Photochemical Synthesis and Stereochemistry of Cobalt(III) Complexes containing Pyrimidine-2-thionate 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, 2 and/or 3; HL = pyrimidine-2-thiol (Hpymt), 4-methylpyrimidine-2-thiol (Hmpymt), or 4,6-dimethylpyrimidine-2-thiol (Hdmpymt); en = ethane-1,2-diamine] have been photochemically prepared from robust $[Co(en)_3]^{3+}$ and the free ligand in moderate yields and characterized by their elemental analyses, UV/VIS absorption and ^1H and ^{13}C NMR spectra. The crystal structure of $[Co(mpymt)(en)_2][ClO_4]_2$ was determined from 3329 reflections to R = 0.043 (R' = 0.062): space group $P2_1/n$ (monoclinic) with a = 10.122(8), b = 9.003(6), c = 20.35(2) Å, β = 100.17(7)° and Z = 4. The mpymt ligand co-ordinates through N and S donors and the complex adopts a remote linkage form where the C^4 methyl group is distant from the en chelate rings. The Co–N bond length *trans* to the sulfur atom is slightly longer (0.013 Å) than the *cis* one.

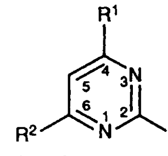
As part of our interest in the chemistry of metal complexes containing N,S-bidentate chelates[1] we report here the preparation of several cobalt(III) complexes with pyrimidine-2-thiol (Hpymt), 4-methylpyrimidine-2-thiol (Hmpymt), and 4,6-dimethylpyrimidine-2-thiol (Hdmpymt). So far, mixed-ligand cobalt(III) complexes of diamine and N,S-bidentate ligands such as 2-aminoethanethiol (Haet),[2] L-cysteine,[3] and pyridine-2-thiol (Hpyt)[4] have been prepared through reduction of the corresponding disulfide by a mixture of cobalt(II) ion and diamine. The procedure, however, was not successful for the present ligand systems.

We have developed a photochemical preparation involving irradiation with a halogen lamp of a solution of $[Co(en)_3]Cl_3$ (en = ethane-1,2-diamine) and a free ligand, which produced a series of $[CoL_n(en)_{3-n}]^{(3-n)+}$ (n = 1, 2 and/or 3) complexes in moderate yields. These cobalt(III) complexes were characterized by elemental analyses, UV/VIS absorption and ^1H and ^{13}C NMR spectra. In $[Co(mpymt)(en)_2][ClO_4]_2$ two linkage isomers are possible considering the disposition of the 4-methyl group of the pyrimidine ring. The assignment was made by ^1H NMR spectra and confirmed by X-ray crystal analysis.

Experimental

All complexes were isolated as the perchlorate salts. **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.

Preparation of Pyrimidine-2-thionato Complexes $[Co(pymt)(en)_2][ClO_4]_2$ **1** *and trans-(S)*-$[Co(pymt)_2(en)]ClO_4$ **2**.—Irradiation with an Eikohsha 500 W halogen lamp through no filter was carried out for eight quartz reaction tubes (30 cm^3) containing $[Co(en)_3]Cl_3$ (0.1 g) and Hpymt (0.03 g) in dinitrogen-purged water (25 cm^3). After 2–3 h the colour of the solution changed from yellow to reddish brown. The resultant reaction solutions were pooled, the unreacted ligand was filtered off, and 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 four coloured bands, green (**2**), light purple (**3**), reddish brown (**1**), and yellow, in this order. The last (yellow) band was confirmed to be the starting material $[Co(en)_3]^{3+}$. Each of the eluates was concentrated with a vacuum rotatory evaporator and the precipitated NaCl was filtered off. By adding an excess of $NaClO_4$ to the filtrate the perchlorate salt was obtained and recrystallized from water and methanol. Isolation of the second light purple band **3** was unsuccessful because of its low formation ratio and instability. The yield was *ca.* 60% for **1** and *ca.* 15% for **2**. Complex **1** (Found: C, 19.70; H, 3.95; N, 17.00. Calc. for $C_8H_{19}Cl_2CoN_6O_8S$: C, 19.65; H, 3.90; N, 17.20%): UV/VIS (water) 20 040 (2.05), 29 400 (sh, 2.94), 33 800 (3.92), 38 900 (4.20), 43 500 (4.27) and 46 700 cm^{-1} (log ε 4.26). Complex **2** (Found: C, 27.50; H, 3.35; N, 18.80. Calc. for $C_{10}H_{14}ClCoN_6O_4S_2$: C, 27.25; H, 3.20; N, 19.05%): UV/VIS (water) 17 010 (2.37), 22 000 (sh, 2.43), 29 800 (4.24), 36 200 (4.34) and 43 700 cm^{-1} (log ε 4.53). Complex **3**: UV/VIS (water) 16 700 (sh), 19 900, 34 500 (sh), 38 200 and 43 100 cm^{-1}.



