Thiosemicarbazones as Co-ordinating Agents. Part 4.[1] Synthesis, Spectroscopic Characterization and X-Ray Structure of two Cobalt(III) Complexes with Pyridoxal Thiosemicarbazone†

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Two pyridoxal (3-hydroxy-5-hydroxymethyl-2-methylpyridine-4-carbaldehyde) thiosemicarbazone (H_2L) complexes of cobalt have been synthesised and structurally characterized by spectroscopic and X-ray diffraction methods. Crystallographic parameters: $[Co(H_{0.5}L)_2]\cdot 3.5H_2O$ **1** space group $C2/c$, $a = 10.335(1)$, $b = 29.026(3)$, $c = 16.564(2)$ Å, $\beta = 94.85(3)°$, $Z = 8$, $R = 0.053$, $R' = 0.057$; $[Co(HL)L]\cdot 4.5H_2O$ **2**, space group $P\bar{1}$ $a = 11.195(1)$, $b = 12.138(2)$, $c = 11.128(1)$ Å, $\alpha = 103.23(3)$, $\beta = 99.42(2)$, $\gamma = 115.49(2)°$, $Z = 2$, $R = 0.051$, $R' = 0.058$. In both compounds the cobalt atom is co-ordinated in a rather distorted octahedron to two molecules of pyridoxal thiosemicarbazone which are not equivalent. They are cobalt(III) complexes although the starting material was a cobalt(II) salt, differing in the H-atom positions of the pyridine nitrogen atoms. In **1** both the pyridine nitrogen atoms are 'semiprotonated': this is responsible for a loss of regularity in the arrangement of the water molecules. In **2** only one pyridine nitrogen atom is protonated. A strong symmetric N···H···N hydrogen bond [2.685(9) Å] is present in complex **1**.

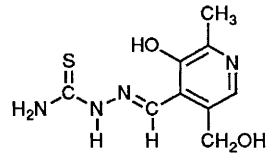
Extensive literature on the antitumour properties of many thiosemicarbazones is available.[2–7] Following our interest in the biological and chemical properties of such compounds, we report the preparation, spectroscopic characterization, crystal and molecular structure determination of two pyridoxal (3-hydroxy-5-hydroxymethyl-2-methylpyridine-4-carbaldehyde) thiosemicarbazone (H_2L) complexes of cobalt(III) $[Co(H_{0.5}L)_2]\cdot 3.5H_2O$ **1** and $[Co(HL)L]\cdot 4.5H_2O$ **2**, with the aim of verifying the non-equivalence of the ligands in these compounds, focusing particularly on their conformations.

In previous papers we have shown that the ligand is always terdentate *via* the S, N (iminic) and O (phenolic) donor atoms, and different types of stoichiometry are observed depending on the nature of the inorganic anion, $M(H_2L)X_2$ (M = Mn, Cu or Zn; X = Cl or NO_3), M(HL)X (M = Co, Cu or Zn; X = Cl or CH_3CO_2) and ML (M = Ni or Cu; from acetate salts).[8–12]

Experimental

Physical Measurements.—Elemental (C, H and N) analyses were made on Perkin-Elmer 240 automatic equipment. Infrared spectra (KBr discs, 4000–200 cm^{-1}) were recorded on a Perkin-Elmer 283 B spectrophotometer. Magnetic susceptibility was measured by the Gouy method on a Newport Instruments balance at 303 K using $[Ni(en)_3]S_2O_3$ (en = ethanol-1,2-diamine) as calibrant.

Preparation of Complexes.—$[Co(H_{0.5}L)_2]\cdot 3.5H_2O$ **1**. To a boiling solution of $H_2L\cdot 3H_2O$ (0.25 g, 0.85 mmol) (obtained as previously reported[10]) in chloroform–methanol (1:1 v/v, 50 cm^3) was added dropwise a solution of $Co(CH_3CO_2)_2\cdot 4H_2O$ (0.21 g, 0.85 mmol) in methanol (10 cm^3). The resulting solution was stirred for 1 h and then after slow evaporation of solvents a viscous product was obtained. Recrystallization from chloroform–methanol (0.75:1 v/v) afforded, in a very small yield, prismatic dark brown crystals of complex **1** suitable for X-ray analysis. Despite several additional attempts we could not isolate sufficient crystals to obtain definitive information by elemental analyses and magnetic studies.



