The First Ligand Oxidation of Cobalt(III) Thiolato Complex by Molecular Dioxygen

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The first ligand oxidation of Co(III)-bound thiolates by molecular dioxygen is realized in the presence of active charcoal. Three oxidation products are characterized by UV/VIS absorption and ^{13}C NMR spectra and X-ray crystal analysis.

The first ligand oxidation in a Nickel(II) thiolato complex by molecular dioxygen O_2 was reported by M.J. Maroney *et al.* in 1989.[1] This reaction is very interesting because it will be a plausible chemical model for the deactivation of many hydrogenase having Ni centers with sulfur ligands by O_2. Since then several examples of such oxidation reactions with O_2 have been reported for a bis(dithiolene) Ni(II) complex[2] and planar *cis*-dithiolato Ni(II) complexes.[3]

In the cobalt(III) thiolato complexes, many papers concerning the preparation and characterization of various kinds of sulfur oxygenates such as sulfenate, sulfinate and their derivatives have been reported so far.[4] However, there have been no reports concerning the direct ligand oxidation by molecular dioxygen. We report here the first examples of the ligand oxidation by molecular dioxygen in *cisciscis*-[Co(pyet)$_2$]$^+$ [pyet = 2-[(2-pyridylmethyl)amino]ethanethiolate (1-)].[5]

The tridentate ligand Hpyet was prepared according to the literature.[6] Abbreviations of the oxidized ligands are as follows; pyese = 2-[(2-pyridylmethyl)amino]ethanesulfenate (1-); pyesi = 2-[(2-pyridylmethyl)amino]ethanesulfinate (1-) .

To an aqueous solution of *cisciscis*-[Co(pyet)$_2$]Cl·2H_2O (1.0 g)[5] was added active charcoal (0.5 g: Wako Pure Chemical Industries LTD.) and the mixed solution was stirred at room temperature for 21 h under air atmosphere. The charcoal was removed by filtration and the brown filtrate was poured onto a column of Dowex 50W × 2 resin (Na$^+$ form, 4 × 8 cm). Elution with 0.4 mol dm^{-3} NaCl gave three bands, orange (**1**, yield 4%), brown (**2**, 82%), and brown (**3**, 14%), in this order. After repeated removal of NaCl each complex was converted to the corresponding perchlorate through a column of QAE-Sephadex A-25 (ClO_4^-) and was crystallized by standing at room temperature.[7]

The Ni(II) thiolato complexes underwent oxidation to the sulfinato complexes simply upon exposure to air[1] or an dioxygen atmosphere.[2,3] However, the oxidation reaction of the present Co(III) thiolato complex did not proceed at all under the same condition. We found that the coexistence of active charcoal is indispensable. It has been well known that active charcoal catalyzes the formation of cobalt(II) species,[8] which may be considered to be the activation species of molecular oxygen. Many examples have been reported for cobalt(II) complexes acting as activators of molecular oxygen.[9] No isomerization of *cisciscis*-[Co(pyet)$_2$]$^+$ was observed during oxidation. The oxidation reaction is much faster in a bis(thiolato) type complex than in a monothiolato one. For example, an aqueous solution of *cisciscis*-[Co(pyet)$_2$]$^+$ in the presence of active charcoal is easily oxidized in several hours, whereas an aqueous solution of [Co(aet)(en)$_2$]$^{2+}$ or [Co(aet)(tren)]$^{2+}$ [aet = 2-aminoethanethiolate(1-), en = 1,2-ethanediamine, and tren = tris(2-aminoethyl)amine] shows almost no sign of oxidation in spite of air bubbling for 1 week.

