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Synthesis and stereochemistry of cobalt(III) complexes containing purine-6-thione and related ligands

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Seven cobalt(III) complexes containing five purinethiones $[Co(L\text{-}N,S)(en)_2]^{n+}$ and [H_nL = H_2put = 9*H*-purine-6(1*H*)-thione, H_2aput = 2-amino-9*H*-purine-6(1*H*)-thione, H_3tpuo = 3,6-dihydro-6-thioxo-9*H*-purine-2(1*H*)-one, H_3oput = 2,3-dihydro-2-thioxo-9*H*-purin-6(1*H*)-one and $H_2pzpymt$ = 1*H*-pyrazolo[3,4-*d*]-pyrimidine-4(5*H*)-thione; en = ethane-1,2-diamine] were thermally or photochemically prepared and characterized by elemental analysis, UV/VIS absorption and ^1H and ^{13}C NMR spectra. The crystal structure of $[Co(put)(en)_2]Cl{\cdot}2H_2O$ was determined. The put ligand co-ordinates through S^6 and N^7 forming a five-membered chelate ring. The other purine-6-thione ligands all adopt this mode rather than the four-membered one of N^1/S^6. Carbon-13 NMR spectroscopy is very useful for the assignment of the above linkage isomers.

Purine-6-thione (H_2put) is an established clinical agent for the therapy of human leukaemias[1] and some metal complexes of put, especially those of platinum and palladium, show antitumour activity.[2] Since this compound has multiple binding sites such as N^1, N^3, S^6, N^7 and N^9 it is interesting to investigate its co-ordination modes.[3] In the metal complexes with a N,S-chelating purine-6-thione ligand, linkage isomerism possibly depends on the N^1/S^6 four- or S^6/N^7 five-membered chelation. Such linkage isomerism is different from that in the pyrimidine-2-thione(Hpymt) system because both N,S modes result in four-membered chelate rings in the latter system.[4]

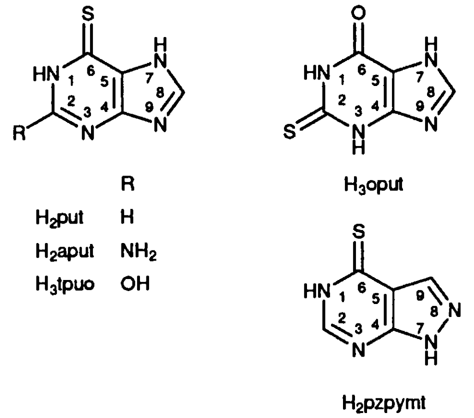
Here we describe the synthesis of bis(ethane-1,2-diamine) type cobalt(III) complexes containing purine-6-thione and related ligands. Five kinds of ligands were used: 9*H*-purine-6(1*H*)-thione (H_2put), 2-amino-9*H*-purine-6(1*H*)-thione (H_2aput), 3,6-dihydro-6-thioxo-9*H*-purin-2(1*H*)-one (H_3tpuo), 2,3-dihydro-2-thioxo-(9*H*)-purin-6(1*H*)-one (H_3oput) and 1*H*-pyrazolo[3,4-*d*]pyrimidine-4(5*H*)-thione ($H_2pzpymt$).

Experimental

All of the thiones (Aldrich) were used without further purification.

Preparation of complexes

$[Co(put)(en)_2]Cl$ 1 and $[Co(Hput)(en)_2]Cl_2$ 2. The compound H_2put (0.68 g, 4 mmol) was suspended in warm water (200 cm^3) and adjusted to pH 8–9 by adding aqueous NaOH. To the above solution was added *rac*-$[Co(en)_3]Cl_3$ (en = ethane-1,2-diamine) (1.6 g, 4 mmol). The mixture was divided into eight portions in quartz reaction tubes (30 cm^3) and nitrogen gas was bubbled through them for 20 min. Irradiation with a Toshiba 500 W halogen lamp in the absence of a filter was carried out 20–22 °C for 2 h, giving clear red solutions. These were combined and poured onto a column of cation exchanger (SP-Sephadex C-25, Na^+ form, 5 × 40 cm). Elution with 0.1 mol dm^{-3} NaCl gave three coloured bands, two red (**1** and **2**) and a yellow one, 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 EtOH to the filtrate, the chloride salt of each complex was obtained and recrystallized from water and methanol. The yield was 15% for **1** and 36% for **2**. Complex **1** {Found: C, 27.00; H, 5.50; N, 27.95. Calc. for $[Co(put)(en)_2]Cl{\cdot}2H_2O$ ($C_9H_{22}ClCoN_8O_2S$): C, 26.95; H, 5.55; N, 27.95%}: UV/VIS (water) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 600 (infl), 496 (140), 400 (sh) (220), 324 (11 600), 305 (10 700) and 265 (sh) (11 000). Complex **2** {Found: C, 26.95; H, 4.80; N, 27.75. Calc. for $[Co(Hput)(en)_2]Cl_2$ ($C_9H_{19}Cl_2CoN_8S$): C, 26.95; H, 4.75; N, 27.95%}: UV/VIS (water) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 502 (130), 390 (sh) (270), 327 (13 800), 295 (10 400), 245 (sh) (14 000) and 222 (25 300).



