Synthesis and Stereochemistry of Cobalt(III) Complexes containing 2-Thiocytocine and Derivatives†

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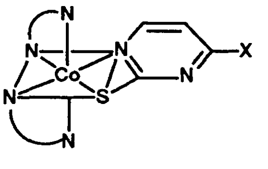
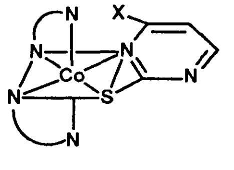
Three series of mixed-ligand cobalt(III) complexes containing four-membered *N,S* chelates $[CoL_n(en)_{3-n}]^{(3-n)+}$ [$n = 1$ or 2; HL = 2-thiocytocine (4-aminopyrimidine-2-thione, Hapymt), 4,6-diaminopyrimidine-2-thione (4,6-Hdapymt) or 2,4-diaminopyrimidine-6-thione (2,4-Hdapymt); en = ethane-1,2-diamine] have been prepared photochemically and/or thermally and characterized by elemental analysis, UV/VIS absorption, and ^1H and ^{13}C NMR spectra. The crystal structure of $[Co(apymt)(en)_2][ClO_4]_2$ was determined from 1897 observed reflections to $R = 0.048$ ($R' = 0.053$): space group *Pbca* (orthorhombic) with $a = 11.849(7)$, $b = 27.551(8)$, $c = 11.201(3)$ Å and $Z = 8$. The apymt ligand co-ordinates through the N^1 and S^2 donors and the complex adopts a remote linkage form where the C^4 amino group is distant from the en chelate rings. A new type of intramolecular hydrogen bond between the co-ordinated sulfur atom of one dapymt ligand and one of the amino groups of the other dapymt ligand was found in *trans*-(*S*)-$[Co(4,6\text{-dapymt})(en)_2]^+$ and *trans*-(*S*)-$[Co(2,4\text{-dapymt})(en)_2]^+$, which is responsible for their relatively high formation yield.

As part of our interest in the chemistry of metal complexes containing *N,S*-bidentate chelates we have prepared several bis(ethane-1,2-diamine)cobalt(III) complexes with 4-methylpyrimidine-2-thionate (mpymt) and its derivatives,[1] 2-thiouracilate (tuc) and its related ligands[2] and 2,4-dithiouracilate (dtuc).[3] In such complexes with an unsymmetrical *N,S* ligand two linkage isomers, adjacent and remote, are possible. It has been found that a substituent group (X) in the 4 position plays an essential role in the stereochemistry: the complexes of tuc (X = O) and dtuc (X = S) adopt an adjacent form whereas those of mpymt (X = Me) adopt a remote form. The existence of a strong intramolecular hydrogen bond was confirmed in the former adjacent complexes, which contributes to stabilize the sterically unfavourable linkage isomer.

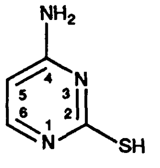
In this paper we describe the cobalt(III) complexes containing 2-thiocytocine (4-aminopyrimidine-2-thione, Hapymt), 4,6-diaminopyrimidine-2-thione (4,6-Hdapymt) and 2,4-diaminopyrimidine-6-thione (2,4-Hdapymt). These three ligands have in common a pyrimidinethionate skeleton with an amino group as the substituent in the 4 position. Therefore, the stereochemical effect of introducing a further amino substituent in the 2 or 6 position should be revealed. Two types of complexes, $[CoL(en)_2]^{2+}$ (en = ethane-1,2-diamine) and $[CoL_2(en)]^+$, were formed in all three systems and were characterized by elemental analysis, UV/VIS absorption spectra, ^1H and ^{13}C NMR spectroscopy and X-ray crystal structure analysis. The stereochemistry of the present systems is compared to that of related complexes.



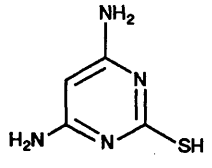
remote



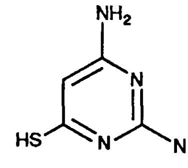
adjacent



Hapymt



4,6-Hdapymt



2,4-Hdapymt

Experimental

Preparation of 2-Thiocytocinato Complexes $[Co(apymt)(en)_2]Cl_2$ **1** *and trans-(S)-*$[Co(apymt)_2(en)]^+$ **2**.—The compound Hapymt (0.56 g, 4.0×10^{-3} mol) was suspended in warm water (200 cm^3) and the pH adjusted to 8–9 by adding aqueous NaOH. To the above solution was added *rac*-$[Co(en)_3]Cl_3$ (1.6 g, 4.0×10^{-3} mol). The mixture was divided into eight portions in quartz reaction tubes (30 cm^3) and nitrogen gas bubbled through them for 20 min. Irradiation with a Toshiba 500 W halogen lamp in the absence of a filter was carried out at 20–22 °C for 40 min, giving clear red solutions. The solutions were pooled and after filtration the filtrate was poured onto a column of cation exchanger (SP-Sephadex C-25, Na^+ form; 4 × 50 cm). Elution with 0.1 mol dm^{-3} NaCl gave three coloured bands, green (**2**; yield 0.8%), red (**1**; 44%) 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 filtered off. Evaporation of the filtrate gave the chloride salt which was recrystallized from a small amount of water. By adding $NaClO_4$ to the filtrate the perchlorate salt of complex **1** was also obtainable and recrystallized from water. The formation yield of complex **2** was very low in this experiment and a more effective photochemical preparation was developed. When a $[Co(en)_3]^{3+}$: Hapymt mole ratio of 1 : 2 was used the yield of complex **2** became 3.7%. After evaporation complex **2** was isolated as the chloride salt. Complex **1** {Found: C, 24.30; H, 5.45; N, 24.85. Calc. for $[Co(apymt)(en)_2]Cl_2$, $C_8H_{22}Cl_2$-