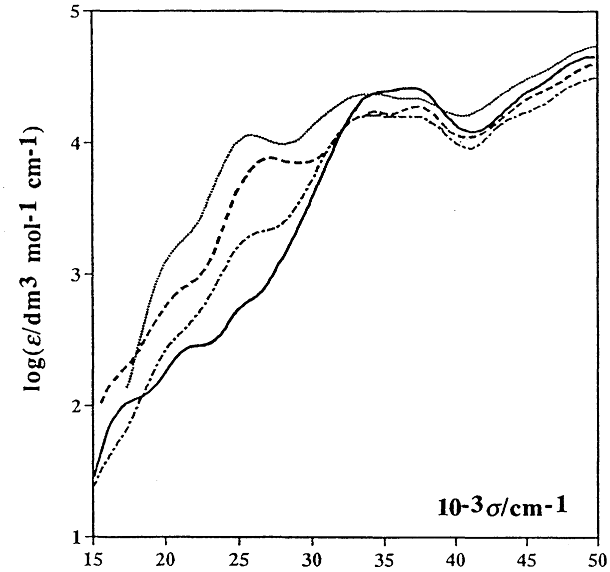

Figure 1. UV/VIS absorption spectra of *cisciscis*-[Co(pyet)$_2$]$^+$ (————) and its oxidation products; complex **1** (········), complex **2** (—·—·—), and complex **3** (--------).

Since two thiolato atoms of *cisciscis*-[Co(pyet)$_2$]$^+$ are chemically nonequivalent, fifteen racemic oxidation products, one bis(sulfinato), two (thiolato)(sulfinato), four (thiolato)-(sulfenato), four bis(sulfenato), and four (sulfenato)(sulfinato), are possible in total. In the column separation three bands were found. The UV/VIS absorption spectra of these complexes as well as that of the starting complex are shown in Figure 1. The presence of a thiolato group is confirmed by a shoulder near 600 nm in complexes **2** and **3**. Another criterion is an intense band at 370-390 nm, which is characteristic for the sulfenato group. The molar absorption coefficients (ε/dm^3 mol^{-1} cm^{-1}) are *ca.*7000 per one sulfenato group.[4] Complexes **1** and **3** exhibited such an intense band but a similar band of complex **2** is assigned to a sulfinato group due to its small molar absorption coefficients.

The second main band showed sixteen ^{13}C signals, which means that this band consists of a single isomer. The signal at δ 26.0 indicates the presence of a thiolato group because a carbon signal bonded to a sulfenato or a sulfinato group shifts to low magnetic field by more than 20 ppm. Figure 2 shows an ORTEP drawing of the cation in complex **2**.[10] Complex **2** takes a *cisciscis* structure, whose geometry is the same as that in *cisciscis*-[Co(pyet)$_2$]$^+$. Though two isomers are possible in *cisciscis*-[Co(pyet)(pyesi)]$^+$ the isolated isomer has a sulfinato group at the S(1) site and a thiolato group at the S(11) site. The

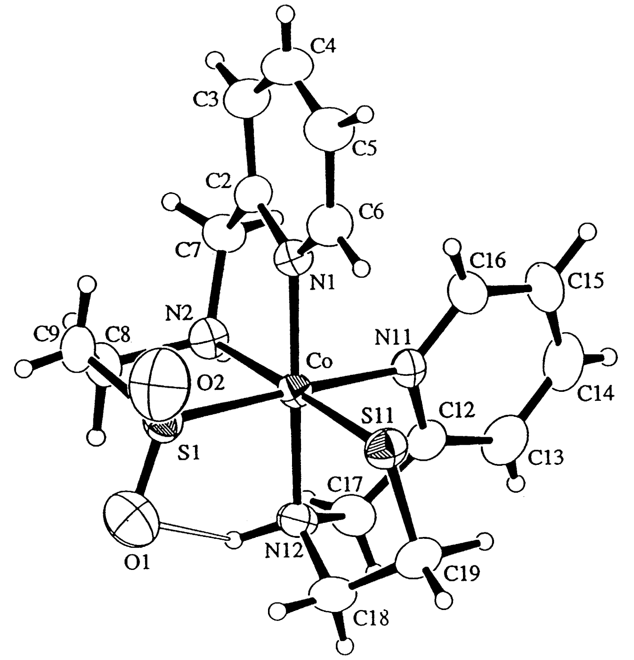

Figure 2. An ORTEP drawing of the cation of *cisciscis*-[Co(pyet)(pyesi)]ClO_4 (complex **2**).

oxidation may be difficult at the S(11) site because there is considerable steric hindrance between the pyridine ring of another pyet ligand and the S(11) donor. It is important that an intramolecular hydrogen bond [O(1)···N(12) = 2.865(4) Å, O(1) ···H-N(12) = 110(3)°] between O(1) and H-N(12) becomes possible in this structure. This may be the reason why only one isomer is found in *cisciscis*-[Co(pyet)(pyesi)]$^+$.