$[Co(Haput)(en)_2]Cl_2$ 3. To a solution of *trans*-$[CoCl_2(en)_2]Cl$ (1.45 g) was added a solution of H_2aput (0.84 g) and NaOH (0.2 g). The mixture was heated at 70 °C for 3 h. After filtration of brown precipitates the filtrate was chromatographed using SP-Sephadex C-25 resin (Na^+ form, 5 × 40 cm) with 0.2 mol dm^{-3} NaCl to give two red bands. The first eluate (**3**) was concentrated with a vacuum rotary evaporator and the white precipitate of NaCl filtered off. Addition of EtOH to the filtrate gave the chloride salt of the complex which was recrystallized from water. The second red band was barely eluted with 2 mol dm^{-3} NaCl and the eluate was allowed to stand at room temperature to give a brown precipitate, of unknown composition. Complex **3** {Found: C, 23.05; H, 5.55; N, 26.85. Calc. for $[Co(Haput)(en)_2]Cl_2{\cdot}3H_2O$ ($C_9H_{26}Cl_2CoN_9O_3S$): C, 23.00; H, 5.55; N, 26.80%}: UV/VIS (water) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 498 (125), 406 (sh) (170), 334 (9690), 325 (sh) (9020), 284 (13 000), 246 (21 000) and 210 (34 000).

$[Co(H_2tpuo)(en)_2][ClO_4]_2$ 4. The reaction solution was prepared in the same way as that for the aput complex. It was

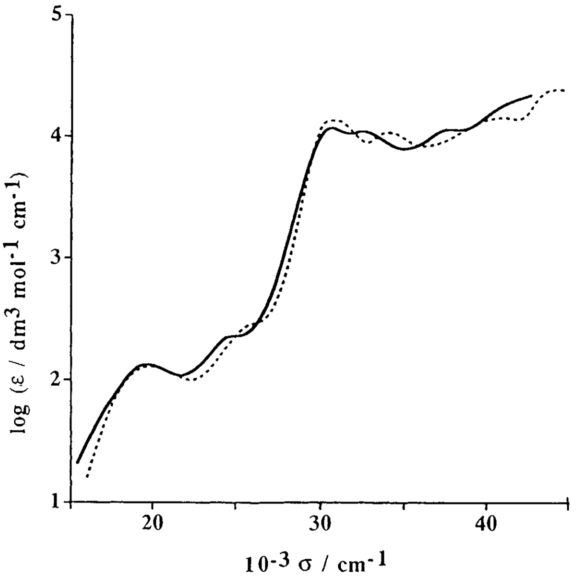


Fig. 1 The UV/VIS absorption spectra of complexes **1** (——) and **2** (- - -)

chromatographed using SP-Sephadex C-25 resin (Na^+ form, 5 × 40 cm) to give a single reddish brown band (**4**). The eluate was concentrated with a vacuum rotary evaporator and the white precipitate of NaCl filtered off. Addition of $NaClO_4$ to the filtrate gave the perchlorate salt which was recrystallized from water (yield: 30%) {Found: C, 19.40; H, 3.70; N, 19.30. Calc. for $[Co(H_2tpuo)(en)_2][ClO_4]_2 \cdot H_2O$ ($C_9H_{21}Cl_2CoN_8O_{10}S$): C, 19.20; H, 3.75; N, 19.90%}: UV/VIS (water), λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 500 (138), 400 (sh) (280), 352 (13 700), 295 (sh) (9400), 273 (15 000), 242 (sh) (16 000) and 216 (28 000).

