An Unusual Dimerization of 6-Amino-2-thiouracilate in a Cobalt(III) Complex†

Kazuaki Yamanari,* Makiko Kida, Masahiro Yamamoto, Takashi Fujihara, Akira Fuyuhiro and Sumio Kaizaki
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

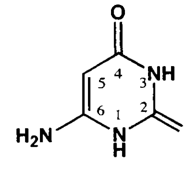
Thermal reaction between *trans*-[CoCl$_2$(en)$_2$]Cl (en = ethane-1,2-diamine), H$_2$atuc (6-amino-2-thiouracil) and NaOH in the presence of activated charcoal produced two red complexes **1** and **2**. The crystal structures of complexes **1** and **2** were determined from 5090 and 4567 reflections to R = 0.048 (R' = 0.052) and 0.055 (0.068), respectively. Complex **1** has the composition [Co(atuc)(en)$_2$]$^+$ where atuc co-ordinates through atoms 2-S and 3-N. Complex **2** has an unusual composition [Co(HL)(en)$_2$]$^+$ {H$_3$L = 6-amino-5-[6-amino-4-oxo-(1*H*)-pyrimidin-2-yl]thio-2,3-dihydro-2-thioxo-(1*H*)-pyrimidin-4-one}: a new bond is formed between the 5-carbon atom of the co-ordinated atuc and the 2-sulfur atom of an unco-ordinated atuc, that is the atuc is dimerized. This complex has self-associated double intermolecular hydrogen bonds in the crystals in addition to an intramolecular hydrogen bond.

The co-ordination chemistry of heterocyclic thione donors is interesting from a biological and pharmaceutical viewpoint.[1] As part of our studies on the co-ordination modes of thioderivatives of the constituent bases of nucleic acids, we attempted the preparation of cobalt(III) complexes containing 6-amino-2-thiouracil [H$_2$atuc = 6-amino-2,3-dihydro-2-thioxo-(1*H*)-pyrimidin-4-one]. This compound is very intriguing because it has characteristics of both 2-thiouracil [H$_2$tuc = 2,3-dihydro-2-thioxo-(1*H*)-pyrimidin-4-one] and of 2-thiocytosine (Hapymt = 4-amino-2,3-dihydropyrimidine-2-thione) and the stereochemistries of tuc[2] and apymt[3] are significantly different from each other.

Two methods were employed, thermal and photochemical, which gave different products. Only the thermal reaction of *trans*-[CoCl$_2$(en)$_2$]Cl (en = ethane-1,2-diamine) and H$_2$atuc in the presence of activated charcoal gave an unusual red cobalt(III) complex [Co(HL)(en)$_2$]$^+$ {H$_3$L = 6-amino-5-[6-amino-4-oxo-(1*H*)-pyrimidin-2-yl]thio-2,3-dihydro-2-thioxo-(1*H*)-pyrimidin-4-one} as well as [Co(atuc)(en)$_2$]$^+$. Here we describe the unique reactivity of H$_2$atuc and the characterization of the resultant complexes by elemental analysis, UV/VIS, ^{1}H and ^{13}C NMR spectroscopy and crystal-structure analysis.

Experimental

Thermal Preparation of [Co(atuc)(en)$_2$]Cl **1** *and* [Co(HL)(en)$_2$]Cl **2**.—An aqueous solution (100 cm^3) of *trans*-[CoCl$_2$(en)$_2$]Cl, H$_2$atuc and NaOH (mole ratio = 1 : 1 : 1) was heated in the presence of activated charcoal at 70 °C for 2 h to give a red solution. The charcoal was removed by filtration and the filtrate poured onto a column of cation exchanger (SP-Sephadex C-25, Na$^+$ form; 4 × 40 cm). Elution with 0.1 mol dm^{-3} NaCl gave three coloured bands, red (**1**, yield 51%), red (**2**, 6.9%) 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 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 **1** {Found: C, 25.95; H, 5.50; N, 26.40. Calc. for [Co(atuc)(en)$_2$]Cl·H$_2$O, C$_8$H$_{21}$ClCoN$_7$O$_2$S: C, 25.70; H, 5.65; N, 26.25. Found: C, 22.15; H, 4.75; N, 22.35. Calc. for [Co(atuc)(en)$_2$]ClO$_4$·H$_2$O, C$_8$H$_{21}$ClCoN$_7$O$_6$S: C, 21.95; H, 4.85; N, 22.40%}: UV/VIS (water) λ_{max} 498 (ε = 138), 360 (sh, 240), 293 (sh, 8800), 270 (12 500), 233 (sh, 28 400) and 209 nm (39 800 dm^3 mol^{-1} cm^{-1}); ^{1}H NMR (D$_2$O) δ 7.50 (s, 1 H, NH$_2$ of en) and 4.98 (s, 1 H, H^5); ^{13}C NMR (D$_2$O) δ 44.8, 45.7, 45.8, 46.6, 85.8, 164.9, 176.7 and 178.9. Complex **2** {Found: C, 26.20; H, 5.10; N, 25.25. Calc. for [Co(HL)(en)$_2$]Cl·3H$_2$O, C$_{12}$H$_{28}$ClCoN$_{10}$O$_5$S$_2$: C, 26.15; H, 5.10; N, 25.40%}: UV/VIS (water) λ_{max} 501 (ε = 141), 360 (sh, 280), 300 (sh, 15 400), 265 (sh, 26 500), 243 (sh, 28 700) and 215 nm (52 200 dm^3 mol^{-1} cm^{-1}); ^{1}H NMR [(CD$_3$)$_2$SO] δ 9.87 (s, 1 H, N$^{1'}$H), 7.60 (s, 1 H, NH$_2$ of en), 6.36 (s, 2 H, NH$_2$), 6.27 (s, 2 H, NH$_2$) and 4.76 (s, 1 H, H$^{5'}$); ^{13}C NMR [(CD$_3$)$_2$SO] δ 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.



