Design of Complex–Ligand Systems based on Thiouracil. A Novel Cyclic Tetramer of Cobalt(III) with 1-(2-Thiouracil-4-methylene)-3,6-diazahexane

Takashi Kajiwara and Tasuku Ito

Department of Chemistry, Faculty of Science, Tohoku University, Aramaki, Aoba-ku, Sendai 980-77, Japan

A Schiff base derived from 2-thiouracil-4-aldehyde and dien reacts with $Co^{II}(CF_3SO_3)_2$ to afford a novel cyclic tetramer of cobalt(III) by self-assembly; the complex has a columnar cavity at its centre with an effective diameter of *ca.* 1.8 Å.

The chemistry of multi-metal-centred complexes or assemblies with highly ordered solid state structures has attracted much attention.[1] Meticulous design of the ligand is important for the construction of such structures and for controlling their properties. One method of forming a multi-metal complex is to use a complex-ligand. In this study, we used 1-(2-thiouracil-4-methylene)-3,6-diazahexane (H_2L), based on 2-thiouracil which forms mononuclear complexes $[M(HL)]^{(n-1)+}$ (Fig. 1).

When the NH proton in $[M(HL)]^{(n-1)+}$ dissociates, the resulting species $[ML]^{(n-2)+}$ is a potential bidentate complex-ligand with free S and N donors which can form a four-membered chelate ring upon coordination to another metal ion. 2-Thoiuracil,[2] pyrimidine-2-thiol[3] and their derivatives[4,5] are known to form such metal complexes with S-containing four-membered chelate rings. Further, self-assembly of the $[ML]^{(n-2)+}$ unit may also occur when M^{n+} prefers six-coordination, although HL^- will occupy only four coordination sites around M^{n+}. In this paper, we report a new cyclic tetramer of $[Co^{III}L]^+$.

Cobalt(II) trifluoromethanesulfonate, prepared from $CoCO_3$ and CF_3SO_3H, was allowed to react with diethylenetriamine in aqueous solution. To this orange solution, 1 equivalent of 2-thiouracil-4-aldehyde monohydrate[6] in methanol was added and the mixture was heated for several minutes. The solution was kept under air at room temperature for several days and gave dark red crystals (Scheme 1).

The single-crystal X-ray analysis† and characterization by means of elemental analysis, UV, IR and ^1H NMR spectroscopy revealed that the product was the cobalt(III) complex $[Co_4L_4](CF_3SO_3)_4 \cdot 8H_2O$.‡ Fig. 2 shows the structure of the cyclic tetramer of the cation which lies on the crystallographic $\bar{4}$ axis.

As expected, L^{2-} acts as a dinucleating hexadentate ligand and $[Co^{III}L]^+$ acts as a bidentate complex-ligand. For the six donor atoms in L^{2-}, four nitrogens [N(2)–N(5)] are coordinated to one cobalt, whereas the uracil nitrogen [N(1)] and sulfur [S(1)] are bound to an adjacent cobalt forming a four-membered chelate ring. Each cobalt is distorted octahedral with an N_5S donor-atom set. The structure of the four-membered chelate ring is very similar to those in complexes of 2-thiouracil,[2] pyrimidine-2-thiol,[3] and their derivatives,[4,5] although all these compounds are mononuclear. Intratetramer hydrogen bonds are formed between uracil oxygen and N(5) of the neighbouring unit [O(1)···N(5) 3.019(5) Å]. These bonds may play a role in the formation of the cyclic tetramer. The Co···Co separations are 5.5408(9) Å (neighbouring) and 7.115(1) Å (diagonal), respectively.

The cyclic tetramer has a relatively large central columnar cavity. Of particular interest is the fact that four thiouracil sulfurs are arranged almost tetrahedrally on the wall of the

