Cobalt(III) Complexes with Thiosemicarbazones as Co-ordinating Agents. Spontaneous Resolution by Crystallization and Absolute Configuration *

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Two new cobalt(III) complexes with pyridoxal [3-hydroxy-5-(hydroxymethyl)-2-methylpyridine-4-carbaldehyde] and pyruvic acid thiosemicarbazones (H_2L and H_2pt) $[Co(HL)_2]Cl{\cdot}EtOH$ **1** and [Co(Hpt)(pt)] **2** respectively, have been synthesized and characterized using single-crystal X-ray diffraction and IR and CD spectroscopic methods. The structure of 2-thio-6-azathymine [6-methyl-3-thioxo-1,2,4-triazin-5-(2*H*,4*H*)-one] obtained upon cyclization of methyl pyruvate thiosemicarbazone in the course of its complexation reaction with cobalt(II) salts is also described. The structure of **1** consists of discrete $[Co(HL)_2]^+$ cations, Cl^- anions and ethanol solvate molecules, that of **2** consists of neutral monomers and the two ligands are not equivalent. In both complexes the co-ordination geometry about cobalt is distorted octahedral and the two ligands are in the *mer* configuration (S and O atoms *cis* to each other and the N atoms *trans*). Complex **1**, an example of optical resolution by preferential crystallization, is chiral.

As part of a programme concerning the behaviour of thiosemicarbazones, which are of great interest because of their chemical and pharmacological properties,[1,2] we have recently studied some pyridoxal [3-hydroxy-5-(hydroxymethyl)-2-methylpyridine-4-carbaldehyde] thiosemicarbazone (H_2L) complexes: $[Co(H_{0.5}L)_2]{\cdot}3.5H_2O$ and $[Co(HL)L]{\cdot}4.5H_2O$,[3] $[Mn(H_2L)(OH_2)Cl]Cl$,[4] $[Cu(HL)(OH_2)]_2Cl_2{\cdot}2H_2O$,[4] $[Cu(H_2L)(OH_2)Cl]Cl$.[5] The copper complexes were found to be more potent inhibitors of Friend cell proliferation[5] than the thiosemicarbazone itself, while the cobalt complex $[Co(HL)L]{\cdot}4.5H_2O$ was inactive against the same cells.

The mechanism by which such copper complexes and others containing the 2-formylpyridine moiety exert their biological activity is not clear. The proposed mechanisms are either the interaction of the complexes with the thiol-containing enzyme [*e.g.* ribonucleoside diphosphate reductase (RDR), which is required for the synthesis of DNA precursors[6-11]] or the generation of active oxygen species.[12,13] In fact the lower oxidation states of several copper and iron complexes which bind to DNA are known to cause cell-free degradation of the macromolecule through redox reactions that activate molecular oxygen.[14]

Many studies have also been reported on the preparation and the magnetic properties of cobalt(II) complexes with Schiff bases, oxygen-carrier compounds,[15] and it is well known that cobalt(III) complexes are obtainable by oxidation of solutions containing cobalt(II) salts and compounds which affect the redox potential of the transition metal.

To extend the knowledge in this research field, particularly with respect to the behaviour of the ligands, stereochemistry of the complex co-ordination and relationship between biological activities and molecular structures, we have now examined two new cobalt(III) complexes, although the starting material was a cobalt(II) salt, with pyridoxal and pyruvic acid thiosemicarbazones (as ligands) respectively; $[Co(HL)_2]Cl{\cdot}EtOH$ **1** and [Co(Hpt)(pt)] **2** (H_2pt = pyruvic acid thiosemicarbazone) and report here their synthesis, spectroscopic characterization and X-ray diffraction study. We also describe the structure of 2-thio-6-azathymine [6-methyl-3-thioxo-1,2,4-triazin-5-(2*H*,4*H*) one] obtained by cyclization of the ligand Hmpt (methyl pyruvate thiosemicarbazone) in the course of the complexation with cobalt(II) salts.

Experimental

Measurements.—Elemental analyses (C, H and N) were carried out on Perkin-Elmer model 240 automatic equipment. Infrared spectra (4000–400 cm^{-1}) for KBr discs were recorded on a Nicolet 5PC FT-IR spectrometer and the electronic spectra on a Uvicon 860 (Kontron Instruments) spectrophotometer. The CD spectra were recorded on a J-500 A JASCO spectropolarimeter using 5×10^{-5} mol dm^{-3} aqueous solutions.

Materials.—Thiosemicarbazide, pyridoxal hydrochloride and methyl pyruvate were commercially available (Aldrich-Chemie) and used without further purification.

