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# OXIDATION OF COORDINATED DITHIOCARBAMATE AND 2-PYRIDINETHIOLATE; SYNTHESIS AND CHARACTERIZATION OF [Co(*N*,*N*-DIMETHYLAMINOTHIOXOMETHANESULFINATO-*S*,*O*)(en)$_2$]$^{2+}$ AND [Co(2-PYRIDINESULFENATO-*S*,*N* OR -*O*,*N*)(en)$_2$]$^{2+}$ COMPLEXES

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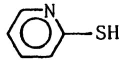
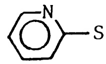
The $H_2O_2$ oxidation of [Co(*N*,*N*-dimethyldithiocarbamato-*S*,*S*′)(en)$_2$]$^{2+}$ and [Co(2-pyridinethiolato-*S*,*N*)(en)$_2$]$^{2+}$ in acid media gave the novel complexes [Co(*N*,*N*-dimethylaminothioxomethanesulfinato-*S*,*O*)(en)$_2$]$^{2+}$ and [Co(2-pyridinesulfenato-*S*,*N*)(en)$_2$]$^{2+}$, respectively. The latter *S*,*N*-chelated isomer was photochemically converted into the *O*,*N*-chelated linkage-isomer [Co(2-pyridinesulfenato-*O*,*N*)(en)$_2$]$^{2+}$, accompanying ring-expansion from a four- to five-membered chelate ring. These complexes were characterized by the absorption, circular dichroism, and X-ray photoelectron spectra.

In a previous communication,$^{1)}$ we reported the synthesis and stereochemistry of cobalt(III) complexes containing 2-pyridinethiolate, which forms a 4-membered chelate ring on *S*,*N*-coordination. The $H_2O_2$ oxidation of thiolato complexes in neutral aqueous solution generally produced the corresponding sulfenato and sulfinato complexes.$^{2)}$ The ordinary oxidation method was ineffective for the pyridinethiolato complexes. However, the modified $H_2O_2$ method in acid media was valid for the oxidation of the thiolato complex containing the 4-membered chelate ring.

We report here the synthesis of novel metal complexes, [Co(*N*,*N*-dimethylaminothioxomethanesulfinato-*S*,*O*)(en)$_2$]$^{2+}$and [Co(2-pyridinesulfenato-*S*,*N*)(en)$_2$]$^{2+}$ by the modified $H_2O_2$ oxidation experiments on [Co(*N*,*N*-dimethyldithiocarbamato-*S*,*S*′)(en)$_2$]$^{2+}$ and [Co(2-pyridinethiolato-*S*,*N*)(en)$_2$]$^{2+}$, respectively. *N*,*N*-Dimethylaminothioxomethanesulfinato(1-) in the former oxidation product is a new compound. The latter oxidation product photoisomerized into its linkage-isomer, [Co(2-pyridinesulfenato-*O*,*N*)(en)$_2$]$^{2+}$. These complexes were characterized by the elemental analysis, and the visible and ultraviolet absorption, circular dichroism (CD), and X-ray photoelectron spectra (XPS). The spectra were recorded on a Hitachi 330 spectrophotometer, JASCO MOE-1 spectropolarimeter, and Shimadzu HIPS 70, respectively. The binding energies relative to the Fermi level were determined by referring to Na-2s (64.0 eV) and S-2p3/2(169.5 eV) of $Na_2SO_4$ mixed with an appropriate amount of each sample. Abbreviations in this letter are as follows: Hdtc, *N*,*N*-dimethyldithiocarbamic acid $(CH_3)_2NCS_2H$; Hdtsi, *N*,*N*-dimethylaminothioxomethanesulfinic acid $(CH_3)_2NC(S)SO_2H$; Hpyt, 2-pyridinethiol  ; Hpyse, 2-pyridinesulfenic acid


—SOH; Haese, 2-aminoethanesulfenic acid $NH_2CH_2CH_2SOH$; Haesi, 2-aminoethanesulfinic acid $NH_2CH_2CH_2SO_2H$.