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

CoN_7OS: C, 24.35; H, 5.60; N, 24.85%. Found: C, 19.25; H, 4.10; N, 19.45. Calc. for $[Co(apymt)(en)_2][ClO_4]_2$, $C_8H_{20}Cl_2CoN_7O_8S$: C, 19.05; H, 4.00; N, 19.45%}. UV/VIS (water): λ_{max}/nm 500 (ε 149), 360 (sh, 260), 302 (10 600), 252 (29 700) and 222 (25 800 $dm^3\ mol^{-1}\ cm^{-1}$). Complex **2** {Found: C, 28.25; H, 4.20; N, 26.55. Calc. for *trans*-(*S*)-$[Co(apymt)_2(en)]Cl{\cdot}H_2O$, $C_{10}H_{18}ClCoN_8OS_2$: C, 28.25; H, 4.25; N, 26.40%}. UV/VIS (water): λ_{max}/nm 589 (ε 211), 445 (sh, 280), 336 (20 100), 303 (sh, 12 700), 255 (31 500) and 222 (40 200 $dm^3\ mol^{-1}\ cm^{-1}$).

Thermal reaction of equimolar amounts of *trans*-$[CoCl_2(en)_2]Cl$, Hapymt and NaOH at 70 °C for 2 h gave the same complexes **1** and **2**: the formation yield is 64% for **1** and **2** is obtained in trace amounts.

Preparation of $[Co(Hapymt)(en)_2][ClO_4]_3$ **3**.—Complex **1** (300 mg) was dissolved in 40% $HClO_4$ 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. Complex **3** {Found: C, 16.20; H, 3.60; N, 16.40. Calc. for $[Co(Hapymt)(en)_2][ClO_4]_3$, $C_8H_{21}Cl_3CoN_7O_{12}S$: C, 15.90; H, 3.50; N, 16.20%}. UV/VIS (10% $HClO_4$): λ_{max}/nm 510 (ε 139), 420 (sh, 82), 325 (11 400), 247 (24 700) and 223 (25 000 $dm^3\ mol^{-1}\ cm^{-1}$).

Preparation of 4,6-*Diaminopyrimidine*-2-*thionato Complexes* $[Co(4,6\text{-}dapymt)(en)_2]Cl_2$ **4** *and trans*-(*S*)-$[Co(4,6\text{-}dapymt)_2(en)]Cl$ **5**.—The complexes were prepared as described above except for the use of 4,6-Hdapymt instead of Hapymt. Column separation using SP-Sephadex C-25 (Na^+ form) gave three bands, green (**5**; yield 37%), red (**4**; 6.1%) and yellow, in this order. The last yellow band was $[Co(en)_3]^{3+}$. The desired complexes were isolated as chloride salts in the same way as described above. Complex **4** {Found: C, 23.70; H, 5.60; N, 27.50. Calc. for $[Co(4,6\text{-}dapymt)(en)_2]Cl_2{\cdot}H_2O$, $C_8H_{23}Cl_2CoN_8OS$: C, 23.50; H, 5.65; N, 27.40%}. UV/VIS (water): λ_{max}/nm 514 (ε 119), 370 (sh, 260), 295 (sh, 9080), 275 (sh, 13 500), 235 (sh, 22 300) and 214 (30 200 $dm^3\ mol^{-1}\ cm^{-1}$). Complex **5** {Found: C, 25.55; H, 4.65; N, 29.65. Calc. for *trans*-(*S*)-$[Co(4,6\text{-}dapymt)_2(en)]Cl{\cdot}2H_2O$, $C_{10}H_{22}ClCoN_{10}O_2S_2$: C, 25.40; H, 4.70; N, 29.60%}. UV/VIS (water): λ_{max}/nm 581 (ε 123), 460 (sh, 170), 334 (14 900), 273 (19 100), 245 (sh, 31 600) and 216 (73 000 $dm^3\ mol^{-1}\ cm^{-1}$).

Heating a solution of equimolar amounts of *trans*-$[CoCl_2(en)_2]Cl$, 4,6-Hdapymt and NaOH at 70 °C for 2 h gave the same complexes **4** and **5**: the formation yield is 30% for **4** and 20% for **5**.