H_2L

$[Co(HL)L]\cdot 4.5H_2O$ **2**. The pyridoxal thiosemicarbazone, $H_2L\cdot 3H_2O$ (0.20 g, 0.68 mmol), was dissolved in water (40 cm^3) by heating for 30 min at 80 °C. To this solution in the open air was added $Co(CH_3CO_2)_2\cdot 4H_2O$ (0.17 g, 0.68 mmol), dissolved in a minimum of the same solvent. The limpid reaction mixture (pH 5–6) turned reddish brown immediately and was stirred for 15 min at room temperature. Upon slow evaporation after several hours, crystals of $[Co(HL)L]\cdot 4.5H_2O$ **2** (Found: C, 35.4; H, 5.1; N, 18.4. $C_{18}H_{30}CoN_8O_{8.5}S_2$ requires C, 35.0; H, 4.9; N, 18.1%) were obtained in *ca.* 94% yield. By the same procedure, when H_2L was treated with $Co(CH_3CO_2)_2\cdot 4H_2O$ in 2:1 molar ratio, the resulting aqueous solution gave crystals of **2** as confirmed by elemental analyses and IR spectral features. The magnetic measurements carried out on the solid sample revealed its diamagnetic nature.

The characterization of complexes **1** and **2** by conventional measurement of melting point (apparatus temperature range: ambient to 300 °C) revealed a thermal stability up to 275 °C for both compounds.

X-Ray Analysis.—The crystal and instrumental parameters used in the unit-cell determination and data collection are

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc. Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Experimental data for the crystallographic analyses[a]

Compound	$[Co(H_{0.5}L)_2]\cdot 3.5H_2O$ **1**	$[Co(HL)L]\cdot 4.5H_2O$ **2**
Formula	$C_{18}H_{28}CoN_8O_{7.5}S_2$	$C_{18}H_{30}CoN_8O_{8.5}S_2$
M	599.5	617.5
Crystal symmetry	Monoclinic	Triclinic
Space group	$C2/c$ (no. 15)	$P\bar{1}$ (No. 2)
a/Å	10.355(1)	11.195(1)
b/Å	29.026(3)	12.138(2)
c/Å	16.564(2)	11.128(1)
α/°	90.0	103.23(3)
β/°	94.85(3)	99.42(2)
γ/°	90.0	115.49(2)
U/Å^3	4951.1(9)	1268.2(5)
Z	8	2
D_m/Mg m^{-3}	1.59	1.64
D_c/Mg m^{-3}	1.61	1.62
$F(000)$	2488	642
Crystal size/mm	0.13 × 0.10 × 0.42	0.11 × 0.07 × 0.13
μ/mm^{-1}	7.76	7.62
h, k, l range	−11 to 11, 0–32, 0–18	−11 to 11, −14 to 14, 0–13
Standard reflection	−2 2 7	3 1 −2
No. of measured reflections	3913	4498
Maximum, minimum height in final difference synthesis/e Å^{-3}	0.46, −0.19	0.38, −0.31
No. of refined parameters	327	343
No. of unique reflections	1921	2465
R	0.053	0.051
R'[b]	0.057	0.058

[a] Details in common: Cu-Kα radiation (λ = 1.541 79 Å); Siemens–AED diffractometer; T = 293 ± 1 K; θ range 2.5–60°; no intensity variation of standards; selection criterion $I \geqslant 2\sigma(I)$. [b] For complex **1** the weighting scheme used was $w = k/[\sigma^2(F_o) + |g|(F_o)^2]$; k was redetermined after each structure-factor calculation and refined by fitting $(|F_o| - |F_c|)^2$ to $[\sigma^2(F_o) + |g|(F_o)^2]/k$. For **2** unit weights were used.

summarized in Table 1. All intensity data were collected by the ω–2θ technique. No correction for absorption was applied.