$R^1 = R^2 = H$	Hpymt
$R^1 = Me, R^2 = H$	Hmpymt
$R^1 = R^2 = Me$	Hdmpymt

Optical Resolution of $[Co(pymt)(en)_2][ClO_4]_2$.—To a solution of complex **1** (2 g) dissolved in water (20 cm^3) was added dropwise a solution of $K_2[Sb_2(D\text{-}tart)_2]\cdot H_2O$ (tart = tartrate) (1.36 g) in water (30 cm^3). A light red diastereomer which exhibited a positive circular dichroism (CD) peak at 520 nm began to deposit. After filtration of the diastereomer, $NaClO_4$ (5 g) was added to the filtrate and the mixture was cooled to give crystals of $(-)_{520}$-$[Co(pymt)(en)_2][ClO_4]_2$ (0.5 g), which were recrystallized from water. The less-soluble diastereomer (2 g) was suspended in water (100 cm^3) and $NaClO_4$ (5 g) was added to give a dark brownish solution. This was evaporated to 20 cm^3

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

and cooled in an ice-bath. The first white precipitates were discarded and the filtrate was kept overnight in a refrigerator to give dark brown crystals of $(+)_{520}$-$[Co(pymt)(en)_2][ClO_4]_2$ (0.6 g); CD (water) 18 940 (+2.93), 23 600 (−0.478), 26 000 (+0.611), 30 000 (sh, −1.7), 33 600 (−13.7) and 40 300 ($\Delta\varepsilon$ −10.5 dm^3 mol^{-1} cm^{-1}) {Found for $\Lambda(-)_{520}$ enantiomer: C, 19.95; H, 4.15; N, 17.20. Found for $\Delta(+)_{520}$ enantiomer: C, 19.90; H, 4.00; N, 17.20. Calc. for $C_8H_{19}Cl_2CoN_6O_8S$: C, 19.65; H, 3.90; N, 17.20%. Found for the less-soluble diastereomer: C, 18.70; H, 3.30; N, 8.20. Calc. for $\Lambda(+)_{520}$-$[Co(pymt)(en)_2][Sb_2(\text{D-tart})_2]\cdot HClO_4\cdot 5H_2O$, $C_{16}H_{34}ClCoN_6O_{21}SSb_2$: C, 18.90; H, 3.35; N, 8.25%}.

Preparation of $[Co(Hpymt)(en)_2][ClO_4]_3$ **4**.—Complex **1** (500 mg) was dissolved in 30% $HClO_4$ solution (5 cm^3) and ethanol–diethyl ether (1:1, 30 cm^3) was added. The mixture was cooled in a refrigerator overnight to give dark brown crystals (0.45 g, 90% yield) {Found: C, 15.65; H, 3.75; N, 13.50. Calc. for $[Co(Hpymt)(en)_2][ClO_4]_3\cdot 1.5H_2O$, $C_8H_{23}Cl_3CoN_6O_{13.5}S$: C, 15.60; H, 3.75; N, 13.65%}; UV/VIS (water) 19 460 (2.10), 30 700 (sh, 3.45), 33 700 (3.99), 37 900 (4.08), 42 200 (4.29) and 44 800 cm^{-1} (log ε 4.30); CD of $(+)_{520}$ enantiomer in water 18 830 (+3.92), 24 500 (−0.3), 28 000 (−1.9), 32 800 (−16.3) and 32 900 cm^{-1} ($\Delta\varepsilon$ −10.7 dm^3 mol^{-1} cm^{-1}).

Preparation of 4-Methylpyrimidine-2-thionato Complexes $[Co(mpymt)(en)_2][ClO_4]_2$ **5** *and trans-*(*S*)-$[Co(mpymt)_2(en)]ClO_4$ **6**.—The complexes were prepared as described above except for the use of an equimolar amount of Hmypmt·HCl and NaOH instead of Hpymt. The column separation using SP-Sephadex C-25 (Na^+ form) showed four bands, green (**6**), light purple (**7**), reddish brown (**5**), and yellow, in this order. The last (yellow) band was $[Co(en)_3]^{3+}$. The isolations of the desired complexes as the perchlorates were carried out as described above. Crystallization of the second band, **7**, was also unsuccessful because of its low formation ratio and instability. Complex **5** (Found: C, 21.55; H, 4.40; N, 16.50. Calc. for $C_9H_{21}Cl_2CoN_6O_8S$: C, 21.50; H, 4.20; N, 16.70%); UV/VIS (water) 19 900 (2.16), 28 600 (2.86), 33 900 (3.99), 38 700 (4.28) and 43 300 (sh, 4.31) and 46 500 cm^{-1} (log ε 4.37). Complex **6** {C, 27.70; H, 4.00: N, 16.10. Calc. for *trans*-(*S*)-$[Co(mpymt)_2(en)]ClO_4\cdot 1.5H_2O\cdot 0.2NaClO_4$, $C_{12}H_{21}Cl_{1.2}CoN_6Na_{0.2}O_{6.3}S_2$: C, 27.70; H, 4.05; N, 16.15%}.