Preparation of 2,4-*Diaminopyrimidine*-6-*thionato Complexes* $[Co(2,4\text{-}dapymt)(en)_2]Cl_2$ **6** *and trans*-(*S*)-$[Co(2,4\text{-}dapymt)_2(en)]Cl$ **7**.—A similar photochemical procedure described above using $[Co(en)_3]^{3+}$, 2,4-Hdapymt$\cdot$0.5H_2SO_4 and NaOH (mole ratio = 1 : 1 : 2) was not effective in this system: irradiation for 2 h gave only brown precipitates which were not identified and the yellow filtrate indicated unreacted starting materials.

Thermal reaction using *trans*-$[CoCl_2(en)_2]Cl$, 2,4-Hdapymt$\cdot$0.5H_2SO_4 and NaOH (mole ratio = 1 : 1 : 2) was then attempted. Heating the solution for 2 h in the presence of activated charcoal gave red solutions. Column separation using SP-Sephadex C-25 (Na^+ form, 4 × 50 cm) showed two bands, green (**7**; yield 7.0%) and red (**6**; 4.2%), in this order. The desired complexes were isolated as chloride salts. Complex **6** {Found: C, 22.25; H, 5.90; N, 26.05. Calc. for $[Co(2,4\text{-}dapymt)(en)_2]Cl_2{\cdot}2H_2O$, $C_8H_{25}Cl_2CoN_8O_2S$: C, 22.50; H, 5.90; N, 26.25%}. UV/VIS (water): λ_{max}/nm 516 (ε 128), 390 (sh, 250), 304 (19 600), 255 (sh, 16 000), 222 (30 400) and 206 (31 800 $dm^3\ mol^{-1}\ cm^{-1}$). Complex **7** {Found: C, 27.20; H, 4.15; N, 31.45. Calc. for *trans*-(*S*)-$[Co(2,4\text{-}dapymt)_2(en)]Cl{\cdot}0.5H_2O$, $C_{10}H_{19}ClCoN_{10}O_{0.5}S_2$: C, 26.95; H, 4.30; N, 31.40%}. UV/VIS (water): λ_{max}/nm 600 (ε 121), 455 (sh, 260), 342 (20 000), 299 (27 400), 223 (49 100) and 206 (54 200 $dm^3\ mol^{-1}\ cm^{-1}$).

Determination of Product Distribution in the 4,6-*dapymt System with Time*.—In order to evaluate the reaction profile of 4,6-dapymt in detail the product distribution was determined with time. Photochemical preparation was achieved in the same way as described above. Samples of the reaction mixture and the absorbance measurements were carried out every 5 min. This system contains only three species, $[Co(4,6\text{-}dapymt)(en)_2]^{2+}$ **4**, *trans*-(*S*)-$[Co(4,6\text{-}dapymt)_2(en)]^+$ **5** and $[Co(en)_3]^{3+}$ (starting material). Therefore, the yield of each complex can be calculated from the absorbances at three different wavelengths. The molar absorption coefficients used were 7.7, 50 and 119 $dm^3\ mol^{-1}\ cm^{-1}$ for complex **4**, 55, 123 and 78 $dm^3\ mol^{-1}\ cm^{-1}$ for complex **5** and 0, 1.1 and 25.6 $dm^3\ mol^{-1}\ cm^{-1}$ for $[Co(en)_3]^{3+}$ at 650, 580 and 515 nm, respectively. The formation yields of **4**, **5** and $[Co(en)_3]^{3+}$ were 2.9, 4.2 and 93% after 5 min, 6.4, 11 and 82% after 10 min, 4.2, 22 and 74% after 15 min, 11, 32 and 57% after 20 min, 9.3, 37 and 54% after 25 min, 13, 38 and 50% after 30 min, 10, 39 and 51% after 35 min and 12, 39 and 49% after 40 min, respectively: the yield of complex **4** found here tends to be higher relative to the isolated experimental yield.

X-Ray Crystal Structure Determination of $[Co(apymt)(en)_2][ClO_4]_2$.—*Crystal data.* $C_8H_{20}Cl_2CoN_7O_8S$, $M = 504.19$, space group *Pbca* (no. 61, orthorhombic), $a = 11.849(7)$, $b = 27.551(8)$, $c = 11.201(3)$ Å, $U = 3657(4)$ Å^3, $Z = 8$, $D_c = 1.832$ g cm^{-3}, $F(000) = 2064$. Red crystal: 0.25 × 0.20 × 0.15 mm, μ(Mo-Kα) = 13.93 cm^{-1}.

Data collection and processing. Rigaku AFC5R diffractometer, ω scan technique with ω scan width = 1.18 + 0.35tanθ, ω scan speed 8.0° min^{-1}, graphite-monochromated Mo-Kα radiation; 3684 reflections measured ($1.5 \leqslant \theta \leqslant 25.0°$), 1897 observed with $I > 3\sigma(I)$, absorption and decay corrections (maximum, minimum transmission factors = 1.00, 0.89 and 0.33% decline).