Similarly, complex **1** was assigned to *cisciscis*-[Co(pyese)$_2$]$^+$ (mixture of four isomers) and complex **3** to *cisciscis*-[Co(pyet)(pyese)]$^+$ (one of four isomers) based on the UV/VIS and NMR spectra and/or crystal structure analysis.[12]

The formation of the (thiolato)(sulfinato) complex *cisciscis*-[Co(pyet)(pyesi)]$^+$ (82%) as a main product is quite normal and it is apparent that the route producing monosulfinato complex is dominant in Co(III) thiolato complex as well as Ni(II) thiolato complexes.[1-3] The most interesting result concerns the isolation of the (thiolato)(sulfenato) complex *cisciscis*-[Co(pyet)(pyese)]$^+$ (14%). This complex is the first example of an oxygenate free from a O_2 unit and the formation is incompatible with the conventional intramolecular mechanisms.[1-3] Hence a new route, *e.g.* an intermolecular mechanism, seems to be necessary to explain the formation of the (thiolato)(sulfenato) complex.

References and Notes

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10 Crystal data for [Co($C_8H_{11}N_2S_2$)($C_8H_{11}O_2N_2S$)]ClO_4 at 296 K: M = 524.88, 0.25 × 0.15 × 0.40 mm, monoclinic, $P2_1/c$ (no.14), a = 9.912(3), b = 6.960(5), c = 28.896(4) Å, β = 94.59(2)°, V = 1987(1) Å^3, Z = 4, and R(Rw) = 0.041 (0.057) for 4056 independent reflections with $I > 3\sigma(I)$. Selected bond distances (Å) and angles (°): Co-S(1) = 2.193 (1), Co-S(11) = 2.263(1), Co-N(1) = 1.945(3), Co-N(2) = 2.031(3), Co-N(11) = 2.000(3), Co-N(12) = 1.988(3), N(1)-Co-N(12) = 175.5(1), N(2)-Co-S(11) = 178.54(9), and S(1)-Co-N(11) = 176.22(8). The structure was solved by direct methods and refined by full-matrix least-squares. The hydrogen atoms are located on calculated positions. All calculations were performed using the TEXSAN[11] crystallographic software package.

11 TEXRAY Structure Analysis Package, Molecular Structure Corporation: 3200A Research Forest Drive, The Woolands, TX 77381(1985).

12 The plate crystal obtained from the third band, however, was composed of two complexes **2** and **3**, whose ratio was determined by its ^{1}H NMR spectrum; complex **2** : **3** = 60% : 40%. The crystal was crystallographically isomorphous to the columnar crystal of *cisciscis*-[Co(pyet)(pyesi)]ClO_4 (complex **2**).[10] Both complexes **2** and **3** occupy the same site in the unit cell and only the occupancy of O(2) is 60%. The result indicates that the sulfenato oxygen in complex **3** occupies the O(1) site in Figure 2. Crystal data for [Co($C_8H_{11}N_2S_2$)($C_8H_{11}O_{1.6}N_2S$)]ClO_4 at 296 K: M = 518.48, 0.15 × 0.07 × 0.2 mm, monoclinic, $P2_1/c$ (no.14), a = 9.912(4), b = 6.983(2), c = 28.909(9) Å, β = 94.51 (3)°, V = 1994(1) Å^3, Z = 4, and R(Rw) = 0.074 (0.100) for 1247 independent reflections with $I > 3\sigma(I)$.