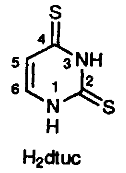
Photochemical Synthesis and Characterization of Linkage Isomers of (2,4-Dithiouracilato-*N*,*S*)bis(ethane-1,2-diamine or propane-1,3-diamine)cobalt(III) Complexes†

Kazuaki Yamanari,* Yoshinori Kushi, Akira Fuyuhiro and Sumio Kaizaki
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

Bis(diamine)cobalt(III) type complexes containing 2,4-dithiouracilate ($dtuc^{2-}$) have been photochemically prepared from robust $[Co(diamine)_3]^{3+}$ [diamine = ethane-1,2-diamine (en) or propane-1,3-diamine (tn)], H_2dtuc and NaOH. Column chromatography yielded two and three linkage isomers of $[Co(dtuc)(en)_2]^+$ and $[Co(dtuc)(tn)_2]^+$, respectively, which were characterized by elemental analysis, UV/VIS absorption and NMR spectroscopy. The crystal structure of $[Co(dtuc)(en)_2]ClO_4$ (main product) was determined from 4952 unique reflections to $R = 0.047$ ($R' = 0.045$): space group *Pa* (monoclinic), $a = 13.394(4)$, $b = 8.819(3)$, $c = 13.813(2)$ Å, $\beta = 102.75(2)°$, and $Z = 4$. The dtuc ligand co-ordinates through the 3-N and 2-S donors and the complex adopts an adjacent linkage form. A characteristic intramolecular hydrogen bond N–H···S [3.210(7) Å] was found between the 4-sulfur atom of the dtuc and an amine proton of en. Proton NMR spectroscopy showed that this hydrogen bond is present even in D_2O and $(CD_3)_2SO$ solutions.

Recently we reported the photochemical synthesis and characterization of bis(ethane-1,2-diamine)cobalt(III) complexes with pyrimidine-2-thionate (pymt) and its derivatives,[1] and 2-thiouracilate (tuc) [2,3-dihydro-2-thioxo-(1*H*)-pyrimidin-4-onate] and related ligands.[2] The results revealed that the stereochemistry of the pymt complexes is very different from that of the tuc complexes. The latter adopt a sterically unfavourable adjacent linkage form, which is stabilized by a characteristic intramolecular hydrogen bond between the 4-oxygen atom of the tuc and one of the amine protons of ethane-1,2-diamine (en).

The presence of two thione sulfur atoms, two imido (>NH) groups, and the ability to co-ordinate in neutral (H_2dtuc) as well as anionic (Hdtuc and $dtuc^{2-}$) forms poses more complex stereochemical possibilities for 2,4-dithiouracil (H_2dtuc). Many metal complexes containing this ligand have been reported so far, but most are polymeric and insoluble in common organic solvents and these characterizations are open to question.[3–5] The only reported crystal structure where $dtuc^{2-}$ functions as a tetradentate bridge is μ-(2,4-dithiouracilato)-bis[bis(η^5-methylcyclopentadienyl)titanium(III)].[6]



H_2dtuc

When 2,4-dithiouracil acts as a four-membered N,S-bidentate ligand three linkage isomers (Fig. 1), one remote isomer **I** with the C^4 substituent group away from the two en chelates and two adjacent isomers **II** and **III** with this group near to them, are possible. There has been no report concerning this linkage isomerism so far. In the present study we describe the photochemical synthesis and characterization of the linkage isomers in the bis(diamine)cobalt(III) complexes containing $Hdtuc^-$ and $dtuc^{2-}$ [diamine = en or propane-1,3-diamine (tn)] based on elemental analysis, UV/VIS absorption, ^1H and ^{13}C NMR spectra and X-ray crystal analysis.

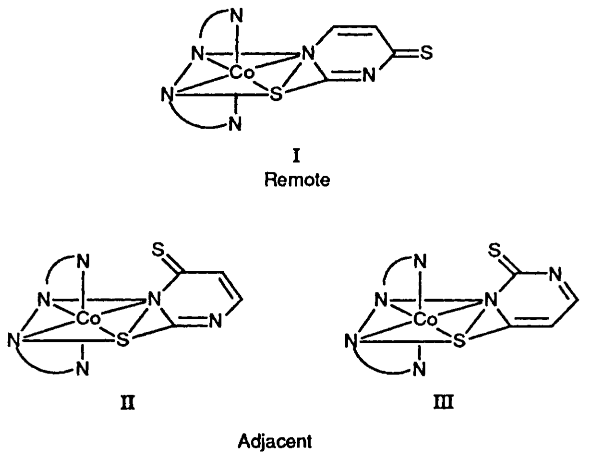


Fig. 1 Three linkage isomers of $[Co(dtuc)(diamine)_2]^+$

Experimental

Preparations.—$[Co(dtuc)(en)_2]^+$ **1** *and* **2**. The compound H_2dtuc (0.56 g, 4.0 mmol) was suspended in warm water (200 cm^3) and the pH adjusted to 8–9 by adding aqueous NaOH solution. To the above solution was added *rac*-$[Co(en)_3]Cl_3$ (1.6 g, 4.0 mmol) and a yellow precipitate, which may be the dithiouracilate salt of $[Co(en)_3]^{3+}$, appeared. This suspension was divided into eight portions in quartz reaction tubes (30 cm^3) and nitrogen gas was bubbled through them for 20 min. Irradiation with an Eikohsha 500 W halogen lamp without a filter was carried out for 3 h, giving dark red solutions with no precipitate. After filtration, the filtrate was poured onto a column of cation exchanger (SP-Sephadex C-25, Na^+ form, 4 × 50 cm). Elution with 0.2 mol dm^{-3} NaCl gave three coloured bands, orange-red (**1**, yield 0.8%), red (**2**, 60%) and yellow, in this order. The third yellow band was the starting material $[Co(en)_3]^{3+}$. The second eluate was concentrated with a vacuum evaporator, and the white precipitate of NaCl was