Structure analysis and refinement. The structure was solved by the Patterson method. The final cycle of block-diagonal matrix least-squares refinements was based on 1897 observed reflections [$I > 3.00\sigma(I)$] and 286 variable parameters. All non-hydrogen atoms were refined anisotropically except for O(8), which was disordered and refined isotropically (see Table 3). All hydrogen atoms were placed at calculated positions except for two hydrogens of N(7) which were refined isotropically. The final R and R' $\{R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}, w = 1/\sigma^2(F_o)\}$ values were 0.048 and 0.053, respectively. All calculations were performed using the TEXSAN[4] 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. Proton and ^{13}C NMR spectra were recorded with JEOL JNM-GSX-270 and GSX-400 spectrometers in D_2O and/or $(CD_3)_2SO$. Perchlorate salts of the complexes, which were obtained from the corresponding chlorides using a column of QAE-Sephadex A-25 (ClO_4^- form), were used for the NMR spectral measurements in $(CD_3)_2SO$. The X-ray crystal structure analysis was performed at the X-ray Diffraction Service of the Department of Chemistry.

Results and Discussion

Preparation and Characterization.—Two kinds of apymt complexes were found during column separation. Their UV/VIS absorption spectra are shown in Fig. 1. The main product **1** shows the first d–d absorption band at 500 nm and an intense sulfur to metal charge-transfer (c.t.) band at 302 nm. These are characteristic for co-ordinated thionate complexes of a CoN_5S

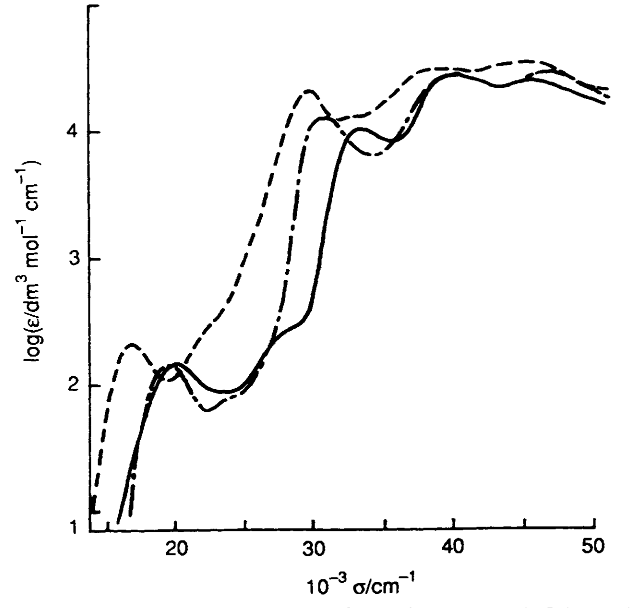
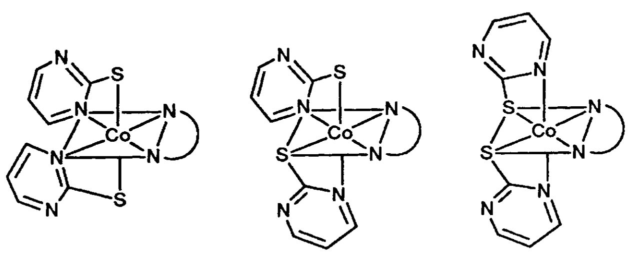


Fig. 1 UV/VIS absorption spectra of complexes **1** (——), **2** (- - - -) and **3** (· — · — ·)

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

Complex	Solvent	^{1}H^a	^{13}C^b
Hapymt^c	$(CD_3)_2SO$	11.99 (s, 1 H, NH) 7.56 (s, 2 H, N^4H_2) 7.43 (d, 2 H, H^6) 5.94 (d, 2 H, H^5)	179.8 (C^2), 162.4 (C^4) 142.4 (C^6), 98.6 (C^5)
1	$(CD_3)_2SO$	7.65 (d, 1 H, H^6) 7.34 (s, 2 H, N^4H_2) 6.07 (d, 1 H, H^5)	180.0 (C^2), 163.3 (C^4) 151.4 (C^6), 101.4 (C^5) 45.5, 45.0, 44.8, 44.3 (en)
2	$(CD_3)_2SO$	7.49 (d, 2 H, H^6) 7.22 (s, 4 H, N^4H_2) 6.02 (d, 2 H, H^5)	180.7 (C^2), 163.4 (C^4) 151.9 (C^6), 101.1 (C^5) 45.7 (en)
3	$(CD_3)_2SO$	7.67 (d, 1 H, H^6) 7.4 (s, 1 H, N^3H) 6.11 (d, 1 H, H^5)	179.7 (C^2), 162.7 (C^4) 151.6 (C^6), 101.4 (C^5) 45.5, 45.0, 44.8, 44.4 (en)
4	$(CD_3)_2SO$	6.60 (s, 2 H, NH_2) 5.80 (s, 2 H, NH_2) 5.15 (s, 1 H, H^5)	178.4 (C^2), 81.9 (C^5) 163.5, 162.8 (C^4 and C^6) 45.1, 45.0, 44.8, 44.7 (en)
5	$(CD_3)_2SO$	7.04 (s, 4 H, NH_2) 6.42 (s, 4 H, NH_2) 5.05 (s, 2 H, H^5)	177.2 (C^2), 79.7 (C^5) 164.3, 162.5 (C^4 and C^6) 45.5 (en)
6	D_2O	5.51 (s, 1 H, H^5)	181.0 (C^6), 163.6 (C^4) 163.4 (C^2), 98.2 (C^5) 46.2, 45.9, 45.7 45.7 (en)
	$(CD_3)_2SO$	6.59 (s, 2 H, N^4H_2) 5.79 (s, 2 H, N^2H_2) 5.49 (s, 1 H, H^5)	
7	$(CD_3)_2SO$	6.79 (s, 4 H, N^2H_2) 6.51 (s, 4 H, N^4H_2) 5.49 (s, 2 H, H^5)	177.8 (C^6), 95.6 (C^5) 163.7, 162.3 (C^2 and C^4) 45.5 (en)

