Photochemical Synthesis and Stereochemistry of Cobalt(III) Complexes containing 2-Thiouracilate and Related Ligands†

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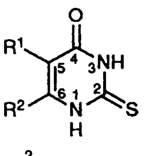
Eight cobalt(III) complexes containing four-membered N,S chelates $[CoL(en)_2]^+$ and $[Co(HL)(en)_2]^{2+}$ {H_2L = 2-thiouracil [2,3-dihydro-2-thioxo-(1*H*)-pyrimidin-4-one] (H_2tuc), 5-methyl-2-thiouracil (5Me-H_2tuc), 6-methyl-2-thiouracil (6Me-H_2tuc) or 2,3-dihydro-2-thioxo-(1*H*)-quinazolin-4-one (H_2quz); en = ethane-1,2-diamine} have been photochemically prepared from robust $[Co(en)_3]Cl_3$ and the ligands in moderate yields and characterized by elemental analyses, UV/VIS absorption and NMR spectroscopy. The crystal structure of $[Co(tuc)(en)_2]ClO_4{\cdot}H_2O$ was determined from 3905 reflections to $R = 0.053$ ($R' = 0.056$): space group $P\bar{1}$ (triclinic) with $a = 9.489(2)$, $b = 10.968(2)$, $c = 8.640(2)$ Å, $\alpha = 101.28(2)$, $\beta = 115.19(1)$, $\gamma = 80.61(2)°$ and $Z = 2$. The tuc ligand co-ordinates through N and S donors and the complex adopts an adjacent linkage form where the C^4 oxygen atom is located near the en chelate ring. A characteristic intramolecular hydrogen bond N–H···O [N···O 2.876(8) Å and N–H···O 143.14°] was found between the oxygen atom of the tuc and an amine proton of en, which contributes to the stabilization of the sterically unfavourable adjacent isomer. Proton NMR spectroscopy showed that the hydrogen bond is also present in D_2O and $(CD_3)_2SO$ solutions.

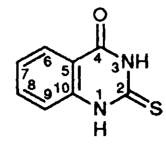
2-Thiouracil [2,3-dihydro-2-thioxo-(1*H*)-pyrimidin-4-one] (H_2tuc) is one of the thio-bases occurring in tRNA and has a therapeutic activity.[1] In neutral media this ligand reacts with metal halides MX_2 producing mostly $M(H_2tuc)_2X_2$ where H_2tuc is believed to be sulfur donating.[2] Most of the reported complexes, however, involve the deprotonated ligand ($Htuc^-$) with transition metals such as Fe^{III}, Rh^{III}, Pt^{II} and Pd^{II}.[3] These complexes are mostly insoluble and polymeric with N,S bridging. Thus, the 2-thiouracilato complexes reported so far have been poorly characterized and stereochemical aspects are not well understood.

Here we report eight bis(ethylenediamine)cobalt(III) complexes containing 2-thiouracil and its related ligands such as 5-methyl-2-thiouracil (5Me-H_2tuc), 6-methyl-2-thiouracil (6Me-H_2tuc) and 2,3-dihydro-2-thioxo-(1*H*)-quinazolin-4-one (H_2quz). These complexes were photochemically prepared by irradiating a solution of $[Co(en)_3]Cl_3$ (en = ethane-1,2-diamine) and the ligand using a halogen lamp. The chromatographic separation shows the existence of two kinds of species of $[CoL(en)_2]^+$ and $[Co(HL)(en)_2]^{2+}$ in each case which have been characterized by elemental analyses, UV/VIS absorption and ^1H and ^{13}C NMR spectra.

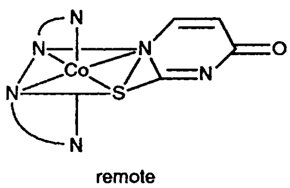
Since the present 2-thiouracilate ligands are unsymmetrical ambidentate, N,S co-ordination to a metal ion generates linkage isomerism, a remote isomer with the C^4 substituent group away from the two en chelates and an adjacent isomer with this group near to them. Proton and ^{13}C NMR spectroscopy showed that all complexes adopt an adjacent form and this was confirmed by an X-ray crystal structure analysis of $[Co(tuc)(en)_2]ClO_4{\cdot}H_2O$ where a characteristic strong hydrogen bond between the C^4 oxygen atom and NH_2 group of en is found. The stereochemistry of the present systems is very different from that of the corresponding complexes with pyrimidine-2-thionate (pymt) and its derivatives[4] irrespective of the similar ligand skeleton.



$R^1 = R^2 = H$	H_2tuc
$R^1 = Me, R^2 = H$	5Me-H_2tuc
$R^1 = H, R^2 = Me$	6Me-H_2tuc



H_2quz



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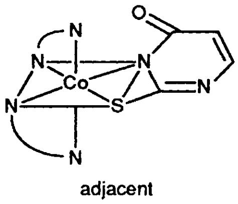

adjacent

CAUTION: In general, perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with great care. The present salts ignite in a Bunsen burner flame but present no hazard in solutions and in normal treatment of the solids.

Experimental

All complexes were isolated as the perchlorate salts.