Preparation of $[Co(Hmpymt)(en)_2][ClO_4]_3$ **8**.—This complex was prepared quantitatively from **5** in an acidic medium by adding an equal volume of ethanol and ether {Found: C, 18.50; H, 4.15; N, 13.70. Calc. for $[Co(Hmpymt)(en)_2][ClO_4]_3\cdot 0.25EtOH$, $C_{9.5}H_{23.5}Cl_3CoN_6O_{12.5}S$: C, 18.55; H, 3.85; N, 13.65%}; UV/VIS (water) 19 500 (2.14), 29 400 (3.66), 34 200 (sh, 4.01), 38 500 (4.15), 42 000 (sh, 4.33) and 44 200 cm^{-1} (log ε 4.36).

Preparation of 4,6-Dimethylpyrimidine-2-thionato Complexes $[Co(dmpymt)(en)_2][ClO_4]_2$ **9** *and fac-*(*S*)-$[Co(dmpymt)_3]$ **10**.—The reaction solution was photochemically prepared in the same way as that for the pymt complexes. A green water-insoluble complex **10** was filtered off. The filtrate was chromatographed to give a single reddish brown band (**9**) besides the starting material. The complex was isolated as the perchlorate salt (8% yield) {Found: C, 22.70; H, 4.80; N, 15.70. Calc. for $[Co(dmpymt)(en)_2][ClO_4]_2\cdot H_2O$ **9**, $C_{10}H_{25}Cl_2CoN_6O_9S$: C, 22.45; H, 4.70; N, 15.70%}; UV/VIS (water) 19 600 (2.00), 25 800 (sh, 2.22), 34 000 (4.01), 39 800 (4.29) and 46 300 cm^{-1} (log ε 4.34). Complex **10** (Found: C, 45.35; H, 4.40; N, 17.80. Calc. for $C_{18}H_{21}CoN_6S_3$: C, 45.35; H, 4.45; N, 17.65%): UV/VIS (EtCH) 16 200 (2.25), 20 200 (2.47), 23 900 (sh, 2.99), 33 000 (4.50) and 36 300 cm^{-1} (log ε 4.62).

Detection of Cobalt(II) *Ion in Reaction Solution.*—Cobalt(II) ion was detected according to the method of Ellis and Gibson[5] which is based on the *o*-dichlorobenzene extraction of the blue $[AsMePh_3]_2[Co(NCS)_4]$ complex formed between aqueous cobalt(II) ion and aqueous methyltriphenylarsonium thiocyanate solution and colorimetric determination. This method is reported to be suitable within a range of 10–100 μg of cobalt(II) per cm^3.

Irradiation with a 500 W halogen lamp was carried out for 3 h using a reaction mixture of $[Co(en)_3]^{3+}$ (100 mg) and Hpymt (30 mg) in water (25 cm^3). This mixture showed no absorption at 627 nm due to $[AsMePh_3]_2[Co(NCS)_4]$. A similar experiment using Λ-$[Co(en)_3]Cl_3$ and Hpymt was performed. After column chromatography the enantiomeric excess of the unreacted Λ-$[Co(en)_3]^{3+}$ was the same as the initial value. These facts indicate that no cobalt(II) species was formed during irradiation.

X-Ray Crystal Structure Determination of $[Co(mpymt)(en)_2][ClO_4]_2$.—*Crystal data.* $C_9H_{21}Cl_2CoN_6O_8S$, M = 503.20, monoclinic, space group $P2_1/n$, a = 10.122(8), b = 9.003(6), c = 20.35(2) Å, β = 100.17(7)°, U = 1825(5) $Å^3$, Z = 4, D_c = 1.831 g cm^{-3}, $F(000)$ = 1032. Red prism. Crystal dimensions: 0.2 × 0.2 × 0.15 mm, μ(Mo-Kα) = 14.33 cm^{-1}.

Data collection and processing. Rigaku AFC-5R diffractometer, ω–2θ mode with ω scan width = 1.05 + 0.30 tan θ, ω scan speed 4.0° min^{-1}, graphite-monochromated Mo-Kα radiation; 4742 reflections measured ($1.5 \leqslant \theta \leqslant 27.5°$), 4496 unique [merging R = 0.014 after absorption correction (maximum, minimum transmission factors = 1.00, 0.00)], giving 3329 with $I > 3\sigma(I)$. Linear and approximately isotropic crystal decay, *ca.* 79%, corrected during processing.

