Synthesis and Crystal Structure of {6-Amino-5-[6-amino-4-oxo-(1*H*)-pyrimidin-2-yl]thio-2-thioxo-pyrimidin-4-onato}[tris(2-aminoethyl)amine]cobalt(III) Perchlorate

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The novel tris(2-aminoethyl)aminecobalt(III) complex containing a dimerized ligand Hatuc-atuc (6-amino-5-[6-amino-4-oxo-(*1H*)-pyrimidin-2-yl]thio-2-thioxo-pyrimidin-4-onate(2-)) was prepared. The crystal structure revealed that Hatuc-atuc coordinates through the S/N donors and exhibits the intermolecular π–π stacking and the double N–H···O hydrogen bond interactions.

As part of our interest in the chemistry of metal complexes containing pyrimidinethione[1] and purinethione,[2] new Co^{III} complexes with 6-amino-2,3-dihydro-2-thioxo-(1*H*)-pyrimidin-4-one [H$_2$atuc] (Chart 1) were prepared. This ligand is very interesting because of exhibiting a novel kind of ring fusion reaction.[3] Thermal reaction between *trans*-[CoCl$_2$(en)$_2$]Cl (en = ethane-1,2-diamine), H$_2$atuc, and NaOH in the presence of activated charcoal produced a new complex [Co(Hatuc-atuc)(en)$_2$]$^+$ (**1**).[4] The complex contains the novel ligand Hatuc-atuc {6-amino-5-[6-amino-4-oxo-(*1H*)-pyrimidin-2-yl]thio-2-thioxo-pyrimidin-4-onate(2−)}, which consists of the dimerized structure of two atuc ligands. We describe here another Co^{III} complex containing Hatuc-atuc.

Thermal reaction between [CoCl$_2$(tren)]Cl [tren = tris(2-aminoethyl)amine], H$_2$atuc, and NaOH in the presence of activated charcoal[5] gave [Co(atuc)(tren)]Cl (**2**) and [Co(Hatuc-atuc)(tren)]$^+$ (**3**: **3a** and **3b**) in moderate yields. The ^{1}H NMR spectrum of **3a** showed a single atuc amino signal at δ 6.35 and one C(5′)H signal at δ 4.76, which are very similar to δ 6.36 and 6.27 for NH$_2$ and δ 4.76 for H$^{5'}$ in **1**. The ^{13}C NMR spectrum of **3a** showed eight signals at the atuc chemical shift region, such a result clearly indicates the presence of two atuc ligands. The molar absorption coefficients of **3** are considerably larger than those of **2** only in the UV region (see Experimental). This is relevant to the presence of two units of the atuc ligand in **3**.

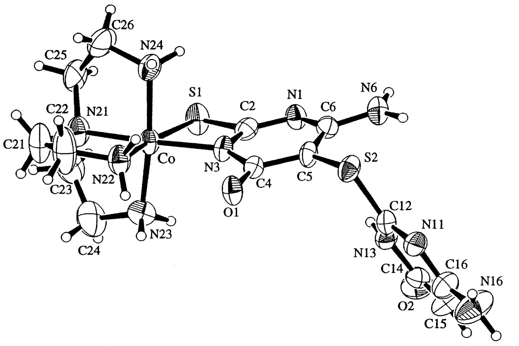
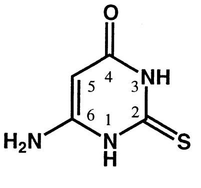


Fig. 1. The ORTEP drawing of the cation in [Co(Hatuc-atuc)(tren)]ClO$_4$·2.5H$_2$O (**3b**).

Table 1. Selected Bond Distances (Å) and angles (°) of [Co(Hatuc-atuc)(tren)]ClO$_4$·2.5H$_2$O (**3b**)