Preparation of 2-*Thiouracilato Complexes* $[Co(tuc)(en)_2]ClO_4$ **1** *and* $[Co(Htuc)(en)_2][ClO_4]_2$ **2**.—In each quartz reaction tube (30 cm^3), $[Co(en)_3]Cl_3$ (0.1 g) and H_2tuc (0.03 g) were dissolved in water (25 cm^3) and nitrogen gas was bubbled through the mixture for 20 min. Irradiation with an Eikohsha 500 W halogen lamp through no filter was carried out for eight reaction tubes for 4 h. The resulting solutions were pooled, concentrated with a vacuum rotary evaporator and insoluble materials were filtered off. The filtrate was poured onto a column of cation exchanger (SP-Sephadex C-25, Na^+ form). Elution with 0.2 mol dm^{-3} NaCl gave three coloured bands, orange-red (**1**), pink (**2**), and yellow, in this order. The last yellow complex was the starting material $[Co(en)_3]^{3+}$. Each eluate was concentrated with a vacuum evaporator, and the white precipitate of NaCl was filtered off. By adding $NaClO_4$ to

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

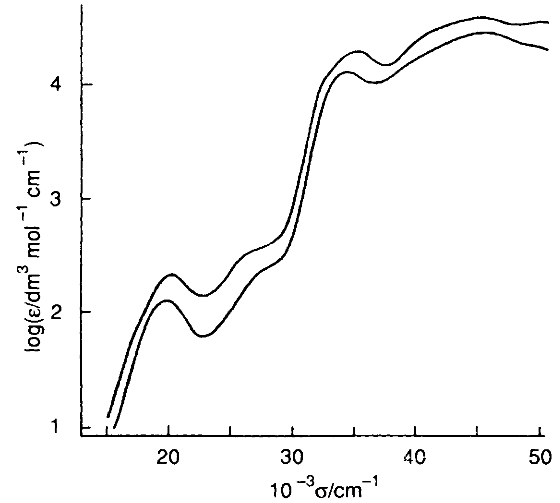


Fig. 1 The UV/VIS absorption spectra of $[Co(tuc)(en)_2]^+$ **1** (upper) and $[Co(Htuc)(en)_2]^{2+}$ **2** (lower). The log ε value of **1** is raised by 0.2 for clarity

the filtrate the perchlorate salt was obtained and recrystallized from water and methanol. The yield was 49% for complex **1** and 10% for **2**. Complex **1** {Found: C, 22.75; H, 4.75; N, 19.80. Calc. for $[Co(tuc)(en)_2]ClO_4{\cdot}H_2O$, $C_8H_{20}ClCoN_6O_6S$: C, 22.75; H, 4.75; N, 19.90%}: UV/VIS (water) λ_{max}/nm 590 (inflection), 496 (ε/dm^3 mol^{-1} cm^{-1} 129), 360 (sh, 250), 305 (sh, 7300), 285 (11 500) and 223 (24 600). Complex **2** {Found: C, 18.85; H, 3.85; N, 16.35. Calc. for $[Co(Htuc)(en)_2][ClO_4]_2{\cdot}0.5H_2O$, $C_8H_{20}Cl_2CoN_6O_{9.5}S$: C, 18.70; H, 3.90; N, 16.35%}: UV/VIS (water) λ_{max}/nm 505 (ε/dm^3 mol^{-1} cm^{-1} 126), 365 (sh, 220), 294 (10 200), 263 (sh, 10 700) and 217 (30 200).

Preparation of 5-*Methyl*-2-*thiouracilato Complexes* $[Co(5Me\text{-}tuc)(en)_2]ClO_4$ **3** *and* $[Co(5Me\text{-}Htuc)(en)_2][ClO_4]_2$ **4**.—The complexes were prepared and separated in a similar way to those above except for the use of 5Me-H_2tuc instead of H_2tuc. Irradiation was continued for 17 h. Two bands, brownish red (**3**) and red (**4**), appeared in this order upon SP-Sephadex column chromatography. Each eluate was concentrated with a vacuum rotary evaporator, and the white precipitate of NaCl was filtered off. By adding $NaClO_4$ to the filtrate the perchlorate salt was obtained and recrystallized from water. Complex **3** {Found: C, 25.80; H, 4.95; N, 19.90. Calc. for $[Co(5Me\text{-}tuc)(en)_2]ClO_4$, $C_9H_{20}ClCoN_6O_5S$: C, 25.80; H, 4.80; N, 20.05%}: UV/VIS (water) λ_{max}/nm 600 (inflection) 494 (ε/dm^3 mol^{-1} cm^{-1} 127), 365 (sh, 220), 350 (inflection), 284 (12 600), 240 (inflection) and 222 (25 300). Complex **4** {Found: C, 20.35; H, 4.15; N, 15.80. Calc. for $[Co(5Me\text{-}Htuc)(en)_2][ClO_4]_2{\cdot}0.5H_2O$, $C_9H_{22}Cl_2CoN_6O_{9.5}S$: C, 20.45; H, 4.20; N, 15.90%}: UV/VIS (water): λ_{max}/nm 502 (ε/dm^3 mol^{-1} cm^{-1} 128), 360 (sh, 240), 291 (11 800) and 219 (26 900).