H$_2$atuc

CAUTION: In general, perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with great care. The present complexes ignite in a Bunsen-burner flame, but are not hazardous in solutions and upon normal treatment of the solid.

Several thermal experiments were undertaken to reveal the factors which affect the yield of complex **2**. The results are collected in Table 6.

Photochemical Preparation.—The ligand H$_2$atuc (1.61 g, 10^{-2} mol) was suspended in warm water (200 cm^3) and adjusted to pH 8–9 by adding aqueous NaOH solution. To this solution was added *rac*-[Co(en)$_3$]Cl$_3$ (3.46 g, 10^{-2} mol) and the solution was divided into eight portions in quartz reaction tubes (30 cm^3) through which dinitrogen gas was bubbled for 20 min. Irradiation of the eight reaction tubes, with an Toshiba 500 W

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

halogen lamp with no filter, was carried out for 3.5 h to give red solutions. Chromatography revealed complex **1** (yield 56%) and the yellow starting material but not **2**.

Crystal Structure Determinations of [Co(atuc)(en)$_2$][ClO$_4$]·H$_2$O **1** *and* [Co(HL)(en)$_2$][ClO$_4$]·3H$_2$O **2**.—Both crystals were grown from aqueous solutions at room temperature: a red prismatic crystal (0.20 × 0.10 × 0.25 mm) for complex **1** and a red lens-like crystal (0.20 × 0.15 × 0.25 mm) for **2**. Diffraction data were collected at 23 °C on a Rigaku AFC5R diffractometer with the ω-scan technique and graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å). Crystallographic data for both complexes are listed in Table 1. Of the 10 803 reflections measured ($1.5 \leqslant \theta \leqslant 30.0°$) for complex **1** 10 534 were unique and of the 8064 reflections measured ($1.5 \leqslant \theta \leqslant 30.0°$) for **2** 7535 were unique. The structure was solved by direct methods. The final cycle of block-diagonal-matrix least-squares refinements was based on 5090 and 4567 observed reflections [$I > 3.00\sigma(I)$] and 635 and 405 variable parameters for **1** and **2**, respectively. The final R (R') values were 0.048 (0.052) for complex **1** and 0.055 (0.068) for **2**. All calculations were performed with the TEXSAN[4] crystallographic software package. The analysis was performed at the X-Ray Diffraction Service of the Department of Chemistry.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters, and remaining bond lengths and angles.

Measurements.—The UV/VIS absorption spectra were measured with a Hitachi 330 spectrophotometer, proton and ^{13}C NMR spectra with JEOL JNM-GSX-270 and GSX-400 spectrometers in D$_2$O and/or (CD$_3$)$_2$SO.

Results and Discussion

Characterization and Crystal Structure of [Co(atuc)(en)$_2$]$^+$ **1**.—Since 6-amino-2-thiouracil is an unsymmetrical ambidentate compound, N,S co-ordination to a metal ion generates linkage isomerism depending upon the 1,2 or the 2,3 co-ordination. It has been found that bis(ethane-1,2-diamine)-cobalt(III) complexes with tuc or its derivatives adopt 2,3 co-ordination without exception and there is a characteristic intramolecular hydrogen bond between the 4-oxygen atom and one of NH$_2$ (en) protons.[2] On the other hand, the apymt complex favours 1,2 co-ordination, the 4-amino group being remote from the two en chelate rings.[3]

In the present system two red complexes **1** and **2** were obtained. The first d–d absorption band of **1** appears at 498 nm (ε = 138 dm^3 mol^{-1} cm^{-1}) and an intense sulfur-to-metal charge-transfer (c.t.) band appears at 270 nm (ε = 12 500 dm^3 mol^{-1} cm^{-1}) (Fig. 1). The shoulder at 293 nm (ε = 8800 dm^3 mol^{-1} cm^{-1}) seems to be an intraligand transition of atuc because the anion of atuc exhibits a similar strong band at 290 nm (ε = 10 100 dm^3 mol^{-1} cm^{-1}). The absorption spectral pattern is characteristic of CoN$_5$S type complexes containing one thionato group.[2,3,5,6] Complex **1** showed eight ^{13}C NMR signals, four in the atuc chemical shift region and four in the en region, and hence assigned to [Co(atuc)(en)$_2$]$^+$. In the ^{1}H NMR spectrum one amine signal of the en is located at exceptionally low 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 as found in analogous complexes.[2] Such a bond is only possible for 2,3 co-ordination.

The crystal data, atomic parameters and bond distances and angles of complex **1** are listed in Tables 1, 2 and 3, respectively. Each unit cell has two kinds of Δ (or Λ) cations which are structurally similar but crystallographically independent (molecules A and B in Table 3). Fig. 2 shows the labelled ORTEP[7] drawing of molecule A. The discussion below concerns mainly molecule A. Complex **1** has a distorted-