Structure analysis and refinement. Direct method followed by normal heavy-atom procedure. The final cycle of full-matrix least-squares refinement was based on the observed reflections and 270 variable parameters. The final values of R and R' were 0.043 and 0.062, respectively. All calculations were performed using the TEXSAN[6] 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 spectra were measured with a Hitachi 330 spectrophotometer, CD spectra with a JASCO J-500 spectropolarimeter, and ^1H and ^{13}C NMR spectra with JEOL JNM-GSX270 and GSX-400 spectrometers in D_2O, $(CD_3)_2SO$ and $(CD_3)_2CO$. The X-ray crystal analysis was made by the X-Ray Diffraction Service of the Department of Chemistry.

Results and Discussion

Characterization of Complexes.—Three kinds of pymt complexes were separated by column chromatography. Their UV/VIS spectra are shown in Fig. 1. The main product **1** shows its first d–d absorption band at 20 040 cm^{-1} and the intense sulfur-to-metal charge-transfer (c.t.) band at *ca.* 33 800 cm^{-1}. These are characteristic of thiolato complexes of CoN_5S type[2–4] such as $[Co(aet)(en)_2]^{2+}$ and $[Co(pyt)(en)_2]^{2+}$. In the ^{13}C NMR spectrum of **1**, eight signals, four in the pymt chemical shift region and four in the en region, were observed (Table 1). Therefore, the composition $[Co(pymt\text{-}N,S)(en)_2]^{2+}$ is assigned in accord with the elemental analysis.

The column chromatographic behaviour shows that the two complexes **2** and **3** seem to have a +1 ionic charge and composition $[Co(pymt)_2(en)]^+$, one *trans*-(*S*) and two *cis*-(*S*) geometrical isomers being possible (Fig. 2). The green complex **2** exhibits two components at 17 010 and *ca.* 22 000 (sh) cm^{-1} in the first d–d absorption band region and a very low-energy sulfur-to-metal c.t. band at 29 800 cm^{-1}. They are characteristic for *trans*-(*S*)-$Co(thiolate)_2N_4$ type complexes.[7] The ^{13}C NMR spectrum of **2** gave only five signals, one in the en region and four in the pymt region. Therefore, the complex is assigned as

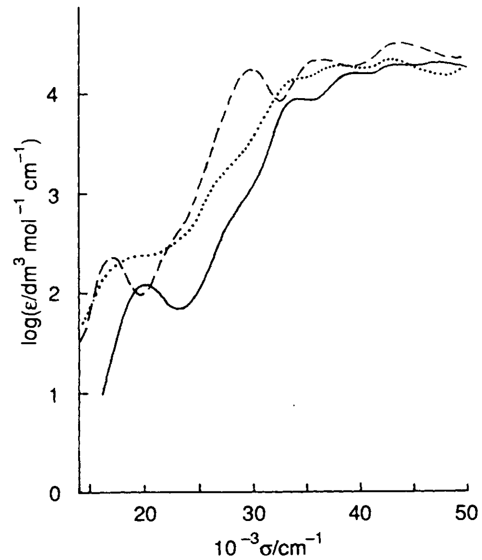


Fig. 1 Ultraviolet/visible absorption spectra of $[Co(pymt)_n(en)_{3-n}]^{(3-n)+}$: **1** (——), **2** (– – – –) and **3** (· · · ·); log ε on arbitrary scale

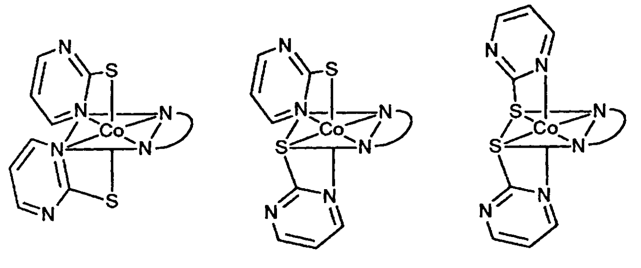
Table 1 Proton and ^{13}C NMR spectral data in D_2O

Complex	$^1H^a$	$^{13}C^b$
1	8.628 (q, 1 H) H^4 8.477 (q, 1 H) H^6 7.157 (t, 1 H) H^5	182.00 C^2, 161.16 C^4 158.56 C^6, 118.32 C^5 46.92, 46.41, 46.31, 45.62 en
2		182.39 C^2 160.03, 159.50 C^4, C^6 117.59 C^5, 46.90 en
4[c]	8.623 (q, 1 H) H^4 8.508 (q, 1 H) H^6 7.759 (s, 1 H) NH 7.112 (t, 1 H) H^5	181.87 C^2, 159.13 C^4 157.56 C^6, 115.84 C^5 45.51, 45.11, 45.00, 44.49 en
5	8.240 (d, 1 H) H^6 7.046 (d, 1 H) H^5 2.502 (s, 3 H) CH_3	181.76 C^2, 172.54 C^4 156.97 C^6, 117.85 C^5 46.48, 46.10, 45.95, 45,46 en 24.09 CH_3
6		181.79 C^2, 171.72 C^4 157.81 C^6, 117.41 C^5 46.65 en, 23.84 CH_3
8[c]	8.316 (d, 1 H) H^6 7.701 (s, 1 H) NH 7.002 (d, 1 H) H^5 2.391 (s, 3 H) CH_3	
9	6.806 (s, 1 H) H^5 2.512 (s, 3 H) C^4H_3 2.351 (s, 3 H) C^6H_3	183.64 C^2, 120.75 C^5 173.01, 172.47 C^4, C^6 48.60, 48.16, 48.05, 47.58 en 25.54 C^4H_3, 23.40 C^6H_3
10[d]		169.20, 168.29 C^4, C^6 116.24 C^5 23.64, 19.76 CH_3