$[Co(Hoput)(en)_2]Cl$ 5 and $[Co(H_2oput)(en)_2][ClO_4]_2$ 6. Complex **5** was prepared and separated in a similar way to the above except for the use of H_3oput instead of H_2put. Irradiation was continued for 17 h. Complex **5** {Found: C, 28.05; H, 4.90; N, 28.30. Calc. for $[Co(Hoput)(en)_2]Cl \cdot 0.5H_2O$ ($C_9H_{19}ClCoN_8O_{1.5}S$): C, 27.75; H, 4.90; N, 28.75%}: UV/VIS (water) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 600 (infl), 494 (133), 370 (sh) (230), 291 (17 000), 240 (sh) (23 500) and 220 (sh) (29 000).

The protonated species **6** was obtained by recrystallizing complex **5** from 10% $HClO_4$ solution. Complex **6** {Found: C, 18.25; H, 3.95; N, 18.60. Calc. for $[Co(H_2oput)(en)_2][ClO_4]_2 \cdot 2.5H_2O$ ($C_9H_{24}Cl_2CoN_8O_{11.5}S$): C, 18.30; H, 4.10; N, 19.00%}: UV/VIS (5% $HClO_4$) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 508 (154), 410 (sh) (100), 360 (sh) (285), 298 (12 400), 270 (sh) (12 600), 246 (23 500) and 218 (sh) (26 400).

$[Co(Hpzpymt)(en)_2]Cl_2$ 7. The complex was prepared and separated in a similar way to the above except for the use of $H_2pzpymt$ instead of H_3oput. After filtration of a brown precipitate the filtrate was chromatographed using SP-Sephadex C-25 resin (Na^+ form, 4 × 20 cm). A non-adsorbing brown band was eluted with water and elution with 0.2 mol dm^{-3} NaCl gave two bands. The last red band has a high charge because it was eluted with 3 mol dm^{-3} NaCl. The first eluate (**7**) was concentrated with a vacuum rotary evaporator and the white precipitate of NaCl was filtered off. Addition of EtOH and cooling produced dark red crystals of complex **7** (yield: 71%) (Found: C, 26.95; H, 4.80; N, 27.75. Calc. for $C_9H_{19}Cl_2CoN_8S$: C, 26.95; H, 4.75; N, 27.95%). UV/VIS (water) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 513 (122.1), 400 (sh) (110), 333 (14 400), 284 (sh) (10 600), 259 (15 400) and 217 (34 400).

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

Crystal structure determination of $[Co(put)(en)_2]Cl \cdot 2H_2O$

Crystal data. $C_9H_{22}ClCoN_8O_2S$, $M = 400.77$, monoclinic, space group $P2_1/c$ (no. 14), $a = 12.639(2)$, $b = 7.507(2)$, $c = 16.404(2)$ Å, $\beta = 92.12(1)°$, $Z = 4$, $U = 1555.3(5)$ Å^3, $D_c = 1.711$ g cm^{-3}, $F(000) = 832$. Red crystal: 0.20 × 0.15 × 0.20 mm, μ(Mo-Kα) = 14.22 cm^{-1}.

Data collection and processing. Rigaku AFC5R diffractometer, 23 °C, ω–2θ mode with ω-scan width = 1.15 + 0.35tan θ, ω-scan speed 6.0° min^{-1}, graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,69$ Å); 5112 reflections measured ($1.5 \leqslant \theta \leqslant 30.0°$, h 0–18, k 0–11, l −23 to +23), 4912 unique [merging $R = 0.026$ after empirical absorption correction (maximum, minimum transmission factors = 1.00, 0.94)], giving 2740 with $I > 3\sigma(I)$. Linear and approximately isotropic crystal decay, *ca.* 1.24%, corrected during processing. The data were also corrected for Lorentz-polarization effects.

Structure analysis and refinement. Direct method followed by normal heavy-atom procedures. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least squares was based on the 2740 observed reflections and 199 variable parameters. The final values of R and R' were 0.044 and 0.046, respectively. The weighting scheme was based on counting statistics. Maximum and minimum peaks in the final Fourier-difference map were 1.07 and −0.50 e Å^{-3}. Neutral atom scattering factors were taken from ref. 5, anomalous dispersion coefficients from ref. 6 and $\Delta f'$ and $\Delta f''$ values from ref. 7. All calculations were performed using the TEXSAN,[8] crystallographic software package.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Measurements

The UV/VIS absorption spectra were measured with a Hitachi 330 spectrophotometer, proton and ^{13}C NMR spectra with a JEOL JNM-GSX-400 spectrometer in D_2O and $(CD_3)_2SO$ at 30 °C.