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

filtered off. By adding $NaClO_4$ to the filtrate the perchlorate salt of complex **2** was obtained and recrystallized from water. Complex **1** could not be isolated because of its low formation ratio. Since the starting material $[Co(en)_3]Cl_3$ was racemic all products were also racemic, which was determined by measuring the circular dichroism (CD) spectrum of each eluate. The formation yield of **1** and **2** were calculated from their absorbances using the molar absorption coefficient $\varepsilon = 109$ $dm^3\ mol^{-1}\ cm^{-1}$ of **2** at 500 nm (Found: C, 22.70; H, 4.40; N, 19.70. Calc. for $[Co(dtuc)(en)_2]ClO_4$, $C_8H_{18}ClCoN_6O_4S_2$ **2**: C, 22.85; H, 4.30; N, 19.95%). UV/VIS: λ_{max}/nm(water) 495, 365 (sh), 310 (sh), 285, 240 (inflection), 222 for **1**; 500 (ε = 109), 390 (inflection), 338 (6250), 292 (14 200), 252 (22 800) and 218 (23 600 $dm^3\ mol^{-1}\ cm^{-1}$) for **2**.

Complex **2** could be thermally obtained in a similar yield by heating the solution (pH 8–9) of $[Co(en)_3]Cl_3$, H_2dtuc, and a catalytic amount of $CoCl_2{\cdot}6H_2O$ (4×10^{-5} mol) at 70 °C for 30 min instead of irradiation.

$[Co(Hdtuc)(en)_2][ClO_4]_2$ **3**. Complex **2** (300 mg) was dissolved in 50% $HClO_4$ solution (10 cm^3) and ethanol–diethyl ether (1:1, 30 cm^3) was added. The mixture was cooled in a refrigerator overnight to give red crystals quantitatively {Found: C, 18.50; H, 3.90; N, 15.80. Calc. for $[Co(Hdtuc)(en)_2][ClO_4]_2{\cdot}0.5H_2O$, $C_8H_{20}Cl_2CoN_6O_{8.5}S_2$: C, 18.10; H, 3.80; N, 15.85%}. UV/VIS: λ_{max}/nm (water) 510 (ε = 109), 400 (inflection), 321 (13 800), 295 (sh, 11 700), 257 (18 000), 230 (21 000) and 210 (22 500 $dm^3\ mol^{-1}\ cm^{-1}$).

Three linkage isomers of $[Co(dtuc)(tn)_2]^+$ **4–6**. The complex *rac*-$[Co(tn)_3]Cl_3$ (1.6 g) and H_2dtuc (0.56 g) were dissolved in water (200 cm^3) with stirring at 60 °C. The solution was divided into eight portions in quartz tubes (30 cm^3) and nitrogen gas was bubbled through them. Irradiation was continued for 12 h to give dark red solutions, and yellow precipitates. After filtration of the precipitates, the filtrate was chromatographed with 0.1 mol dm^{-3} NaCl to give four bands, orange-red (**4**, yield 6%), pink (**5**, 18%), red (**6**, 36%), and orange, in this order, though the second and third bands were partly overlapped. The last orange band was the starting material $[Co(tn)_3]Cl_3$. Each eluate was concentrated with a vacuum evaporator, and the white precipitate of NaCl was filtered off. By standing the filtrate in a refrigerator the chloride salt was obtained and recrystallized from water. Complexes **4** and **5** could not be isolated because of their thermal instability. The formation yields of **4–6** were calculated from their absorbances using the molar absorption coefficient $\varepsilon = 102$ $dm^3\ mol^{-1}\ cm^{-1}$ of **6** at 515 nm {Found: C, 31.10; H, 5.85; N, 21.40. Calc. for $[Co(dtuc)(tn)_2]Cl$, $C_{10}H_{22}ClCoN_6S_2$ **6**: C, 31.20; H, 5.75; N, 21.85%}. UV/VIS: λ_{max}/nm(water) 512, 348 (sh), 312 (sh), 290, 242 (sh), 224 for **4**; 519, 335, 295 (sh), 252 (sh), 232 for **5**; 515 (ε = 102), 336 (6900), 294 (16 300), 257 (27 400) and 224 (26 100 $dm^3\ mol^{-1}\ cm^{-1}$) for **6**.

$[Co(Hdtuc)(tn)_2][ClO_4]_2$ **7**. Complex **6** (500 mg) was dissolved in 50% $HClO_4$ solution (10 cm^3) and ethanol (20 cm^3) was added. The mixture was cooled in a refrigerator to give red crystals quantitatively. This complex is very unstable and decomposes in water in a day and even in the solid state in a week {Found: C, 20.95; H, 4.40; N, 14.60. Calc. for $[Co(Hdtuc)(tn)_2][ClO_4]_2{\cdot}1.5H_2O$, $C_{10}H_{26}Cl_2CoN_6O_{9.5}S_2$ **7**: C, 20.85; H, 4.55; 14.60%}. UV/VIS: λ_{max}/nm(water) 525 (ε = 146), 320 (sh) (15 400), 300 (16 100), 263 (22 900), 237 (27 900) and 210 (sh) (20 300 $dm^3\ mol^{-1}\ cm^{-1}$).

X-Ray Crystal Structure Determination of $[Co(dtuc)(en)_2]ClO_4$ **2**.—*Crystal data.* $C_8H_{18}ClCoN_6O_4S_2$, $M = 420.77$, monoclinic, space group Pa, $a = 13.394(4)$, $b = 8.819(3)$, $c = 13.813(2)$ Å, $\beta = 102.75(2)°$, $U = 1591(1)$ Å^3, $Z = 4$, $D_c = 1.756$ g cm^{-3}, $F(000) = 864$, red prism, dimensions $0.2 \times 0.15 \times 0.07$ mm, μ(Mo-Kα) = 15.21 cm^{-1}.