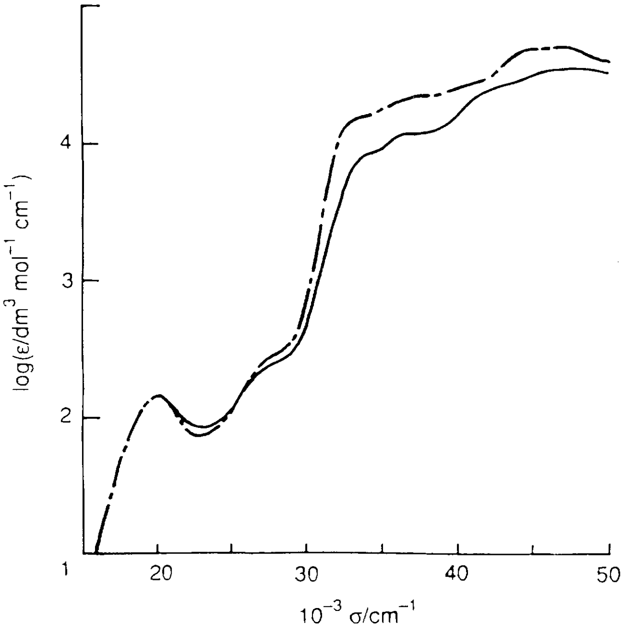


Fig. 1 The UV/VIS absorption spectra of complexes **1** (———) and **2** (- — - —)

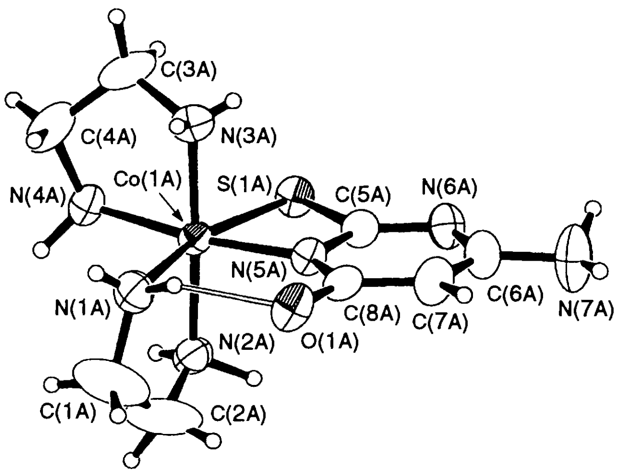


Fig. 2 An ORTEP drawing of the [Co(atuc)(en)$_2$]$^+$ cation **1**

Table 1 Crystallographic data for [Co(atuc)(en)$_2$]ClO$_4$·H$_2$O **1** and [Co(HL)(en)$_2$]ClO$_4$·3H$_2$O **2**

	1	**2**
Formula	C$_8$H$_{21}$ClCoN$_7$O$_6$S	C$_{12}$H$_{28}$ClCoN$_{10}$O$_9$S$_2$
M	437.74	614.94
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/a$	$P2_1/c$
a/Å	19.982(3)	7.25(1)
b/Å	8.403(2)	29.390(8)
c/Å	22.193(2)	11.930(6)
β/°	114.932(7)	98.66(7)
U/Å^3	3379.2(8)	2513(4)
Z	8	4
D_c/g cm^{-3}	1.721	1.625
F(000)	1808	1272
μ(Mo-Kα)/cm^{-1}	13.31	10.07
R^a	0.048	0.055
R'^b	0.052	0.068

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$, $w = 1/\sigma^2|F_o|$.

Table 2 Positional parameters for $[Co(atuc)(en)_2]ClO_4 \cdot H_2O$ **1**

Atom	x	y	z
Co(1A)	0.383 40(3)	0.136 89(7)	0.056 51(3)
S(1A)	0.261 76(6)	0.185 3(1)	−0.012 77(6)
O(1A)	0.452 9(2)	−0.167 6(4)	−0.000 6(2)
N(1A)	0.481 9(2)	0.042 3(5)	0.105 9(2)
N(2A)	0.352 1(2)	−0.003 4(5)	0.110 3(2)
N(3A)	0.416 7(2)	0.281 3(5)	0.006 5(2)
N(4A)	0.403 9(2)	0.313 4(5)	0.119 3(2)
N(5A)	0.353 1(2)	−0.014 5(4)	−0.015 2(2)
N(6A)	0.238 1(2)	−0.040 5(5)	−0.108 2(2)
N(7A)	0.220 7(3)	−0.240 1(7)	−0.184 9(2)
C(1A)	0.481 1(4)	−0.063(1)	0.158 4(4)
C(2A)	0.410 8(4)	−0.115(1)	0.146 2(4)
C(3A)	0.420 9(3)	0.445 7(6)	0.032 3(3)
C(4A)	0.449 2(3)	0.434 3(7)	0.106 0(3)
C(5A)	0.283 5(2)	0.026 6(6)	−0.051 9(2)
C(6A)	0.269 3(3)	−0.161 9(7)	−0.128 6(2)
C(7A)	0.340 9(3)	−0.208 0(6)	−0.095 3(3)
C(8A)	0.386 5(2)	−0.133 3(6)	−0.035 5(2)
Co(1B)	0.166 12(3)	0.360 35(7)	0.554 08(3)
S(1B)	0.225 95(6)	0.318 1(1)	0.486 77(6)
O(1B)	0.045 1(2)	0.669 7(4)	0.499 0(2)
N(1B)	0.110 3(2)	0.446 1(5)	0.601 9(2)
N(2B)	0.245 3(2)	0.503 0(5)	0.611 2(2)
N(3B)	0.087 7(2)	0.216 8(5)	0.500 3(2)
N(4B)	0.202 9(2)	0.181 3(5)	0.616 2(2)
N(5B)	0.131 3(2)	0.515 3(4)	0.484 2(2)
N(6B)	0.161 6(2)	0.547 8(5)	0.392 2(2)
N(7B)	0.108 5(3)	0.746 0(6)	0.316 9(2)
C(1B)	0.158 3(3)	0.546 3(7)	0.658 2(3)
C(2B)	0.212 3(3)	0.626 8(7)	0.638 0(3)
C(3B)	0.107 5(3)	0.051 8(6)	0.522 4(3)
C(4B)	0.145 0(3)	0.055 5(7)	0.596 0(3)
C(5B)	0.167 7(2)	0.477 9(5)	0.447 3(2)
C(6B)	0.111 6(2)	0.668 7(6)	0.371 6(2)
C(7B)	0.069 6(2)	0.713 0(6)	0.405 1(2)
C(8B)	0.079 6(2)	0.637 2(5)	0.464 1(2)
Cl(1)	0.495 54(8)	0.355 8(2)	0.308 80(7)
O(11)	0.479 1(3)	0.494 8(7)	0.267 0(3)
O(12)	0.571 1(3)	0.351(1)	0.344 1(4)
O(13)	0.463 8(4)	0.223 7(7)	0.270 1(3)
O(14)	0.468 3(4)	0.380 0(9)	0.356 8(3)
Cl(2)	0.329 88(8)	0.345 9(2)	0.815 55(7)
O(15)	0.279 6(3)	0.372 3(8)	0.842 6(3)
O(16)	0.307 7(4)	0.218 8(8)	0.770 5(3)
O(17)	0.327 9(4)	0.480(1)	0.776 5(3)
O(18)	0.399 9(3)	0.328(1)	0.863 2(3)
O(71)	0.140 7(4)	0.201(1)	0.730 7(3)
O(72)	0.620 1(6)	0.163(2)	0.238 7(5)