Results and Discussion

Characterization of the put complexes and crystal structure of $[Co(put)(en)_2]Cl$

Two red complexes **1** and **2** were found in the column separation of the put system. The chromatographic behaviour shows that **1** is an uni- and **2** a di-positive species. The UV/VIS absorption spectra of complexes **1** and **2** are shown in Fig. 1. The first d–d band appears at 496 nm (ε 140 dm^3 mol^{-1} cm^{-1}) for **1** and 502 nm (130 dm^3 mol^{-1} cm^{-1}) for **2**. An intense sulfur to metal charge-transfer (c.t.) band appears at 305 nm (10 700 dm^3 mol^{-1} cm^{-1}) for **1** and at 295 nm (10 400 dm^3 mol^{-1} cm^{-1}) for **2**. These absorption spectra are characteristic for CoN_5S-type complexes containing one thionato group.[4,9] In the ^{13}C NMR spectra both complexes showed nine signals, five in the put chemical shift region and four in the en region (Table 1). Thus complexes **1** and **2** are assigned to $[Co(put\text{-}N,S)(en)_2]^+$ and $[Co(Hput\text{-}N,S)(en)_2]^{2+}$, respectively. These formulations are also confirmed by the elemental analysis.

Fig. 2 shows an ORTEP[10] drawing of $[Co(put\text{-}N,S)(en)_2]^+$. The atomic parameters and selected bond distances and angles are listed in Tables 2 and 3, respectively. The put ligand co-

Table 1 Proton and ^{13}C NMR spectral data (δ)[a] of purinethione complexes

		^{13}C NMR							^{1}H NMR		
Compound	Solvent	C^2	C^4	C^5	C^6	C^8 (C^9)	en		H^2	H^8 (H^9)	NH_2 (en)
H_2put	$(CD_3)_2SO$	150.6	144.7	128.5	170.9	144.5					
1 $[Co(put)(en)_2]^+$	$(CD_3)_2SO$	151.8	156.8	140.2	165.5	151.6	45.8 44.9	45.4 44.1	8.25 (s, 1 H)	8.01 (s, 1 H)	6.18–4.51 (m, 8 H)
2 $[Co(Hput)(en)_2]^{2+}$	D_2O	148.2	154.2	139.4	171.6	147.9	46.8 46.1	46.4 45.4	8.46 (s, 1 H)	8.34 (s, 1 H)	
3 $[Co(Haput)(en)_2]^{2+}$[b]	$(CD_3)_2SO$	163.2	148.8	131.4	170.9	140.6				8.38 (s, 1 H)	6.23–4.66 (m, 8 H)
4 $[Co(H_2tpuo)(en)_2]^{2+}$	$(CD_3)_2SO$	151.1	155.0	132.5	168.2	149.2	46.0 44.7	45.2 44.0		8.08 (s, 1 H)	5.32–4.53 (m, 8 H)
5 $[Co(Hoput)(en)_2]^+$	$(CD_3)_2SO$	171.5	152.9	116.4	166.8	136.7	46.0 43.5	44.8[c]		7.79 (s, 1 H)	7.79 (s, 1 H) 5.18–4.04 (m, 7 H)
6 $[Co(H_2oput)(en)_2]^{2+}$	$(CD_3)_2SO$	172.6	147.1	111.1	162.0	140.0	45.8 44.9	45.1 44.2		8.25 (s, 1 H)	6.35 (s, 1 H) 5.66–4.34 (m, 7 H)
7 $[Co(Hpzpymt)(en)_2]^{2+}$	$(CD_3)_2SO$[d]	150.8	152.8	114.3	181.6	131.5	45.7 45.0	45.5 44.9	8.53 (s, 1 H)	8.46 (s, 1 H)	7.36–5.36 (m, 8 H)

[a] Downfield relative to $SiMe_4$ in $(CD_3)_2SO$, and dioxane (δ 67.4) was used as internal standard in D_2O. [b] δ 6.39 (s, 2 H) for NH_2 (put). [c] Relatively strong. [d] Downfield relative to acetate ($MeCO_2^-$: δ 2.00).