Data collection and processing. A red crystal, grown by standing a saturated aqueous solution of complex **2** in a refrigerator for several days, was mounted on a glass fibre. All measurements were made on a Rigaku AFC-5R diffractometer with graphite-monochromated Mo-Kα radiation. The data were collected at 23 ± 1 °C using the ω–2θ scan technique to a maximum 2θ of 60°. Of the 5139 reflections collected, 4952 were unique. The structure was solved by the direct method. The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were placed at calculated positions. The final cycle of block-diagonal-matrix least-squares refinements was based on 2413 observed reflections $[F_o^2 > 3\sigma(F_o^2)]$. Redundant data were removed and corrections for decay and absorption were not applied. The final R and R' values were 0.047 and 0.045, respectively $\{R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$; $w = 1/\sigma^2(F_o)\}$. All calculations were performed using the TEXSAN [7] crystallographic software package.

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 and CD spectra with a JASCO J-500 spectropolarimeter. The ^1H and ^{13}C NMR spectra were recorded with JEOL JNM-GSX-270 and JNM-GSX-400 spectrometers in D_2O and $(CD_3)_2SO$.

Results and Discussion

Characterization of $[Co(dtuc)(en)_2]^+$ **1** *and* **2** *and* $[Co(Hdtuc)(en)_2]^{2+}$ **3**.—The column separation of this system gave two red complexes **1** and **2**. Both exhibit the first d–d absorption band near 500 nm [495 for **1** and 500 nm (ε = 109 $dm^3\ mol^{-1}\ cm^{-1}$) for **2**] and an intense sulfur-to-metal charge-transfer (c.t.) band near 290 nm [285 for **1** and 292 nm (ε = 14 200 $dm^3\ mol^{-1}\ cm^{-1}$) for **2**]. These are characteristic for CoN_5S type complexes containing one thionate group.[8] Another intense c.t. band was observed near 350 nm for both complexes. This can be assigned to the intraligand transition of dtuc because the neutral molecule and an anion of 2,4-dithiouracil are known to show intense absorption bands at 361 (ε = 8770) and 360 nm (8900 $dm^3\ mol^{-1}\ cm^{-1}$),[9] respectively. In the ^{13}C NMR spectrum complex **2** gave eight signals, four in the dtuc chemical shift region and four in the en region (Table 1). Elemental analysis of **2** also confirms the formulation $[Co(dtuc)(en)_2]^+$. Therefore, complexes **1** and **2** can be assigned to linkage isomers of $[Co(dtuc)(en)_2]^+$.

The corresponding protonated species $[Co(Hdtuc)(en)_2]^{2+}$ **3** was obtained by recrystallizing complex **2** from 50% $HClO_4$ solution. The first d–d absorption band of this complex is red-shifted by 8 nm compared with that of **2**. Similar red shifts upon protonation have been observed for complexes containing pymt[1] and tuc.[2]

As shown in Fig. 1, three linkage isomers are possible for $[Co(dtuc)(en)_2]^+$ and $[Co(Hdtuc)(en)_2]^{2+}$. Complex **3** was quantitatively obtained from **2** in an acidic medium. Since the reaction is instantaneous it is reasonable to consider that no isomerization occurs during the crystallization and both complexes adopt the same co-ordination mode. Complex **3** showed a new imine proton signal at δ 13.3 and a marked upfield shift of the C^6 carbon signal (*ca.* 14 ppm) compared with **2**. This means that protonation occurs at the 1-nitrogen atom because the large upfield shifts of the α-carbon have been confirmed in pyridine[10] and cobalt(III) complexes with tuc and related ligands.[2] Thus, both complexes **2** and **3** are one of the adjacent isomers **II** and **III**. The final assignment to adjacent **II** was made from the X-ray crystal analysis described below.

In the present preparations the photochemical method was used. As stated elsewhere,[1] the thermal reactions between $[Co(en)_3]Cl_3$ and the thione ligands did not proceed at all even at 80 °C. The advantage of the present method is the non-existence of by-products, and the product control enabled by changing the irradiation time and/or amount of ligand. Since

Table 1 Proton and ^{13}C NMR spectral data (δ)

Complex	Solvent	^1H [a]	^{13}C [b]
2	D_2O	7.575 (d, 1 H, H^6) 6.642 (d, 1 H, H^5)	192.20 (C^4), 180.16 (C^2), 150.18 (C^6), 123.87 (C^5), 47.73, 46.06, 45.83, 44.62 (en)
	$(CD_3)_2SO$	7.410 (d, 1 H, H^6) 6.348 (d, 1 H, H^5)	191.96 (C^4), 179.21 (C^2), 148.63 (C^6), 122.84 (C^5), 46.81, 45.23, 44.71, 43.06 (en)
3	$(CD_3)_2SO$	13.34 (s, 1 H, NH) 7.526 (d, 1 H, H^6) 6.555 (d, 1 H, H^5)	197.49 (C^4), 175.40 (C^2), 134.37 (C^6), 121.64 (C^5), 46.42, 45.22, 44.96, 43.91 (en)
4	$(CD_3)_2SO$	7.498 (d, 1 H, H^6) 5.438 (d, 1 H, H^5)	178.32, 174.01 (C^2 and C^4), 152.92 (C^6), 107.81 (C^5), 41.47, 40.71, 38.32, 38.10, 25.46, 25.27 (tn)
5	$(CD_3)_2SO$	7.738 (s, 1 H, H^6) 5.816 (s, 1 H, H^5)	183.95, 167.46 (C^2 and C^4), 156.41 (C^6), 107.79 (C^5), 42.00, 40.32, 38.45, 38.38, 25.39, 25.12 (tn)
6	D_2O	7.426 (d, 1 H, H^6) 6.476 (d, 1 H, H^5)	191.49 (C^4), 180.27 (C^2), 150.26 (C^6), 124.02 (C^5), 41.19, 40.71, 38.74, 38.43, 26.29, 25.73 (tn)
7 [c]	$(CD_3)_2SO$	13.33 (d, 1 H, NH) 7.706 (t, 1 H, H^6)	194.37 (C^4), 178.48 (C^2), 142.06 (C^6), 113.37 (C^5), 42.00, 38.22, 37.54, 24.88 (tn)