[a] Downfield relative to sodium 4,4-dimethyl-4-silapentene-1-sulfonate as internal standard. [b] Downfield relative to $SiMe_4$ by use of dioxane (δ 67.35) as internal standard. [c] In $(CD_3)_2SO$ containing $SiMe_4$. [d] In $(CD_3)_2CO$.

trans-(*S*)-$[Co(pymt)_2(en)]^+$. The light purple complex **3** was not isolated because of its low yield and instability, but was assigned to *cis*-(*S*)-$[Co(pymt)_2(en)]^+$ based on its absorption spectrum.

The complexes of mpymt and dmpymt were characterized by their absorption and NMR spectra in a similar manner. The main products **5** and **9** were monosubstituted complexes of $[Co(N\text{-}S)(en)_2]^{2+}$ type. Complex **10** was confirmed to be $[Co(dmpymt)_3]$ by elemental analysis; two geometrical isomers, *fac*-(*S*) and *mer*-(*S*), are possible. The absorption spectrum showed a single component in the first d–d transition region and the ^{13}C NMR spectrum gave five resonance lines but the lack of a C^2 signal. These facts indicate that **10** has the *fac*-(*S*) geometry. Its acetone adduct is known to be *fac*-(*S*) through the X-ray structural analysis by Cartwright *et al.*[8]



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

Fig. 2 Three possible geometrical isomers of $[Co(pymt)_2(en)]^+$

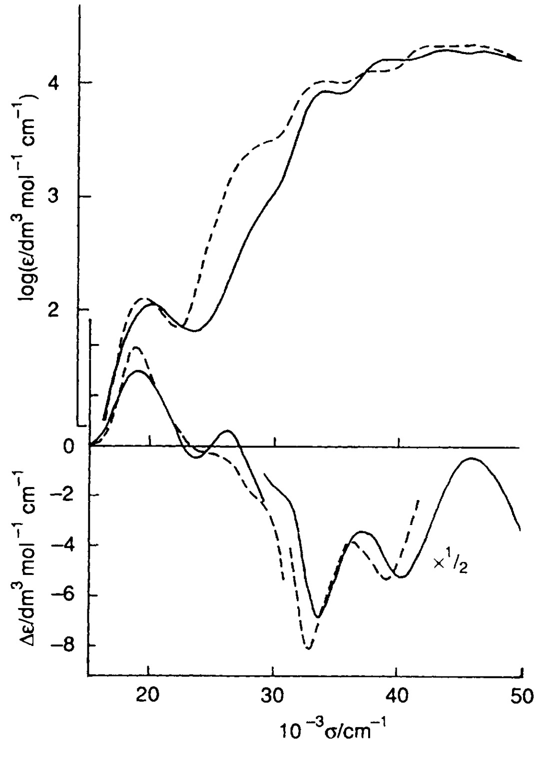


Fig. 3 Ultraviolet/visible absorption and CD spectra of $[Co(pymt)(en)_2]^{2+}$ (——) and $[Co(Hpymt)(en)_2]^{3+}$ (– – – –)

Recrystallization of $[Co(pymt)(en)_2]^{2+}$ or $[Co(mpymt)(en)_2]^{2+}$ from an acidic medium produced the corresponding protonated species $[Co(Hpymt)(en)_2]^{3+}$ or $[Co(Hmpymt)(en)_2]^{3+}$, respectively. The protonation occurs at the uncoordinated imine nitrogen atom. This is confirmed by the ^1H NMR spectrum: a new NH signal was observed at δ 7.7–7.8 in $(CD_3)_2SO$. The protonated complexes also exhibit characteristic features in the UV/VIS absorption spectra. The first d–d absorption band is red-shifted by 10–15 nm compared with the original band, and a new intense band (log ε = 3.4–3.6) appears at 29 000–31 000 cm^{-1} as shown in Fig. 3. The latter bathochromic shift has been reported in the protonation of pyrimidine-2-thiol itself.[9]

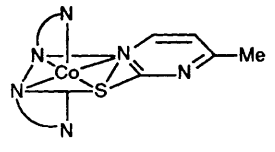
The CD spectrum of $(+)_{520}$-$[Co(pymt)(en)_2]^{2+}$ is shown in Fig. 3. The complex exhibits two CD components, (+) and (−), at lower energy with respect to the first d–d band region. The CD pattern is very similar to that of Λ-$(+)_{520}$-$[Co(pyt)(en)_2]^{2+}$.[4] Thus the $(+)_{520}$ enantiomer obtained from the less-soluble diastereomer is assigned the Λ absolute configuration.