Table 3 Selected bond distances (Å) and angles (°) of $[Co(atuc)(en)_2]ClO_4 \cdot H_2O$ **1**

Co(1A)–S(1A)	2.299(1)	Co(1B)–S(1B)	2.300(2)
Co(1A)–N(1A)	1.971(4)	Co(1B)–N(1B)	1.971(5)
Co(1A)–N(2A)	1.958(5)	Co(1B)–N(2B)	1.958(5)
Co(1A)–N(3A)	1.942(5)	Co(1B)–N(3B)	1.939(4)
Co(1A)–N(4A)	1.957(4)	Co(1B)–N(4B)	1.962(4)
Co(1A)–N(5A)	1.925(4)	Co(1B)–N(5B)	1.917(4)
S(1A)–C(5A)	1.744(5)	S(1B)–C(5B)	1.751(4)
O(1A)–C(8A)	1.257(5)	O(1B)–C(8B)	1.266(7)
N(5A)–C(5A)	1.329(5)	N(5B)–C(5B)	1.341(7)
N(5A)–C(8A)	1.378(7)	N(5B)–C(8B)	1.388(6)
N(6A)–C(5A)	1.321(5)	N(6B)–C(5B)	1.315(7)
N(6A)–C(6A)	1.367(7)	N(6B)–C(6B)	1.355(8)
N(7A)–C(6A)	1.384(6)	N(7B)–C(6B)	1.355(8)
C(6A)–C(7A)	1.361(7)	C(6B)–C(7B)	1.387(8)
C(7A)–C(8A)	1.402(6)	C(7B)–C(8B)	1.392(7)
S(1A)–Co(1A)–N(1A)	165.7(1)	S(1B)–Co(1B)–N(1B)	166.6(1)
S(1A)–Co(1A)–N(5A)	71.9(1)	S(1B)–Co(1B)–N(5B)	72.0(1)
N(1A)–Co(1A)–N(2A)	85.3(2)	N(1B)–Co(1B)–N(2B)	85.0(2)
N(2A)–Co(1A)–N(3A)	177.6(2)	N(2B)–Co(1B)–N(3B)	178.1(2)
N(3A)–Co(1A)–N(4A)	85.1(2)	N(3B)–Co(1B)–N(4B)	85.5(2)
N(4A)–Co(1A)–N(5A)	171.2(1)	N(4B)–Co(1B)–N(5B)	171.9(2)
Co(1A)–S(1A)–C(5A)	77.5(1)	Co(1B)–S(1B)–C(5B)	77.8(2)
Co(1A)–N(5A)–C(5A)	102.6(3)	Co(1B)–N(5B)–C(5B)	103.2(3)
C(5A)–N(5A)–C(8A)	120.9(4)	C(5B)–N(5B)–C(8B)	119.9(4)
C(5A)–N(6A)–C(6A)	113.9(4)	C(5B)–N(6B)–C(6B)	114.4(5)
S(1A)–C(5A)–N(5A)	108.0(3)	S(1B)–C(5B)–N(5B)	107.0(3)
N(5A)–C(5A)–N(6A)	126.3(5)	N(5B)–C(5B)–N(6B)	126.9(4)
N(6A)–C(6A)–C(7A)	123.7(4)	N(6B)–C(6B)–C(7B)	122.9(5)
C(6A)–C(7A)–C(8A)	120.0(5)	C(6B)–C(7B)–C(8B)	120.2(4)
N(5A)–C(8A)–C(7A)	115.0(4)	N(5B)–C(8B)–C(7B)	115.6(5)

octahedral structure: the angle N(2A)–Co(1A)–N(3A) is 177.6(2)° whereas S(1A)–Co(1A)–N(1A) and N(4A)–Co(1A)–N(5A) are 165.7(1) and 171.2(1)°, respectively. The crystal-structure analysis confirms that **1** adopts 2-S, 3-N co-ordination. The bite angle S(1A)–Co(1A)–N(5A) of the atuc, 71.9(1)°, is almost the same as the 72.4(1)° in $[Co(mpymt)(en)_2][ClO_4]_2$ (mpymt = 4-methylpyrimidine-2-thionate)[5] and 72.7(2)° in $[Co(tuc)(en)_2]ClO_4$.[2]