For both compounds, three-dimensional Patterson maps were computed and the positions of the Co atoms determined. Successive Fourier syntheses revealed the positions of all other non-hydrogen atoms and the disordered distribution of water molecules, O(4) and O(6) for complex **1**, O(7) for **2**. In **1** the hydrogen atoms were located from a Fourier difference synthesis, except that of O(2) and those of the water molecules [only one hydrogen, H(13) of the water molecule O(3), was found]. Surprisingly the hydrogen atom bonded to O′(2) (alcoholic) was found in the difference synthesis statistically distributed in two positions [H′(5), H″(5)] with half the occupancy of that of the hydrogen atom bonded to the pyridine atom N(4). Their position was confirmed on the basis of the hydrogen bonds present. In **2** all the hydrogen atoms were similarly located except those of the disordered water molecule O(7).

Refinements were carried out by block-matrix least-squares cycles using the SHELX 76 system of computer programs.[13] The hydrogen atoms were not refined. Six reflections, which suffered errors during data reduction, were omitted in the last cycle for **1**. Scattering factors for all atoms were taken from ref. 14 and both the real and imaginary components of the anomalous dispersion factor were included.

The final positional parameters for the non-hydrogen atoms are given in Tables 2 and 3 for complexes **1** and **2** respectively. All calculations were performed on the GOULD-SEL 77/22 computer of the Centro di Studio per la Strutturistica Diffrattometrica del C.N.R. (Parma) using the PARST[15] program for the geometrical description of the structure, and PLUTO[16] for the structural 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

In contrast with the results obtained in absolute ethanol,[10] when H_2L and $Co(CH_3CO_2)_2\cdot 4H_2O$ were allowed to react in water or in chloroform–methanol the cobalt(II) ion always underwent an oxidation process leading to a cobalt(III) complex species with a different extent of hydration.

Infrared spectra—Assignments of the characteristic IR bands of H_2L and its cobalt(III) complexes are given in Table 4. The spectra of both complexes exhibit a broad band in the region 3640–3000 cm^{-1} with three distinct peaks around 3380, 3330 and 3180 cm^{-1}. The broad bands provide evidence of hydrate nature and are assigned to the O–H stretching vibration of un-co-ordinated water molecules, while the three medium-intensity absorptions are due to the N–H modes of the terminal NH_2 group. It is interesting that the band at 3160 cm^{-1} disappears on complexation, which indicates the removal of the proton of the secondary amine nitrogen. The characteristic band at 2860 cm^{-1} of the pyridoxal moiety is shifted in the spectra of the complexes (maximum ±20 cm^{-1}) and suggests, from the dipolar nature of H_2L in the crystalline state in accordance with observations and X-ray studies on previously reported complexes,[9,10] that the phenolic oxygen is involved in the co-ordination. The spectra of the two complexes exhibit a systematic shift in the positions of the bands in the 1620–1300 cm^{-1} region due to ν(C=C) and ν(C=N) vibrational modes, and their mixing patterns are different from those present in the ligand spectrum but very similar in profile for both complexes. The two very intense bands at 1495 and 1465 cm^{-1} for $[Co(HL)L]\cdot 4.5H_2O$ and the single band at 1470 cm^{-1} for $[Co(H_{0.5}L)_2]\cdot 3.5H_2O$ seem to show the presence of different delocalized ligand molecules linked to the metal through the imine nitrogen. The medium-intensity band in the spectra of both complexes at *ca.* 1150 cm^{-1} is considered to derive a portion of its intensity from the carbon–sulphur stretching mode. This new band together with the small shift toward lower energy of the band at 920 cm^{-1} and the new peaks which appear in the region 880–840 cm^{-1} suggest an S-co-ordinating ligand. In addition, the band at 360 cm^{-1} in the spectra of the complexes is assigned to a ν(Co–S) mode.[17,18]

Table 2 Fractional atomic coordinates ($\times 10^5$ for Co and S; $\times 10^4$ for others) in $[Co(H_{0.5}L)_2]\cdot 3.5H_2O$ **1**