Preparation of Complexes.—Table 2 collects the formation ratios of the complexes. Monosubstituted complexes of $[Co(N\text{-}S)(en)_2]^{2+}$ type are the main products in all cases. The formation ratios decrease in the order pymt > mpymt >

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

N-S ligand	Mono ($n = 1$)	Bis ($n = 2$)*	Tris ($n = 3$)	Irradiation time (h)
pymt	65	30	0	3.0
mpymt	57	16	0	2.5
dmpymt	12	trace	5	2.0

* Total amount of *trans*-(*S*) and *cis*-(*S*) isomers.



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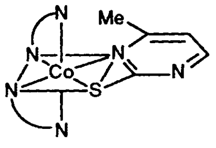


adjacent

dmpymt, which may reflect steric crowding. It should be noted that the only complexes found belong to the series $[Co(N\text{-}S)_n(en)_{3-n}]^{(3-n)+}$ ($n = 1$, 2 and/or 3). The photochemical reactions between pyrimidine-2-thiolate ligands and $[Co(en)_3]Cl_3$ were extremely clean without any by-product as revealed by column chromatography. Product control is possible to some extent by changing the irradiation time and/or an amount of ligand. It is noteworthy that the thermal reactions between $[Co(en)_3]Cl_3$ and the present ligands did not proceed at all even at 80 °C. Analogous photochemical preparations are effective for N,S-containing ligands such as pyridine-2-thiol, its derivatives, 2-aminoethanethiol, and L-cysteine, but not for N,O-containing ligands such as amino acids.

The low sensitivity of cobalt(III) polyamine complexes to irradiation in the ligand-field spectral region has been generally recognized. According to Balzani and Carassiti,[10] the quantum yield for aquation of $[Co(en)_3]^{3+}$ is $\approx 10^{-4}$ in the $^1T_{2g} \longleftarrow {}^1A_{1g}$ band, $< 10^{-5}$ in the $^1T_{1g} \longleftarrow {}^1A_{1g}$ band, and for both bands no redox decomposition was observed. There is a possibility that a catalytic amount of cobalt(II) species is formed in the systems. Cobalt(II) ion was tested for by the method of Ellis and Gibson[5] (see Experimental section). The fact that the unreacted optically active $[Co(en)_3]^{3+}$ exhibits no racemization after irradiation excludes the above possibility. Thus, the reaction seems to be purely photochemical, though the exact mechanism is not clear.

Heating a solution containing an equimolar amount of $[Co(en)_3]^{3+}$ and Hpymt and a catalytic amount of $CoCl_2 \cdot 6H_2O$ {*ca.* 1 mg per 100 mg of $[Co(en)_3]^{3+}$} produced a similar reaction mixture to that obtained upon irradiation. The thermal reaction between $[Co(en)_3]^{3+}$ and Hpymt in the presence of activated carbon also gave a brown solution. However, these reaction mixtures often contain some by-products besides the desired complexes, in contrast with the photochemical one.

Linkage Isomerism.—Since 4-methylpyrimidine-2-thionate is an unsymmetrical ambidentate ligand its N,S-bidentate co-ordination to a metal ion generates linkage isomerism. There is a remote isomer with the C^4 methyl group of the pyrimidine ring distant from the two en chelates and an adjacent isomer with the methyl group near the en chelates. The difference nuclear Overhauser effect (NOE) technique with the ^1H NMR spectra is very useful for assignments of this kind of isomerism. Irradiation at the C^6 proton frequency of $[Co(mpymt)(en)_2][ClO_4]_2$ results in enhancement of the methylene resonances of en at δ 2.6–3.0 but irradiation at the C^4 methyl frequency does not. This means that the C^6 proton is spacially located near the en chelate rings and the C^4 methyl group away from them, and therefore the mpymt complex is assigned the remote form. This was confirmed by the X-ray crystal analysis described below.

