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First Observation of Metal-Mediated Interligand Tautomerism. Cobalt(III) Complexes Containing Mixed Pyridine-2-thiol and Pyridine-2-thione Ligands

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This work stems from our interest on the unprecedented molecular nonrigidity directed toward metal-mediated interligand tautomerism between mixed-tautomeric ligands in metal complexes. Tautomeric equilibria have often been used to deduce general structure-stability relationships,[1,2] and the results have been extended beyond the initial studies to such diverse areas as quantum mechanical calculations,[3] molecular switches,[4] tautomeric catalysts,[5] and theories of genetic mutation.[1] Many important biological molecules have been found to exist as tautomers and their chemistry is of considerable interest. For instance, the tautomeric equilibria of purine and pyrimidine bases have been suggested to affect RNA transcription and DNA replication in biological systems,[1] behaviors of nucleic acids,[6,7] and *etc.* In particular, thio-bases such as thiouracil and thiocytosine that can be tautomerized are normal constituents of some *t*-RNA species.[8,9] Among such tautomeric systems, the simplest example is pyridine-2-thiol and its analogs, which are capable of chelating to metals as either pyridine-2-thiol (A, thiol) or pyridine-2-thione (B, thion).[10,11] The coordination
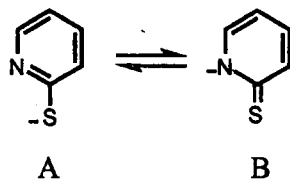
modes of the ligand are directed by various factors such as the basicity of the central metal, the overall charge of the complex, and medium effects *etc.*[12-20] Some metal complexes of the ligands have been structurally elucidated in the solid state, but their solution-behaviors are not evaluated unambiguously due to surprisingly delicate NMR spectra in solution.[21-24] In this communication, we describe a preliminary investigation of a unique molecular fluxionality in cobalt(III) complexes containing mixed-tautomeric thiol-thion ligands.

The present synthetic procedure[25] of the title complexes afforded the same *mer*-Co(N-S)₃ isomer (N-S=pyridine-2-thio (PyS); pyrimidine-2-thio (PymS)[26]) as the literature procedures.[22,24] Intricate signals of ¹H NMR (CDCl₃) result from three non-equivalent ligands in Co(PyS)₃, indicating that the *mer* isomer is still retained without any geometrical isomerism accompanied by a bond-rupture in the solution. Among the signals, in particular, two broad resonances at 8.28 ppm and 7.09 ppm in a 2 : 1 integral ratio are notable and somewhat illegible. From ¹H/¹³C 2D-heteronuclear spectrum of Co(PyS)₃ (Figure 1), the two signals are clearly characterized as the protons of ring carbons adjacent to nitrogen atoms of PyS ligands along with the assignment of
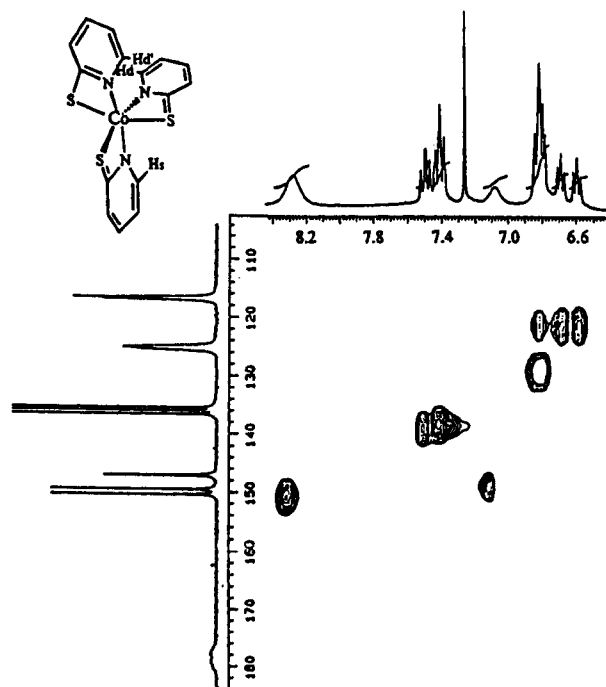

Figure 1. ¹H/¹³C heteronuclear correlation spectrum (300 MHz, CDCl₃) of Co(PyS)₃.

