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An Unusual Self-Assembly of 2-Thiouracil Derivative. Synthesis and Crystal Structure of Bis(ethane-1,2-diamine)[5-((1'H)-4'-oxo-6'-aminopyrimidin-2'-yl)thio]-6-amino-2-thiouracilatocobalt(III) Perchlorate

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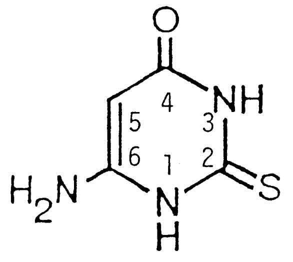
An unusual red complex [Co(di-Hatuc)(en)$_2$]$^+$ (di-Hatuc = [5-((1'H)-4'-oxo-6'-aminopyrimidin-2'-yl)thio]-6-amino-2-thiouracilate (2-); en = ethane-1,2-diamine) is formed by a simple thermal reaction. This complex has both a intramolecular hydrogen bond and novel linear intermolecular hydrogen bonds, the latter being analogous to hydrogen bonding in nucleic acids.

As part of our studies on the coordinating modes of thio-derivatives of nucleic acid constituent bases, we attempted the preparation of cobalt(III) complexes containing 6-amino-2-thiouracil [H_2atuc = 2,3-dihydro-2-thioxo-(1H)-6-aminopyrimidin-4-one]. This ligand is very interesting because it has both characteristics of 2-thiouracil [H_2tuc = 2,3-dihydro-2-thioxo-(1H)-pyrimidin-4-one]$^{1)}$ and 2-thiocytocine (Htcy = 4-aminopyrimidine-2-thione).$^{2)}$ Thermal reaction of trans-[$CoCl_2$(en)$_2$]Cl (en = ethane-1,2-diamine), H_2atuc and NaOH in the presence of activated charcoal gave a novel cobalt(III) complex containing [5-((1'H)-4'-oxo-6'-aminopyrimidin-2'-yl)thio]-6-amino-2-thiouracilate (di-Hatuc^{2-}). Here we describe the synthesis, characterization and X-ray crystal structure of [Co(di-Hatuc)(en)$_2$]$^+$.



An aqueous solution (100 cm^3) of trans-[$CoCl_2$(en)$_2$]Cl, H_2atuc and NaOH (mole ratio = 1:1:1) was heated in the presence of activated charcoal at 70 °C for 2 h to give the red solution. After filtration, the filtrate was poured onto a column of cation exchanger (SP-Sephadex C-25, Na$^+$ form; ϕ4 x 40 cm). Elution with 0.1 mol dm^{-3} NaCl gave three colored bands, red (1, yield 51%),$^{3)}$ red (2, 6.9%)$^{4)}$ and yellow, in this order. The third yellow band was $[Co(en)_3]^{3+}$. Each red eluate was concentrated with a vacuum evaporator and the white precipitate NaCl was filtered off. Evaporation of the filtrate gave the chloride salt. By adding $NaClO_4$ to the filtrate, the perchlorate salt was also obtainable.

In the present system two red complexes 1 and 2 were obtained. The first d-d absorption band appears at 498 nm and an intense sulfur-to-metal charge transfer band appears at 293(sh) nm for 1.[3)] They are characteristic of CoN_5S type complexes containing one thionato group.[1)] Based on the ^{13}C NMR spectrum complex 1 is assigned to $[Co(atuc)(en)_2]^+$. Complex 1 showed one amine ^1H NMR signal of the en at exceptionally lower magnetic field (δ 7.50): this indicates the existence of an intramolecular hydrogen bond between the 4-oxygen atom and one of the NH_2(en) protons.[1)] Thus complex 1 adopts the 2,3-coordination.

Complex 2 showed twelve ^{13}C NMR signals, eight in the atuc chemical shift region and four in the en region. This indicates that complex 2 contains two units of the atuc ligand. UV/VIS absorption spectrum of complex 2 is similar to that of complex 1 and therefore complex 2 also has a CoN_5S chromophore.[4)] However, it should be noted that the molar absorption coefficients of complex 2 are considerably larger than those of complex 1 only in the UV region. This is relevant to the presence of two