Preparation of 6-*Methyl*-2-*thiouracilato Complexes* $[Co(6Me\text{-}tuc)(en)_2]ClO_4$ **5** *and* $[Co(6Me\text{-}Htuc)(en)_2][ClO_4]_2$ **6**.—A procedure similar to the above was followed with 6Me-H_2tuc in place of 5Me-H_2tuc. Two complexes, a brownish red band (**5**) and a red one (**6**), appeared in this order upon column chromatography. After removal of most NaCl, the addition of $NaClO_4$ and cooling gave each perchlorate salt. Complex **5** {Found: C, 24.65; H, 5.15; N, 19.25. Calc. for $[Co(6\text{-}Me\text{-}tuc)(en)_2]ClO_4{\cdot}H_2O$, $C_9H_{22}ClCoN_6O_6S$: C, 24.75; H, 5.10; N, 19.25%}: UV/VIS (water) λ_{max}/nm 600 (inflection), 496 (ε/dm^3 mol^{-1} cm^{-1} 128), 360 (sh, 240), 305 (inflection), 284 (11 800) and 221 (25 200). Complex **6** {Found: C, 20.90; H, 4.10; N, 16.05. Calc. for $[Co(6Me\text{-}Htuc)(en)_2][ClO_4]_2$, $C_9H_{21}Cl_2CoN_6O_9S$: C, 20.80; H, 4.10; N, 16.20%}: UV/VIS (water): λ_{max}/nm 504 (ε/dm^3 mol^{-1} cm^{-1} 128), 360 (sh, 230), 292 (10 500), 250 (inflection) and 218 (28 200).

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

Complex	Solvent	^1H[a]	^{13}C[b]
1	D_2O	7.708 (d, 1 H) H^6 5.793 (d, 1 H) H^5	179.51 C^2, 176.14 C^4 153.62 C^6, 108.63 C^5 46.76, 45.90, 45.81, 44.79 en
	$(CD_3)_2SO$	7.494 (d, 1 H) H^6 5.441 (d, 1 H) H^5	
2	D_2O	7.654 (d, 1 H) H^6 5.932 (d, 1 H) H^5	178.23 C^2, 173.14 C^4 142.44 C^6, 108.16 C^5 47.08, 46.25, 46.22, 45.44 en
	$(CD_3)_2SO$	7.700 (d, 1 H) H^6 5.777 (d, 1 H) H^5	
3	D_2O	7.583 (s, 1 H), H^6 1.874 (s, 3 H) CH_3	176.10 C^2, 175.36 C^4 145.48 C^6, 117.95 C^5 46.70, 45.82, 44.89 en 13.38 CH_3
4	D_2O	7.548 (s, 1 H) H^6 1.884 (s, 3 H) CH_3	175.40 C^2, 173.65 C^4 138.25 C^6, 118.10 C^5 47.06, 46.29, 46.20, 45.52 en 23.46 CH_3
	$(CD_3)_2SO$	12.916 (s, 1 H) NH 7.631 (d, 1 H) H^6 1.814 (d, 3 H) CH_3	
5	D_2O	5.656 (s, 1 H) H^5 2.107 (s, 3 H) CH_3	178.45 C^2, 176.46 C^4 165.02 C^6, 106.77 C^5 46.73, 45.78, 44.77 en 23.00 CH_3
6	D_2O	5.761 (s, 1 H) H^5 2.243 (s, 3 H) CH_3	177.60 C^2, 173.68 C^4 154.29 C^6, 106.64 C^5 47.08, 46.29, 46.23, 45.50 en 18.66 CH_3
	$(CD_3)_2SO$	13.004 (s, 1 H) NH 5.653 (s, 1 H), H^5 2.132 (s, 3 H) CH_3	176.30 C^2, 169.61 C^4 150.99 C^6, 105.66 C^5 45.77, 44.95, 44.11 en 17.68 CH_3
7	$(CD_3)_2SO$	7.816 (q, 1 H) 7.511 (m, 1 H) 7.240 (q, 1 H) 7.151 (m, 1 H)	174.91 C^2, 171.60 C^4 150.57 C^{10}, 132.12 C^5 124.40, 124.23 C^7 and C^8 122.31, 120.66 C^6 and C^9 45.94, 44.81, 44.75, 43.46 en
8	$(CD_3)_2SO$	13.506 (s, 1 H) NH 7.959 (q, 1 H) 7.806 (m, 1 H) 7.472 (m, 1 H) 7.370 (d, 1 H)	176.84 C^2, 167.82 C^4 139.22 C^{10}, 134.66 C^3, 125.76 125.63 C^7 and C^8, 117.40, 116.32 C^6 and C^9 45.75, 45.06, 44.97, 44.43 en

[a] Downfield relative to sodium 4,4-dimethyl-4-silapentane-1-sulfonate as internal standard. [b] Downfield relative to $SiMe_4$ using dioxane (δ 67.35) as internal standard.

Preparation of 2-*Thioxo*-4-*quinazolinonato Complexes* $[Co(quz)(en)_2]ClO_4$ **7** *and* $[Co(Hquz)(en)_2][ClO_4]_2$ **8**.—Complex **7** was prepared and separated in a similar way to the above except for the use of an equimolar amount of H_2quz and NaOH instead of H_2tuc. The reaction mixture was irradiated for 6 h. A single red band appeared upon column chromatography. After removal of most NaCl, addition of $NaClO_4$ and cooling produced dark red crystals of the perchlorate dihydrate salt (yield: 71%) (Found: C, 29.75; H, 4.90; N, 17.35. Calc. for $C_{12}H_{24}ClCoN_6O_7S$: C, 29.35; H, 4.95; N, 17.10%): UV/VIS (water): λ_{max}/nm 580 (inflection), 494 (ε/dm^3 mol^{-1} cm^{-1} 145), 370 (sh, 280), 335 (inflection), 298 (19 500) and 227 (36 200).