[a] In ppm downfield relative to sodium 4,4-dimethyl-4-silapentane-1-sulfonate (D_2O) or $SiMe_4$ [$(CD_3)_2SO$]. [b] Reference is 1,4-dioxane (δ 67.40) in D_2O and $(CD_3)_2SO$ (δ 39.50) in $(CD_3)_2SO$. [c] One signal is overlapped with the signals of $(CD_3)_2SO$ and the signal at δ 24.88 is twice as intense as the others.

Table 2 Positional parameters for complex **2**

Atom	*x*	*y*	*z*
Co(1)	0	0.1786(1)	0
S(1)	0.0030(2)	0.1860(4)	−0.1644(2)
S(2)	−0.2564(2)	0.1859(3)	0.0618(2)
N(1)	−0.0129(5)	0.1544(9)	0.1375(5)
N(2)	0.0031(6)	−0.0418(8)	−0.0018(6)
N(3)	0.0026(7)	0.3988(8)	0.0091(7)
N(4)	0.1527(6)	0.196(1)	0.0453(5)
N(5)	−0.1398(6)	0.1809(9)	−0.0726(6)
N(6)	−0.1971(7)	0.186(1)	−0.2493(6)
C(1)	0.0004(7)	−0.006(1)	0.1679(7)
C(2)	−0.0445(8)	−0.096(1)	0.0784(8)
C(3)	0.1051(8)	0.453(1)	0.0043(8)
C(4)	0.1804(8)	0.352(1)	0.0723(9)
C(5)	−0.1262(8)	0.184(1)	−0.1686(7)
C(6)	−0.2919(9)	0.186(1)	−0.2320(8)
C(7)	−0.3157(7)	0.191(1)	−0.1433(8)
C(8)	−0.2360(7)	0.186(1)	−0.0548(7)
Co(2)	−0.0225(1)	0.3512(1)	0.4954(1)
S(3)	−0.0858(2)	0.2952(3)	0.3328(2)
S(4)	0.1691(2)	0.6696(3)	0.5414(2)
N(11)	0.0381(6)	0.429(1)	0.6307(6)
N(12)	−0.1286(5)	0.494(1)	0.4955(6)
N(13)	0.0944(6)	0.207(1)	0.5029(6)
N(14)	−0.0886(6)	0.184(1)	0.5493(5)
N(15)	0.0418(5)	0.4914(8)	0.4147(5)
N(16)	0.0183(6)	0.493(1)	0.2389(6)
C(11)	−0.0384(8)	0.523(1)	0.6642(8)
C(12)	−0.0947(8)	0.607(1)	0.5768(8)
C(13)	0.057(1)	0.054(1)	0.510(1)
C(14)	−0.015(1)	0.056(1)	0.578(1)
C(15)	−0.0032(6)	0.444(1)	0.3212(6)
C(16)	0.0855(8)	0.607(1)	0.2503(7)
C(17)	0.1311(7)	0.667(1)	0.3394(8)
C(18)	0.1113(7)	0.607(1)	0.4280(7)

Table 3 Selected intramolecular bond distances (Å) for complex **2**

Molecule 1		Molecule 2	
Co(1)–S(1)	2.281(3)	Co(2)–S(3)	2.273(3)
Co(1)–N(1)	1.956(8)	Co(2)–N(11)	1.987(7)
Co(1)–N(2)	1.944(7)	Co(2)–N(12)	1.900(8)
Co(1)–N(3)	1.946(7)	Co(2)–N(13)	2.002(8)
Co(1)–N(4)	2.009(7)	Co(2)–N(14)	1.953(8)
Co(1)–N(5)	1.919(7)	Co(2)–N(15)	1.984(8)
S(1)–C(5)	1.72(1)	S(3)–C(15)	1.75(1)
S(2)–C(8)	1.69(1)	S(4)–C(18)	1.68(1)
N(1)–C(1)	1.47(1)	N(11)–C(11)	1.47(1)
N(2)–C(2)	1.48(1)	N(12)–C(12)	1.49(1)
N(3)–C(3)	1.47(1)	N(13)–C(13)	1.45(1)
N(4)–C(4)	1.45(1)	N(14)–C(14)	1.49(1)
N(5)–C(5)	1.38(1)	N(15)–C(15)	1.37(1)
N(5)–C(8)	1.36(1)	N(15)–C(18)	1.37(1)
N(6)–C(5)	1.30(1)	N(16)–C(15)	1.30(1)
N(6)–C(6)	1.34(2)	N(16)–C(16)	1.34(1)
C(1)–C(2)	1.48(1)	C(11)–C(12)	1.47(1)
C(3)–C(4)	1.51(1)	C(13)–C(14)	1.49(2)
C(6)–C(7)	1.33(2)	C(16)–C(17)	1.36(1)
C(7)–C(8)	1.44(1)	C(17)–C(18)	1.41(1)

the starting material $[Co(en)_3]Cl_3$ was racemic all products were also racemic.

X-Ray Crystal Structure of $[Co(dtuc)(en)_2]ClO_4$ **2**.—The atomic parameters, bond distances and angles of complex **2** are listed in Tables 2, 3 and 4, respectively. Since complex **2** belongs to the space group *Pa* with $Z = 4$ each unit cell is composed of two Δ and two Λ complex ions. The two Δ (or Λ) cations are structurally similar but crystallographically independent (molecules 1 and 2 in Tables 2–4). Fig. 2 shows the numbered ORTEP[11] drawing of molecule 1. Hereinafter the discussion concerns molecule 1 and then the differences between molecules 1 and 2 will be described.