The starting complexes, Δ-$[\mathrm{Co(dtc)(en)_2}](\mathrm{ClO_4})_2$ 3) and Δ-$[\mathrm{Co(pyt)(en)_2}](\mathrm{ClO_4})_2$, 1) were prepared and optically resolved according to the separately reported procedures. For the oxidation, a solution of 30% aqueous $H_2O_2$ (10 g) and 60% aqueous $HClO_4$ (10 g) was added to the solution of Δ-$[\mathrm{Co(dtc)(en)_2}](\mathrm{ClO_4})_2$ (5 g) in 50 $cm^3$ of dimethyl sulfoxide (DMSO) with stirring below 5 °C to give an orange-red solution instantly. To the resulting solution was immediately added a mixture of diethyl ether (700 $cm^3$) and ethanol (300 $cm^3$). Orange-red crystals separated out on the inside wall of a beaker within a few minutes and were filtered off. The yield was *ca.* 1 g. The oxidation product of Δ-$[\mathrm{Co(pyt)(en)_2}](\mathrm{ClO_4})_2$ could be obtained in the same manner as orange crystals. Found for the former product: C, 16.19; H, 4.20; N, 13.18%. Calcd for $(-)^{\mathrm{CD}}_{490}$-$[\mathrm{Co(dtsi)(en)_2}](\mathrm{ClO_4})_2$ = $C_7H_{22}N_5O_{10}S_2Cl_2Co$: C, 15.86; H, 4.18; N, 13.20%. Found for the latter product: C, 21.44; H, 3.93; N, 13.53%. Calcd for $(-)^{\mathrm{CD}}_{507}$-$[\mathrm{Co(pyse)(en)_2}](\mathrm{ClO_4})_2$ = $C_9H_{20}N_5O_9SCl_2Co$: C, 21.44; H, 4.00; N, 13.89%.

The orange pyse complex was converted into the green one under solid condition by the irradiation of white light; in the dark, the color of the complex did not change. Elemental analysis of the photoproduct was consistent with the formula $[\mathrm{Co(pyse)(en)_2}](\mathrm{ClO_4})_2$. The DMSO or aqueous solution of the orange pyse complex became dark brownish on exposure to light and even in the dark. Such color change in solution was caused probably by redox decomposition and/or solvolysis. However, the green pyse complex was stable in aqueous or DMSO solution at room temperature. The orange-red dtsi complex was stable in solid state on exposure to light but

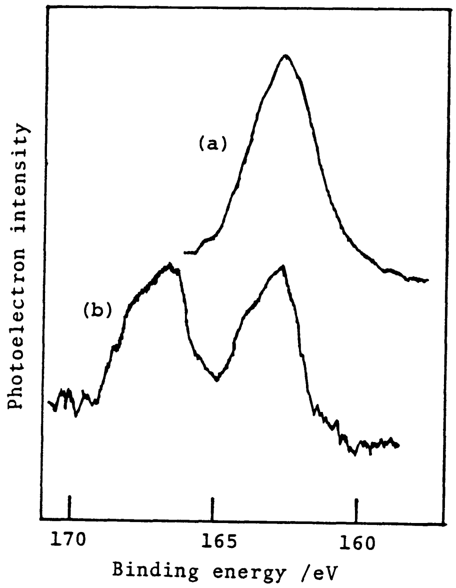


Fig. 1. The XPS spectra of $[\mathrm{Co(dtc)(en)_2}](\mathrm{ClO_4})_2$ (a) and $[\mathrm{Co(dtsi)(en)_2}](\mathrm{ClO_4})_2$ (b) in the region of S-2p binding energy.

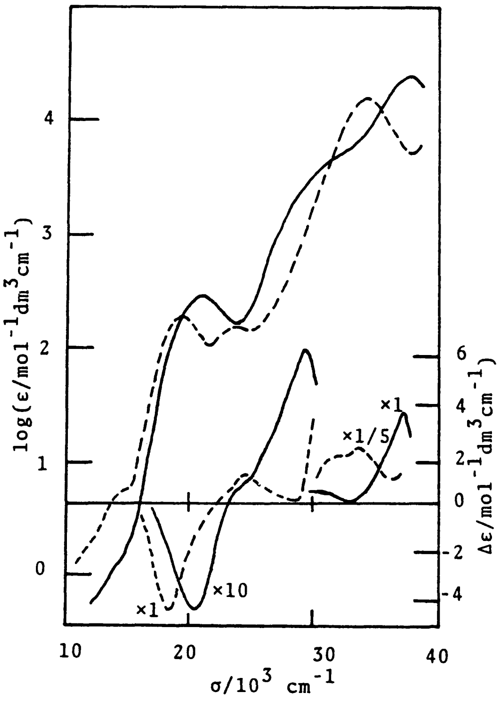


Fig. 2. The absorption and CD spectra of Δ-$[\mathrm{Co(dtsi)(en)_2}](\mathrm{ClO_4})_2$ (——) and Δ-$[\mathrm{Co(dtc)(en)_2}](\mathrm{ClO_4})_2$ (---) in DMSO solution.

unstable in aqueous or DMSO solution even in the dark.