Preparations.—Pyridoxal thiosemicarbazone and methyl pyruvate thiosemicarbazone were prepared using published procedures.[16,17]

$[Co(HL)_2]Cl{\cdot}EtOH$ **1**. To a boiling ethanolic solution (30 cm^3) of pyridoxal thiosemicarbazone (0.14 g, 0.58 mmol) was added an ethanolic solution (10 cm^3) of cobalt(II) chloride hexahydrate (1:1 molar ratio) at room temperature. The resultant blue solution changed to brown at room temperature. After slow evaporation of the solvent, brown crystals were isolated (m.p. > 280 °C) (Found: C, 39.05; H, 4.65; N, 17.85. $C_{20}H_{28}ClCoN_8O_5S_2$ requires C, 38.80; H, 4.55; N, 18.10%).

[Co(Hpt)(pt)] **2**. To a methanolic solution (20 cm^3) of methyl pyruvate thiosemicarbazone (0.06 g, 0.32 mmol) was added solid cobalt(II) chloride hexahydrate (0.08 g, 0.30 mmol) at room temperature. The resultant blue solution (pH ≈5)

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc. Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

changed to red and was then stirred for *ca.* 10 min. After some days red prismatic crystals were isolated (m.p. > 280 °C). The analytical data were consistent with the formula [Co(Hpt)(pt)], established by X-ray analysis (Found: C, 25.50; H, 3.35; N, 21.70. $C_8H_{11}CoN_6O_4S_2$ requires C, 25.40; H, 2.95; N, 22.20%).

Compound **2** was also isolated by changing the experimental conditions such as the metal:ligand molar ratio (1:2), the temperature (at reflux in methanol) or the solvent (in water at 80 °C). In the last case a white product was also obtained which, on the basis of X-ray diffraction analysis, has been revealed to be the 2-thio-6-azathymine.

In order to clarify the formation of the thymine compound by cyclization of Hmpt, some tests were made on Hmpt under different conditions. In particular, the thymine was not isolated upon treating Hmpt as follows: stirring of an aqueous solution at room temperature (r.t.) for several hours; heating a 0.1 mol dm^{-3} $MeCO_2H$ solution (pH 6) at 70 °C for 1 h; heating a 0.1 mol dm^{-3} HCl solution (pH 4.5) at 70 °C for 1 h; and heating a methanol solution at reflux for several hours. On the contrary, the thymine was formed upon heating an aqueous solution of Hmpt at reflux for a few minutes. Moreover, the presence of a small amount of an inorganic salt, such as cobalt or zinc chloride or manganese or zinc acetate led to its formation at r.t. both in aqueous and in methanolic solution.

X-Ray Analysis.—The crystal and instrumental parameters used in the unit-cell determination and data collection are summarized in Table 1. All intensity data were collected by the θ–2θ technique. No correction for absorption was applied.

The structures were solved by three-dimensional Patterson analysis for complex **1** and by direct methods (SHELX 86, MULTAN)[18,19] for **2** and the thymine. Refinements were carried out by full-matrix least-squares cycles (SHELX 76).[20] Anisotropic thermal motion was assumed for all non-hydrogen atoms. The hydrogen atoms, located on a difference map, were refined isotropically only for complex **2** and the thymine.

The atomic scattering factors used in the calculations take into account anomalous scattering effects,[21] which have been utilized for determination of the absolute configuration of complex **1**, an example of optical resolution by preferential crystallization and of chirality because of the appropriate arrangement of the two terdentate ligands. The absolute configuration was determined by considering the mirror image of the structure. The resulting values $R = 0.092$ and 0.049 for the two enantiomers showed that the configuration with the lower R value is the correct one.

A Powernode computer of the Centro di Studio per la Strutturistica Diffrattometrica del C.N.R. (Parma) was employed with the PARST[22] program for the geometrical description of the structure and ORTEP[23] and PLUTO[24] for the structure drawings.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Crystal and Molecular Structure.—In both complexes **1** and **2** the cobalt atom is co-ordinated, in a distorted octahedron, to two terdentate thiosemicarbazone ligands, each of which is joined to the metal *via* the sulfur, the nitrogen of the hydrazinic chain and the phenolic oxygen in **1** or the carboxylate oxygen in **2**.

The structure of **1** consists of discrete $[Co(HL)_2]^+$ cations, Cl^- anions and ethanol molecules as solvate. The complex is chiral and Fig. 1 shows it in its correct absolute configuration. Both ligands (HL) are monodeprotonated and equivalent, in contrast to the two cobalt(III) complexes with pyridoxal thiosemicarbazone previously studied.[3] Final atomic coordinates are given in Table 2, selected bond lengths and angles in Table 4.

The structure of complex **2** consists of a neutral monomer and the two ligands are not equivalent because one of them has lost only the carboxylic proton (Hpt), whereas the other (pt) loses also the proton of the hydrazinic nitrogen N(2′) (Fig. 2), in accord with the oxidation state III for cobalt. Final atomic coordinates are given in Table 3, selected bond lengths and angles in Table 4.