[a] Downfield relative to sodium 4,4-dimethyl-4-silapentane-1-sulfonate (D_2O) or $SiMe_4$ [$(CD_3)_2SO$]. [b] Referenced to 1,4-dioxane (δ 67.40) in D_2O or $SiMe_4$ in $(CD_3)_2SO$. [c] Ref. 6.



trans-(*S*) C_1-*cis*-(*S*) C_2-*cis*-(*S*)

Table 2 Formation yields (%) of complexes $[Co(N\text{-}S)_n(en)_{3-n}]^{(3-n)+}$

	Photochemical		Thermal	
N-S ligand	Mono (n = 1)	Bis(*trans*) (n = 2)	Mono (n = 1)	Bis(*trans*) (n = 2)
apymt	44	0.8	64	Trace
4,6-dapymt	6.1	37	30	20
2,4-dapymt	0	0	4.2	7.0

type such as $[Co(pyt)(en)_2]^{2+}$ (pyt = pyridine-2-thionate)[5] and $[Co(tuc)(en)_2]^{2+}$.[2] In the ^{13}C NMR spectrum of complex **1**, eight signals, four in the apymt chemical shift region and four in the en region, were observed (Table 1). Therefore, complex **1** has the composition $[Co(apymt\text{-}N,S)(en)_2]^{2+}$ which is in accord with its elemental analysis. The column chromatographic behaviour suggests that complex **2** has a +1 ionic charge with the composition $[Co(apymt)_2(en)]^+$, where one *trans*-(*S*) and two *cis*-(*S*) geometrical isomers are possible. The green complex **2** exhibits a main component at 589 nm in the first d–d absorption band region and a low energy sulfur-to-metal c.t. band at 336 nm characteristic of *trans*-(*S*)-$[Co(thionato)_2(N)_4]$ type complexes.[5,7]

In the systems of 4,6-dapymt and 2,4-dapymt, the red (**4** and **6**) and green (**5** and **7**) complexes were similarly assigned to $[Co(N\text{-}S)(en)_2]^{2+}$ and *trans*-(*S*)-$[Co(N\text{-}S)_2(en)]^+$, respectively. The first d–d absorption peaks of complexes **4** and **6** at *ca.* 515 nm are shifted by *ca.* 15 nm relative to complex **1** (500 nm) owing to the presence of the additional amino group in the dapymt ligands. A similar red shift has been observed between the complexes with methyl substituents, $[Co(mpymt)(en)_2]^{2+}$ (502 nm) and $[Co(dmpymt)(en)_2]^{2+}$ (510 nm) (dmpymt = 4,6-dimethylpyrimidine-2-thionate).[1]

Recrystallization of $[Co(apymt)(en)_2]^{2+}$ **1** in a concentrated acidic medium produced the corresponding protonated species $[Co(Hapymt)(en)_2]^{3+}$ **3**. Complex **3** is however deprotonated to **1** even in 0.01 mol dm^{-3} HCl. A new broad proton signal for **3** which is assignable to N^3H was observed at δ *ca.* 7.4 in $(CD_3)_2SO$. In the protonated complex, the first d–d absorption peak is red-shifted by *ca.* 10 nm compared with the peak of complex **1** and the sulfur-to-metal c.t. band is also red-shifted as shown in Fig. 1.

Table 2 collects the formation yields of the complexes. Total yields for the apymt system are very similar to those of the 4,6-dapymt system using both experimental methods. On the other hand, the reactivity of 2,4-dapymt is very low compared with the other two ligands. This indicates that the co-ordinating ability of 2-thionate is higher than that of 6-thionate.

In the present systems mono- and bis-substituted complexes $[CoL_n(en)_{3-n}]^{(3-n)+}$ (n = 1 or 2) were formed when the starting complex : ligand mole ratio was 1 : 1, a similar situation to that found for the pymt, mpymt and dmpymt systems. However, the products in the tuc and dtuc systems are different from the present systems: only two types of mono-substituted complexes $[CoL(en)_2]^{2+}$ and $[Co(HL)(en)_2]^+$ were formed and no bis-substituted complexes were found under the same conditions as used here.

