed. We have previously reported the synthesis of these complexes and also the crystal and molecular structure of $[Co^{III}(s\text{-}BQDI)_2(Ph_3P)]ClO_4$, which is square-pyramidal in the solid state, with Ph_3P in the axial position.[8]

There is continuing interest in the synthesis and structure of s-BQDI metal complexes,[9−13] as well as in the mechanisms of their catalytic transformations.[7] However, no information is available on their behavior in ligand substitution reactions. In this paper, we report for the first time kinetic data on the substitution of axial ligand L in $[LCo^{III}(s\text{-}BQDI)_2]ClO_4$.

Experimental Section

Spectrophotometric measurements were performed on a Hewlett-Packard 8452A diode array UV−vis instrument. Kinetic experiments were carried out in a Hi-Tech Scientific SFA-II rapid kinetics accessory using the HP 8452A as detector. Rate constants were calculated from the known integrated rate equation for a reversible one-step reaction second order in both directions,[15] using the kinetic software of the HP 8452A spectrophotometer.

$[LCo^{III}(s\text{-}BQDI)_2]ClO_4$, where L = Ph_3P, Ph_3As, and Ph_3Sb, were synthesized as described earlier[8], *viz.* by air oxidation of OPD in the presence of L. This procedure gave no satisfactory results in the case of L = pyridine, pyrrolidine, *N*-Me-imidazole, and $P(OEt)_3$. However, we have found that the latter ligands can be introduced via direct replacement of Ph_3Sb in $[Co^{III}(s\text{-}BQDI)_2(Ph_3Sb)]ClO_4$ according to the following general procedure. To 1 mmol (0.724 g) of $[Co^{III}(s\text{-}BQDI)_2(Ph_3Sb)]ClO_4$ suspended in 50 mL of benzene−MeOH (9:1) under N_2, a 10−50-fold excess of the ligand was added. The mixture was vigorously stirred for 3−8 hours. The solid $[LCo^{III}(s\text{-}BQDI)_2]ClO_4$ was filtered and washed thoroughly with benzene (CAUTION, benzene is carcinogenic). The procedure was repeated until the visible spectrum of the product complex in MeOH did not change upon adding excess L, *i.e.* axial ligand exchange had gone to completion. The products gave satisfactory elemental analyses; the UV−vis (diimine band), IR and ^1H NMR spectra were consistent with the above structure. Some typical data are listed in Table 1.

Results and Discussion

Octahedral cobalt(III) complexes are known to be substitutionally inert.[14] This behavior could also be expected for our $[LCo^{III}(s\text{-}BQDI)_2]^+$ complexes, which upon dissolution in MeOH (a convenient solvent) coordinate a solvent molecule in the sixth octahedral position. We have found, however, that replacement of the axial ligand is quite facile and can be readily observed when the solution of $[LCo^{III}(s\text{-}BQDI)_2]^+$ in MeOH or CH_2Cl_2 contains also one of the ligands listed in Table 2. Upon mixing methanol solutions of $[(Ph_3As)Co^{III}(s\text{-}BQDI)_2]ClO_4$ (5×10^{-5} M) and $P(OEt)_3$ (1.0×10^{-4} M), the spectral changes shown in Figure 1 can be observed (HP 8452 diode array spectrophotometer). The presence of several isosbestic points is consistent with a single reaction with products in constant proportion. Reversibility has been demonstrated by adding excess Ph_3As to the product solution, when the starting spectrum of the complex was regenerated. A similar behavior has been found with the other ligands studied, typical equilibration times being of the order of 1−5 min. The spectra obtained at various ligand and complex concentrations after allowing sufficient time for the equilibrium to be reached have been used to calculate the equilibrium constant *K*, assuming substitution of the axial ligand L by L*, as described by eq 2. The resulting

$$[LCo^{III}(s\text{-}BQDI)_2]^+ + L^* \overset{K}{\rightleftharpoons} [L^*Co^{III}(s\text{-}BQDI)_2]^+ + L \quad (2)$$

K values for the ligand/complex combinations studied are listed in Table 2. For identical entering ligands L*, the ratio of the *K* values corresponding to L = Ph_3Sb and Ph_3As is equal to 4.7 ± 0.7. This is the equilibrium constant of reaction 2 for L* = Ph_3As and L = Ph_3Sb, which has been found to be 4.8 ± 0.8 from independent measurements. The agreement provides additional support for the validity of reaction 2.