Table 1 Experimental data for the crystallographic analyses*

Compound	$[Co(HL)_2]Cl{\cdot}EtOH$ **1**	[Co(Hpt)(pt)] **2**	2-Thio-6-azathymine
Formula	$C_{20}H_{28}ClCoN_8O_5S_2$	$C_8H_{11}CoN_6O_4S_2$	$C_4H_5N_3OS$
M	619.0	378.27	143.16
Space group	$P2_12_12_1$	$C2/c$	$P\bar{1}$
a/Å	21.304(2)	16.676(2)	8.386(1)
b/Å	10.045(1)	9.248(1)	8.337(1)
c/Å	12.789(1)	17.985(2)	4.635(1)
α/°			77.62(2)
β/°		104.90(2)	88.42(2)
γ/°			87.75(2)
U/Å^3	2736.8(4)	2679.7(6)	316.21(9)
λ/Å	1.541 78 (Cu-Kα)	0.710 69 (Mo-Kα)	0.710 69 (Mo-Kα)
Z	4	8	2
D_m/Mg m^{-3}	1.42	1.83	1.48
D_c/Mg m^{-3}	1.44	1.88	1.50
F(000)	1232	1536	148
Crystal size/mm	0.26 × 0.13 × 0.05	0.33 × 0.13 × 0.16	0.49 × 0.20 × 0.03
μ/mm^{-1}	7.85	1.60	0.41
θ range/°	3–70	3–30	3–33
hkl Ranges	0–25, 0–12, 0–15	−23 to 22, 0–13, 0–25	−10 to 11, −9 to 11, 0–6
Standard reflection	8 0 1	−4 0 0	−4 1 1
No. of measured reflections	2973	7854(triclinic)	2387
Maximum, minimum height in final ΔF map/e Å^{-3}	0.27, −0.23	1.10, −0.66	0.10, −0.10
No. of refined parameters	324	190	82
No. of unique reflections [$I > 2\sigma(I)$]	1571	2683	639
R,R'	0.050, 0.058	0.040, 0.043	0.035, 0.039

* Data common to all three compounds: $T = 293 \pm 1$ K; unit weights used.

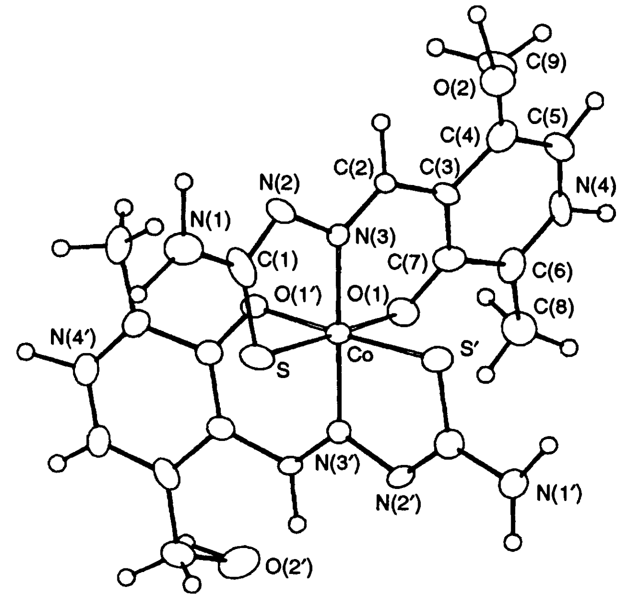

Fig. 1 Perspective view of the chiral $[Co(HL)_2]^+$ cation in its correct absolute configuration

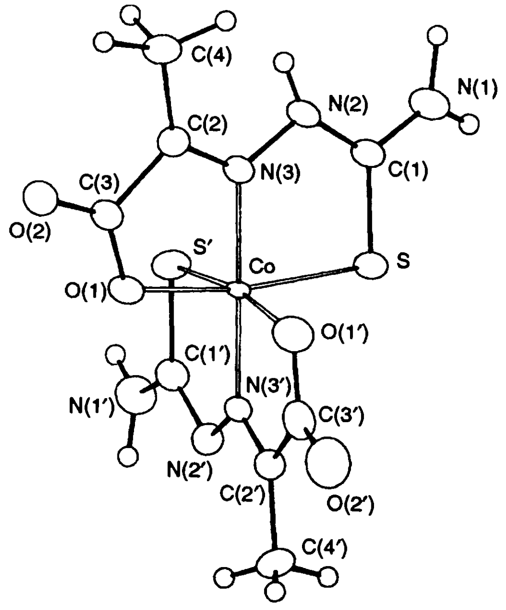

Fig. 2 Perspective view of the neutral complex [Co(Hpt)(pt)] **2**

A comparison of the bond parameters shows that there are no great differences between the two complexes and the Co–S, Co–N and Co–O distances are in the ranges 2.198(1)–2.212(3), 1.881(9)–1.889(8) and 1.933(7)–1.956(3) Å respectively as expected for cobalt(III) complexes.[3]