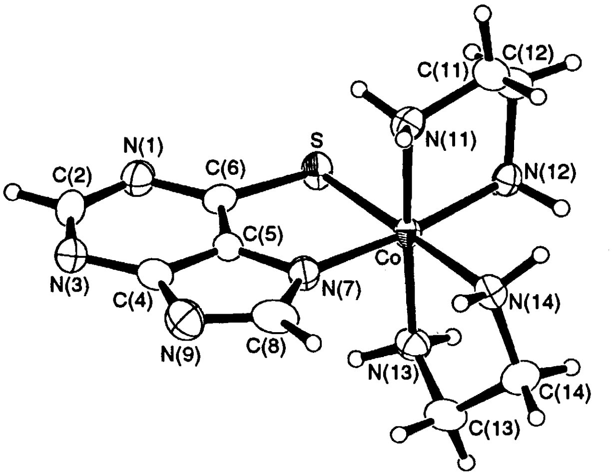


Fig. 2 An ORTEP drawing of $[Co(put)(en)_2]Cl·2H_2O$ **1**

Table 2 Positional parameters for $[Co(put)(en)_2]Cl_2·2H_2O$

Atom	*x*	*y*	*z*
Co	0.229 73(4)	0.133 04(7)	0.199 40(3)
Cl	0.466 74(9)	0.417 7(2)	0.352 38(7)
S	0.067 93(7)	0.002 8(1)	0.228 37(6)
O(1)	−0.183 4(2)	0.121 6(4)	0.204 4(2)
O(2)	0.497 9(5)	0.206 9(9)	0.517 7(3)
N(1)	−0.028 9(3)	−0.213 4(5)	0.113 0(2)
N(3)	0.043 9(3)	−0.258 8(5)	−0.021 4(2)
N(7)	0.216 8(2)	0.029 3(5)	0.090 3(2)
N(9)	0.210 8(3)	−0.095 0(5)	−0.037 0(2)
N(11)	0.308 7(2)	−0.075 1(4)	0.237 9(2)
N(12)	0.237 9(2)	0.211 9(4)	0.312 8(2)
N(13)	0.157 1(2)	0.349 9(4)	0.161 2(2)
N(14)	0.362 0(2)	0.264 1(4)	0.175 6(2)
C(2)	−0.024 7(3)	−0.282 0(6)	0.036 5(2)
C(4)	0.124 0(3)	−0.149 6(6)	0.002 7(2)
C(5)	0.128 0(3)	−0.074 1(5)	0.079 9(2)
C(6)	0.050 9(3)	−0.104 7(5)	0.135 4(2)
C(8)	0.263 9(3)	0.012 4(6)	0.019 1(2)
C(11)	0.353 1(3)	−0.044 1(6)	0.321 2(3)
C(12)	0.271 5(3)	0.060 1(6)	0.366 3(2)
C(13)	0.229 8(3)	0.456 0(6)	0.112 6(3)
C(14)	0.336 0(3)	0.451 7(6)	0.156 0(3)

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

Co–S	2.331(1)	Co–N(7)	1.953(3)
Co–N(11)	1.947(3)	Co–N(12)	1.951(3)
Co–N(13)	1.961(3)	Co–N(14)	1.991(3)
S–C(6)	1.732(4)	N(1)–C(2)	1.360(5)
N(1)–C(6)	1.338(5)	N(3)–C(2)	1.320(5)
N(3)–C(4)	1.351(5)	C(4)–C(5)	1.386(5)
C(5)–C(6)	1.377(5)	N(7)–C(5)	1.370(5)
N(7)–C(8)	1.337(5)	N(9)–C(4)	1.360(5)
N(9)–C(8)	1.378(6)		
S–Co–N(7)	88.6(1)	Co–S–C(6)	95.6(1)
S–C(6)–C(5)	115.9(3)	C(6)–C(5)–N(7)	127.5(3)
C(5)–N(7)–Co	112.4(2)	C(5)–C(6)–N(1)	117.7(4)
C(2)–N(1)–C(6)	115.4(3)	N(1)–C(2)–N(3)	131.6(4)
C(2)–N(3)–C(4)	112.0(3)	N(3)–C(4)–C(5)	121.1(4)
C(4)–C(5)–C(6)	122.2(4)	C(5)–N(7)–C(8)	103.1(3)
N(7)–C(8)–N(9)	114.7(4)	C(4)–N(9)–C(8)	103.8(3)
N(9)–C(4)–C(5)	108.2(3)	C(4)–C(5)–N(7)	110.3(3)
S–Co–N(14)	175.2(1)	N(7)–Co–N(12)	173.9(1)
N(11)–Co–N(13)	177.0(1)	N(11)–Co–N(12)	85.8(1)
N(13)–Co–N(14)	85.0(1)		