Recrystallization of complex **7** from *ca.* 20% $HClO_4$ gave quantitatively the corresponding red protonated species $[Co(Hquz)(en)_2][ClO_4]_2$ **8** (Found: C, 26.00; H, 3.90; N, 15.05. Calc. for $C_{12}H_{21}Cl_2CoN_6O_9S$: C, 25.95; H, 3.80; N, 15.15%): UV/VIS (0.01 mol dm^3 HCl): λ_{max}/nm 506 (ε/dm^3 mol^{-1} cm^{-1} 138), 360 (sh, 300), 310 (sh, 13 000), 292 (15 400), 235 (35 900) and 227 (36 200).

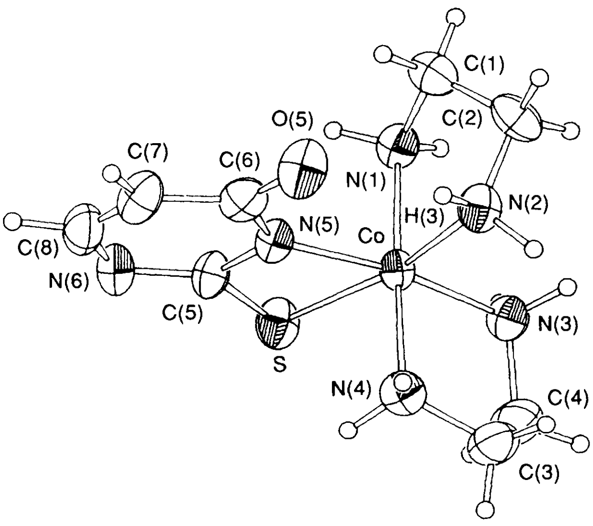


Fig. 2 An ORTEP drawing of $[Co(tuc)(en)_2]ClO_4{\cdot}H_2O$ **1**

X-Ray Crystal Structure Determination of $[Co(tuc)(en)_2]ClO_4{\cdot}H_2O$.—*Crystal data.* $C_8H_{20}ClCoN_6O_6S$, $M = 422.73$, triclinic, space group $P\bar{1}$, $a = 9.489(2)$, $b = 10.968(2)$, $c = 8.640(2)$ Å, $\alpha = 101.28(2)$, $\beta = 115.19(1)$, $\gamma = 80.61(2)°$, $U = 794.7(3)$ Å^3, $Z = 2$, $D_c = 1.77$ g cm^{-3}, $F(000) = 416$. Red crystal: $0.3 \times 0.3 \times 0.5$ mm, μ(Mo-Kα) = 14.02 cm^{-1}.

Data collection and processing. Rigaku AFC5R diffractometer, ω–2θ mode with ω scan width = $1.05 + 0.30 \tan\theta$, ω scan speed 8.0° min^{-1}, graphite-monochromated Mo-Kα radiation; 3905 reflections measured ($1.5 \leqslant \theta \leqslant 27.5°$), 3680 unique [merging $R = 0.047$ after absorption correction (maximum, minimum transmission factors = 1.00, 0.90)], giving 1852 with $I > 3\sigma(I)$. Linear and approximately isotropic crystal decay, *ca.* 39%, corrected during processing.

Structure analysis and refinement. Direct methods followed by normal heavy-atom procedures. The final cycle of full-matrix least-squares refinement was based on the observed reflections and 230 variable parameters. The final values of R and R' were 0.053 and 0.056, respectively. All calculations were performed using the TEXSAN[5] crystallographic software package of Molecular Structure Corporation.

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 recorded with a Hitachi 330 spectrophotometer, ^{1}H and ^{13}C NMR spectra with a JEOL JNM-GSX-400 spectrometer in D_2O and $(CD_3)_2SO$. X-Ray crystal analysis was made at the X-Ray Diffraction Service of the Department of Chemistry.

Table 2 Positional parameters for complex **1**

Atom	*x*	*y*	*z*
Co	0.586 7(1)	0.217 64(9)	0.330 7(1)
Cl	0.200 0(2)	0.258 8(2)	0.682 7(3)
S	0.426 6(2)	0.060 5(2)	0.235 0(3)
O(1)	0.305(1)	0.295(1)	0.640(1)
O(2)	0.253(1)	0.153 8(7)	0.771(1)
O(3)	0.080(1)	0.232(2)	0.542(2)
O(4)	0.166(2)	0.350 2(8)	0.790(2)
O(5)	0.381 5(6)	0.503 6(4)	0.291 7(7)
O(10)	−0.113 6(6)	0.066 5(5)	0.105 8(7)
N(1)	0.583 9(7)	0.207 1(5)	0.101 4(7)
N(2)	0.688 6(7)	0.373 3(5)	0.385 7(7)
N(3)	0.784 4(7)	0.112 5(5)	0.414 0(7)
N(4)	0.599 2(7)	0.234 8(5)	0.565 4(8)
N(5)	0.376 4(6)	0.292 7(5)	0.251 2(7)
N(6)	0.140 4(7)	0.193 4(6)	0.126 7(8)
C(1)	0.616(1)	0.329 3(7)	0.081(1)
C(2)	0.742(1)	0.376 7(7)	0.250(1)
C(3)	0.755(1)	0.183 5(8)	0.681(1)
C(4)	0.809(1)	0.076 4(8)	0.580(1)
C(5)	0.293 7(8)	0.192 1(6)	0.198(1)
C(6)	0.304 4(9)	0.412 6(7)	0.243 0(9)
C(7)	0.137 5(8)	0.417 5(7)	0.174(1)
C(8)	0.066 9(9)	0.310 8(8)	0.117(1)