Table 2 Fractional atomic co-ordinates for non-hydrogen atoms for complex **1**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Co	−0.821 20(7)	−0.501 6(2)	−0.221 2(1)
Cl	−1.037 6(1)	−0.369 5(3)	0.282 0(2)
S	−0.917 9(1)	−0.489 9(4)	−0.283 6(2)
O(1)	−0.739 1(3)	−0.509 0(9)	−0.157 1(5)
O(2)	−0.727 7(4)	−1.001 3(11)	−0.307 8(5)
O(3)	−0.906 8(4)	−1.006 7(13)	−0.293 5(8)
C(10)	−0.903 3(1)	−1.011 1(36)	−0.403 6(19)
C(11)	−0.891 1(2)	−0.909 0(41)	−0.461 2(22)
N(1)	−0.995 6(5)	−0.697 0(11)	−0.269 1(11)
N(2)	−0.892 8(4)	−0.742 6(9)	−0.228 9(8)
N(3)	−0.832 0(4)	−0.688 3(8)	−0.220 0(7)
N(4)	−0.599 2(4)	−0.690 8(12)	−0.152 8(8)
C(1)	−0.934 3(6)	−0.650 8(14)	−0.257 5(9)
C(2)	−0.787 6(5)	−0.776 1(10)	−0.205 2(8)
C(3)	−0.721 7(6)	−0.742 5(11)	−0.187 0(8)
C(4)	−0.677 1(6)	−0.848 7(13)	−0.193 4(9)
C(5)	−0.615 0(6)	−0.815 8(13)	−0.174 4(10)
C(6)	−0.637 1(6)	−0.583 4(14)	−0.146 4(10)
C(7)	−0.704 3(6)	−0.610 9(12)	−0.166 6(9)
C(8)	−0.614 4(7)	−0.453 0(14)	−0.123 1(13)
C(9)	−0.695 5(6)	−0.988 8(14)	−0.209 1(10)
S′	−0.777 4(1)	−0.509 8(3)	−0.377 0(2)
O(1′)	−0.855 8(3)	−0.500 2(10)	−0.081 2(5)
O(2′)	−0.815 9(4)	−0.013 7(10)	−0.008 5(6)
N(1′)	−0.717 2(5)	−0.301 3(10)	−0.454 2(7)
N(2′)	−0.773 6(5)	−0.259 6(9)	−0.303 6(7)
N(3′)	−0.810 2(4)	−0.315 8(8)	−0.224 3(6)
N(4′)	−0.947 4(4)	−0.318 9(11)	0.096 4(7)
C(1′)	−0.755 9(6)	−0.347 9(12)	−0.375 9(8)
C(2′)	−0.830 2(5)	−0.228 1(10)	−0.159 1(8)
C(3′)	−0.869 0(5)	−0.265 4(12)	−0.067 1(9)
C(4′)	−0.895 5(6)	−0.158 2(12)	−0.008 2(9)
C(5′)	−0.934 8(6)	−0.190 8(13)	0.074 6(9)
C(6′)	−0.921 7(6)	−0.423 0(13)	0.048 4(9)
C(7′)	−0.879 0(5)	−0.397 9(12)	−0.039 1(8)
C(8′)	−0.936 3(8)	−0.561 0(16)	0.080 2(11)
C(9′)	−0.882 0(6)	−0.015 3(14)	−0.027 4(9)

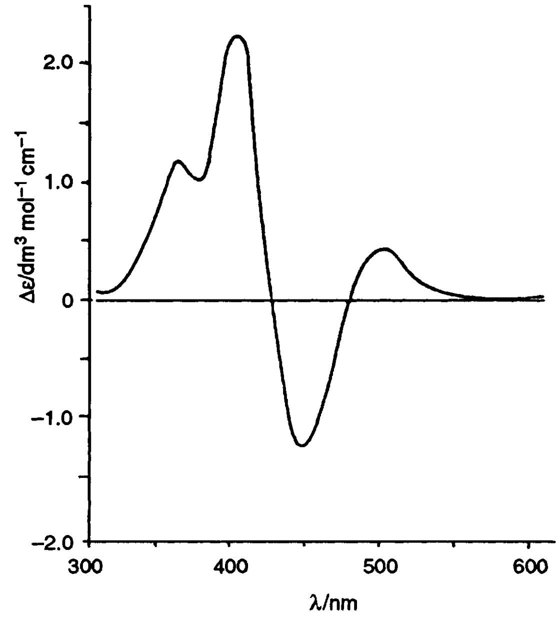

Fig. 3 The CD spectrum of complex **1**

In both complexes the two ligands are in the *mer* configuration (S and O atoms *cis* to each other and the N atoms *trans*) as found in other octahedral cobalt complexes. Using the Cahn–Ingold–Prelog (CIP) system[25] it is possible to describe the complexes as *mer*-(*OC*-6-22) isomers. On the basis of the IUPAC rule[26] and of a dominating positive circular dichroism spectrum (Fig. 3), we can state that complex **1** has the chirality symbol *A* [according to the pairs of skew lines S–N(3), S′–N(3′) and N(3)–O(1), N(3′)–O(1′) the absolute configuration is Λ].[27] In complex **1** five- and six-membered chelate rings are present which show an envelope and twist-boat conformation respectively in both ligands. In **2** instead four five-membered chelate rings are present [Co–S–C(1)–N(2)–N(3): twist, φ_2 = 19.7(1.7) (unprimed); envelope, φ_2 = 39.5(3.7) (primed). Co–N(3)–C(2)–C(3)–O(1): envelope, φ_2 = −178.4(6.1) (unprimed); twist, φ_2 = 122.5(4.5)° (primed)].