In the present complex an intramolecular hydrogen bond was found between O(1A) and N(1A)–H of en. The N ··· O distance 2.806(6) Å is shorter than the sum of the van der Waals radii (N–H ··· O 2.90 Å).[8] The en chelate ring involved in the hydrogen bond adopts an ob conformation (where the C–C bond of the en ligand is *oblique* to the pseudo-C_3 axis),[9] which results in one of the NH_2 protons being in a suitable position for hydrogen bonding with the 4-oxygen of the atuc. A similar intramolecular hydrogen bond N–H ··· O has been found in the adjacent isomer of $[Co(tuc)(en)_2]ClO_4$ where the en chelate ring also adopts an ob conformation.[2] This bond exists even in solutions such as D_2O and $(CD_3)_2SO$ as described above.

In the pyrimidine ring the two C–N bond distances C(5A)–N(5A) and C(5A)–N(6A) [1.329(5) and 1.321(5) Å] are appreciably shorter than the other two bonds [1.367(7) and 1.378(7) Å], and C(6A)–C(7A) [1.361(7) Å] is also shorter than C(7A)–C(8A) [1.402(6) Å]. That is, the four bonds C(5A)–N(5A), C(5A)–N(6A), C(6A)–C(7A) and C(8A)–O(1A) have localized double-bond character. The same situation is found for the tuc[2] and dtuc (H_2dtuc = 1,3-dihydro-2,4-dithioxopyrimidine)[6] complexes.

The bond distances and angles of molecule B are similar to those of A. The C(6B)–N(7B) distance is slightly shorter than C(6A)–N(7A) (Table 3).

Characterization and Crystal Structure of $[Co(HL)(en)_2]^+$ **2**.—The first d–d absorption band of complex **2** appears at 501 nm (ε = 141 $dm^3\ mol^{-1}\ cm^{-1}$) and there is an intense c.t. band at *ca.* 270 nm (ε = 26 500 $dm^3\ mol^{-1}\ cm^{-1}$). Thus complex **2** has a CoN_5S chromophore like that of **1**.[2,3,5,6] Complex **2** showed twelve ^{13}C NMR signals, eight in the atuc chemical shift region and four in the en region, which means that it contains one bis(ethane-1,2-diamine) unit and two atuc units. Fig. 3 shows the ^1H NMR spectrum. Since this complex contains two atuc ligands two amino signals are observed at δ 6.36 (2 H) and 6.27 (2 H) but only one proton signal due to H^5 was observed. These facts indicate the participation of the 5-carbon in bond formation. The amine signal of en at δ 7.60 indicates the existence of an intramolecular hydrogen bond between the 4-oxygen atom and one of the NH_2 (en) protons and hence complex **2** also adopts 2,3 co-ordination. Its molar absorption coefficients are considerably larger than those of complex **1** only in the UV region (Fig. 1). This is relevant to the presence of two atuc units.

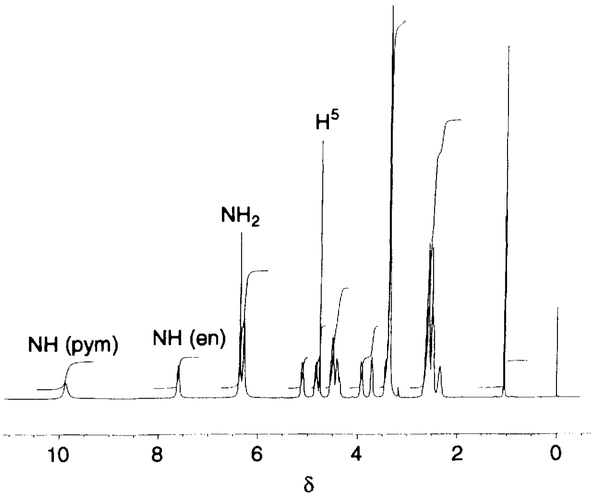


Fig. 3 Proton NMR spectrum of complex **2**

Table 4 Positional parameters for [Co(HL)(en)$_2$]ClO$_4$·3H$_2$O **2**

Atom	*x*	*y*	*z*
Co(1)	0.157 31(8)	0.354 19(2)	0.187 47(5)
S(1)	−0.146 0(2)	0.357 76(4)	0.214 6(1)
S(2)	−0.039 8(2)	0.483 05(4)	−0.180 1(1)
O(1)	0.235 8(4)	0.423 2(1)	−0.032 8(3)
O(2)	−0.079 5(6)	0.453 2(1)	−0.586 2(3)
N(1)	0.396 2(6)	0.356 8(2)	0.130 7(4)
N(2)	0.103 9(7)	0.303 9(2)	0.082 7(4)
N(3)	0.225 7(7)	0.403 4(2)	0.296 3(3)
N(4)	0.243 4(7)	0.313 2(2)	0.313 6(4)
N(5)	0.032 8(5)	0.396 1(1)	0.078 0(3)
N(6)	−0.286 1(5)	0.418 7(1)	0.054 3(3)
N(7)	−0.406 4(6)	0.465 7(2)	−0.088 7(4)
N(8)	−0.065 6(6)	0.461 1(1)	−0.395 6(3)
N(9)	−0.150 2(6)	0.403 8(1)	−0.277 9(3)
N(10)	−0.241(1)	0.334 4(2)	−0.350 2(5)
C(1)	0.417 8(8)	0.317 6(2)	0.057 5(5)
C(2)	0.229(1)	0.305 8(3)	−0.002 7(6)
C(3)	0.332(1)	0.384 8(3)	0.401 7(5)
C(4)	0.260(1)	0.339 0(3)	0.421 8(6)
C(5)	−0.140 7(6)	0.395 6(2)	0.103 4(3)
C(6)	−0.255 8(6)	0.445 1(1)	−0.034 8(3)
C(7)	−0.078 8(6)	0.449 0(1)	−0.066 3(3)
C(8)	0.074 1(6)	0.423 4(1)	−0.009 2(3)
C(9)	−0.091 8(6)	0.444 2(2)	−0.294 0(4)
C(10)	−0.185 0(8)	0.376 6(2)	−0.371 2(4)
C(11)	−0.165 3(8)	0.391 5(2)	−0.478 8(4)
C(12)	−0.103 8(7)	0.435 1(2)	−0.493 6(4)
Cl	0.734 6(2)	0.251 12(5)	0.378 4(1)
O(3)	0.759 0(7)	0.203 6(1)	0.398 0(4)
O(4)	0.902 5(8)	0.273 7(2)	0.397 4(7)
O(5)	0.622(1)	0.269 6(3)	0.452 5(7)
O(6)	0.635(1)	0.257 5(2)	0.271 9(6)
O(11)	0.563 7(6)	0.455 6(1)	0.247 7(3)
O(12)	0.193(1)	0.287 9(2)	−0.301 7(5)
O(13)	0.350(1)	0.378 4(3)	−0.235 3(6)