Co–S(1)	2.305(2)	Co–N(3)	1.920(4)
Co–N(21)	1.934(5)	Co–N(22)	1.948(5)
Co–N(23)	1.955(5)	Co–N(24)	1.969(5)
S(1)–C(2)	1.749(6)	S(2)–C(5)	1.749(5)
S(2)–C(12)	1.754(6)	O(1)–C(4)	1.232(6)
O(2)–C(14)	1.247(7)	N(1)–C(2)	1.303(7)
N(1)–C(6)	1.356(7)	N(3)–C(2)	1.342(7)
N(3)–C(4)	1.386(6)	N(6)–C(6)	1.347(7)
N(11)–C(12)	1.313(7)	N(11)–C(16)	1.372(7)
N(13)–C(12)	1.333(7)	N(13)–C(14)	1.393(7)
N(16)–C(16)	1.329(8)	N(21)–C(21)	1.498(8)
C(4)–C(5)	1.432(7)	C(5)–C(6)	1.401(8)
C(14)–C(15)	1.384(8)	C(15)–C(16)	1.382(9)
S(1)–Co–N(3)	72.1(1)	S(1)–Co–N(22)	171.4(1)
N(3)–Co–N(21)	172.8(2)	N(21)–Co–N(22)	87.5(2)
N(23)–Co–N(24)	171.7(2)	N(21)–Co–N(24)	86.0(2)
Co–S(1)–C(2)	77.2(2)	C(5)–S(2)–C(12)	104.2(3)
Co–N(3)–C(2)	102.4(3)	C(2)–N(3)–C(4)	120.0(5)
C(2)–N(1)–C(6)	114.9(5)	N(3)–C(4)–C(5)	113.6(5)
S(1)–C(2)–N(3)	107.5(4)	N(1)–C(2)–N(3)	127.8(5)
N(1)–C(6)–C(5)	121.7(5)	C(4)–C(5)–C(6)	120.6(5)
C(12)–N(11)–C(16)	115.9(5)	C(12)–N(13)–C(14)	124.0(5)
N(13)–C(14)–C(15)	113.4(6)	C(14)–C(15)–C(16)	120.6(6)
C(15)–C(16)–N(11)	122.8(6)	N(11)–C(12)–N(13)	123.1(5)



H$_2$atuc

Chart 1.

An ORTEP drawing of **3b** together with the numbering scheme is shown in Fig. 1. The selected bond distances and angles are listed in Table 1. Complex **3b** has the novel dimeric ligand Hatuc-atuc: a new bond is formed between the C(5) of the coordinated atuc and the S(2) of the pendant atuc. Coordination occurs through the S(1) and N(3) donor atoms and a weak intramolecular hydrogen bond exists between O(1) and N(22)H$_2$(tren) [N(22)···O(1) = 3.050(6) Å]. The bond lengths and angles of two pyrimidine rings in **3b** are very similar to those in **1**.[4] In the coordinated pyrimidine ring the two bonds, C(5)–N(6) and C(4)–O(1), have a localized double bond character and the bond lengths and angles of the pendant atuc ring

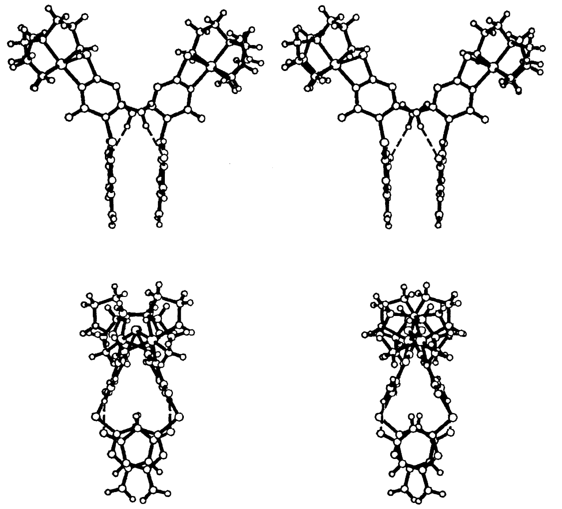


Fig. 2. The intermolecular π–π stacking and the double N–H···O hydrogen bonds in **3b**: top view (above) and side view (below).

are a little different from those of the coordinated ring. Protonation occurs at N(13). The most striking difference is the mutual orientation of two atuc rings: the torsion angle of two atuc rings is 68.46° for **3b** but is 91.6° for **1**. The torsion angles C(4)–C(5)–S(2)–C(12) and C(6)–C(5)–S(2)–C(12) are 107.5(4) and −79.2(5)° for **3b** and 89.8(4) and −87.2(4)° for **1**, respectively. This may be because of different intemolecular interactions.

An interesting structural feature of the present complex concerns the intermolecular π–π stacking and the double N–H···O hydrogen bonds, as shown in Fig. 2. The π–π stacking contact of the two pendant atuc rings becomes minimum at C(15)···C(15) [3.33(1) Å] and maximum at N(13)···N(13) [3.64(1) Å]. The double intermolecular hydrogen bonds are formed between N(6)H and O(2) of one complex and O(2) and N(6)–H of the adjacent complex, and the N(6)–H···O(2) distance is 3.193(6) Å. Such a different type of double intermolecular hydrogen bonds has been found in **3b**: both N(13)H and O(2) atoms of the pendant atuc ring are relevant to the interaction and there is no intermolecular π–π stacking in **1**.[4] It is interesting that the intermolecular interaction modes of Hatuc-atuc are quite different from each other between **1** and **3b**. This suggests that the substitution of the remaining amine ligand moieties, en or tren, leads to the exploitation of new intermolecular interaction modes.