A comparison of the bond distances in the side chain for the two complexes is shown in Table 4.

Table 3 Fractional atomic coordinates for non-hydrogen atoms for complex **2** and the thymine derivative

Atom	*X/a*	*Y/b*	*Z/c*
Complex **2**			
Co	0.130 46(3)	0.102 07(6)	0.157 04(3)
S	0.101 02(5)	0.101 3(1)	0.269 96(5)
O(1)	0.178 0(1)	0.108 4(3)	0.069 0(1)
O(2)	0.302 0(2)	0.100 4(4)	0.043 2(2)
N(1)	0.209 1(2)	0.010 1(5)	0.395 0(2)
N(2)	0.260 6(2)	0.044 5(5)	0.289 2(2)
N(3)	0.241 6(2)	0.073 8(4)	0.212 1(2)
C(1)	0.196 9(2)	0.047 1(5)	0.322 1(2)
C(2)	0.297 0(2)	0.077 4(4)	0.173 1(2)
C(3)	0.257 8(2)	0.098 0(4)	0.087 7(2)
C(4)	0.388 2(2)	0.060 0(6)	0.205 6(2)
S′	0.106 61(6)	−0.131 3(1)	0.142 78(6)
O(1′)	0.132 1(2)	0.313 4(3)	0.155 1(2)
O(2′)	0.049 7(2)	0.498 3(4)	0.105 7(2)
N(1′)	−0.042 0(2)	−0.229 6(4)	0.070 9(2)
N(2′)	−0.035 0(2)	0.016 8(4)	0.079 0(2)
N(3′)	0.018 8(2)	0.128 2(3)	0.102 2(2)
C(1′)	0.002 0(2)	−0.110 0(4)	0.093 7(2)
C(2′)	−0.005 9(2)	0.260 3(4)	0.088 0(2)
C(3′)	0.061 3(3)	0.368 3(4)	0.116 7(2)
C(4′)	−0.091 3(2)	0.303 8(5)	0.046 1(2)
2-Thio-6-azathymine			
S	0.342 4(2)	0.195 2(2)	0.250 0(3)
N(1)	0.546 3(4)	0.327 4(5)	−0.174 2(8)
N(2)	0.800 2(4)	0.133 9(5)	0.058 4(9)
N(3)	0.650 0(5)	0.122 5(5)	0.179 8(9)
O(1)	0.703 2(4)	0.446 1(4)	−0.562 8(7)
C(1)	0.985 2(6)	0.257 3(9)	−0.319 4(15)
C(2)	0.519 4(5)	0.214 2(6)	0.080 1(9)
C(3)	0.822 0(5)	0.242 0(6)	−0.180 3(11)
C(4)	0.689 1(5)	0.349 2(5)	−0.326 8(10)

Table 4 Selected bond distances (Å) and angles for complexes **1** and **2**

	$[CO(HL)_2]Cl{\cdot}Et_2OH$ **1**		$[Co(Hpt)(pt)]$ **2**	
Co–S	2.212(3)	2.202(3)*	2.209(1)	2.198(1)*
Co–O(1)	1.933(7)	1.936(6)	1.946(3)	1.956(3)
Co–N(3)	1.889(8)	1.881(9)	1.882(3)	1.884(3)
S–C(1)	1.69(1)	1.69(1)	1.707(4)	1.752(3)
C(1)–N(1)	1.39(2)	1.38(1)	1.318(6)	1.333(6)
C(1)–N(2)	1.33(1)	1.33(1)	1.342(6)	1.319(5)
N(2)–N(3)	1.41(1)	1.40(1)	1.368(4)	1.360(4)
N(3)–C(2)	1.31(1)	1.29(1)	1.296(5)	1.293(5)
C(2)–C(3)	1.46(2)	1.48(2)	1.520(5)	1.491(6)
C(2)–C(4)			1.490(5)	1.485(5)
C(3)–O(1)			1.290(4)	1.306(5)
C(3)–O(2)			1.218(5)	1.226(5)
C(3)–C(4)	1.43(2)	1.43(2)		
C(4)–C(5)	1.38(2)	1.39(2)		
C(5)–N(4)	1.33(2)	1.34(2)		
C(6)–N(4)	1.35(2)	1.33(2)		
C(6)–C(8)	1.43(2)	1.48(2)		
C(6)–C(7)	1.48(2)	1.46(2)		
C(7)–C(3)	1.40(2)	1.40(2)		
C(7)–O(1)	1.27(1)	1.26(1)		
C(4)–C(9)	1.47(2)	1.48(2)		
C(9)–O(2)	1.44(1)	1.46(2)		
O(1)–Co–N(3)	93.9(4)	93.4(4)*	83.2(1)	83.0(1)*
S–Co–N(3)	86.7(3)	88.0(3)	86.4(1)	86.6(1)
O(1)–Co–S	176.0(2)	176.8(2)	169.1(1)	169.3(1)
O(1′)–Co–N(3)	87.3(4)		97.6(2)	
O(1)–Co–N(3′)	86.2(4)		97.1(1)	
N(3)–Co–S′	91.3(3)		92.8(1)	
N(3′)–Co–S	93.2(3)		93.4(1)	
S–Co–O(1′)	88.8(2)		91.5(1)	
S′–Co–O(1)	90.0(2)		91.4(1)	
N(3)–Co–N(3′)	179.2(4)		179.4(2)	
S–Co–S′	94.0(1)		91.6(1)	
O(1)–Co–O(1′)	87.3(3)		86.8(1)	