Crystallization from an aqueous perchlorate solution of complex **2** produced crystals with apparently two kinds of morphologies: square-columnar crystals appeared first and then lens-like crystals. Both types exhibited the same ^{13}C NMR and infrared spectra. X-Ray diffraction analysis showed that the crystals had the same structure. Crystal data, atomic parameters and bond distances and angles of complex **2** are listed in Tables 1, 4 and 5, respectively. Fig. 4 shows the labelled ORTEP[7] drawing of complex **2**. Surprisingly, complex **2** has a novel dimeric atuc ligand: a new bond is formed between the 5-carbon atom of one and the 2′-sulfur of another atuc. Co-ordination occurs through the 2-S and 3-N donor atoms and an intramolecular hydrogen bond exists between O(1) and N(1)H (en) [N(1)···O(1) 2.878(6) Å and N(1)–H···O(1) 146.8°] as found in complex **1**. The en chelate ring involving the hydrogen bond adopts the ob conformation.[9]

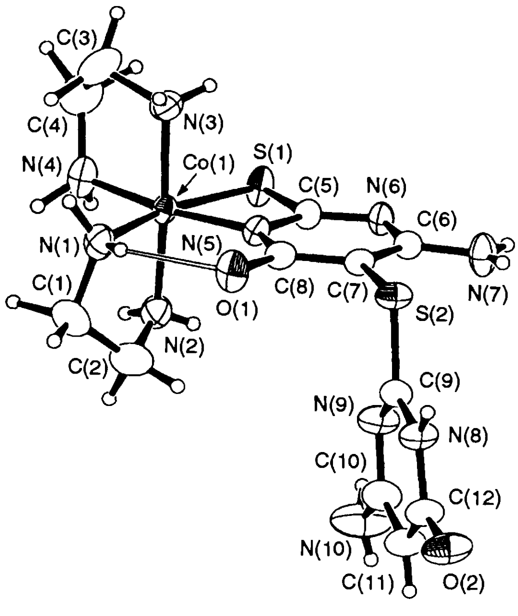


Fig. 4 An ORTEP drawing of the [Co(HL)(en)$_2$]$^+$ cation **2**

Table 5 Selected bond distances (Å) and angles (°) of [Co(HL)-(en)$_2$]ClO$_4$·3H$_2$O **2**

Co(1)–S(1)	2.273(3)	Co(1)–N(1)	1.954(5)
Co(1)–N(2)	1.937(5)	Co(1)–N(3)	1.957(4)
Co(1)–N(4)	1.955(5)	Co(1)–N(5)	1.919(4)
S(1)–C(5)	1.736(4)	S(2)–C(7)	1.745(4)
S(2)–C(9)	1.771(5)	O(1)–C(8)	1.246(5)
O(2)–C(12)	1.262(5)	N(5)–C(5)	1.337(5)
N(5)–C(8)	1.382(5)	N(6)–C(5)	1.314(5)
N(6)–C(6)	1.360(5)	N(7)–C(6)	1.327(6)
N(8)–C(9)	1.349(5)	N(8)–C(12)	1.389(6)
N(9)–C(10)	1.362(6)	N(10)–C(10)	1.341(7)
C(6)–C(7)	1.396(6)	C(7)–C(8)	1.425(6)
C(10)–C(11)	1.383(6)	C(11)–C(12)	1.379(7)
S(1)–Co(1)–N(1)	167.1(2)	S(1)–Co(1)–N(5)	72.6(1)
N(1)–Co(1)–N(2)	84.7(2)	N(2)–Co(1)–N(3)	176.6(2)
N(3)–Co(1)–N(4)	85.7(2)	N(4)–Co(1)–N(5)	169.2(2)
Co(1)–S(1)–C(5)	77.7(2)	C(7)–S(2)–C(9)	100.8(2)
Co(1)–N(5)–C(5)	101.6(3)	C(5)–N(5)–C(8)	119.6(4)
C(5)–N(6)–C(6)	115.4(4)	C(9)–N(8)–C(12)	121.2(4)
C(9)–N(9)–C(10)	116.4(4)	N(1)–C(1)–C(2)	107.3(5)
N(3)–C(3)–C(4)	108.8(5)	S(1)–C(5)–N(5)	108.0(3)
N(5)–C(5)–N(6)	127.8(4)	N(6)–C(6)–C(7)	121.4(4)
C(6)–C(7)–C(8)	120.6(4)	O(1)–C(8)–N(5)	119.0(4)
O(1)–C(8)–C(7)	125.8(4)	N(5)–C(8)–C(7)	115.2(4)
N(8)–C(9)–N(9)	124.6(4)	N(9)–C(10)–C(11)	122.7(4)
C(10)–C(11)–C(12)	119.6(5)	O(2)–C(12)–N(8)	118.0(4)
O(2)–C(12)–C(11)	126.5(4)	N(8)–C(12)–C(11)	115.5(4)