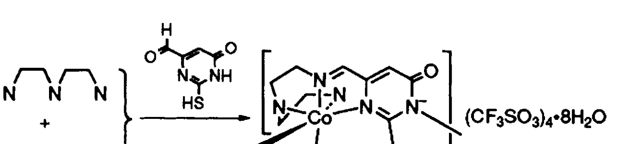

Fig. 1

Scheme 1

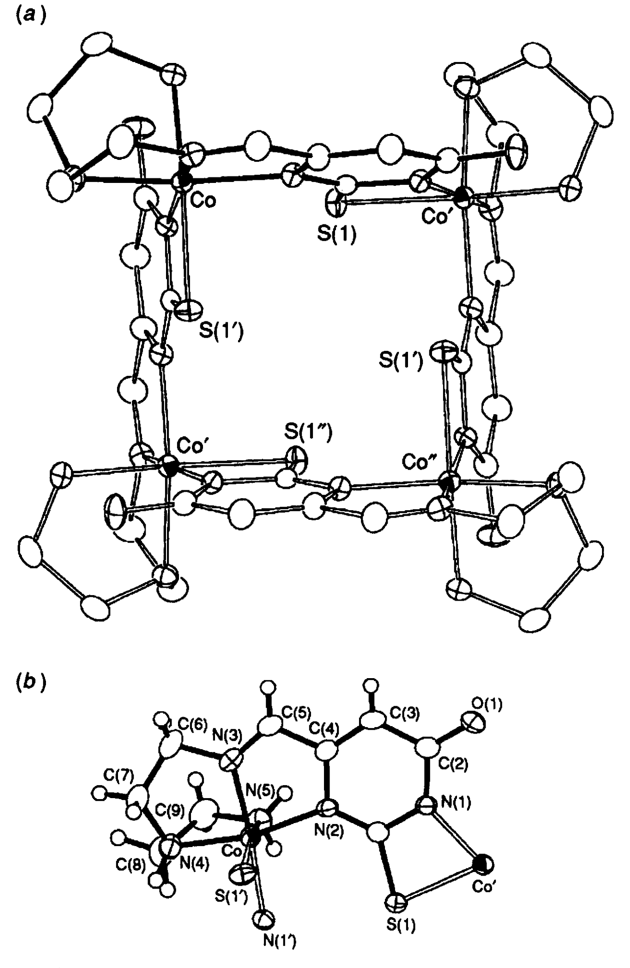

Fig. 2 (*a*) ORTEP drawing of $[Co_4L_4]^{4+}$ with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity; S(1)–S(1′) 4.615(2), S(1)–S(1″) 4.267(2), Co–Co′ 5.5408(9), Co–Co″ 7.115(1) Å. (*b*) The monomeric (asymmetric) unit in $[Co_4L_4]^{4+}$. Thermal ellipsoids are at the 50% probability level. Selected bond distances (Å) and bond angles (°): Co–S(1′) 2.296(1), Co–N(1′) 1.929(3), Co–N(2) 1.970(3), Co–N(3) 1.876(3), Co–N(4) 1.943(3), Co–N(5) 1.956(4), S(1)–C(1) 1.737(4), S(1′)–Co–N(1′) 71.9(1), S(1′)–Co–N(2) 90.9(1), S(1′)–Co–N(3) 98.9(1), S(1′)–Co–N(4) 93.1(1), S(1′)–Co–N(5) 168.7(1), N(1′)–Co–N(2) 101.5(1), N(1′)–Co–N(3) 170.1(1), N(1′)–Co–N(4) 91.3(1), N(1′)–Co–N(5) 96.9(2), N(2)–Co–N(3) 82.1(1), N(2)–Co–N(4) 167.2(1), N(2)–Co–N(5) 91.9(1), N(3)–Co–N(4) 85.3(2), N(3)–Co–N(5) 92.3(2), N(4)–Co–N(5) 86.6(2), Co′–S(1)–C(1) 78.3(1) S(1)–C(1)–N(1) 107.3(3), S(1)–C(1)–N(2) 127.7(3).

cavity. The S···S separations are 4.615(2) Å [neighbouring, S(1)–S(1′)] and 4.267(2) Å [S(1)–S(1″)]. The cavity present in this compound might lead to the potential for host–guest chemistry as found for metallacrowns.[7]

In MeCN, $[Co_4L_4](CF_3SO_3)_4 \cdot 8H_2O$ shows an intense absorption around 280 nm (sh, ε = *ca.* 1400 $dm^3\ mol^{-1}\ cm^{-1}$) and a weak shoulder around 500 nm (ε = *ca.* 40 $dm^3\ mol^{-1}\ cm^{-1}$), which can be ascribed to S → Co^{III} charge transfer and d–d transitions, respectively, on the basis of the assignments reported for $Co^{III}N_5S$ type complexes.[5]

To our knowledge, this is the first example where the thiouracil group acts as a bridging ligand. In view of the fact that the reaction of HL^- with Ni^{2+} gives a mononuclear complex, $[Ni(HL)(H_2O)_2]^-$,§ it would appear that the present cyclic cobalt(III) tetramer is formed by self-assembly of an initially formed $[CoL]^+$ species in a head-to-tail manner.