The kinetics of reaction 2 was investigated by monitoring the variation of visible spectra in time. Second order behavior

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Table 1. Physical Data for $[LCo^{III}(s\text{-}BQDI)_2]ClO_4$ Complexes

L	λ_{max}/nm (ϵ/M^{-1} cm^{-1})	IR/cm^{-1}	^1H NMR/ppm
py	746 (13 800), 538 (15 000), 416 (4670)	3258, 1520, 1440, 1365, 1195	
pyrrolidine	732 (14 500), 535 (14 500), 420 (3920)	3280, 2960, 2855, 1515(sh), 1445, 1410, 1360, 1210, 1190	
N-Me−Im	740 (14 800), 536 (15 800), 418 (4210)	3290, 2945, 2900, 1520, 1440, 1365, 1225, 1195	12.7 (s, 4H), 7.85 (m, 4H), 7.45 (m, 4H), 7.30 (s, 1H), 6.98−6.80 (m, 2H), 3.40 (s, 3H)
$P(OEt)_3$	706 (35 600), 432 (9060), 382 (4810)	3329, 2975, 2910, 2890, 1520, 1440, 1330, 1190	11.17 (s, 4H), 7.48 (M, 4H), 7.14 (m, 4H), 3.58 (q, 6H), 0.95 (t, 9H)

Table 2. Rate and Equilibrium Constants of Axial Substitution in (Ligand)bis(*o*-benzosemiquinonediiminato)cobalt(III) Complexes[a]

entering ligand (L^*)	$10^{-3}k_f$ (M^{-1} s^{-1})	$10^{-3}k_r$ (M^{-1} s^{-1})	*K*	n°_{Pt}[e]
		L = Ph_3Sb[b]		
Ph_3P	14.5	0.485	30	8.79
N-Me-imidazole[d]	4.97	0.316	16	
$P(OEt)_3$	4.75	0.190	25	7.08
N-Me-imidazole	1.21	4.05	0.3	
pyridine[d]	1.0	1.42	0.71	
SCN^-	0.910	4.80	0.19	5.65
pyrrolidine	0.295	1.01	0.29	
I^-	0.055	2.04	0.027	5.42
pyridine	0.035	1.29	0.027	3.13
benzimidazole	0.032	1.28	0.025	
imidazole	0.027	1.13	0.024	
		L = Ph_3As[c]		
Ph_3P	3.68	0.720	5.1	
$P(OEt)_3$	2.20	0.365	6.0	
N-Me-imidazole[d]	1.71	0.450	3.8	
pyridine[d]	0.415	2.44	0.17	
N-Me-imidazole	0.347	5.34	0.065	
pyrrolidine	0.174	3.34	0.052	
SCN^-	0.031	6.22	0.048	
pyridine	0.019	2.34	0.008	
imidazole	0.014	2.81	0.0048	
benzimidazole	0.013	2.65	0.0049	
I^-	0.009	1.70	0.0053	

[a] Solvent MeOH; t = 25 °C; $[\{LCo^{III}(s\text{-}BQDI)_2\}ClO_4]_o = (1.0-10.0) \times 10^{-5}$ M; $[L^*]_o = (1.0-500) \times 10^{-5}$ M. Each rate constant is the average of 5 determinations reproducible to within ±12%. [b] n°_{Pt} for Ph_3Sb = 6.65. [c] n°_{Pt} for Ph_3As = 6.75. [d] Solvent CH_2Cl_2. [e] Data from ref 16.

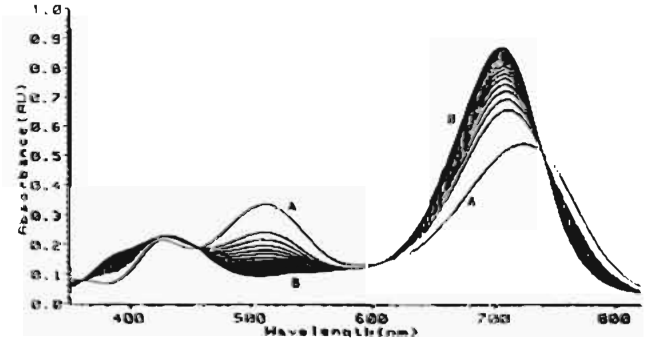

Figure 1. Successive spectra recorded during the reaction of 5×10^{-5} M $[(Ph_3As)Co^{III}(s\text{-}BQDI)_2]ClO_4$ with 1×10^{-4} M $P(OEt)_3$ in MeOH at 25 °C (A, 1 s after mixing; B, 90 s after mixing).

was found in both directions. The rate constants for the forward (k_f) and reverse (k_r) reaction have been calculated from the time dependence of the successive spectra, using the integrated rate equation corresponding to a reversible second order reaction 2,[15] and the independently determined equilibrium constants ($K = k_f/k_r$). The kinetic behavior was found to be consistent with the proposed reaction 2. There was no indication of a two-term rate law with a dissociative contribution. The results are listed in Table 2.