ordinates in a bidentate manner *via* the S and N(7) atoms and forms a five-membered chelate ring. Its bite angle S–Co–N(7) is 88.6(1)°, which is much larger than the values for four-membered chelate rings in $[Co(mpymt\text{-}N,S)(en)_2][ClO_4]_2$ [72.4(1)°, mpymt = 4-methylpyrimidine-2-thionate(1 −)],[4] $[Co(tuc\text{-}N,S)(en)_2]ClO_4$ [72.7(2)°, H_2tuc = 2,3-dihydro-2-thioxo-1*H*-pyrimidin-4-one (2-thiouracil)][9] and $[Co(apymt\text{-}N,S)(en)_2][ClO_4]_2$ [72.2(2)°, apymt = 4-aminopyrimidine-2-thionate(1 −)].[11] Consequently the central cobalt(III) ion of complex **1** has a nearly regular octahedral structure: the N(11)–Co–N(13), N(7)–Co–N(12) and S–Co–N(14) angles [177.0(1), 173.9(1) and 175.2(1)°, respectively] are close to 180°. Though two co-ordination modes N(1)/S^6 and S^6/N(7) are possible in the put N,S chelation, only the former five-membered mode is known so far including the present study.[12] This is due to the less-strained structure of the latter mode.

Three crystal structures have been reported for complexes with S^6/N^7 chelated put[12–14] but this is the first example with the dinegative put ligand. The Co–S and Co–N(7) lengths [2.331(1) and 1.953(3) Å] are slightly different from the 2.294(2) and 1.936(3) Å in $[Co(mpymt\text{-}N,S)(en)_2][ClO_4]_2$,[4] and 2.292(2) and 1.933(5) Å in $[Co(apymt\text{-}N,S)(en)_2][ClO_4]_2$,[11] respectively, but are considerably longer than 2.278(2) and 1.911(5) Å in $[Co(tuc\text{-}N,S)(en)_2]ClO_4$,[9] respectively. The C(6)–S bond length 1.732(4) Å of complex **1** is considerably longer than 1.679(1) Å of the free thione[15] and is the longest value among the known put complexes.[12] Hence the double-bond character is probably altered much by co-ordination. However it should be noted that this C–S bond lengthening upon co-ordination has been commonly found in other cobalt(III) complexes. The corresponding C–S distance is 1.732(4) in [Co(mpymt-*N*,*S*)(en)$_2$][ClO$_4$]$_2$,[4] 1.738(7) in [Co(tuc-*N*,*S*)(en)$_2$]ClO$_4$[9] and 1.742(7) Å in [Co(apymt-*N*,*S*)(en)$_2$][ClO$_4$]$_2$.[11]

The en chelate rings of the present complex adopt a *lel* and an *ob* conformation (where the C–C bonds of the en ligands are parallel and oblique, respectively, to the pseudo-C_3 axis).[16] These conformations are commonly seen in [Co(mpymt-*N*,*S*)(en)$_2$][ClO$_4$]$_2$,[4] [Co(tuc-*N*,*S*)(en)$_2$]ClO$_4$[9] and [Co(apymt-*N*,*S*)(en)$_2$][ClO$_4$]$_2$.[11]

Intermolecular stacking

An interesting feature of purine compounds is the solid-state stacking.[17] The range of interplanar stacking distances is considered to be 3.25–3.50 Å. The present complex **1** has such a stacking interaction. Fig. 3 shows stereoviews of the π–π contact in two directions. It is clear that there is a considerable overlap between the two purine rings. The complex cations are related by a symmetry centre and the intermolecular distance between the two least-square planes comprising the nine atoms of the purines is 3.40 Å. The shortest interatomic distances are 3.426(5) for N(3)···C(5), 3.463(5) for N(1)···N(9) and 3.494(5) Å for N(3)···C(6). There was no clear evidence of intermolecular stacking from the ^{1}H and ^{13}C NMR spectra (concentration *ca.* 0.1 mol dm^{-3}).