The structures of the two pyrimidine rings of complex **2** are considerably different from each other. In the co-ordinated pyrimidine ring the three bonds C(5)–N(6), C(6)–C(7) and C(8)–O(1) have localized double-bond character as found in **1**. The bond lengths of the second ring are a little different from those of the co-ordinated ring. Protonation occurs at N(8) and the atoms O(2) and N(8)H participate in novel intermolecular hydrogen bonds to the adjacent complex. The second pyrimidine ring is almost perpendicular to the co-ordinated pyrimidine ring: the torsion angles C(6)–C(7)–S(2)–C(9),

Table 6 Yields of complexes **1** and **2** in various experiments

Experiment	Mole ratio *trans*-$[CoCl_2(en)_2]Cl$	H_2atuc	NaOH	Activated charcoal[a]	O_2[b]	Yield of complex (%) **1**	**2**
1	1	1	1	+	−	51	6.9
2	1	2	2	+	−	56	18
3	1	2	2	+	+	32	40
4	1	2	2	+	=	70	5.3
5	1	2	2	−	+	88	0
6	1	2	4	+	−	15	0

[a] +, Presence of activated charcoal; −, absence of activated charcoal. [b] +, Air-bubbled; −, open to the atmosphere; =, deoxygenated by dinitrogen.

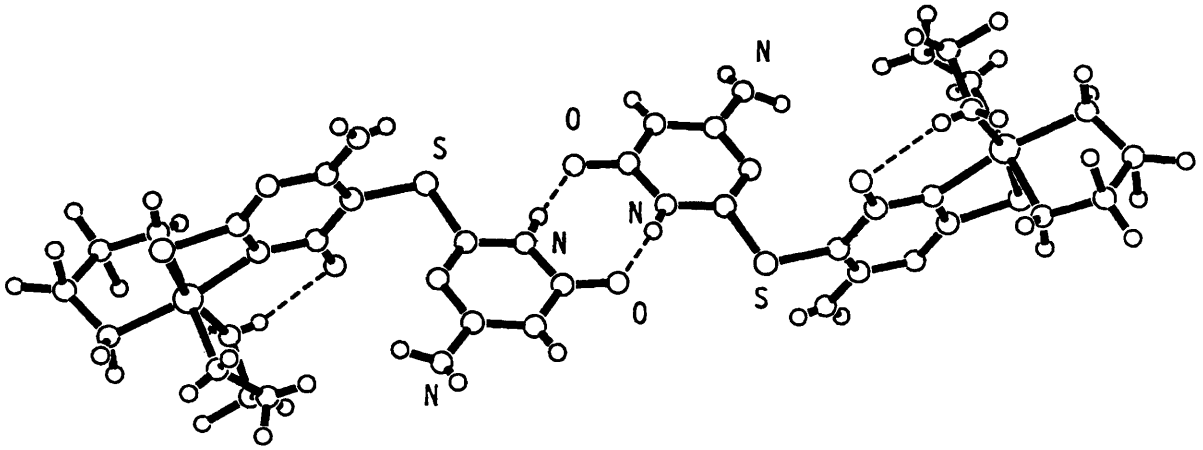
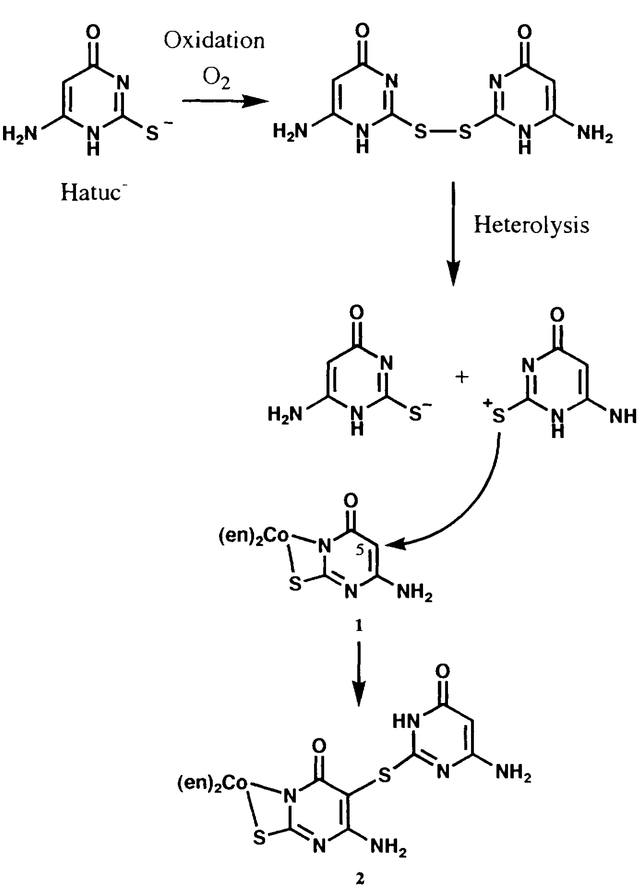


Fig. 5 Linear intermolecular hydrogen bonds in $[Co(HL)(en)_2]^+$



Scheme 1 Possible mechanism of formation of $[Co(HL)(en)_2]^+$

C(8)–C(7)–S(2)–C(9), C(7)–S(2)–C(9)–N(8) and C(7)–S(2)–C(9)–N(9) are −87.2(4), 89.8(4), −177.4(4) and 3.1(5)°, respectively.