Experimental

Preparations. [Co(atuc)(tren)]Cl (**2**), [Co(Hatuc-atuc)(tren)]Cl (**3a**), and [Co(Hatuc-atuc)(tren)]ClO_4 (**3b**). An aqueous solution (100 cm^3) of [$CoCl_2$(tren)]Cl, H_2atuc and NaOH (mole ratio = 1:2:2) was heated in the presence of activated charcoal at 80 °C for 4 h to give a red solution. After the charcoal was removed by filtration the filtrate was poured onto a column of cation exchanger (SP-Sephadex C-25, Na^+ form; $\phi 4 \times 40$ cm). Elution with 0.1 mol dm^{-3} NaCl gave two dominant bands, red (**2**, yield 52%) and red (**3**, 30%), in this order. Each red eluate was concentrated with a vacuum evaporator and the white precipitate of 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. Complex **2** {Found: C, 27.50; H, 6.46; N, 22.45%. Calcd for [Co(atuc)(tren)]Cl·$3H_2O$ = $C_{10}H_{27}ClCoN_7O_4S$: C, 27.56; H, 6.24; N, 22.50%. UV/vis (water) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 485 (157), 293sh (9100), 270sh (12500), 233 (33400), 218 (34800)}. Complex **3a** {Found: C, 28.09; H, 5.44; N, 23.43%. Calcd for [Co(Hatuc-atuc)(tren)]Cl·$4H_2O$ = $C_{14}H_{32}ClCoN_{10}O_6S_2$: C, 28.26; H, 5.42; N, 23.54%}. Complex **3b** {Found: C, 26.70; H, 4.53; N, 22.28%. Calcd for [Co(Hatuc-atuc)(tren)]ClO_4·$2.5H_2O$ = $C_{14}H_{29}ClCoN_{10}O_{8.5}S_2$: C, 26.61; H, 4.63; N, 22.16%}. UV/vis (**3a**/water) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 488 (162), 299sh (16500), 264sh (24400), 240sh (37700), 225 (53100), 215 (51600). NMR (**3a**) δ_H (DMSO-d_6) 9.52 (NH; s, 1H), 6.35 (NH_2(atuc); s, 4H), 5.41 (NH_2(tren); s, 2H), 4.76 (NH_2(tren); s, 2H), 4.76($H^{5'}$; s, 1H), 4.50 (NH_2(tren); s, 2H); δ_C (DMSO-d_6) 178.2, 170.5, 166.4, 163.6, 162.5, 162.0, 81.1, 75.9, 62.9, 58.6, 44.6}.

Caution: In general, perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with great care.

Crystallography. Crystal data for [Co(Hatuc-atuc)(tren)]ClO_4·$2.5H_2O$ **3b** were collected on a Rigaku AFC-5R diffractometer with graphite-monochromated Mo-$K\alpha$ radiation (λ = 0.71069 Å); $C_{14}H_{29}ClCoN_{10}O_{8.5}S_2$, Mw = 631.95, crystal size 0.25 × 0.20 × 0.10 mm; T = 23 °C; monoclinic, space group $P2/c$ (No. 13), a = 9.830(2), b = 14.562(3), c = 16.973(2) Å, β = 92.14(2)°, Z = 4, V = 2427.8(8) $Å^3$, D_c = 1.729 g cm^{-3}, $F(000)$ = 1308. Of the 6165 reflections, 5902 were unique ($R_{int.}$ = 0.050). Reflection data were collected for both Lorentz and polarization effects and an empirical absorption correction was applied (transmission factors ranging from 0.7861 to 0.8999). Final $R1$ = 0.067 for 3035 reflections with $I > 2\sigma(I)$ (336 parameters) and $wR2$ = 0.148 [$w = 1/\sigma^2(F_o^2)$] for all reflections. The half water of crystallization indicates that one water occupies two sites with occupancy = 0.5 which are related by a C_2 axis. The oxygen atoms of ClO_4^- and O(53) were refined isotropically due to disorder and the rest of the nonhydrogen atoms were refined anisotropically. H(13) atom was refined isotropically and the three hydrogen atoms of $2.5H_2O$ were located but not refined. The rest of the hydrogen atoms were located on the calculated positions. Refinements were carried out by a full-matrix least squares method based on F^2. All calculations were performed using the teXsan[6] crystallographic software package.

Measurements. UV/vis absorption spectra were measured with a Hitachi 330 spectrophotometer, ^1H and ^{13}C NMR spectra with a JEOL JNM-GSX-400 spectrometer in $(CD_3)_2SO$ at 30 °C.

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5 Detail mechanism due to charcoal is still unsolved.

6 TEXSAN-TEXRAY Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1985 & 1992.