Since put is a dinegative ligand in complex **1** all sites at N(1), N(3) and N(9) are deprotonated. The bond angles C(2)–N(1)–C(6) 115.4(3) and C(2)–N(3)–C(4) 112.0(3)° are consistent with Singh's rule that the valence angles for nitrogen without an extra-annular hydrogen atom are within 116 ± 3° for a six-membered ring.[18] The N(1) and N(9) sites participate in intermolecular hydrogen bonding between H–N(12)[N(1)···N(12) 3.002(5)] and H–O(1)[N(9)···O(1) 2.762(4) Å], respectively, whereas the N(3) site has no such interaction.

Characterization of other complexes

In the column separations of the other four systems, aput (**3**), tpuo (**4**), oput (**5**, **6**) and pzpymt (**7**) only one red complex with a mono- or a di-positive charge was obtained for each system. They were characterized in the same way as that for the put complexes based on elemental analysis, UV/VIS, ^{1}H and ^{13}C NMR spectra. Thus complex **3** is assigned to [Co(Haput-*N*,*S*)(en)$_2$]Cl$_2$, **4** to [Co(H$_2$tpuo-*N*,*S*)(en)$_2$][ClO$_4$]$_2$, **5** to [Co(Hoput-*N*,*S*)(en)$_2$]Cl, **6** to [Co(H$_2$oput-*N*,*S*)(en)$_2$][ClO$_4$]$_2$ and **7** to [Co(Hpzpymt-*N*,*S*)(en)$_2$]Cl$_2$.

In complex **7** the pzpymt ligand co-ordinates through the N^1 and S^6 atoms and forms a four-membered chelate ring. In **5**, the oput co-ordinates through N^1/S^2 or S^2/N^3. This complex shows one of the amine protons of en at exceptionally low magnetic field (δ 7.79) compared with the other seven signals (7 H, δ 5.18–4.04). Such a large downfield shift indicates the existence of an intramolecular hydrogen bond as found in 2-thiouracilato complexes.[6] Since an intramolecular hydrogen bond C=O···H–N (en) is only possible for the N^1/S^2 co-ordination mode, this is adopted by Hoput.

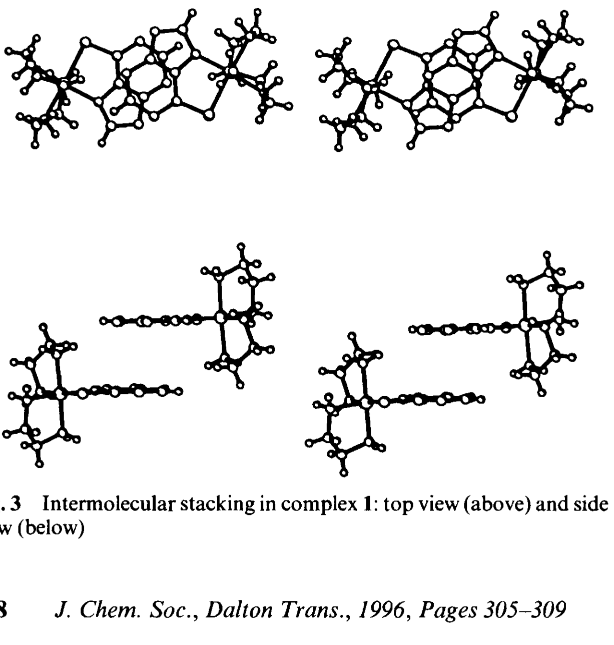


Fig. 3 Intermolecular stacking in complex **1**: top view (above) and side view (below)

One or two strong absorption bands are observed at longer wavelengths than the intense sulfur-to-metal c.t. band for the complexes with 6-thione ligands: 324 nm (ε = 11 600) for complex **1**, 327 (13 800) for **2**, 334 (9690) and 325 (sh) (9020) for **3**, 352 (13 700) for **4** and 333 (14 400 dm^3 mol^{-1} cm^{-1}) for **7**. These bands are assignable to intraligand transitions because the anions of purine-6-thiones show similar strong absorptions at 340–347 nm but the anion of purine-2-thione does not show such a strong band in the region 300–350.[19]