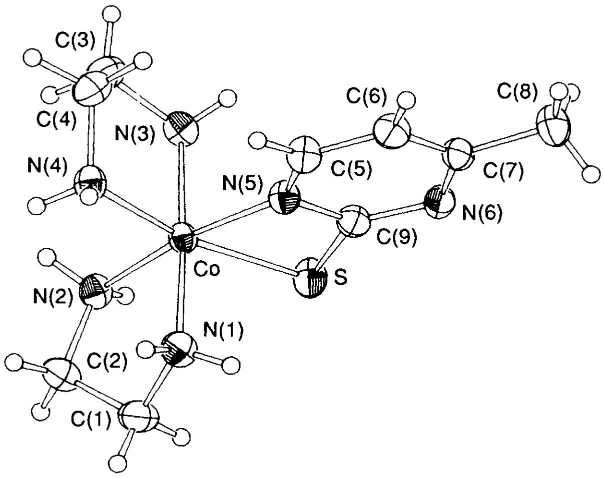


Fig. 4 An ORTEP drawing of $[Co(mpymt)(en)_2][ClO_4]_2$ **5**

Table 3 Positional parameters for complex **5**

Atom	*x*	*y*	*z*
Co	0.106 74(4)	0.292 03(5)	0.339 23(2)
Cl(1)	0.058 4(1)	0.201 0(1)	0.602 86(4)
Cl(2)	0.614 92(9)	0.312 1(1)	0.377 27(5)
S	0.214 7(1)	0.176 6(1)	0.263 28(4)
O(1)	−0.020 1(3)	0.204 7(4)	0.537 1(2)
O(2)	−0.026 6(4)	0.164 2(4)	0.649 4(2)
O(3)	0.161 6(3)	0.092 6(4)	0.606 1(2)
O(4)	0.115 5(4)	0.344 8(3)	0.618 2(2)
O(5)	0.598 6(7)	0.198(1)	0.328 7(4)
O(6)	0.523 4(4)	0.276 4(6)	0.419 1(2)
O(7)	0.578 6(5)	0.435 2(6)	0.339 0(4)
O(8)	0.749 8(4)	0.304 7(6)	0.407 0(2)
N(1)	−0.054 8(3)	0.171 1(3)	0.313 3(2)
N(2)	0.012 4(3)	0.443 6(3)	0.279 1(1)
N(3)	0.262 9(3)	0.420 7(3)	0.364 1(1)
N(4)	0.045 4(3)	0.373 9(3)	0.418 4(1)
N(5)	0.206 3(3)	0.126 4(3)	0.384 1(1)
N(6)	0.359 1(3)	−0.033 9(3)	0.342 2(1)
C(1)	−0.135 8(4)	0.234 8(4)	0.251 8(2)
C(2)	−0.131 3(3)	0.400 9(4)	0.258 7(2)
C(3)	0.242 3(4)	0.525 0(4)	0.417 7(2)
C(4)	0.162 3(4)	0.444 1(4)	0.462 0(2)
C(5)	0.232 6(3)	0.060 5(4)	0.443 6(2)
C(6)	0.326 8(4)	−0.051 3(4)	0.455 5(2)
C(7)	0.391 6(3)	−0.093 9(4)	0.403 3(2)
C(8)	0.502 5(4)	−0.205 5(4)	0.413 0(2)
C(9)	0.268 6(3)	0.074 5(4)	0.335 2(2)

In a case of *trans*-(*S*)-$[Co(mpymt)_2(en)]^+$ three pairs of linkage isomers, (adjacent, adjacent), (adjacent, remote), (remote, remote), are possible. The ^{13}C NMR spectra of this complex shows seven signals, five in the mpymt ring region and two in the en and methyl regions, which mean that this complex has C_2 symmetry. Since the remote configuration is sterically more favoured, we conclude that this *trans*-(*S*) complex takes a (remote, remote) structure.

Crystal Structure of $[Co(mpymt)(en)_2][ClO_4]_2$.—Fig. 4 shows an ORTEP[11] drawing of the title complex ion. The atomic parameters and bond distances and angles are listed in Tables 3 and 4, respectively. A distorted octahedral structure is found: the N(1)–Co–N(3) angle is 177.4(1)°, whereas the S–Co–N(4) and N(5)–Co–N(2) angles are 167.84(8) and 169.8(1)°, respectively. As had been expected from the spectroscopic data, the mpymt ligand co-ordinates in a bidentate manner through the nitrogen and sulfur donors and adopts the remote linkage form. Its bite angle S–Co–N(5) is 72.4(1)°, almost the same as the 72° (average) in *fac*-(*S*)-$[Co(dmpymt)_3]$.[7]

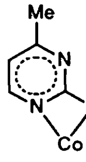
Table 4 Selected intramolecular bond distances (Å) and angles (°) for complex **5**