Table 3 Selected intramolecular bond distances (Å) and angles (°) for complex **1**

Co–S	2.278(2)	N(1)–C(1)	1.48(1)
Co–N(1)	1.951(7)	N(2)–C(2)	1.47(1)
Co–N(2)	1.977(6)	N(3)–C(4)	1.48(1)
Co–N(3)	1.959(5)	N(4)–C(3)	1.480(9)
Co–N(4)	1.953(7)	N(5)–C(5)	1.350(9)
Co–N(5)	1.911(5)	N(5)–C(6)	1.379(9)
Cl–O(1)	1.33(1)	N(6)–C(5)	1.315(9)
Cl–O(2)	1.409(9)	N(6)–C(8)	1.36(1)
Cl–O(3)	1.29(1)	C(1)–C(2)	1.50(1)
Cl–O(4)	1.33(1)	C(3)–C(4)	1.47(1)
O–C(6)	1.234(9)	C(6)–C(7)	1.43(1)
N(2)–H(3)	0.778	C(7)–C(8)	1.35(1)
S–C(5)	1.738(7)		
S–Co–N(1)	90.8(2)	Co–N(3)–C(4)	108.7(5)
S–Co–N(2)	168.7(2)	Co–N(4)–C(3)	109.9(6)
S–Co–N(3)	96.6(2)	Co–N(5)–C(5)	101.9(4)
S–Co–N(4)	92.5(2)	Co–N(5)–C(6)	136.2(5)
S–Co–N(5)	72.7(2)	N(1)–C(1)–C(2)	106.6(6)
N(1)–Co–N(2)	85.5(3)	N(2)–C(1)–C(2)	106.7(7)
N(1)–Co–N(3)	93.2(2)	N(3)–C(4)–C(3)	108.8(6)
N(1)–Co–N(5)	90.5(3)	N(4)–C(3)–C(4)	108.4(6)
N(1)–Co–N(4)	176.6(3)	N(5)–C(5)–N(6)	126.1(6)
N(2)–Co–N(3)	94.2(2)	N(5)–C(5)–S	107.5(5)
N(2)–Co–N(4)	91.3(3)	N(5)–C(6)–O	121.1(7)
N(2)–Co–N(5)	96.6(2)	N(5)–C(6)–C(7)	113.4(7)
N(3)–Co–N(4)	85.9(3)	N(6)–C(5)–S	126.3(6)
N(3)–Co–N(5)	168.8(3)	N(6)–C(8)–C(7)	125.8(7)
N(4)–Co–N(5)	91.0(3)	O–C(6)–C(7)	125.5(7)
Co–S–C(5)	77.8(3)	C(5)–N(5)–C(6)	121.8(6)
Co–N(1)–C(1)	109.0(5)	C(5)–N(6)–C(8)	113.0(7)
Co–N(2)–C(2)	108.3(4)	C(6)–C(7)–C(8)	119.7(7)

Results and Discussion

Characterization of Complexes.—Two red tuc complexes **1** and **2** were found in the column separation. The chromatographic behaviour shows that **1** is a uni- and **2** a di-positive species. Complex **1** exhibits the first and the second d–d bands at 496 (129) and *ca.* 360 nm (ε = 250 dm^3 mol^{-1} cm^{-1}), respectively, and **2** at 505 (126) and *ca.* 365 nm (ε = 220 dm^3 mol^{-1} cm^{-1}), respectively (Fig. 1). An intense sulfur-to-metal charge-transfer (c.t.) band appears at 285 (11 500) for **1** and 294 nm (ε = 10 200 dm^3 mol^{-1} cm^{-1}) for **2**. These absorption spectra are characteristic for CoN_5S type complexes containing one thionato (or thiolato) group.[6] In the ^{13}C NMR spectra both complexes showed eight signals, four in the tuc chemical shift region and four in the en region (Table 1). Therefore, **1** and **2** are assigned to $[Co(tuc)(en)_2]ClO_4$ and $[Co(Htuc)(en)_2][ClO_4]_2$, respectively. Elemental analyses are consistent with these formulations.

In the system of 5Me-H_2tuc or 6Me-H_2tuc the first eluted orange-red complex was assigned to $[CoL(en)_2]^+$ and the second red complex to $[Co(HL)(en)_2]^{2+}$. In the column separation of the H_2quz system, only the unipositive complex $[Co(quz)(en)_2]^+$ **7** was found. The corresponding protonated species $[Co(Hquz)(en)_2]^{2+}$ was obtained from **7** in an acidic medium but is unstable in neutral aqueous solution, reverting to the deprotonated species. Comparing the absorption spectra of $[CoL(en)_2]^+$ and $[Co(HL)(en)_2]^{2+}$, the first d–d band of the