Intermolecular Hydrogen bonds in $[Co(HL)(en)_2]^+$.—An interesting feature of complex **2** concerns the double linear N–H ··· O intermolecular hydrogen bonds (Fig. 5). The self-associated double hydrogen bonds are formed between N(8)H and O(2) of one molecule and O(2) and N(8)H of another. They are related by an inversion centre and in the same plane. The mean deviation from a least-squares plane composed of twelve atoms of the two pyrimidine rings is 0.021 Å. The distances between N(8) and O(2) and the plane are only 0.026(4) and −0.075 Å, respectively. The N(8)H ··· O(2) distance is 2.750(5) Å which is very similar to the values found in nucleic acids.[10] However, the hydrogen-bonding mode of the present complex is of a self-associated type between the same molecules and is different from the modes in nucleic acids. A similar hydrogen bonding has been reported for the dimers of uracil derivatives in $CDCl_3$.[11]

In addition to the above nucleic acid-like contact, another intermolecular interaction exists. A π–π stacking related by an inversion centre is formed between the planes of the two co-ordinated atuc. The C(7) ··· C(7), S(2) ··· C(7) and S(2) ··· C(8) distances are 3.502(8), 3.552(4) and 3.591(5) Å, respectively.

Mechanism of Formation of $[Co(HL)(en)_2]^+$.—In the original thermal reaction between *trans*-$[CoCl_2(en)_2]Cl$, H_2atuc and NaOH (mole ratio = 1 : 1 : 1) in the presence of activated charcoal (experiment 1) the yield of complex **2** was only 6.9%. In order to reveal the mechanism of formation of **2** several other experiments were undertaken and the results are collected in Table 6. As expected from the complex composition a high mole ratio {experiment 2; *trans*-

$[CoCl_2(en)_2]Cl:H_2atuc:NaOH = 1:2:2\}$ raised the yield to 18%. Air oxidation of the same solution (experiment 3) substantially raised the yield to 40%. Under anaerobic conditions (experiment 4) the yield was very low (5.3%) compared with that (18%) in air, though it was not possible completely to remove adsorbed dioxygen from the activated charcoal. These facts mean that dioxygen is essential for the formation of complex **2**. Since the absence of activated charcoal gave no **2** (experiment 5) activated charcoal is also indispensable. An equimolar ratio of hydroxide ion to ligand is necessary but excess of it was harmful for the formation of complex **2** (experiment 6). In the absence of *trans*-$[CoCl_2(en)_2]Cl$, no HL was detected in the ^1H NMR spectrum, which means that the dimeric ligand is formed only by the reaction of co-ordinated atuc.

It is well known that electrophilic substitution occurs at the 5 position in pyrimidine and the presence of functional groups such as OH and/or NH_2 in the 4 and 6 positions elevates the reactivity of the 5 position.[12] The present unusual dimerization may belong to the same category. The above experiments revealed four essential factors for the formation of complex **2**: the prior co-ordination of atuc, activated charcoal, dioxygen and an appropriate amount of OH^-. One possible mechanism is shown in Scheme 1. The disulfide of 6-amino-2-thiouracil may be formed by air oxidation and then heterolytically cleaved. Activated charcoal seems to be relevant to the latter process. The resultant electrophiles attack the 5-carbon of the co-ordinated pyrimidine ring of complex **1** to give **2** with HL. The photochemical experiment, in the absence of activated charcoal and dioxygen, where no complex **2** was formed, is compatible with this scheme.

References

1 E. S. Raper, *Coord. Chem. Rev.*, 1985, **61**, 115; R. E. Handschumacher and D. E. Welch, *The Nucleic Acids*, Academic Press, New York, 1960, vol. 3.
2 K. Yamanari, K. Okusako, Y. Kushi and S. Kaizaki, *J. Chem. Soc., Dalton Trans.*, 1992, 1621.
3 K. Yamanari, M. Yamamoto, M. Kida, T. Fujihara, A. Fuyuhiro and S. Kaizaki, *J. Chem. Soc., Dalton Trans.*, 1993, 1651.
4 TEXAN TEXRAY, Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1985.
5 K. Yamanari, K. Okusako and S. Kaizaki, *J. Chem. Soc., Dalton Trans.*, 1992, 1615.
6 K. Yamanari, Y. Kushi, A. Fuyuhiro and S. Kaizaki, *J. Chem. Soc., Dalton Trans.*, 1993, 403.
7 C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
8 W. C. Hamilton and J. A. Ibers, *Hydrogen Bonding in Solids*, Benjamin, New York, 1968, ch. 5.
9 S. F. Mason, *Molecular Optical Activity and the Chiral Discriminations*, Cambridge University Press, 1982, p. 109.
10 S. Arnott and D. W. Hukins, *J. Mol. Biol.*, 1979, **81**, 93.
11 Y. Kyogoku, R. C. Lord and A. Rich, *J. Am. Chem. Soc.*, 1967, **89**, 496.
12 R. M. Acheson, *An Introduction to the Chemistry of Heterocyclic Compounds*, Wiley, New York, 1976, ch. 8.

Received 22*nd March* 1995; *Paper* 5/01851J