The XPS spectra of the [Co(dtc)(en)$_2$](ClO$_4$)$_2$ and [Co(dtsi)(en)$_2$](ClO$_4$)$_2$ are shown in Fig. 1, which indicates the presence of two kinds of sulfur in the latter complex. The lower S-2p3/2 binding energy (162.7 eV) in the dtsi complex is the same as that in the dtc complex. The higher peak (166.6 eV) corresponds to the oxidized sulfur atom with two oxygen atoms because the S-2p3/2 binding energy increases in proportion to the sulfur oxidation numbers.4) Since the intensities of the lower and higher energy bands are approximately equal, the dtsi complex has both the oxidized and non-oxidized sulfur atoms. Thus, the dtsi ligand is represented by the formula $(CH_3)_2NC(S)SO_2^-$. The present dtsi complex exhibits a new absorption band at *ca.* 29000 cm$^{-1}$ as a broad shoulder (and a positive extremum in CD spectrum of the Δ isomer) in addition to the Co(σ*) ← S(σ) ligand-to-metal charge transfer (LMCT) band at 37000 cm$^{-1}$ as shown in Fig. 2. The *O*-bonded sulfinato cobalt(III) complex, [Co(aesi-*O*,*N*)(en)$_2$]$^{2+}$, shows a similar absorption band at 31000 cm$^{-1}$ without the Co(σ*) ← S(σ) LMCT band.5) Therefore, it is reasonable to consider that the dtsi ligand coordinates through the sulfinato oxygen and thiocarbonyl sulfur atoms. The optically active complex $(-)^{CD}_{490}$-[Co(dtsi)(en)$_2$]$^{2+}$ is assigned to the Δ-configuration on the basis of the CD sign at 20400 cm$^{-1}$ in the first spin-allowed d-d band region (Fig. 2). This assignment is consistent with the retention of the initial configuration of Δ-[Co(dtc)(en)$_2$]$^{2+}$, whose configuration was determined by the X-ray structure analysis.3)

The XPS spectra of the orange and green isomers of [Co(pyse)(en)$_2$](ClO$_4$)$_2$ in the S-2p binding energy region are shown in Fig. 3. The orange complex exhibits

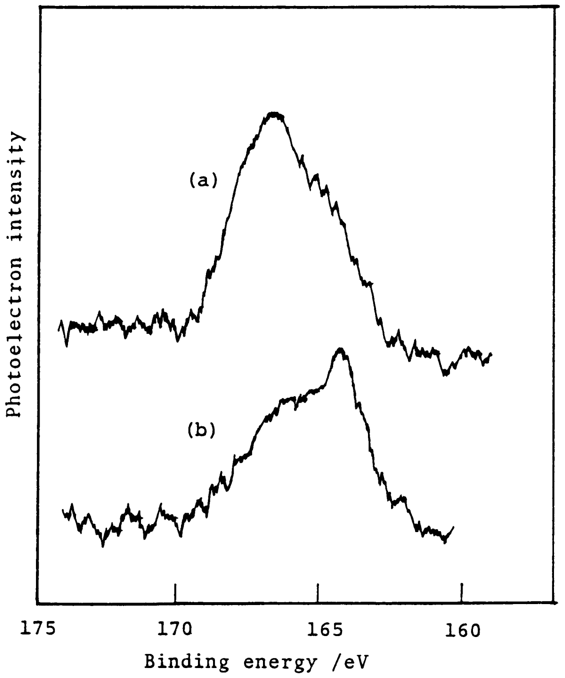


Fig. 3. The XPS spectra of orange (a) and green (b) isomers of [Co(pyse)(en)$_2$](ClO$_4$)$_2$ in the region of S-2p binding energy.