Assignment of linkage isomers based on ^{13}C NMR spectra

The ^{13}C NMR spectral data are collected in Table 1. The signals of [Co(put)(en)$_2$]$^+$ **1** were assigned by long-range ^{13}C–^{1}H correlation spectroscopy (COSY) and the assignments of other complex signals were made by referring to the literature.[20] Except for the pzpymt ligand in **7**, linkage isomerism is possible for all the other four ligands. The possible N,S-co-ordination modes are N^1/S^6 and S^6/N^7 for put (**1**, **2**), aput (**3**) and tpuo (**4**), and N^1/S^2 and S^2/N^3 for oput (**5**, **6**). The two four-membered co-ordination modes are possible for oput but one five- and one four-membered mode for put, aput and tpuo. X-Ray diffraction analysis confirmed that the put ligand adopts the S^6/N^7 five-membered mode. Both the 4- and 5-carbon atom signals of complexes **1** and **2** are shifted by 10–20 ppm to low field compared with those of free put. This fact means that the S^6/N^7 five-membered chelating mode causes the downfield shifts of the 4- and 5-carbon atoms. Since the signal of the C^5 atom of a free purinethione appears at an isolated region of δ 110–120, the low-field shift of this signal is a good criterion for the S^6/N^7 five-membered mode.

Fig. 4 shows a schematic representation of the ^{13}C NMR spectra. The pzpymt ligand in complex **7** adopts unequivocally the N^1/S^2 mode and the C^5 signal is located at δ 114.3. The co-ordination mode of oput in **5** and **6** is assigned to N^1/S^2 because of the existence of an intramolecular hydrogen bond C=O···H–N (en). The C^5 signals of complexes **5** and **6** appear at δ 116.4 and 111.1, respectively. Significant downfield shifts were not observed for these three complexes because it is clear that the 7-N atom is not involved in co-ordination.

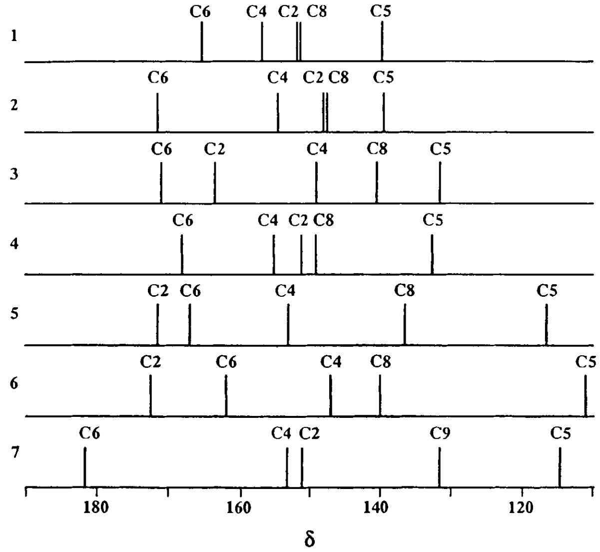


Fig. 4 Schematic representation of ^{13}C NMR spectra of the purinethione region (δ 110–190) of complexes **1**–**7**

On the other hand, the two complexes of aput and tpuo showed the C^5 signals at δ 131.4 and 132.5, respectively. The downfield shift of the C^5 signal for complex **4** is 14.3 ppm compared with that of free tpuo. These large shifts are very similar to those for the put complexes **1** and **2** and accordingly we concluded that $[Co(Haput\text{-}N,S)(en)_2]^{2+}$ and $[Co(H_2tpuo\text{-}N,S)(en)_2]^{2+}$ adopt the S^6/N^7 five-membered co-ordination mode. Thus ^{13}C NMR spectra are very useful for the assignment of the linkage isomers of purinethione ligands.

The non-bonding bite distance between 6-S and 7-N is 3.35 Å in $H_2put{\cdot}2H_2O$.[15] When S^6/N^7 chelation occurs this bite distance is significantly decreased: 3.32–3.34 Å for Cd^{II} (ionic radius r = 0.95 Å), 3.06–3.03 Å for Pd^{II} (r = 0.86 Å) and 3.04 Å for Cu^{II} (r = 0.73 Å).[12] Since the ionic radius of Co^{III} is 0.545 Å the extent of this decrease will be more pronounced in the present complex: the distance is 3.004(3) Å. The same trend is observed for the C(6)–C(5)–N(7) angle. The angle is 132.52(8)° in $H_2put{\cdot}2H_2O$, 129.7(1)° in $[Cd(H_2put)_4Cl_2]$[12] and 127.5(3)° in the present $[Co(put)(en)_2]Cl$. These facts explain the substantial downfield shifts of the 4- and 5-carbon signals of cobalt(III) purine-6-thionato complexes.

Acknowledgements

This work was partly supported by a Grant-in-Aid for Scientific Research (No. 07640750 for K. Y.) from the Ministry of Education, Science, Sports and Culture.

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Received 5th July 1995; *Paper* 5/04352B