Atom	*X/a*	*Y/b*	*Z/c*
Co	20 270(11)	12 825(4)	9 272(7)
S	40 510(19)	14 215(6)	13 977(13)
O(1)	248(4)	1 151(2)	487(3)
O(2)	2 504(6)	49(2)	−1 584(4)
N(1)	5 775(7)	753(2)	1 616(5)
N(2)	3 835(6)	534(2)	977(4)
N(3)	2 659(6)	695(2)	643(4)
N(4)	−1 517(6)	645(2)	−1 220(4)
C(1)	4 554(7)	862(3)	1 332(5)
C(2)	2 049(8)	422(2)	114(5)
C(3)	828(7)	515(2)	−347(5)
C(4)	461(8)	243(2)	−1 026(5)
C(5)	−737(9)	312(3)	−1 448(5)
C(6)	−1 205(7)	927(2)	−593(5)
C(7)	−4(7)	873(2)	−117(5)
C(8)	−2 143(8)	1 292(3)	−410(5)
C(9)	1 337(8)	−128(2)	−1 316(5)
S′	15 954(19)	10 446(6)	21 371(12)
O′(1)	2 309(4)	1 507(2)	−151(3)
O′(2)	−1 435(6)	2 635(2)	466(4)
N′(1)	1 518(6)	1 637(2)	3 370(4)
N′(2)	1 588(6)	1 967(2)	2 112(4)
N′(3)	1 535(5)	1 872(2)	1 288(4)
N′(4)	416(6)	2 111(2)	−1 710(4)
C′(1)	1 551(7)	1 595(2)	2 545(5)
C′(2)	1 176(7)	2 203(2)	815(5)
C′(3)	952(7)	2 172(2)	−62(4)
C′(4)	111(7)	2 498(2)	−476(5)
C′(5)	−135(7)	2 454(2)	−1306(5)
C′(6)	1 212(7)	1 800(2)	−1345(5)
C′(7)	1 524(7)	1 815(2)	−498(5)
C′(8)	1 729(9)	1 430(3)	−1 853(5)
C′(9)	−567(8)	2 861(3)	−32(5)
O(3)	1 582(8)	2 833(3)	2 979(5)
O(4A)	1 363(13)	4 673(5)	2 906(8)
O(4B)	885(19)	4 258(8)	2 979(12)
O(5)	0	3 498(8)	2 500
O(6A)	637(17)	3 977(6)	917(10)
O(6B)	218(19)	5 306(7)	−481(11)

Table 3 Fractional atomic coordinates ($\times 10^5$ for Co and S; $\times 10^4$ for others) in $[Co(HL)L]\cdot 4.5H_2O$ **2**

Atom	*X/a*	*Y/b*	*Z/c*
Co	7 268(11)	30 702(10)	23 913(11)
S	−12 571(17)	13 827(16)	10 911(18)
O(1)	2 490(4)	4 555(4)	3 496(4)
O(2)	4 755(5)	2 153(4)	871(5)
N(1)	−1 650(6)	−1 015(5)	677(6)
N(2)	555(5)	575(5)	1 806(5)
N(3)	1 421(5)	1 889(5)	2 234(5)
N(4)	6 066(5)	6 005(5)	3 714(5)
C(1)	−734(7)	258(6)	1 198(6)
C(2)	2 752(7)	2 225(6)	2 511(6)
C(3)	3 846(6)	3 535(6)	2 939(6)
C(4)	5 199(7)	3 746(6)	2 885(6)
C(5)	6 266(7)	4 972(6)	3 304(6)
C(6)	4 808(7)	5 874(6)	3 744(6)
C(7)	3 673(7)	4 634(6)	3 396(6)
C(8)	4 710(7)	7 077(7)	4 135(8)
C(9)	5 442(7)	2 658(6)	2 261(7)
S′	524(18)	26 903(18)	40 999(18)
O′(1)	1 331(4)	3 439(4)	900(4)
O′(2)	1 891(5)	8 056(5)	3 199(5)
N′(1)	−1 797(6)	3 320(6)	4 803(6)
N′(2)	−1 002(5)	4 087(5)	3 229(6)
N′(3)	−44(5)	4 190(5)	2 529(5)
N′(4)	3 223(6)	6 190(5)	16(6)
C′(1)	−981(6)	3 427(6)	3 996(7)
C′(2)	265(7)	5 109(6)	2 075(7)
C′(3)	1 280(7)	5 467(6)	1 361(7)
C′(4)	1 804(7)	6 670(6)	1 218(7)
C′(5)	2 785(7)	7 013(7)	559(7)
C′(6)	2 710(7)	5 026(6)	98(7)
C′(7)	1 743(6)	4 586(6)	836(6)
C′(8)	3 167(8)	4 115(7)	−544(8)
C′(9)	1 408(8)	7 660(7)	1 802(8)
O(3)	667(6)	9 509(5)	3 727(5)
O(4)	2 013(5)	1 519(5)	6 060(6)
O(5)	5 430(8)	15(8)	6 223(9)
O(6)	3 364(9)	267(9)	7 194(10)
O(7)	4 863(15)	47(13)	9 319(14)