Received, 17th May 1994; Com. 4/02923B

Footnotes

† *Crystal data*: $C_{40}H_{72}Co_4F_{12}N_{20}O_{24}S_8$, M = 1937.3, crystal size 0.40 × 0.40 × 0.20 mm, tetragonal, space group $I4_1/a$ (no. 88), a = 22.305(3), c = 14.769(2) Å, V = 7347(1) $Å^3$, Z = 4. D_c = 1.751 g cm^{-3}, $F(000)$ = 3952.00, μ(Mo-Kα) = 12.30 cm^{-1}, with the use of 3155 unique reflections [$I > 3\sigma(I)$] collected at room temperature with Mo-Kα radiation (λ = 0.71069 Å) up to 2θ = 55.0° on a Rigaku AFC 7S diffractometer, the structure was solved by the Patterson Method (DIRDIF92 PATTY) and refined by full-matrix least squares analysis with anisotropic thermal parameters for the non-hydrogen atoms to a final R value of 0.047 (R_w = 0.041). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‡ Cyclic voltammetry of this compound in 0.1 mol dm^{-3} aqueous $NaClO_4$ shows two redox waves at $E_{\frac{1}{2}}(1) = -0.64$ V *vs.* SSCE and $E_{pc}(2)$ = 1.13 V. Process 1 is reversible whereas process 2 is irreversible. Judging from a comparison of peak current intensities with the $[Fe^{II}(CN)_6]^{4-}$–$[Fe^{III}(CN)_6]^{3-}$ couple under the same conditions, redox process 1 involves two electrons and is ascribed to the Co^{III}_4–$Co^{II}_2Co^{III}_2$ couple. The tetranuclear complex ion can gain two electrons maintaining its cyclic structure.

§ *Crystal data* for $[Ni(HL)(H_2O)_2](ClO_4)$: $C_9H_{18}ClN_5NiO_7S$, monoclinic, space group $P2_1/c$ (no. 14), a = 15.891(5), b = 7.2641(9), c = 16.145(4) Å, β = 116.77(2)°, V = 1664.0(8) $Å^3$, Z = 4, R = 0.040. The coordination mode of HL^- in the nickel(II) complex is the same as that found in the $[M(LH)]^{(n-1)+}$ unit in Fig. 1. Two *cis* aqua ligands occupy the remaining positions.

References

1 For example, H. O. Stumpf, L. Ouahab, Y. Pei, D. Grandjean and O. Kahn, *Science*, 1993, **261**, 447; S. L. Suib, *Chem. Rev.*, 1993, **93**, 803.

2 K. Yamanari, K. Okusako, Y. Kushi and S. Kaizaki, *J. Chem. Soc., Dalton Trans.*, 1992, 1621.

3 K. Yamanari, K. Okusako and S. Kaizaki, *J. Chem. Soc., Dalton Trans.*, 1992, 1615; F. A. Cotton and W. H. Ilsley, *Inorg. Chem.*, 1981, **20**, 614.

4 J. F. Villa and H. C. Nelson, *J. Indian Chem. Soc.*, 1978, 631; W. O. Foye and J.-R. Lo, *J. Pharm. Sci.*, 1972, **8**, 1209; B. A. Cartwright, P. O. Langguth Jr. and A. C. Skapski, *Acta Crystallogr., Sect B*, 1979, **35**, 63; D. M. L. Goodgame and G. A. Leach, *J. Chem. Soc., Dalton Trans.*, 1978, 1705; *Inorg. Chim. Acta*, 1979, **32**, 69.

5 K. Yamanari, M. Kida, M. Yamamoto, T. Fujihara, A. Fuyuhiro and S. Kaizaki, *Chem. Lett.*, 1993, 1865; K. Yamanari, M. Yamamoto, M. Kida, T. Fujihara, A. Fuyuhiro and S. Kaizaki, *J. Chem. Soc., Dalton Trans.*, 1993, 1651.

6 T. B. Johnson and E. F. Schroeder, *J. Am. Chem. Soc.*, 1931, **53**, 1989; T. B. Johnson and L. A. Mikeska, *J. Am. Chem. Soc.*, 1919, **41**, 810.

7 B. R. Gibney, A. J. Stemmler, S. Pilotek, J. W. Kampf and V. L. Pecoraro, *Inorg. Chem.*, 1993, **32**, 6008.