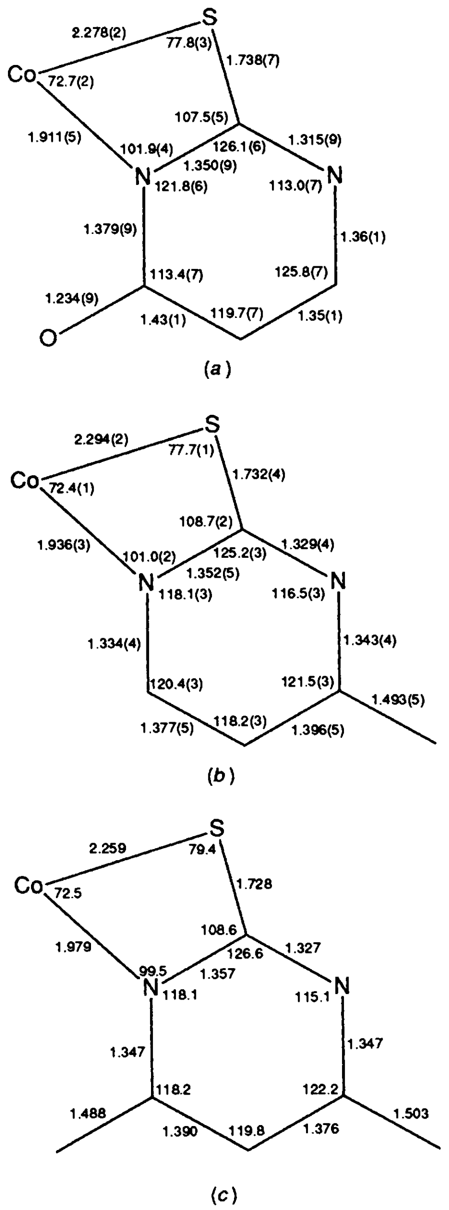


Fig. 3 Comparison of bond lengths (Å) and angles (°) in related four-membered ligand systems: (*a*) $[Co(tuc)(en)_2]ClO_4$, (*b*) $[Co(mpymt)(en)_2][ClO_4]_2$ and (*c*) *fac*-(*S*)-$[Co(dmpymt)_3]$ (average values)

latter is red-shifted by 8–12 nm in each case. A similar red shift caused by protonation was observed in the pyrimidine-2-thionato system.[4] The inflection at *ca.* 305 nm (ε = 6500–7300 dm^3 mol^{-1} cm^{-1}) of **1**, **3** or **5** seems to be due to an intra-ligand transition of the tuc because an anion of 2-thiouracil exhibits a similar strong band at 310 nm (ε = 6950 dm^3 mol^{-1} cm^{-1}).[7]

Preparation of Complexes.—In the present systems of tuc and related ligands only monosubstituted complexes of $[CoL(en)_2]^+$ or $[Co(HL)(en)_2]^{2+}$ type were obtained photochemically. Relatively long irradiation times (4–17 h) was necessary. Thermal reactions of an equimolar amount of $[Co(en)_3]Cl_3$ and the ligand and a catalytic amount of $CoCl_2{\cdot}6H_2O$ {1 mg per 100 mg of $[Co(en)_3]Cl_3$} did not produce any desired complexes in these systems.

The above results are in contrast to those of pyrimidine-2-thionate and related ligand systems.[4] In the pymt systems, mono(n = 1)-, bis(n = 2)- and/or tris(n = 3)-substituted complexes $[CoL_n(en)_{3-n}]^{(3-n)+}$ were all formed in relatively short irradiation times (2–3 h). Thermal reaction with a catalytic amount of $CoCl_2{\cdot}6H_2O$ gave the same complexes. Thus, the introduction of an oxygen atom at C^4 changes greatly the chemistry of the pymt and related ligand systems, though we still cannot explain such differences clearly.

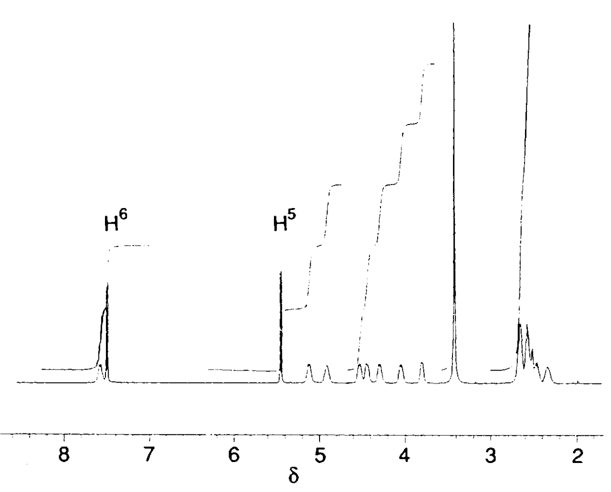


Fig. 4 The ^1H NMR spectrum of complex **1** in $(CD_3)_2SO$

Linkage Isomerism.—Recrystallization of complex **1** in an acidic medium gave quantitatively the corresponding protonated species $[Co(Htuc)(en)_2]^{2+}$ whose ^1H and ^{13}C NMR spectra are the same as those of **2**. The same situation was found for the other complexes. This means that no structural change occurs during protonation and the two types of complexes belong to the same linkage isomer.

The difference nuclear Overhauser effect (NOE) technique with the ^1H NMR spectra was used for the assignment. Radiofrequency irradiation at the C^6 proton frequency of complex **1** caused no enhancement of the methylene resonances of en at δ 2.6–3.0. No interaction between the C^6 substituent group and the en chelate ring was found also in **3** and **5**. The results indicate that this group is spacially located away from the en chelate rings, that is, **1**, **3** and **5** adopt the adjacent form.