Table 4 Selected vibrational bands (cm^{-1}) of H_2L and the complexes of Co^{III}

Compound	ν(NH$_2$), ν(OH)	ν(NH)	ν(NH$^+$), ν(OH)	ν(C=N), ν(C=C)	Ring	ν(C=N)	Ring	δ(OH)	δ(NCS)	ν(C=S)	δ(CH)
$H_2L\cdot 3H_2O$	3390m, 3250m	3160m	2860(sh)	1600s	1570mw	1540s	1505(sh), 1495s, 1465m, 1430m, 1415m	1375vs	1250s, 1220m, 1090s, 1035vs	920m	825m, 815(sh)
$[Co(H_{0.5}L)_2]\cdot 3.5H_2O$	3390m(br), 3300m, 3180m	—	2880w	1615s(br), 1600(sh)	1565mw(br)	1555(sh)	1505(sh), 1495(sh), 1470vs(br), 1440(sh)	1375s	1250ms, 1210m, 1145ms, 1080mw, 1000m(br)	910w, 855vw	825vw
$[Co(HL)L]\cdot 4.5H_2O$	3370mw(br), 3300ms, 3190m	—	2880w, 2840w	1620vs(br), 1600(sh)	1565mw	1525(sh)	1505(sh), 1495vs(br), 1465vs(br), 1435(sh)	1370s	1260ms, 1245ms, 1205ms, 1155ms, 1080mw, 1010s(br)	910mw, 880w, 840w	820vw

Crystal and Molecular Structure.—In both compounds 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 sulphur, the nitrogen atom from the hydrazine chain and the phenolic oxygen of the pyridoxal group. Co-ordination bond lengths are reported in Table 5 for both compounds **1** and **2**. A comparison of these values shows that there are no great differences between the two complexes and the Co–S, Co–N and Co–O distances are in the expected ranges of 2.201–2.230, 1.891–1.901, 1.945–1.964 Å respectively already noted for several cobalt(III) complexes.[19–21] In both compounds the two ligands, which are not equivalent because of variation in the pyridine H-atom positions, are in the *meridional* configuration (S and O atoms *cis* to each other and the N atoms *trans*). In **1** they could be considered as 1.5 deprotonated in acco dance with the oxidation state three of cobalt, *i.e.* in both