Complex **2** adopts a distorted-octahedral structure: the angle N(2)–Co(1)–N(3) is 176.7(3)° whereas S(1)–Co(1)–N(1) and N(4)–Co(1)–N(5) are 173.9(2) and 166.2(3)°, respectively. The crystal analysis confirms that the dtuc ligand co-ordinates in a bidentate manner *via* S(1) and N(5) and complex **2** adopts the adjacent **II** form. The bite angle S(1)–Co(1)–N(5) 73.1(3)° of the dtuc is almost the same as the 72.4(1)° in $[Co(mpymt)(en)_2][ClO_4]_2$ (mpymt = 4-methylpyrimidine-2-thionate)[1] and 72.7(2)° in $[Co(tuc)(en)_2]ClO_4$.[2]

In the present complex a marked intramolecular hydrogen bond was found between S(2) and N(1)–H(2) of en. The N ··· S distance 3.210(7) Å is considerably shorter than the sum of the van der Waals radii (N–H ··· S 3.40 Å).[12] The en chelate ring relevant to the hydrogen bond adopts an ob[13] conformation (where the C–C bond of the en ligand is oblique to the pseudo C_3 axis), which results in one of the NH_2 protons being in a suitable position for hydrogen bonding with the sulfur of the dtuc. The hydrogen bond contributes to the stabilization of the sterically unfavourable adjacent isomer. 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] The existence of the intramolecular hydrogen bond in solutions such as D_2O and $(CD_3)_2SO$ was identified in the present complexes by ^1H NMR spectroscopy as described below.

Table 4 Selected bond angles (°) for complex **2**

Molecule 1		Molecule 2	
S(1)–Co(1)–N(1)	173.9(2)	S(3)–Co(2)–N(11)	171.9(3)
S(1)–Co(1)–N(2)	90.6(3)	S(3)–Co(2)–N(12)	91.6(2)
S(1)–Co(1)–N(3)	91.8(3)	S(3)–Co(2)–N(13)	91.7(2)
S(1)–Co(1)–N(4)	93.9(2)	S(3)–Co(2)–N(14)	96.3(2)
S(1)–Co(1)–N(5)	73.1(3)	S(3)–Co(2)–N(15)	72.2(2)
N(1)–Co(1)–N(2)	84.8(4)	N(11)–Co(2)–N(12)	85.5(3)
N(1)–Co(1)–N(3)	92.9(4)	N(11)–Co(2)–N(13)	91.0(3)
N(1)–Co(1)–N(4)	90.5(3)	N(11)–Co(2)–N(14)	91.5(3)
N(1)–Co(1)–N(5)	102.9(3)	N(11)–Co(2)–N(15)	100.2(3)
N(2)–Co(1)–N(3)	176.7(3)	N(12)–Co(2)–N(13)	176.5(3)
N(2)–Co(1)–N(4)	93.3(3)	N(12)–Co(2)–N(14)	95.7(3)
N(2)–Co(1)–N(5)	91.4(3)	N(12)–Co(2)–N(15)	90.3(3)
N(3)–Co(1)–N(4)	84.3(4)	N(13)–Co(2)–N(14)	85.1(3)
N(3)–Co(1)–N(5)	91.4(3)	N(13)–Co(2)–N(15)	89.7(3)
N(4)–Co(1)–N(5)	166.2(3)	N(14)–Co(2)–N(15)	167.3(3)
Co(1)–S(1)–C(5)	78.2(3)	Co(2)–S(3)–C(15)	79.7(3)
Co(1)–N(1)–C(1)	110.5(6)	Co(2)–N(11)–C(11)	108.8(5)
Co(1)–N(2)–C(2)	107.6(6)	Co(2)–N(12)–C(12)	109.7(5)
Co(1)–N(3)–C(3)	109.1(6)	Co(2)–N(13)–C(13)	108.4(7)
Co(1)–N(4)–C(4)	109.7(6)	Co(2)–N(14)–C(14)	110.0(7)
Co(1)–N(5)–C(5)	100.5(6)	Co(2)–N(15)–C(15)	100.7(6)
Co(1)–N(5)–C(8)	139.2(7)	Co(2)–N(15)–C(18)	139.2(6)
C(5)–N(5)–C(8)	120.2(7)	C(15)–N(15)–C(18)	120.1(8)
C(5)–N(6)–C(6)	112.9(9)	C(15)–N(16)–C(16)	114.6(8)
N(1)–C(1)–C(2)	106.1(7)	N(11)–C(11)–C(12)	106.9(9)
N(2)–C(2)–C(1)	106.7(8)	N(12)–C(12)–C(11)	107.6(8)
N(3)–C(3)–C(4)	106.2(9)	N(13)–C(13)–C(14)	108(1)
N(4)–C(4)–C(3)	107.7(8)	N(14)–C(14)–C(13)	109(1)
S(1)–C(5)–N(5)	108.3(6)	S(3)–C(15)–N(15)	107.4(7)
S(1)–C(5)–N(6)	124.8(9)	S(3)–C(15)–N(16)	126.4(7)
N(5)–C(5)–N(6)	127(1)	N(15)–C(15)–N(16)	126.0(8)
N(6)–C(6)–C(7)	126.2(9)	N(16)–C(16)–C(17)	124(1)
C(6)–C(7)–C(8)	120(1)	C(16)–C(17)–C(18)	120.5(9)
S(2)–C(8)–N(5)	121.9(7)	S(4)–C(18)–N(15)	122.0(8)
S(2)–C(8)–C(7)	124.4(8)	S(4)–C(18)–C(17)	123.3(7)
N(5)–C(8)–C(7)	113.7(9)	N(15)–C(18)–C(17)	114.6(8)