* The second set of values are for the ligands with primed labels.

In complex **1** an average geometry is observed for both monodeprotonated ligands corresponding to dipolar ions. The two hydroxylic groups adopt different conformations. In fact O(2) and O(2′) are + synclinal and − synclinal with regard to C(3) and C(3′) respectively [C(3)–C(4)–C(9)–O(2) 61.4(1.5), C(3′)–C(4′)–C(9′)–O(2′) −63.6(1.5)°] and H(2O), H(2O′) are −anticlinal and −synclinal to C(4) and C(4′) [C(4)–C(9)–O(2)–H(2O) −168.2(8), C(4′)–C(9′)–O(2′)–H(2O′) −78.4(9)°]. These conformations, as in previous cobalt(III) complexes,[3] are probably adopted in order to form intermolecular hydrogen bonds (Table 5). In fact in this compound an efficient hydrogen-bonding network is present (Fig. 4). This may also account for the spontaneous resolution upon crystallization of complex **1**, probably determined by lower free energy compared to that of the racemic structure. A strong symmetric hydrogen bond O(2) ··· H(2O) ··· N(2′) $(x, y - 1, z)$ [2.77(1) Å] is present with the hydrogen atom half-way between oxygen and nitrogen (Table 5). Both ligands deviate considerably from planarity. The pyridine and thiosemicarbazide moieties are planar but the hydrazinic chain gives a curvature to the whole ligand which assumes a boat-like conformation.[3,4] The dihedral angles between the three planes of the system are 18.0(9), 5.5(8) and 11.1(7), 4.6(7)° for the 'unprimed' and 'primed' ligands respectively.

Complex **2** contains both tautomeric forms of the ligand, thione (Hpt) and thiol (pt). The two ligand molecules are not planar, even though the thiourea moiety and the pyruvic group are planar. The dihedral angles between them are 11.7(2) (thione) and 6.9(2)° (thiol) respectively. The bond distances are affected by the different behaviour of the two ligands (for example): S–C(1) 1.707(4), C(1)–N(2) 1.342(6) Å (thione); S′–C(1′) 1.752(3), C(1′)–N(2′) 1.319(5) Å (thiol) (Table 4).

A cobalt complex $[Co(Hpt)(pt)]{\cdot}H_2O$ was also obtained from the reaction of $CoCl_2{\cdot}6H_2O$ with $H_2NC(S)NHN{=}C(Me)$-$C(O)NHN{=}C(Me)C(O)OMe$[28] which, in aqueous solution, yielded H_2pt as a result of hydrolysis. This compound, which differs from **2** by a water molecule, is isostructural with the chromium complex $[Cr(Hpt)(pt)]{\cdot}H_2O$.[29] The crystallographic parameters are: a = 11.174(2), b = 10.674(2), c = 13.194(3) Å, β = 103.14(2)°, space group $P2_1/n$ (chromium compound); a = 11.308(2), b = 10.350(2), c = 12.851(2) Å, β = 102.88(2)°, space group $P2_1/n$ (cobalt compound). The structural details of $[Co(Hpt)(pt)]{\cdot}H_2O$ suffer from the poor level of refinement (R = 0.120) of the disordered water molecule or the use of a geminate crystal.

The crystallographic parameters and space group of non-hydrated complex **2** probably isostructural with [Fe(Hpt)-(pt)][29] are very different from those of $[Co(Hpt)(pt)]{\cdot}H_2O$ though the environment of the metals in all these solids is essentially the same. Probably the water molecule of crystallization completely changes the packing. In **2** this is determined by hydrogen bonds between nitrogens of amine groups and the carboxylate oxygen atoms (Fig. 5 and Table 5), while in the hydrated cobalt compound, isostructural with the chromium complex, it is the water molecule that determines the packing in order to form a more open structure.