Another useful criterion for the structural assignment was obtained from the ^{13}C NMR spectra. Protonation is possible on the unco-ordinated nitrogen atom in the pyrimidine ring of complexes **1**, **3**, **5** and **7**. In fact, a new imine proton signal was observed at δ 13–13.5 for **4**, **6** and **8** with HL^-. It is well known that methylation or protonation on a pyridine ring nitrogen leads to shielding of the α carbon relative to the free ligand.[8] Of the tuc complexes, **2** exhibited the C^6 carbon signal at 11 ppm to higher magnetic field than that of **1**. Similar upfield shifts at the C^6 carbon of **4** and **6** and at C^{10} of **8** (7–12 ppm) were observed for each pair of complexes with L^{2-} and HL^-. Thus, these facts confirm that protonation occurs at the nitrogen atom at the 1 position in the present complexes, which leads to the conclusion that the bidentate chelation occurs through the 2-S and 3-N donor atoms and that all complexes adopt the adjacent linkage form.

Crystal Structure of $[Co(tuc)(en)_2]ClO_4{\cdot}H_2O$.—Fig. 2 shows the ORTEP[9] drawing of this complex. The atomic parameters and the bond distances and angles are listed in Tables 2 and 3, respectively. The complex has a distorted octahedral structure: the N(1)–Co–N(4) angle is 176.6(3)° whereas S–Co–N(2) and N(3)–Co–N(5) are 168.7(2) and 168.8(3)°, respectively. The crystal analysis confirms that the tuc ligand co-ordinates in a bidentate manner *via* the 2-S and 3-N donors. The bite angle of the tuc 72.7(2)° is almost the same as that of 72.4(1)° in $[Co(mpymt)(en)_2][ClO_4]_2$ (mpymt = 4-methylpyrimidine-2-thionate)[4] and 72° (average) in *fac*-(*S*)-$[Co(dmpymt)_3]$ (dmpymt = 4,6-dimethylpyrimidine-2-thionate).[10]

As expected from NMR spectroscopy, the adjacent form is

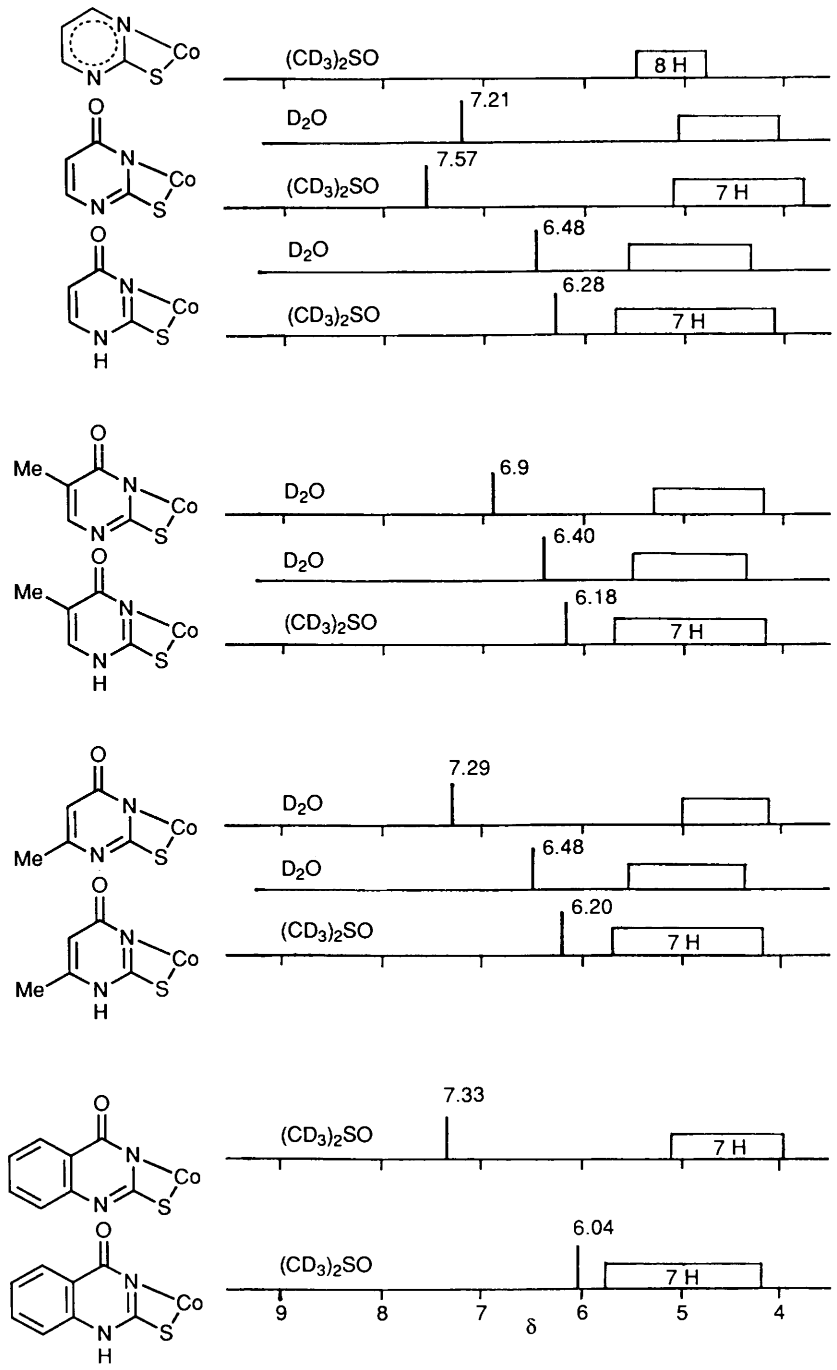
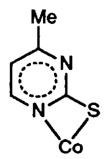