The photochemical reactions between $[Co(en)_3]^{3+}$ and the thionato ligands are extremely clean without any by-products being observed on the chromatography column. The thermal reactions between $[CoCl_2(en)_2]Cl$ and the ligands in the

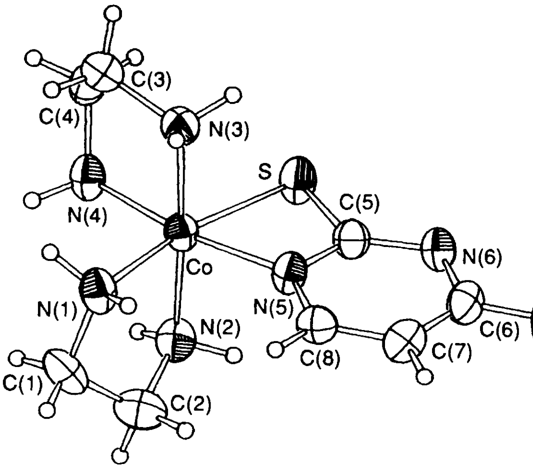


Fig. 2 An ORTEP drawing of $[Co(apymt)(en)_2]^+$ with thermal ellipsoids drawn at the 50% probability level

Table 3 Positional parameters for $[Co(apymt)(en)_2][ClO_4]_2$

Atom	*x*	*y*	*z*
Co	0.150 31(7)	0.142 09(3)	0.044 86(8)
S	0.038 7(1)	0.164 52(7)	0.202 7(2)
N(1)	0.220 9(4)	0.116 1(2)	−0.102 2(5)
N(2)	0.178 3(4)	0.077 7(2)	0.111 1(5)
N(3)	0.130 7(4)	0.206 6(2)	−0.026 2(5)
N(4)	0.292 3(4)	0.167 3(2)	0.109 5(5)
N(5)	−0.003 1(4)	0.123 5(2)	0.008 0(5)
N(6)	−0.167 7(4)	0.132 6(2)	0.128 5(5)
N(7)	−0.334 5(5)	0.099 7(2)	0.063 4(5)
C(1)	0.273 8(6)	0.068 4(3)	−0.076 4(7)
C(2)	0.199 4(7)	0.042 9(3)	0.011 7(7)
C(3)	0.237 1(6)	0.235 0(2)	−0.012 9(7)
C(4)	0.288 8(6)	0.221 1(3)	0.105 4(7)
C(5)	−0.058 7(5)	0.137 8(2)	0.106 6(6)
C(6)	−0.226 2(5)	0.108 5(2)	0.043 7(6)
C(7)	−0.174 2(5)	0.092 0(2)	−0.062 1(6)
C(8)	−0.062 3(5)	0.100 3(2)	−0.076 2(6)
Cl(1)	0.014 1(1)	0.178 86(6)	0.659 4(2)
O(1)	0.008 3(5)	0.202 1(3)	0.547 8(5)
O(2)	−0.069 9(6)	0.193 1(3)	0.738 5(6)
O(3)	0.119 1(6)	0.183 7(4)	0.703 9(6)
O(4)	−0.004(1)	0.130 6(2)	0.642 4(8)
Cl(2)	0.445 5(2)	0.009 99(7)	0.214 0(2)
O(5)	0.389 5(8)	−0.030 0(3)	0.191 3(9)
O(6)	0.436 3(7)	0.054 0(3)	0.159 6(8)
O(7)	0.542 6(7)	0.001 6(3)	0.269(1)
O(8A)*	0.443(1)	0.026 8(6)	0.344(2)
O(8B)*	0.335(1)	0.024 4(6)	0.274(2)
O(8C)*	0.487(2)	−0.003(1)	0.088(2)

* The occupancies of O(8A), O(8B) and O(8C) are 0.4, 0.3 and 0.3, respectively.

Table 4 Selected bond distances (Å) and angles (°) for $[Co(apymt)(en)_2][ClO_4]_2$