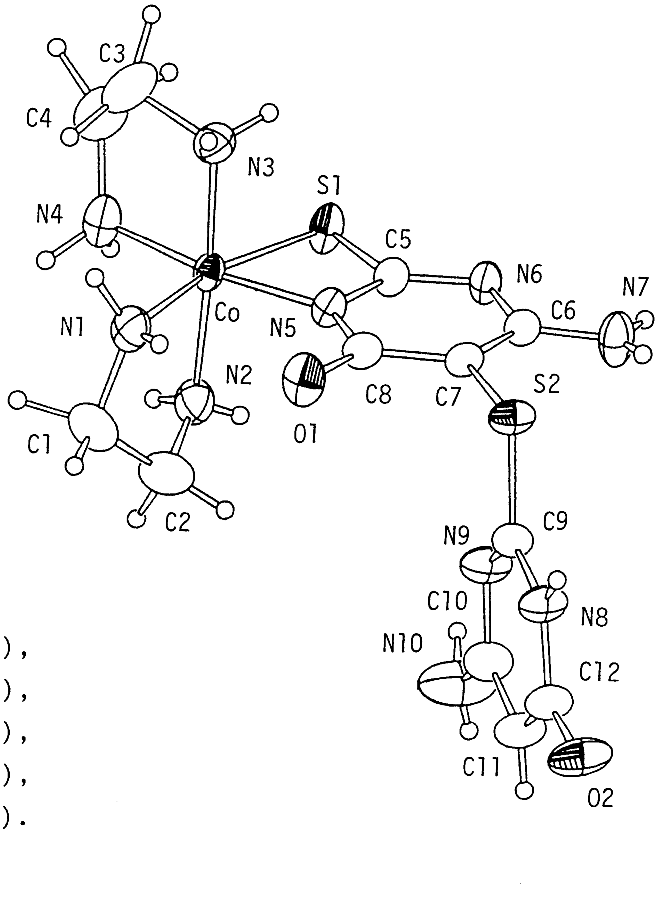


Fig. 1. An ORTEP view of $[Co(di\text{-}Hatuc)(en)_2]^+$ (2) with the atomic labeling scheme. Selected bond lengths (Å) and angles (°): Co-S1 2.273(3), Co-N1 1.954(5), Co-N2 1.937(5), Co-N3 1.957(4), Co-N4 1.955(5), Co-N5 1.919(4), S1-C5 1.736(4), C5-N5 1.337(5), N5-C8 1.382(5), C8-O1 1.246(5), C7-C8 1.425(6), C5-N6 1.314(5), N6-C6 1.360(5), C6-N7 1.327(6), C6-C7 1.396(6), S2-C7 1.745(4), S2-C9 1.771(5), C9-N8 1.349(5), N8-C12 1.389(6), O2-C12 1.262(5), C9-N9 1.286(6), N9-C10 1.362(6), C10-N10 1.341(7), C10-C11 1.383(6), C11-C12 1.379(7), S1-Co-N1 167.1(2), N2-Co-N3 176.6(2), N4-Co-N5 169.2(2), S1-Co-N5 72.6(1), Co-S1-C5 77.7(2), S1-C5-N5 108.0(3), Co-N5-C5 101.6(3).

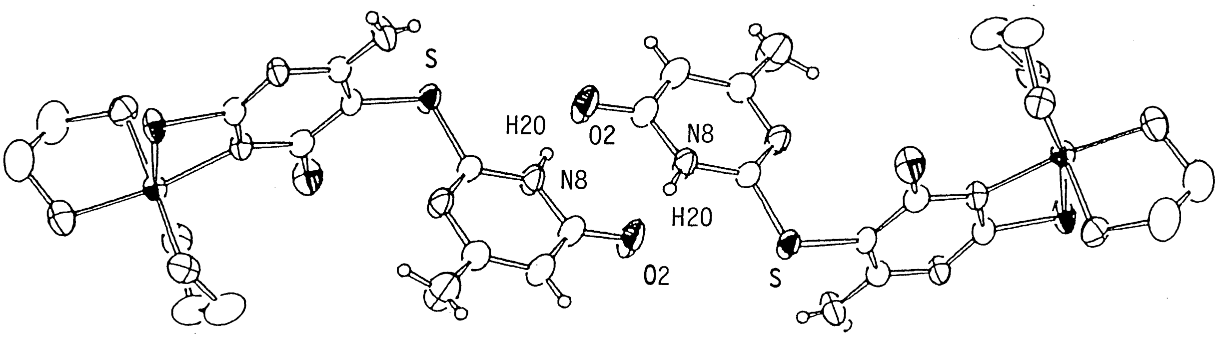


Fig. 2. Linear intermolecular hydrogen bonds of complex **2**.

