ChemComm

Insertion of a metal-bound nitrogen atom into a disulfide (S–S) bond. Synthesis and characterisation of $[Co^{III}L_2]ClO_4$ [HL = di(2-pyridylthio)amine]

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Received (in Cambridge, UK) 22nd February 1999, Accepted 10th March 1999

Reaction of *cis*-$[Co^{III}(NH_3)_4(H_2O)_2](ClO_4)_3$ with 2,2′-dithiodipyridine (2,2′-DTDP) in nearly equimolar proportion generates $[Co^{III}L_2]ClO_4$ where HL (H = dissociable proton) is di(2-pyridylthio)amine, resulting in an unprecedented insertion of a coordinated ammine N into the S–S bond of 2,2′-DTDP.

Reactions of a disulfide bond (S–S) are of much biological importance.[1] This bond usually undergoes reductive cleavage giving rise to sulfur radicals, thiols/thioethers or thiolate anions.[1] Herein we describe a novel reaction of the disulfide bond.

Reaction of *cis*-$[Co^{III}(NH_3)_4(H_2O)_2](ClO_4)_3$ with 2,2′-dithiodipyridine (2,2′-DTDP) leads to the isolation of diamagnetic $[Co^{III}L_2]ClO_4$ **1** [HL = di(2-pyridylthio)amine ≡ $HN\{(2\text{-}C_5H_4N)S\}_2$] [eqn. (1)].

$$\begin{array}{c} cis\text{-}[Co^{III}(NH_3)_4(H_2O)_2](ClO_4)_3 \;+\; 2\,(2,2'\text{-DTDP}) \\ \downarrow \\ Co^{III}[N\{(2\text{-}C_5H_4N)S\}_2]_2{\bullet}ClO_4 \;+\; 2\,NH_4ClO_4 \\ \mathbf{1} \end{array} \qquad (1)$$

In this reaction, two coordinated ammine N atoms are inserted into the S–S bonds of two molecules of 2,2′-DTDP, *i.e.* two of the three hydrogen atoms of two coordinated ammine nitrogens are replaced by the sulfur atoms of 2,2′-DTDP and the remaining hydrogen atom of each of the two disulfur substituted amino nitrogens dissociate as protons resulting in two L^- units. Though eqn. (1) suggests a 1 : 2 reaction stoichiometry between the metal and 2,2′-DTDP, the optimum yield of **1** is obtained by reacting almost equimolar amounts of the cobalt tetraammine complex and 2,2′-DTDP.†

The structure of **1** as determined by X-ray crystallography‡ is shown in Fig. 1. The cobalt atom lies at the center of a distorted but centric octahedron of six N (four pyridyl and two amide) atoms. Interestingly, each L^- fragment does not span a meridian but caps a face of the octahedron. If a Co–N(amide) bond is placed along the *y*-axis, then the two pyridyl rings of the L^- moiety lie quite close to the *xy* and *yz* planes, and one of the two sulfur atoms lies in the *xy* plane and the other in the *yz* plane. The average bond length of Co–N(pyridyl) is 1.963 Å and that of Co–N(amide) is 1.951 Å. The amide N is pyramidal with valence angles in the range 111.5(2)–112.0(2)° which are slightly larger than the ideal tetrahedral angle of 109.5°.

X-Ray photoelectron spectra of **1** show normal[2] binding energies: 62 (Co 3p), 164 (S 2p), 227 (S 2s), 284 (C 1s), 398 (N 1s), 533 (O 1s), 782 (Co 2p) and 929 eV (Co 2s). The absence of the spin multiplicity splitting in Co 3p confirms diamagnetism of the complex.[2] A broadening of the linewidth was observed at the lower binding energy side in the N 1s signal. This is possibly due to the difference in the binding energies of pyridyl N (401 eV) and dithioamide N (399 eV).

^1H and ^{13}C NMR spectral data for **1** in $(CD_3)_2SO$ are given in Table 1 together with their assignments. The two pyridyl rings become equivalent in solution, though they are not so in the crystal. The doublet signals are assigned to H4 and H1, while triplet signals are assigned to H2 and H3; these assignments are confirmed by 2D NMR. The ^{13}C signals are assigned considering the ^1H signals and the electron withdrawing effect of S on the C1 (or C6) atom. For ready comparison, ^1H and ^{13}C NMR data for 2,2′-DTDP are also given in Table 1.[3]