Table 5 Selected interatomic bond distances (Å) within 3.40 Å

Molecule 1		Molecule 2	
N(2)–H $\cdots$ O(6^{I})	3.11(1)	N(11)–H $\cdots$ O(7)	3.07(1)
N(3)–H $\cdots$ O(8^{III})	3.25(2)	N(12)–H $\cdots$ O(3^{II})	3.22(1)
N(4)–H $\cdots$ O(4)	3.08(1)	N(13)–H $\cdots$ O(1)	3.04(1)
N(4)–H $\cdots$ O(5^{V})	2.97(1)	N(13)–H $\cdots$ O(2)	3.29(1)
		N(13)–H $\cdots$ O(7)	3.35(1)
		N(14)–H $\cdots$ O(2^{IV})	3.08(1)

Symmetry-related positions: I $x - \frac{1}{2}, -y, z - 1$; II $x - \frac{1}{2}, 1 - y, z$; III $x - \frac{1}{2}, 1 - y, z - 1$; IV $x - \frac{1}{2}, -y, z$; V $x, y, z - 1$.

The structure of molecule 1 is very similar to that of molecule 2 as seen in Tables 2–4. However, the Co–N distances are very different. For example, Co(1)–N(4) and Co(2)–N(13) distances are 2.009(7) and 2.002(8) Å, respectively and considerably longer than the corresponding Co(2)–N(14) [1.953(8) Å] and Co(1)–N(3) [1.946(7) Å]. The lengthening of the Co(1)–N(4) and Co(2)–N(13) bonds can be ascribed to the intermolecular hydrogen bonds. Table 5 shows selected intermolecular hydrogen bonds within 3.40 Å. The N(4) and N(13) atoms are involved in two and three hydrogen bonds between oxygen atoms of the perchlorate ions, respectively, whereas the corresponding atoms N(14) and N(3) are involved in only one hydrogen bond. Therefore the Co(1)–N(4) and Co(2)–N(13) bonds are lengthened and simultaneously Co(1)–N(5) and Co(2)–N(12) *trans* to the long Co(1)–N(4) and Co(2)–N(13) bonds are shortened.

Fig. 3 shows a comparison of some bond lengths and angles in related four-membered ligand systems. In the dtuc complex (*a*) the C(5)–N(6) distance [1.30(1) Å] is appreciably shorter than the other three C–N distances [1.34(2), 1.36(1) and 1.38(1) Å] and the C(6)–C(7) distance [1.33(2) Å] is also shorter than C(7)–C(8) 1.44(1) Å. That is, the three bonds C(8)–S(2), C(5)–N(6) and C(6)–C(7) have a localized double-bond character. The same situation is found for the tuc complex (*b*). In the mpymt complex (*c*) four C–N and two C–C bond distances resemble each other, respectively. Thus this complex has a delocalized pyrimidine ring structure. Differences are found in the bond angles: the bond angles of mpymt except for N–C–N angle are close to 120° whereas the C(5)–N(6)–C(6) 112.9(9) and N(5)–C(8)–C(7) 113.7(9)° of dtuc and the corresponding angles of tuc 113.0(7) and 113.4(7)° are lower than 120°. This reflects the deviations of the bond distances of the pyrimidine ring in the dtuc and tuc complexes.

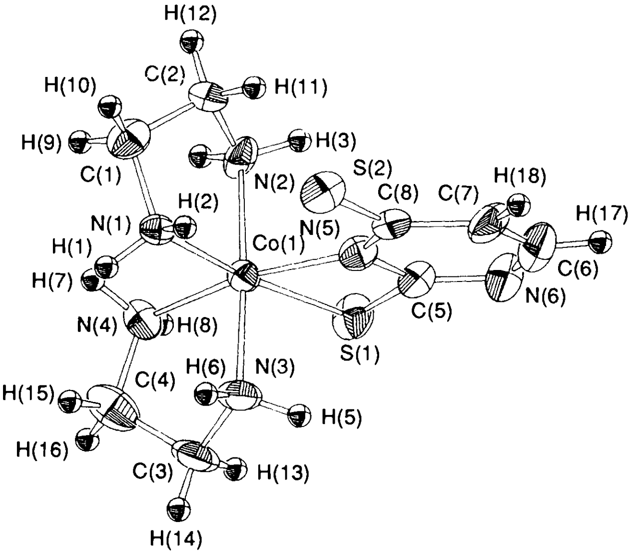


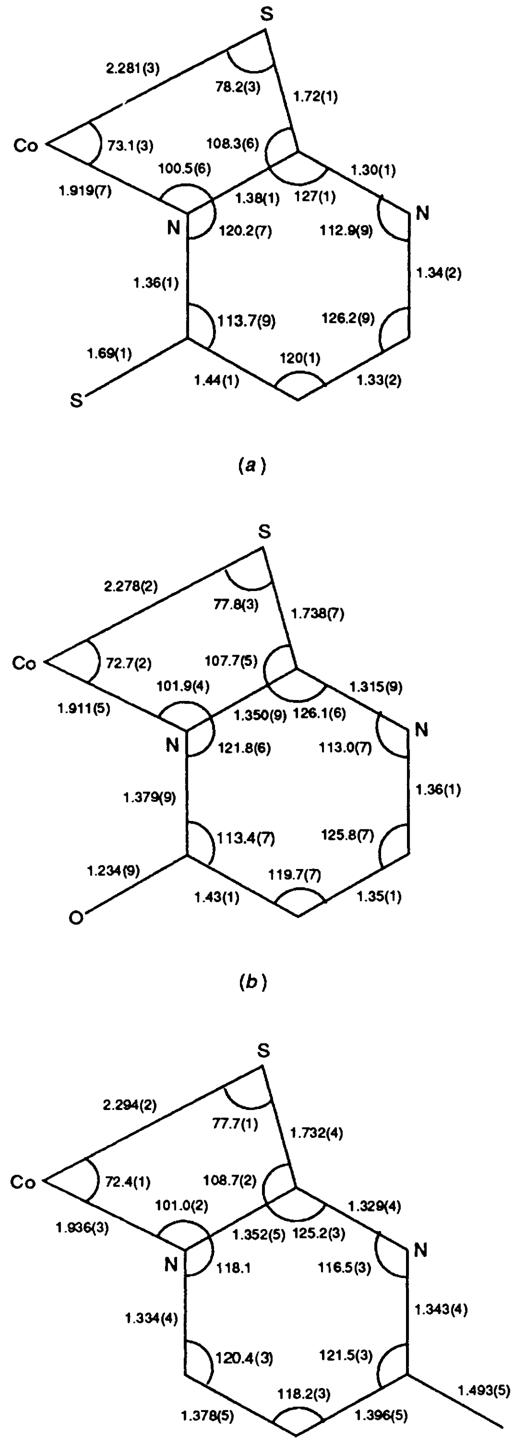
Fig. 2 An ORTEP drawing of [Co(dtuc)(en)$_2$]$^+$ (molecule 1) with thermal ellipsoids drawn at the 50% probability level