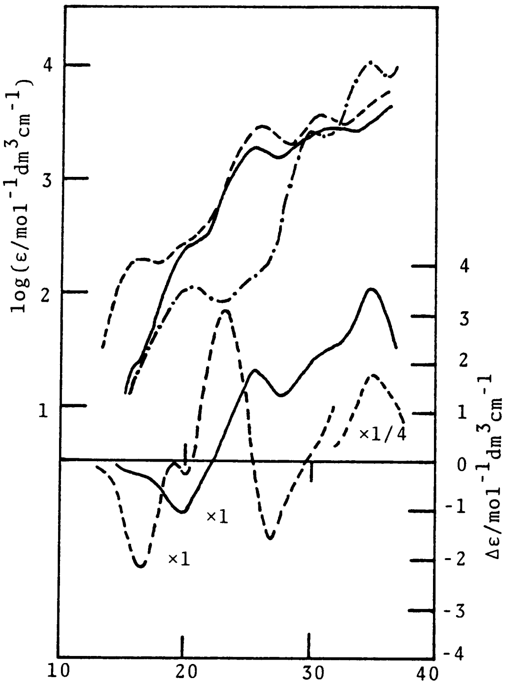


Fig. 4. Absorption and CD spectra of Δ-[Co(pyse-*S*,*N*)(en)$_2$](ClO$_4$)$_2$ (——), Δ-[Co(pyse-*O*,*N*)(en)$_2$](ClO$_4$)$_2$ (---), and [Co(pyt)(en)$_2$](ClO$_4$)$_2$ (—·—) in DMSO solution.

the peak at 166.7 eV with a shoulder at *ca.* 164 eV. The green complex shows the peak at 164.3 eV with a shoulder at *ca.* 167 eV. These results indicate that both the samples used for the measurements are a mixture and that the pure orange complex should show the peak at 166.7 eV and the pure green one at 164.3 eV. Since the *O,N*-coordinated pyse must show the lower sulfur binding energy owing to the decrease of partial charge on the sulfur atom as compared with the *S,N*-coordinated pyse, the orange and green isomers can be assigned to possess the *S,N*- and *O,N*-chelated structures, respectively. Thus, the light-irradiation to *S,N*-chelated pyse complex caused the linkage-isomerization to give the *O,N*-chelate; this is the first example of linkage-isomerism in a sulfenato complex. The isomerization corresponds to the change from the 4-membered to 5-membered chelate ring. In general, the strain energy of a chelate ring is much eliminated in 5-membered chelation as compared with 4-membered. Therefore, the present photoisomerization seems to be energetically favorable one. A similar photoisomerization was recently reported in $[Co(aesi\text{-}S,N)(en)_2]^{2+}$, though the corresponding sulfenato complex $[Co(aese\text{-}S,N)(en)_2]^{2+}$ didn't.6)

The green complex exhibits a ligand-field transition at 16600 $cm^{-1}$ as shown in Fig. 4.7) It seems that the ligand-field strength of the oxygen atom of *O*-bonded sulfenato complex is weak because of the repulsion between the oxygen and adjacent sulfur lone-pairs. The pyse-*S,N* and -*O,N* complexes exhibit an intense absorption band at *ca.* 25000 $cm^{-1}$ and *ca.* 26000 $cm^{-1}$, respectively. All the known *S*-bonded sulfenato complexes showed a similar absorption band at *ca.* 27000 $cm^{-1}$.2) Such a intense band was observed in some complexes with the Co-X-Y array, where X and Y are oxygen and/or sulfur atom having lone-pair electrons.8) The parent complex $[Co(pyt\text{-}S,N)(en)_2]^{2+}$ didn't show the intense band in the region below 30000 $cm^{-1}$ (Fig. 4). The optically active complexes, $(-)^{CD}_{507}\text{-}[Co(pyse\text{-}S,N)(en)_2]^{2+}$ and its linkage-isomer $(-)^{CD}_{603}\text{-}[Co(pyse\text{-}O,N)(en)_2]^{2+}$, are assigned to the Δ-configuration on the basis of the dominant negative CD sign at 19700 $cm^{-1}$ and at 16600 $cm^{-1}$ in the first spin-allowed d-d band region, respectively.

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