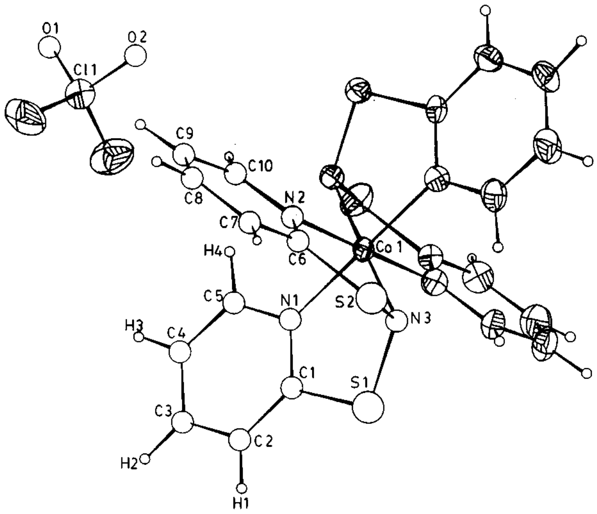

Fig. 1 X-Ray crystal structure of **1**. Selected bond distances (Å) and angles (°): Co1–N1 1.960(3), Co1–N2 1.966(3), Co1–N3 1.951(3), S1–N3 1.711(3), S2–N3 1.718(3), S1–C1 1.747(4), S2–C6 1.742(4); N1–Co1–N2 86.1(1), N1–Co1–N3 88.2(1), N2–Co1–N3 87.9(1), S1–N3–S2 111.5(2), Co1–N3–S1 111.6(2), Co1–N3–S2 112.0(2), N3–S1–C1 100.6(2), N3–S2–C6 101.0(2).

The known complexes of 2,2′-DTDP can be divided into two classes. In one class, metal complexes are formed after reductive cleavage of the S–S bond of 2,2′-DTDP. In such cases, 2-pyridylthiolato complexes are generated with four membered M–N–C–S chelate rings[4] or unidentate thiolato moieties.[4,5] The other class consists of metal complexes of 2,2′-DTDP itself in which the ligand can act in an N,N-bidentate,[6,7]

Table 1 ^1H and ^{13}C NMR spectral data for **1** and 2,2′-DTDP in $(CD_3)_2SO$ (δ in ppm from TMS)[a]

	H4	H2	H3	H1	
1	9.13	7.68	7.28	7.47	
2,2′-DTDP	8.4	7.6	7.1	7.2	
	C1	C5	C3	C4	C2
1	177.31	153.24	138.73	118.47	122.04
2,2′-DTDP	158.85	149.45	137.26	119.62	121.02

[a] The atom labelling scheme for **1** is shown in Fig. 1 and similar labelling applies to 2,2′-DTDP; Spectral data for 2,2′-DTDP are taken from ref. 3.

N,S-bidentate[7] or N-unidentate[7] mode. In the N,N-bidentate mode, it can act as a bridging ligand giving rise to polymeric species.[8] Our present complex belongs to a new class of complex of 2,2′-DTDP where a donor atom is inserted into the S–S bond. Such insertion of an atom into an S–S bond in the absence or presence of a metal is, to our knowledge, hitherto unknown.

H. N. thanks the Kagawa Nutrition College, Japan and the Japan Private School Promotion Foundation for support on an outside studies program. Thanks are also due to Dr M. Koizumi, Central Research Laboratory of Mitsubishi Materials Co., Omiya, Saitama, Japan for helping with the X-ray photoelectron spectra and to Dr T. Ekita, Tosoh Co., Ayase, Kanagawa, Japan for helping with the NMR spectra.

Notes and references

† 4.6 g (10 mmol) of *cis*-[Co^{III}(NH$_3$)$_4$(H$_2$O)$_2$](ClO$_4$)$_3$, synthesised by a reported procedure,[9] and 2.8 g (13 mmol) of 2,2′-DTDP was dissolved in 12 ml of DMF and heated at 100 °C for 1 h. Within 30 min of heating, a shiny dark compound started to separate. The reaction mixture was cooled to room temp. and 6 ml of ethyl acetate was added dropwise with stirring. The precipitate was allowed to settle for 15 min. It was filtered, washed first with 15 ml of DMF–ethylacetate (1 : 2) and then with ethyl acetate, and was dried in air. The crude product was recrystallised from DMF–ethyl acetate. Yield, 1.2 g (20%). Colour: shining brown. Anal. Found (calc.): Co, 9.33(9.41); C, 38.14(38.29); H, 2.42(2.57); N, 13.50(13.40)%. Diamagnetic. Single crystals were grown by direct diffusion of ethyl acetate into a dilute DMF solution of **1**.

‡ *Crystal data* for $CoC_{20}N_6S_4H_{16}O_4Cl$ **1**: M_w = 626.86, monoclinic, space group $C2/c$, a = 21.049(3), b = 12.603(2), c = 9.523(2) Å, β = 97.39(4)°, U = 2505.3 Å^3, Z = 4, D_c = 1.662 g cm^{-3}. The data were collected on a CAD-4 diffractometer with Cu-Kα radiation (λ = 1.54178 Å) at 295 K. Absorption correction: empirical T_{min} = 0.7082, T_{max} = 1.6595. The crystal structure was solved by direct methods (SHELXS) and refined by full matrix least squares methods with first isotropic then anisotropic displacement parameters. The hydrogen atoms were located from difference electron density function after the isotropic refinement and placed geometrically, and their isotropic displacement parameters were refined. R = 0.0524 (R_w = 0.0632) for 1908 observed reflections with $F > 3\sigma(F)$. CRYSTALS[10] was used for calculations and CAMERON[11] for diagrams. CCDC 182/1194.

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Communication 9/01442J