The structure of the thymine derivative is shown in Fig. 6. The bond lengths and angles (Fig. 6) are in agreement with values found by Voutsas *et al.*[30] for the 2:1 adduct of 2-thio-6-azathymine and triethylamine. The nearly planar rings are joined together through hydrogen bonds N–H ··· O and N–H ··· S (Table 5) to form zigzag chains running parallel to [010].

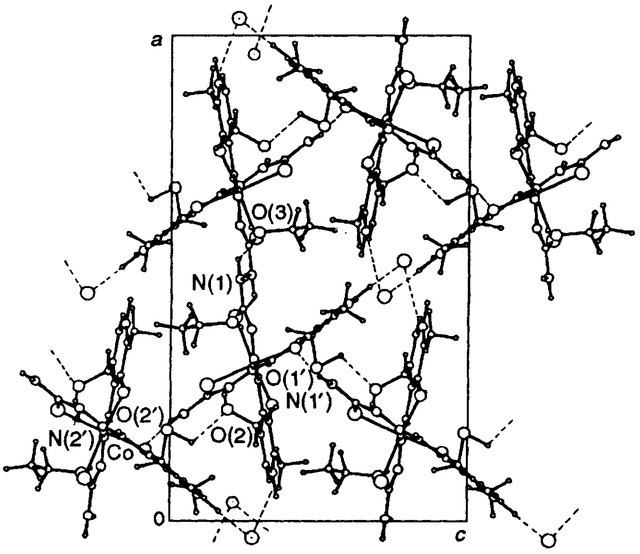

Fig. 4 Packing arrangement of complex **1**

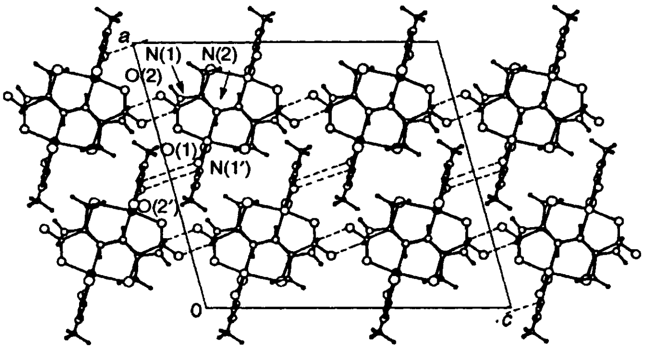

Fig. 5 Projection of the structure of complex **2** on the (010) plane

Table 5 Relevant hydrogen bond distances (Å) and angles (°) (D = donor atom, A = acceptor atom)

D–H···A	D···A	D–H···A
Complex **1**		
N(4′)–H(4′)···Cl	3.10(1)	172
N(1)–H(21)···O(3^{I})	2.94(2)	145
O(2)···H(2O)···N(2$^{II'}$)	2.77(1)	161
N(4)–H(4)···Cl^{III}	3.07(1)	142
N(1′)–H(11′)···O(1^{III})	3.35(1)	126
N(1′)–H(11′)···O(1$^{III'}$)	3.00(1)	156
N(1′)–H(21′)···O(2$^{IV'}$)	3.06(1)	161
O(2′)–H(2O′)···O(2^{V})	2.74(1)	110
O(3)–H(3)···N(2^{V})	2.80(1)	174
Complex **2**		
N(1)–H(11)···O(2^{I})	2.904(5)	139(5)
N(1)–H(21)···N(2$^{II'}$)	3.058(5)	154(5)
N(2)–H(2)···O(1$^{III'}$)	2.802(5)	151(5)
N(2)–H(2)···O(2$^{III'}$)	3.267(5)	141(4)
N(1′)–H(11′)···O(2$^{IV'}$)	2.928(5)	167(5)
N(1′)–H(21′)···O(1^{V})	3.129(4)	144(6)
N(1′)–H(21′)···O(2^{VI})	2.969(5)	124(5)
2-Thio-6-azathymine		
N(1)–H(1)···O(1^{I})	2.876(5)	179(5)
N(3)–H(3)···S^{II}	3.316(4)	168(5)

Symmetry operations: **1**, I $x - \frac{1}{2}, -y - \frac{1}{2}, -z$; II $x, y - 1, z$; III $-x - \frac{3}{2}, -y - 1, z - \frac{1}{2}$; IV $-x - \frac{3}{2}, -y, z - \frac{1}{2}$; V $-x - \frac{3}{2}, -y - 1, \frac{1}{2} + z$; **2**; I $x, -y, \frac{1}{2} + z$; II $-x, y, \frac{1}{2} - z$; III $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; IV $x, y - 1, z$; V $-x, -y, -z$; VI $x - \frac{1}{2}, y - \frac{1}{2}, z$; **3**; I $1 - x, 1 - y, -z - 1$; II $1 - x, -y, 1 - z$.