Fig. 5 The amine proton signals of en in the present complexes. In D_2O some of the signals corresponding to 7 H at higher magnetic field were not observed because of rapid H–D exchange

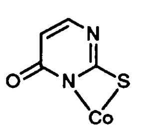
found for complex **1**. This isomer seems to be unfavourable because of steric repulsion between the C^4 substituent group of the pyrimidine ring and one of the en chelates. Only the remote isomer was found for $[Co(mpymt)(en)_2]^{2+}$.[4] The most striking characteristic found in the present complex is the presence of a strong intramolecular hydrogen bond between C(6)–O and N(2)–H(3) of en [O $\cdots$ H(3) 2.22, O $\cdots$ N(2) 2.876(8) Å; N(2)–H(3) $\cdots$ O 143.14°]. This contributes to the stabilization of the sterically unfavourable adjacent isomer. The en chelate ring corresponding to the hydrogen bond adopts an *ob* conformation (*i.e.* the C–C bond of the en is oblique to the C_3 axis, see ref. 11), which directs one of the NH_2 protons to the hydrogen bond with the oxygen of the tuc. Similar N–H $\cdots$ O distances have been reported for the intermolecular hydrogen bonds of $(NH_4)_2H_3IO_6$ [2.860(2) Å][12] and cyanuric acid [1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione] [2.778(3) and 2.798(3) Å],[13] respectively.

The Co–N(2) distance *trans* to sulfur is 1.977(6) Å, and the average of Co–N(1) and Co–N(4) *cis* to sulfur is 1.952 Å; the difference between the *trans* and *cis* bond lengths is 0.025 Å. This *trans* influence is less than the 0.041 Å of the 2-aminoethanethiolate (aet),[14] is equal to the 0.023 Å of the pyridine-2-thiolate (pyt),[15] and slightly larger than the 0.013 Å of the mpymt[4] in the corresponding $[Co(N–S)(en)_2]^{n+}$ type complexes.

Fig. 3 shows a comparison of some bond lengths and angles in related four-membered ligand systems. The Co–S and Co–N distances are similar to each other. In the tuc complex the C(5)–N(6) distance [1.315(9) Å] is appreciably shorter than the other three C–N distances [1.350(9), 1.36(1) and 1.379(9) Å]



a



b

and the C(7)–C(8) bond [1.35(1) Å] is also shorter than C(6)–C(7) [1.43(1) Å]. The three bonds C(6)–O, C(5)–N(6) and C(7)–C(8) have a localized double-bond character as shown in **b**. In the mpymt and dmpymt complexes four C–N and two C–C bond distances resemble each other, respectively. These complexes have the delocalized pyrimidine ring structure **a**. Differences are found in the bond angles: all angles except for N–C–N in the mpymt and dmpymt complexes are close to 120°, whereas in the tuc complex N(5)–C(6)–C(7) [113.4(7)°] and C(5)–N(6)–C(8) [113.0(7)°] are considerably smaller than 120° because of the deviations of the adjacent bond distances.

The above structural difference in the pyrimidine ring is reflected in the ^{1}H NMR spectra. The proton signals of the 5 and 6 positions in $[Co(pymt)(en)_2]^{2+}$ are located at δ 7.16 and 8.48, respectively, whereas the corresponding signals of the tuc complexes are located at δ 5.5–5.7 and 7.5–7.7, respectively. Large upfield shifts were observed for both signals. This means that the delocalized ring structure of the pymt is altered into the localized one of tuc by introducing an oxygen atom as a C^4 substituent.

Intramolecular Hydrogen Bond detected by ^{1}H *NMR Spectra.*—As described above, the X-ray crystal structure analysis of complex **1** shows the existence of a strong intramolecular hydrogen bond between C(6)–O and one of the NH_2 protons of en. This is relevant to the stabilization of the adjacent linkage isomer. The hydrogen bond was identified in solutions by ^{1}H NMR spectroscopy. Fig. 4 shows the spectrum of **1** in $(CD_3)_2SO$. Eight broad signals due to the NH_2 protons of en were observed besides two sharp doublets due to H^5 and H^6. Of these, one signal (δ 7.57) is located at an exceptionally lower magnetic field compared with the other seven signals (7 H, δ 3.79–5.11). Since eight amine signals of $[Co(pymt)(en)_2]^{2+}$, in which there is no intramolecular hydrogen bond, appear at δ 4.80–5.50 (8 H), it is reasonable to conclude that such a large shift indicates the existence of an intramolecular hydrogen bond. Thus, the en chelate ring relevant to the hydrogen bond keeps the *ob* conformation in dimethyl sulfoxide.

In D_2O solution most of the amine signals could not be observed because of rapid H–D exchange. However, the lowest-field signal showed the slowest H–D exchange rate: the amine signals at higher magnetic field of complex **5** almost disappeared in 40 min after dissolution in D_2O, whereas the signal at δ 7.29 still showed 92% intensity in 40 min and 52% intensity in 160 min relative to the signal intensity of H^5.

The same situation was found for the other complexes as shown graphically in Fig. 5. The downfield shifts are larger for **1**, **3**, **5** and **7** with L^{2-} than for **2**, **4**, **6** and **8** with HL^-. Smaller shifts of the latter complexes reflect the decrease in electron density on the oxygen atom in tuc caused by proton addition to the 1-N atom. The marked downfield shift of one of the amine protons, which is an indication of the adjacent form, can be also a good criterion for the assignment of linkage isomerism.

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