units of the atuc ligand. Figure 1 shows an ORTEP drawing of the cation of [Co(di-Hatuc)(en)$_2$]ClO$_4$·3H$_2$O (**2**).$^{5)}$ Surprisingly, complex **2** has a novel dimeric Hatuc ligand: a new bond is formed between the 5-carbon atom and the 2'-sulfur one. Cooordination occurs through the 2-S and 3-N donor atoms. An intramolecular hydrogen bond is found between O1 and N1H(en) [N···O = 2.878(6) Å and N-H···O = 146.8°]. The en chelate ring relevant to the hydrogen bond adopts ob conformation (i.e. the C-C bond of the en is oblique to the pseudo C3 axis), which makes one of the NH$_2$ protons direct to the suitable hydrogen bond with the oxygen atom. The characteristic downfield shift of one amine proton (δ 7.60) indicates that the intramolecular hydrogen bond exists also in (CD$_3$)$_2$SO solution.$^{1)}$ In the coordinated pyrimidine ring three bonds, C5-N6, C6-C7 and C8-O1, have a localized double bond character. The second pyrimidine ring is almost perpendicular to the coordinated pyrimidine ring: the torsion angles of C6-C7-S2-C9, C8-C7-S2-C9, C7-S2-C9-N8 and C7-S2-C9-N9 are -87.2(4), 89.8(4), -177.4(4) and 3.1(5)°, respectively.

A particularly interesting feature of this structure concerns the linear N-H···O double intermolecular hydrogen bonds. Figure 2 reveals clearly these self-associated hydrogen bonds: two hydrogen bonds between N8 and O2 of one complex and O2 and N8 of another complex, respectively, are formed. They are in the same plane and are related by an inversion center. The N8···O2, N8-H20 and H20···O2 distances are 2.750(5), 0.87(5) and 1.88(5) Å, respectively, which are very similar values found in nucleic acids.$^{7)}$

Some experiments to raise the yield of complex **2** were attempted. In the reaction with mole ratio = 1:2:2 the yield increased to 16%. Furthermore air oxidation of the same solution caused a drastic change that complex **2** becomes a major product: the yield was 32 and 40% for complexes **1** and **2**, respectively. Photochemical preparation using [Co(en)$_3$]Cl$_3$,

H_2atuc and NaOH was also carried out.[1,2] This method gave only complex **1** (56%) but not complex **2**. It has been well known that electrophilic substitution reaction occurs at the 5-position in pyrimidine.[8] The mechanistic study for the present unusual self-assembly reaction of 6-amino-2-thiouracil is now in progress.

References

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3) Anal. Found: C, 25.93; H, 5.50; N, 26.40%. Calcd for [Co(atuc)-(en)$_2$]Cl·H_2O = $C_8H_{21}ClCoN_7O_2S$: C, 25.71; H, 5.66; N, 26.23%. UV/VIS: λ_{max}/nm (water) 498 (ε= 138), 360 (sh, 240), 293 (sh, 8800), 270 (12500), 233 (sh, 28400) and 209 (39800 dm^3 mol^{-1} cm^{-1}). ^{1}H NMR 400 MHz, D_2O, ppm from DSS): 7.50 (s, 1H: NH_2(en)) and 4.98 (s, 1H: H5). ^{13}C NMR [100 MHz, D_2O, 1,4-dioxane(δ 67.40) as an internal standard]: 44.8, 45.7, 45.8, 46.6, 85.8, 164.9, 176.7 and 178.9.
4) Anal. Found: C, 26.21; H, 5.12; N, 25.25%. Calcd for [Co(di-Hatuc)(en)$_2$]Cl·3H_2O = $C_{12}H_{28}ClCoN_{10}O_5S_2$: C, 26.16; H, 5.12; N, 25.42%. UV/VIS: λ_{max}/nm (water) 501 (ε= 141), 360 (sh, 280), 300 (sh, 15400), 265 (sh, 26500), 243 (sh, 28700) and 215 (52200 dm^3 mol^{-1} cm^{-1}). ^{1}H NMR [400 MHz, $(CD_3)_2SO$, ppm from TMS]: 9.87 (s, 1H: N1'H), 7.60 (s, 1H: NH_2(en)), 6.36 (s, 2H: NH_2), 6.27 (s, 2H: NH_2) and 4.76 (s, 1H: H5'). ^{13}C NMR [100 MHz, $(CD_3)_2SO$, ppm from TMS]: 43.3, 44.5, 44.7, 45.6, 75.9, 81.1, 162.0, 162.5, 163.4, 165.9, 172.4 and 180.0.
5) Crystal data for $[Co(C_8H_6N_6O_2S_2)(C_2H_8N_2)_2]ClO_4\cdot 3H_2O$: M = 614.9, monoclinic, $P2_1/c$ (No.14), a = 7.25(1), b = 29.390(8), c = 11.930(6) Å, β = 98.66(7)°, V = 2513(4) Å^3, Z = 4, Dcalcd = 1.625 g/cm^3, λ(MoKα) = 0.71069 Å, R(R_w) = 0.055(0.068) for 4567 independent reflections with Fo > 3σFo. All calculations were performed using the TEXSAN[6] crystallographic software package.
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