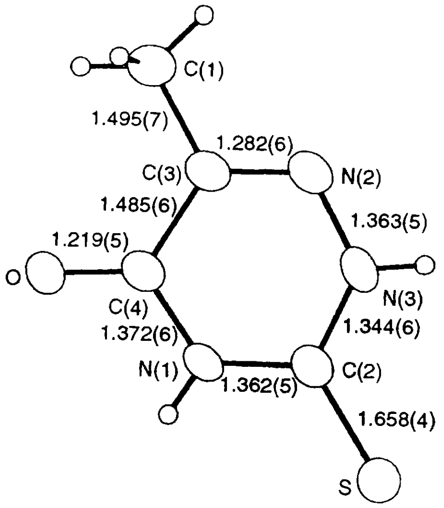

Fig. 6 An ORTEP drawing of the 2-thio-6-azathymine showing bond distances (Å) the atomic numbering scheme

Table 6 Selected vibrational bands (cm^{-1}) of Hmpt, [Co(Hpt)(pt)] and [Zn(Hpt)$_2$]

Assignment	Hmpt[17]	[Co(Hpt)(pt)]	[Zn(Hpt)$_2$][31]
ν(NH$_2$)	3510m	3370m	3490ms
	3290m	3290ms	3290m
	3230ms	–	–
ν(NH)	3150ms	3180m	3170s
ν(CO)	1720vs	1660s	1655s
	–	1630 (sh)	1630vs
ν(CN)	1625s	1610s	1580s
	1610s	1585 (sh)	–
ν(NCS)	1435s	1430m	1420m
δ(NCS)	1290vs	1290m	1230s
	1260vs	1220s	1195m
	1105vs	1015m	1050w
ν(CS)	965m	880m	870ms
	860ms	860m	–

Infrared Spectra.—The main vibrational bands of free Hmpt and [Co(Hpt)(pt)], together with those of a zinc complex previously studied,[31] are compared in Table 6. The comparison is made difficult owing to the modification that Hmpt has undergone during the complex formation. Moreover, owing to the presence in the cobalt complex of both the mono- and bi-deprotonated forms of H_2pt, it is impossible to evidence the deprotonation of the NH group. A negative shift of the ν(CO) band (Δν 60 cm^{-1}) is observed in connection with the change of the ester to the corresponding carboxylic group and as a consequence of the participation of the oxygen atom in co-ordination to cobalt. Significant shifts of the ν(CN) and ν(CS) bands are observed in accord with the ONS terdentate ligand behaviour.

In Table 7 selected vibrational bands of [Co(HL)$_2$]Cl·EtOH are compared with those of free H_2L and two cobalt complexes, [Co(HL)(L)]·4.5H_2O and [Co(H$_{0.5}$L)$_2$]·3.5H_2O, the structures of which have been previously described.[3] In particular, in the 4000–3000 cm^{-1} region, three bands, due to stretching of the NH$_2$ group, are present, while the band at 3160 cm^{-1} in the spectrum of free H_2L disappears as a consequence of deprotonation. The absorptions in the 1700–1300 cm^{-1} region are similar in the spectra of all the cobalt complexes. Participation of the phenolic oxygen and the sulfur atoms in co-ordination is suggested by the splitting of the ν(NH$^+$) band at 2860 cm^{-1} and by the presence of the δ(NCS) and ν(CS) bands at 1160, 925 and 890 cm^{-1} respectively.

Table 7 Selected vibrational bands (cm^{-1}) of H_2L and cobalt complexes

Assignment	$H_2L\cdot3H_2O$[16]	$[Co(HL)_2]Cl\cdot EtOH$	$[Co(HL)L]\cdot4.5H_2O$[3]	$[Co(H_{0.5}L)_2]\cdot3.5H_2O$[3]
ν(OH), ν(NH_2)	3390m	3370m	3370m	3390m
	3250m	3290ms	3300m	3300m
	—	3180ms	3190m	3180m
ν(NH)	3160m	—	—	—
ν(NH^+)	2860 (sh)	2870mw	2880w	2880w
	—	2840mw	2840w	—
ν(CN), ν(CC)	1600s	1630ms	1620vs	1615s
	—	1620s	1600 (sh)	1600 (sh)
	—	1600 (sh)	—	—
ν(CN)	1540s	1535m	1525(sh)	1555 (sh)
δ(NCS)	1250s	1250ms	1260ms	1250m
	1229m	1160s	1205ms	1145ms
	1090s	1030s	1155ms	1000m
	1035vs	1020s	1010s	—
ν(CS)	920m	925mw	910mw	910w
	—	890mw	880w	855w
	—	855w	—	—

Acknowledgements

This work was financially supported by the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (40%), Italy. We also thank D. Belletti, A. Cantoni and G. Pasquinelli for their valuable technical assistance.

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Received 4*th April* 1995; *Paper* 5/02162F