Co–S	2.292(2)	N(4)–C(4)	1.49(1)
Co–N(1)	1.981(5)	N(5)–C(5)	1.346(8)
Co–N(2)	1.953(6)	N(5)–C(8)	1.338(8)
Co–N(3)	1.962(5)	N(6)–C(5)	1.321(8)
Co–N(4)	1.959(5)	N(6)–C(6)	1.352(8)
Co–N(5)	1.933(5)	N(7)–C(6)	1.325(8)
S–C(5)	1.742(7)	C(1)–C(2)	1.50(1)
N(1)–C(1)	1.48(1)	C(3)–C(4)	1.51(1)
N(2)–C(2)	1.49(1)	C(6)–C(7)	1.41(1)
N(3)–C(3)	1.490(9)	C(7)–C(8)	1.35(1)
S–Co–N(1)	169.2(2)	Co–N(3)–C(3)	109.6(4)
S–Co–N(2)	92.9(2)	Co–N(4)–C(4)	108.6(4)
S–Co–N(3)	90.0(2)	Co–N(5)–C(5)	102.0(4)
S–Co–N(4)	96.6(2)	Co–N(5)–C(8)	140.4(4)
S–Co–N(5)	72.2(2)	C(5)–N(5)–C(8)	117.5(5)
N(1)–Co–N(2)	85.2(2)	C(5)–N(6)–C(6)	115.1(5)
N(1)–Co–N(3)	92.3(2)	N(1)–C(1)–C(2)	107.2(6)
N(1)–Co–N(4)	94.2(2)	N(2)–C(2)–C(1)	106.9(6)
N(1)–Co–N(5)	97.1(2)	N(3)–C(3)–C(4)	107.4(6)
N(2)–Co–N(3)	176.7(2)	N(4)–C(4)–C(3)	107.0(6)
N(2)–Co–N(4)	92.1(2)	S–C(5)–N(5)	107.8(4)
N(2)–Co–N(5)	90.0(2)	S–C(5)–N(6)	125.4(5)
N(3)–Co–N(4)	86.0(2)	N(5)–C(5)–N(6)	126.8(6)
N(3)–Co–N(5)	92.5(2)	N(6)–C(6)–N(7)	118.0(6)
N(4)–Co–N(5)	168.7(2)	N(6)–C(6)–C(7)	121.7(5)
Co–S–C(5)	78.0(2)	N(7)–C(6)–C(7)	120.4(6)
Co–N(1)–C(1)	109.6(4)	C(6)–C(7)–C(8)	118.2(6)
Co–N(2)–C(2)	109.2(4)	N(5)–C(8)–C(7)	120.7(6)

presence of activated charcoal also gave the same products and this method is rather useful for the poorly reactive 2,4-dapymt. However, the thermal reactions sometimes lead to small amounts of by-products.

Crystal Structure of $[Co(apymt)(en)_2][ClO_4]_2$ **1**.—Since 4-aminopyrimidine-2-thionate is an unsymmetrical ambidentate ligand its bidentate-*N*,*S* co-ordination to a metal ion generates linkage isomerism: a remote isomer with the C^4 amino group of the pyrimidine ring distant from the two en chelates and an adjacent isomer with the amino group near the en chelates. In order to determine the bonding mode an X-ray crystal structure analysis of complex **1** was undertaken.

Fig. 2 shows an ORTEP[8] drawing of complex **1**. The atomic parameters and selected bond distances and angles are listed in Tables 3 and 4, respectively. A distorted octahedral structure is found for this complex: the N(2)–Co–N(3) angle is 176.7(2)°, whereas the S–Co–N(1) and N(4)–Co–N(5) angles are 169.2(2) and 168.7(2)°, respectively. The apymt ligand co-ordinates in a bidentate manner through the N^1 and S^2 donors and complex **1** adopts the remote linkage form. The bite angle S–Co–N(5) is 72.2(2)°, whose value is almost the same as that of 72.4(1)° found in $[Co(mpymt)(en)_2][ClO_4]_2$[1] and 72.7(2)° in $[Co(tuc)(en)_2]ClO_4$.[2] Since we cannot find any evidence for the presence of an adjacent isomer under neutral or alkaline conditions, such complete stereoselective formation may be ascribed to steric effects. The same situation is found for $[Co(mpymt)(en)_2][ClO_4]_2$.[1]

The Co–S and Co–N(5) bond lengths of 2.292(2) and 1.933(5) Å, respectively, are in good agreement with the corresponding values of 2.294(2) and 1.936(3) Å in $[Co(mpymt)(en)_2][ClO_4]_2$[1] and 2.282(2) and 1.929(5) Å in $[Co(pyt)(en)_2][ClO_4]_2$.[5]

In the pyrimidine ring the C(5)–N(6) bond length [1.321(8) Å] is a little shorter than the other three C–N lengths [1.338(8), 1.346(8) and 1.352(8) Å]. The C(7)–C(8) bond length [1.355(9) Å] is also shorter than C(6)–C(7) [1.410(9) Å]. The C(6)–N(7) bond length [1.325(8) Å] is considerably shorter than those in aniline [1.398(6) and 1.386(6) Å].[9] The sum of the three bond angles around N(7) is 360°, whereas the corresponding angles are 346 and 338° in aniline. These facts indicate that the C(6)–N(7) bond has a double bond character. The N(5)–C(5)–N(6) angle becomes in general larger than 120° due to the co-ordination of the sulfur atom. The other five angles are close to 120°.

Linkage Isomerism.—The X-ray crystal analysis indicates that $[Co(apymt)(en)_2]^{2+}$ adopts a remote form. The assignment of linkage isomerism is possible from NMR spectroscopy. Our previous studies show that a strong intramolecular hydrogen bond –NH(en)···X=C (X = O or S) exists in the adjacent complexes of $[Co(tuc)(en)_2]^+$ and $[Co(dtuc)(en)_2]^+$. The amine proton and the carbon atom of C=X relevant to the hydrogen bond exhibited a characteristic downfield shift: *ca.* 2 and *ca.* 10–15 ppm in the ^1H and ^{13}C NMR spectra,

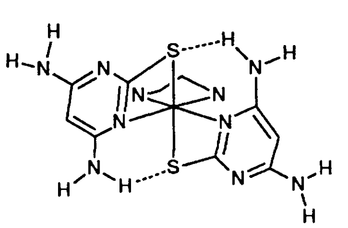


Fig. 3 Proposed intramolecular hydrogen bonds in *trans*-(*S*)-[Co(4,6-dapymt)$_2$(en)]$^+$

respectively.[2,3] Such a hydrogen bond is impossible in complex **1** in which the NH$_2$ peak, δ 7.34, is close to that (δ 7.56) of the free ligand. Therefore, the 4-amino group does not participate in hydrogen bonding and complex **1** adopts a sterically favourable remote form.