Co–S	2.294(2)	N(4)–C(4)	1.489(5)
Co–N(1)	1.958(3)	N(5)–C(5)	1.334(4)
Co–N(2)	1.964(3)	N(5)–C(9)	1.352(5)
Co–N(3)	1.953(3)	N(6)–C(7)	1.343(4)
Co–N(4)	1.969(3)	N(6)–C(9)	1.329(4)
Co–N(5)	1.936(3)	C(1)–C(2)	1.502(5)
S–C(9)	1.732(4)	C(3)–C(4)	1.501(6)
N(1)–C(1)	1.485(5)	C(5)–C(6)	1.377(5)
N(2)–C(2)	1.491(4)	C(6)–C(7)	1.396(5)
N(3)–C(3)	1.483(5)	C(7)–C(8)	1.493(5)
S–Co–N(1)	92.3(1)	Co–N(3)–C(3)	110.7(2)
S–Co–N(2)	97.6(1)	Co–N(4)–C(4)	108.3(2)
S–Co–N(3)	89.0(1)	Co–N(5)–C(5)	140.9(3)
S–Co–N(4)	167.84(8)	Co–N(5)–C(9)	101.0(2)
S–Co–N(5)	72.4(1)	C(5)–N(5)–C(9)	118.1(3)
N(1)–Co–N(2)	85.8(1)	C(7)–N(6)–C(9)	116.5(3)
N(1)–Co–N(3)	177.4(1)	N(1)–C(1)–C(2)	107.6(3)
N(1)–Co–N(4)	93.5(1)	N(2)–C(2)–C(1)	107.1(3)
N(1)–Co–N(5)	92.2(1)	N(3)–C(3)–C(4)	107.1(3)
N(2)–Co–N(3)	91.8(1)	N(4)–C(4)–C(3)	107.8(3)
N(2)–Co–N(4)	93.5(1)	N(5)–C(5)–C(6)	120.4(3)
N(2)–Co–N(5)	169.8(1)	C(5)–C(6)–C(7)	118.2(3)
N(3)–Co–N(4)	85.6(1)	N(6)–C(7)–C(6)	121.5(3)
N(3)–Co–N(5)	90.3(1)	N(6)–C(7)–C(8)	116.6(3)
N(4)–Co–N(5)	96.6(1)	C(6)–C(7)–C(8)	121.9(3)
Co–S–C(9)	77.7(1)	S–C(9)–N(5)	108.7(2)
Co–N(1)–C(1)	108.8(2)	S–C(9)–N(6)	126.1(3)
Co–N(2)–C(2)	109.7(2)	N(5)–C(9)–N(6)	125.2(3)

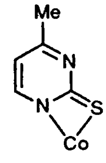
Since we cannot find any evidence for the presence of the adjacent linkage isomer under neutral and alkaline conditions, such complete stereoselectivity may be ascribed to the steric effect. Shepherd and co-workers[12] reported a similar kind of linkage isomerism in pentaammine(4-methylimidazole)-cobalt(III), though 4-methylimidazole is an unidentate ligand. In their system, both adjacent and remote isomers were obtained and the latter is estimated to be thermodynamically more favoured for steric reasons.

The Co–S and Co–N(5) lengths [2.294(2) and 1.936(3) Å, respectively] are in good agreement with 2.282(2) and 1.929(5) Å in $[Co(pyt)(en)_2]^{2+}$,[3] but are slightly different from 2.259 and 1.979 Å (averages) in *fac*-(*S*)-$[Co(dmpymt)_3]$ because of the presence of the *trans* influence for the latter complex.

The four C–N [1.329(4), 1.334(4), 1.343(4) and 1.352(5) Å] and two C–C [1.377(5) and 1.396(5) Å] bond lengths of the mpymt ligand do not deviate much from those of 1.340(2) and 1.393(2) Å,[13] respectively, of pyrimidine itself which has a delocalized structure. The bond lengths of the dmpymt ligands in *fac*-(*S*)-$[Co(dmpymt)_3]$ are also very similar to the above values. These facts indicate that the complexes containing pymt, mpymt and dmpymt adopt mainly the resonance structure **a** and the contribution of **b** is very small, if any. The ^1H NMR chemical shifts of complex **1** (δ 8.628 for H^4, 8.477 for H^6, and 7.157 for H^5) are almost the same as δ 8.6 for H^4 and H^6 and δ 7.1 for H^5 of the pyrimidine. This supports the delocalized structure of the pymt complex.



a



b

The Co–N(4) bond length *trans* to sulfur is 1.969(3) Å, and the average of Co–N(1) and Co–N(3) *cis* to sulfur is 1.956 Å; the difference between the *trans* and *cis* bond lengths is 0.013 Å. This *trans* influence is less than the 0.041 Å of aet thiolate[14] and slightly less than the 0.023 Å of the pyt thiolate[4] in the corresponding $[Co(N–S)(en)_2]^{2+}$ type complexes.

Acknowledgements

We thank Mr. T. Yamamoto of the X-ray Diffraction Service of the Department of Chemistry, Dr. A. Fuyuhiro in our group, and Professor Y. Kushi and Dr. H. Tamura of the Institute of Chemistry of the College of General Education of our University for X-ray crystal analysis.

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Received 20th October 1991; *Paper* 1/05526G