Intramolecular Hydrogen Bond in Solutions.—The X-ray crystal analysis of complex **2** revealed the existence of a strong intramolecular hydrogen bond between S(2) and N(1)–H(2). This was also identified in solutions by ^{1}H NMR spectroscopy. In the ^{1}H NMR spectrum in $(CD_3)_2SO$ one broad amine signal is located at an exceptionally low magnetic field (δ 9.20) compared with other signals corresponding to seven protons (7 H, δ 3.67–5.17). Since eight signals of [Co(pymt)(en)$_2$]$^{2+}$, where there is no intramolecular hydrogen bond, appear at δ 4.80–5.50, such a large shift indicates the existence of an intramolecular hydrogen bond.

In D_2O solution the amine signal intensity decreases with time because of rapid H/D exchange. However, the exchange rate is not as rapid as that involving the intramolecular hydrogen bond. For example, complex **2** showed the slowest H/D exchange rate for the signal at δ 8.95 and it took 9 h at 40 °C to disappear completely.

Fig. 4 shows graphically the amine signals of complexes **2**–**4**, **6** and **7**. For all the complexes one amine signal is located at an exceptionally low magnetic field δ *ca.* 8–9 compared with the other seven amine signals. This signal corresponds to the N–H $\cdots$ S hydrogen bond, which is only possible for the two adjacent forms **II** and **III** in Fig. 1. Therefore, the downfield shift of the amine proton is a good criterion for the assignment of linkage isomerism.

Characterization of Three Linkage Isomers of [Co(dtuc)(tn)$_2$]$^+$ **4**–**6**.—The column separation revealed the presence of three bands, **4**–**6**, and the elution behaviour suggests that all complexes have a charge of 1+. Fig. 5 shows their UV/VIS absorption spectra. Each complex exhibits the first d–d



(*a*)

(*b*)

(*c*)

Fig. 3 Comparison of bond lengths (Å) and angles (°) in related four-membered ligand systems: (*a*) $[Co(dtuc)(en)_2]ClO_4$ (molecule 1), (*b*) $[Co(tuc)(en)_2]ClO_4$, and (*c*) $[Co(mpymt)(en)_2][ClO_4]_2$

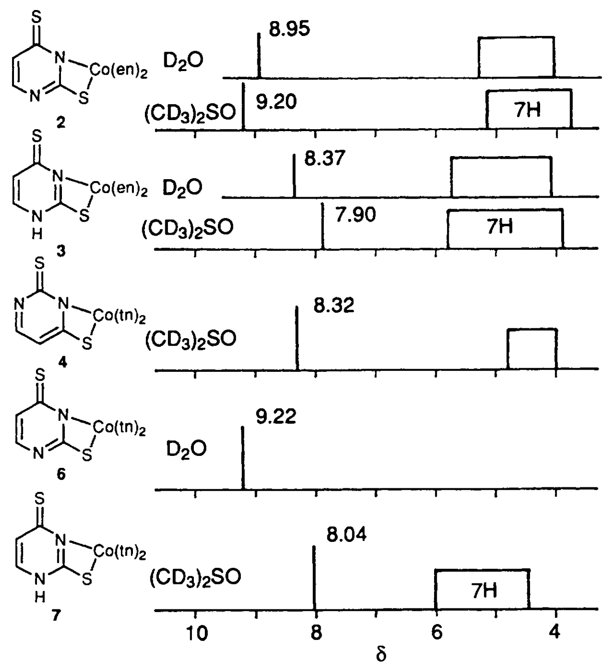


Fig. 4 Schematic presentation of the amine proton signals in the dtuc complexes. Some of the amine signals corresponding to seven H atoms at the higher magnetic field were not observed because of rapid H/D exchange in D_2O

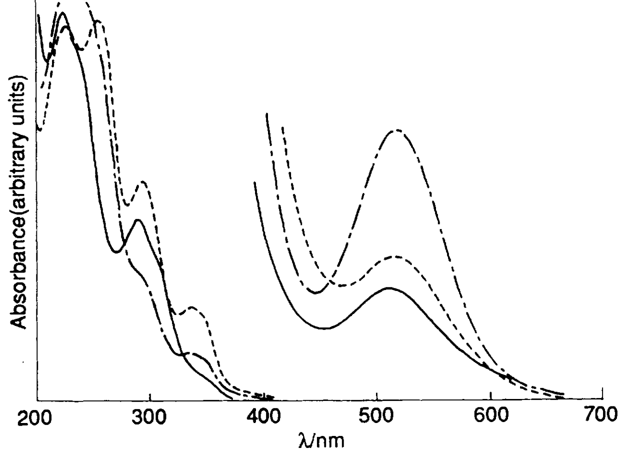


Fig. 5 The UV/VIS absorption spectra of the three linkage isomers **4** (——), **5** (— · — · —) and **6** (- - - -) of $[Co(dtuc)(tn)_2]^+$

absorption band at 510–520 nm. The red shifts (*ca.* 10–20 nm) compared with $[Co(dtuc)(en)_2]^+$ are due to the weak ligand field of tn. Two intense bands at *ca.* 350 and 290 nm due to the intraligand transition of dtuc and the sulfur-to-metal c.t., respectively, are also present for all complexes. These features are characteristic of CoN_5S type complexes.[8] Therefore, we conclude that the three complexes **4**–**6** are linkage isomers of $[Co(dtuc)(tn)_2]^+$.