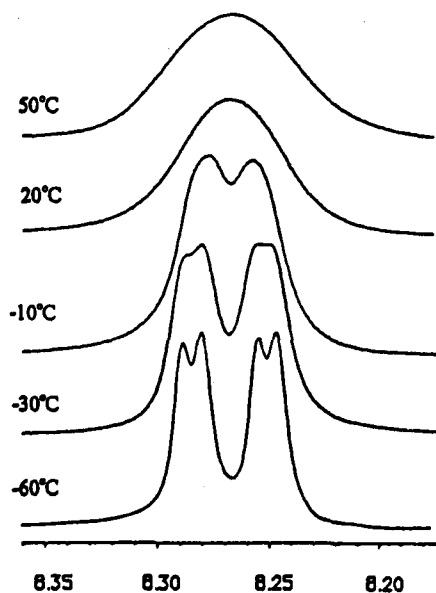*Author to whom correspondence should be addressed

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Figure 2. Variable-temperature ^{1}H NMR (600 MHz, CDCl$_3$) of the signal at 8.28 ppm in Co(PyS)$_3$.

Scheme 1.

the other peaks.[25] The high field shift of one proton (7.09 ppm) relative to the other two protons (8.28 ppm) is explained in terms of a π-shielding effect: in the *mer* configuration one of the three protons lies perpendicularly above the plane of another PyS ligand and experiences an upfield shift due to the magnetic anisotropy. If so, why are only the two signals so broad even though the basic structure is retained in solution ? The peak broadening provokes the most striking question in the present work.[27] The two broad peaks exhibit a marked temperature-dependence in the range of -60-50 °C. Variable temperature ^{1}H NMR spectra for the signal at 8.28 ppm in chloroform are shown in Figure 2. The peak (H_d and $H_{d'}$) at 20 °C shows a broad resonance. The signal has a coalescent temperature at 10 °C with a free energy of activation $\Delta G^{\neq}$=14.4 kcal/mol,[28] and begins to separate into two chemical shifts of equal intensity corresponding to H_d and $H_{d'}$, respectively. Each chemical shift finally appears as a doublet (*via* coupling with a neighboring proton) as the temperature is decreased down to -60 °C. The peak at 7.09 ppm (Hs) has similar behavior that appears as a doublet at -60 °C. Behaviors of the two peaks rule out the possibilities of an isomerism between *fac* and *mer* isomer and a typical ligand exchanging. From the C-S bond lengths (1.753(3) Å, 1.724(4) Å, and 1.720(4) Å) of Co(PyS)$_3$,[21] to our knowledge, two mixed tautomeric ligands exist in the solid state: one (1.753(3) Å) has a significant amount of a thiol whereas the other two ligands (1.724(4) Å and 1.720(4) Å) are functioning as thion. Thus, the NMR studies in combination with the X-ray data reflect a tautomerism between the two pliable tautomeric ligands via the cobalt(III) atom. The dynamical interligand processes of the cobalt(III) complex containing the mixed-tautomeric thiol (A)-thion (B) ligands are summarized in Scheme 1: for the complex, one thiol (A) and two thion (B) ligands are retained even in solution, but they are tautomerized each other at room temperature. However, at below -60 °C Co(PyS)$_3$ in solution is locked
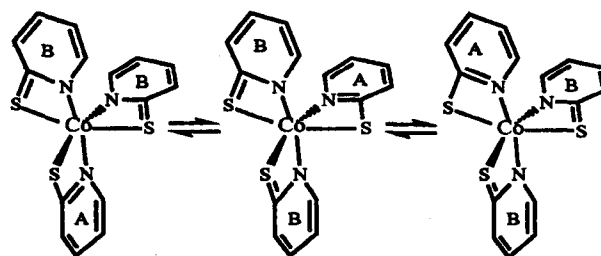
in the crystal structure. In particular, the broad signals are gradually broadened as the temperature is raised up to 50 °C (limiting temperature in chloroform solution) in contrast to general fluxional motion that exhibits signal sharpening at above the coalescent temperature. This explains the fact that the tautomerism still occurs at a reasonable rate even at 50 °C. However, the broad signals may be sharpened at much higher temperature, indicating that the tautomeric rate is faster. On the other hand, significant change for other protons (C$_3$-H, C$_4$-H, and C$_5$-H) was hardly observed in the range -60-50 °C. This fact indicates that the tautomeric equilibria of the pyridine-2-thio group predominantly occur in the following N-C-S subunit: this is an example of typical tautomerism.[1]

A   B
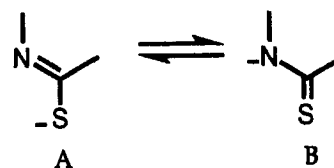
Moreover, a considerable broadening of the ^{13}C signal at 178.15 ppm (Figure 1) assigned as the C-S of PyS ligand[29] may also be responsible for the tautomerism.