For *trans*-(*S*)-[Co(apymt)$_2$(en)]$^+$, three pairs of linkage isomers, (adjacent, adjacent), (adjacent, remote) and (remote, remote), are possible. The ^{13}C NMR spectrum of this complex shows five signals, four in the apymt ring region and one in the en region. This indicates that the complex has C_2 symmetry. If complex **2** adopts the (adjacent, adjacent) form, two intramolecular hydrogen bonds (described below) would be formed and a large downfield shift of the amine proton would be observed. The NH$_2$ peak for complex **2**, δ 7.22, however, is close to that (δ 7.34) of complex **1** with a remote form. Thus, the *trans*-(*S*) complex **2** is assigned the (remote, remote) structure.

Importance of Intramolecular Hydrogen Bonding in trans-(*S*)*-*[Co(4,6-dapymt)$_2$(en)]$^+$ *and trans-*(*S*)*-*[Co(2,4-dapymt)$_2$(en)]$^+$.—In all the en systems of pymt, mpymt and dmpymt the monosubstituted complex [CoL(en)$_2$]$^{2+}$ was the main product.[1] However, in the present photochemical preparation of the 4,6-dapymt system the main product was *trans*-(*S*)-[Co(4,6-dapymt)$_2$(en)]$^+$ even though the mole ratio of [Co(en)$_3$]$^{3+}$: 4,6-Hdapymt was 1 : 1. The formation yields were determined every 5 min of irradiation, the main product always being the bis-substituted *trans*-(*S*) isomer **5** irrespective of irradiation time (see Experimental section). The *trans*-(*S*) isomer **7** is also the major product in the thermal reaction in the 2,4-dapymt system.

Both dapymt complexes **5** and **7** have two amino groups and an interesting common structural feature. As shown in Fig. 3 two intramolecular hydrogen bonds $-NH_2 \cdots S{-}Co$ are forced to form in the *trans*-(*S*)-[Co(4,6-dapymt)$_2$(en)]$^+$ structure. In complex **5** the hydrogen bonds are formed between the co-ordinated S^2 atom of one 4,6-dapymt and an amino group of the other 4,6-dapymt, while in complex **7** they are formed between the co-ordinated S^6 atom of one 2,4-dapymt and the 2-amino group of the other 2,4-dapymt. Proton NMR spectra gave direct evidence of this mode of co-ordination. One of the NH$_2$ protons shows a characteristic downfield shift from δ 5.80 in complex **4** to δ 7.04 in complex **5** while the other appears at the same region for both complexes (δ 6.60 in complex **4** and 6.42 in complex **5**). Similarly the N^{2}H$_2$ proton also exhibits a large downfield shift from δ 5.79 in complex **6** to δ 6.79 in complex **7** though the N^{4}H$_2$ signal appears at the same region (δ 6.59 in complex **6** and δ 6.51 in complex **7**). Such a downfield shift indicates the existence of an intramolecular hydrogen bond.[10] An analogous hydrogen bond does not exist in the (remote, remote) form of complex **2**. This may be the reason why the yield of the *trans*-(*S*) isomer is relatively high in the 4,6- and 2,4-dapymt systems compared to the apymt system.

Conclusion

We can now compare the four systems of en with mpymt (X = Me),[1] tuc (X = O),[2] dtuc (X = S)[3] and apymt (X = NH$_2$). The behaviour of the tuc and dtuc systems is very similar. The stereochemistry of apymt differs from that of tuc and dtuc but is very similar to that of mpymt and shows similar ligand reactivity, product distribution and linkage isomerism. The pyrimidine ring in the [Co(N–S)(en)$_2$]$^{n+}$ complexes has a localized structure in the tuc and dtuc derivatives but is delocalized in the case of mpymt and apymt. The most striking difference between the mpymt and apymt systems is in the different bonding modes of the amino substituent groups. The amino group generally (like alkyl) acts sterically but sometimes participates in hydrogen bonding. Novel intramolecular hydrogen bonding between the co-ordinated sulfur atom and the amino group is expected in *trans*-(*S*)-[Co(4,6-dapymt)$_2$(en)]$^+$ and *trans*-(*S*)-[Co(2,4-dapymt)$_2$(en)]$^+$, and this is directly confirmed in (CD$_3$)$_2$SO solution by proton NMR spectroscopy.

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Received 22nd *December* 1992; *Paper* 2/06797H