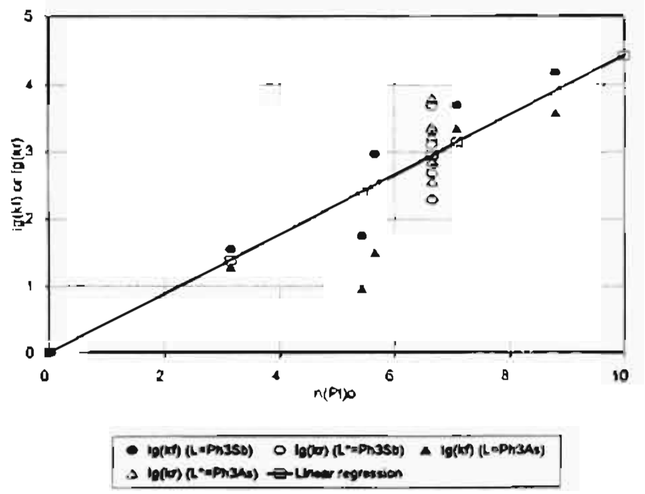

Figure 2. Plot of log k_f and log k_r against the nucleophilic reactivity constant n°_{Pt} of the entering ligand.

Table 2 reveals some trends that merit consideration. A noteworthy feature is the fairly pronounced dependence of k_f on the nature of the entering ligand (500-fold variation). This behavior points to an associatively activated interchange mechanism (I_a) for the square-pyramidal complexes studied in this work. Indeed, k_f and k_r in Table 2 parallel the *trans*-effect of the entering ligand deduced from studies on substitution in square-planar Pt(II) complexes, where this correlation has been rationalized in terms of a trigonal bipyramidal transition state in which one axial ligand labilizes the other.[17]

As good *trans*-labilizers are at the same time good entering groups, we have attempted to find a quantitative correlation of our rate constants with the nucleophilic reactivity constant n°_{Pt} derived from kinetic data for Cl^- substitution in *trans*-$[Ptpy_2Cl_2]$ by various entering ligands.[16] In Figure 2, log k_f and log k_r are plotted against n°_{Pt} for the entering ligand (where available), resulting in a fairly good linear relationship. On these grounds we propose a mechanism involving rapid dissociation equilibrum 3 with the solvent to afford a 5-coordinate species **X**, followed by rate-determining ligand entry (eq 4) via a 6-coordinate transition state **Y**:

$$[LCo^{III}(s\text{-}BQDI)_2S]^+ \underset{+S}{\overset{-S}{\rightleftharpoons}} \underset{\mathbf{X}}{[LCo^{III}(s\text{-}BQDI)_2]^+} \quad (3)$$

$$\mathbf{X} \underset{-L^*}{\overset{+L^*}{\rightleftharpoons}} \underset{\mathbf{Y}}{[LCo^{III}(s\text{-}BQDI)_2L^*]^{\ddagger(+)}} \underset{+L}{\overset{-L}{\rightleftharpoons}} [Co^{III}(s\text{-}BQDI)_2L^*]^+ \quad (4)$$

By analogy to square planar substitution, the *trans*-effect of the entering ligand in both directions is exerted in the 6-coor-

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dinate transition state **Y** when it determines how fast the other axial ligand is expelled.

The moderate changes in rate constants upon changing the solvent are in accordance with the above picture.

The central atom in the 5-coordinate species may exhibit some cobalt(II) character due to an intramolecular redox equilibrium similar to that described for [Co^{III}(3,5-DBSQ)(3,5-DBCat)(bpy)].[18] In that case the kinetic lability could be ascribed to the cobalt(II) species **Z** present in small amounts.

$$\underset{\mathbf{X}}{[\mathrm{LCo^{III}(s\text{-}BQDI)_2}]^+} \rightleftharpoons \underset{\mathbf{Z}}{[\mathrm{LCo^{II}(s\text{-}BQDI)(BQDI)}]^+}$$

Metal−BQDI electron transfer between central metal atom and coordinated s-BQDI$^-$ or BQMI may also produce reactive intermediates at low concentrations, involved in various catalytic oxidations of OPD and its derivatives.[19]

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