Complexes **4** and **5** could not be isolated but NMR spectroscopy clearly supports the above formulation. Each isomer exhibits ten ^{13}C NMR signals, four in the dtuc chemical shift region and six in the tn region (Table 1). The ^1H and ^{13}C NMR signal patterns of **6** in the dtuc region resemble those of $[Co(dtuc)(en)_2]^+$ **2** which adopts the adjacent **II** form as shown by the X-ray crystal analysis. The absorption spectrum in the UV region of **6** is also analogous to that of **2**. Therefore, complex **6** is assigned to the adjacent **II** form. This co-ordination mode seems to be the most stable because it is found predominantly in both en and tn complexes.

Complex **4** exhibits a broad amine band at δ 8.30 and is assigned to the other adjacent **III** isomer. The absorption spectrum of **1** in the UV region is similar to that of **4**. Therefore, we conclude that complex **1** also adopts the adjacent **III** form. Complex **5** is assigned to the remaining remote isomer **I**.

The absorption spectrum of complex **7** in the UV region is very similar to that of $[Co(Hdtuc)(en)_2]^{2+}$ **3** which adopts the adjacent **II** form. The ^1H and ^{13}C NMR spectral patterns in the

Hdtuc region of **7** are also similar to those of **3**: a new signal appears at δ 13.33 due to the imine proton and the signal of H^6 became a triplet (δ 7.706) upon protonation. This means that the protonation occurs at the 1-nitrogen atom. Therefore, complex **7** is assigned to the adjacent **II** form.

Linkage Isomerism.—The fact that 2,4-dithiouracilate acts as a four-membered N,S-chelate was confirmed in the present study. However, there are a few differences between the en and tn ligand systems: the major adjacent **II** and minor adjacent **III** form were found for $[Co(dtuc)(en)_2]^+$, whereas all three isomers were found for $[Co(dtuc)(tn)_2]^+$. The formation of all possible isomers in the latter system may be ascribed to the conformational flexibility of tn compared with en. In the en system the co-ordination modes **I** and **III** seem to be formed but they react further to give dinuclear complexes containing both modes **I** and **III**, which will be reported elsewhere.

Thermal reaction between *trans*-$[CoCl_2(tn)_2]^+$ and H_2dtuc at pH 3–4 produced three linkage isomers of $[Co(Hdtuc)(tn)_2]^{2+}$, but the protonated isomers were very unstable and all decomposed during the isolation process.

The main product was the adjacent **II** form in both systems. This indicates the importance of the strong intramolecular hydrogen bond between the sulfur in the 4 position and one of the amine protons of en, which stabilizes this form. Crystal structure analysis of 2,4-dithiouracil reveals that the sulfur in the 4 position adopts a zwitterionic amidic configuration, $-^+NH{=}C(-S^-)-$, to a greater extent than the sulfur in the 2 position and that hydrogen bonds involving S^4 are significantly shorter than those involving S^2.[12] A comparison of the two adjacent complexes of **4** and **6** shows that the downfield shift of the amine proton in **6** is larger than in **4** (Fig. 4). Thus, the trend with the dtuc ligand that the hydrogen bond involving S^4 is stronger than that involving S^2 does not change much after complexation, as seen in the present complexes.

References

1 K. Yamanari, K. Okusako and S. Kaizaki, *J. Chem. Soc., Dalton Trans.*, 1992, 1615.
2 K. Yamanari, K. Okusako, Y. Kushi and S. Kaizaki, *J. Chem. Soc., Dalton Trans.*, 1992, 1621.
3 J. S. Dwivedi and U. Agarwala, *Aust. J. Chem.*, 1972, **10**, 652, 657.
4 J. S. Dwivedi and U. Agarwala, *Z. Anorg. Allg. Chem.*, 1973, **397**, 74.
5 H. C. Nelson and J. F. Villa, *Inorg. Chim. Acta*, 1979, **34**, L235.
6 D. R. Corbin, L. C. Francesconi, D. N. Hendrickson and G. D. Stucky, *Inorg. Chem.*, 1979, **18**, 3069.
7 TEXSAN–TEXRAY Structure Analysis Package, Molecular Structure Corporation, TX, 1985.
8 K. Yamanari, J. Hidaka and Y. Shimura, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 2299; M. Kita, K. Yamanari and Y. Shimura, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 2873.
9 H. Mautner and G. Bergson, *Acta Chem. Scand.*, 1963, **17**, 1694.
10 O. K. Lavallee, M. D. Baugman and M. P. Phillips, *J. Am. Chem. Soc.*, 1977, **99**, 718; J. E. Figars, J. V. Paukstelis, E. F. Byrne and J. D. Petersen, *J. Am. Chem. Soc.*, 1977, **99**, 8417.
11 C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
12 W. C. Hamilton and J. A. Ibers, *Hydrogen Bonding in Solids*, Benjamin, New York, 1968, ch. 5.
13 S. F. Mason, *Molecular Optical Activity and the Chiral Discriminations*, Cambridge University Press, 1982, p. 109.
14 E. Shefter and H. G. Mautner, *J. Am. Chem. Soc.*, 1967, **89**, 1249.

Received 2nd June 1992; *Paper* 2/03175B