On the other hand, *fac*-Co(PySO)$_3$, (PySO=pyridine-2-thio N-oxide, which is also a similar tautomeric system) containing 5-membered chelate ring does not exhibit the unique fluxionality in the range of the same temperature.[30] Thus, the protomeric tautomerism is very sensitive to the structure of the ligand including the angle strain of chelate. Furthermore, such a phenomenon was found to depend strongly on solvents. For instance, addition of water into the organic solution results in decreasing the rate of the tautomeric fluxional motion, presumably due to the solvation effects of the water. The detailed change depending on the ligand structure and solvents will be published separately. The cognate analog, Rh(PyS)$_3$ also did not reveal the interligand protomeric tautomerism.[13,15] Assuming that only cobalt(III) analogs exhibit the interligand tautomerism at the present temperature range, its driving force may be deduced. First of all, for the present system, mixed tautomeric ligands are essential for the tautomerism. Second, a considerable strain in the ligand framework by the formation of four-membered chelate ring may be in part responsible for it. Third, the cobalt(III) species surrounded by three sulfur and three nitrogen atoms may be labile in solution, *i.e.* central metal atom may be a crucial factor. Further studies on solvent and ligand effects within this series will provide more detailed information about the origin of this unprecedented molec-

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ular motion. The molecular structure and its related flux-
ionality of Co(PymS)₃ (PymS=pyrimidine-2-thio) are in pro-
gress, and will be published in a separate paper.

In conclusion, the present system is a rare verified ex-
ample of metal complexes containing mixed tautomeric li-
gands. This unique nonrigidity is direct evidence for metal-
mediated interligand tautomerism in metal complexes. The
first observation may provide a clue to understand the
unusual molecular fluxionality occurring in biological metal
molecules.

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25. Synthetic procedures of Co(PyS)₃ and Co(PymS)₃ are re-ported in ref. 21 and 23, respectively. The present mod-ified synthetic route: CoCl₂·6H₂O (1 mmol) and po-tassium salt of each ligand (3.1 mmol) were combined in 30 mL of water. The mixture was stirred for 1 h at room temperature. The precipitate was filtered and dried to obtain crude solids. Recrystallization from aceto-nitrile gave dark brown crystals suitable for X-ray crys-tallography of the complexes in 85-90% yields.
26. Studies on Co(PymS)₃ are in progress. ^1H NMR (CDCl₃, ppm): 6.59 (t, C₄-H), 6.69 (t, C₄-H), 6.80 (t, C₄-H), 6.82 (t, 3C₅-H), 7.09 (br, C₆-H), 7.41 (t, 2C₃-H), 7.50 (t, C₃-H), 8.28 (br, 2C₆-H). ^{13}C NMR (CDCl₃, ppm): 116.84 (2C₄), 117.16 (C₄), 125.33 (3C₅), 135.60 (C₃), 136.14 (C₃), 136.75 (C₃), 150.54 (C₆), 149.61 (C₆), 147.19 (C₆), 178.15 (3C₂). Pleliminary crystal data: monoclinic P2₁/c, a=10.476(4) Å, b=10.669(6) Å, c=13.601(7) Å, b=95.99(4)°, V=1512(1) Å³, Z=4, R1≈0.072, GOF=1.336 for 199 parameters and 757 unique data (I>3σ). Howev-er, the X-ray structure with the large esd's is not suit-able for publication.
27. The authors of ref. 21 considered that the broadening is a consequence of the temperature independent param-agnetism of the cobalt atom.
28. $\Delta G^{\ne}$ values were calculated from $k_c = \pi \cdot \Delta v / 2$; $\Delta G^{\ne} = 2.3RT_c(10.32 + \log T_c / k_c)$.
29. The authors of ref. 23 and 24 did not observe the peak presumably due to its broadening.
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