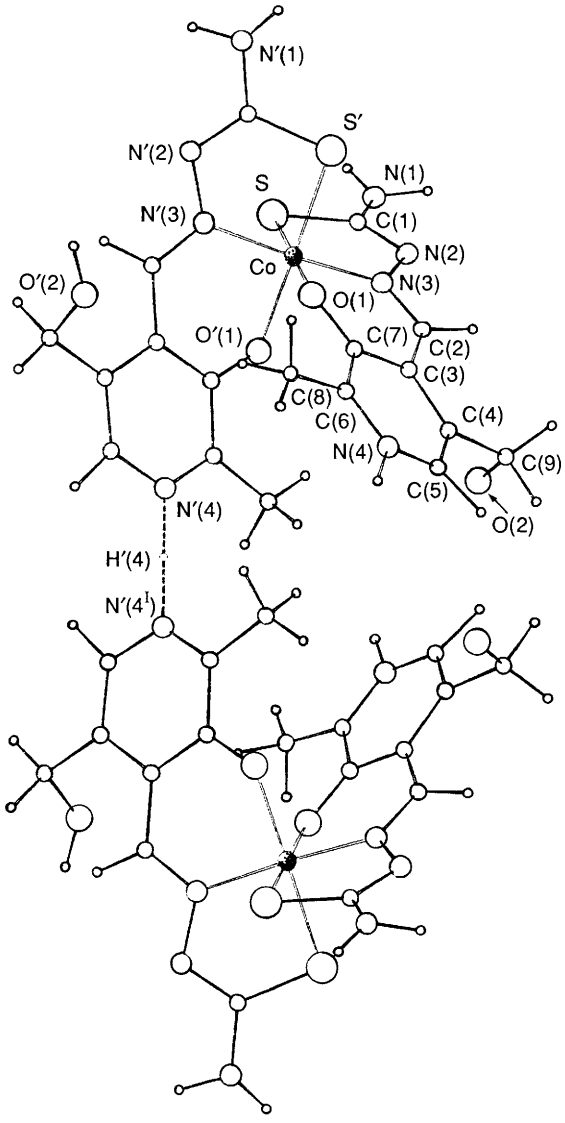
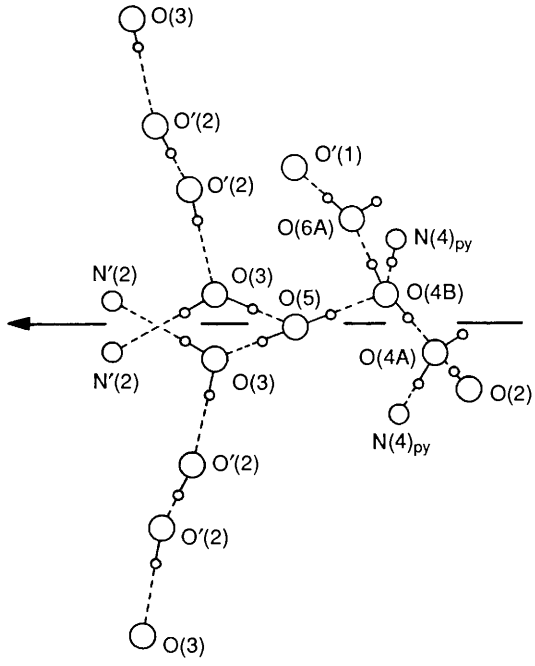


Fig. 1 Perspective view of two molecules of complex **1** linked by a very short symmetric hydrogen bond



Scheme 1

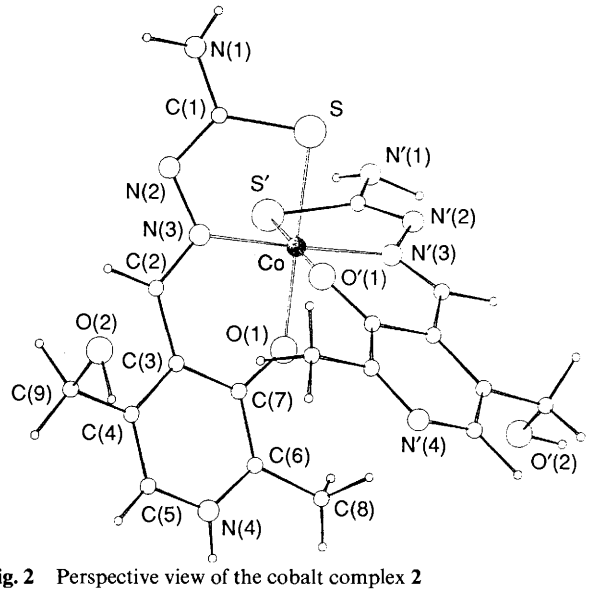


Fig. 2 Perspective view of the cobalt complex **2**

ligands the hydrazine nitrogen atom is deprotonated, but the pyridine atoms N(4) and N'(4) would be statistically deprotonated. In fact the complexes are linked in pairs *via* the pyridine rings of one of the ligands by a strong symmetric hydrogen bond N'(4)···H'(4)···N'(4) $(-x, y, -z-\frac{1}{2})$ [2.685(9) Å] (Fig. 1). The hydrogen atom lies on a two-fold axis, but it could be considered as disordered, vibrating around two equally probable positions on either side of the axis. The N(4) atom of the other ligand, also statistically deprotonated, forms two hydrogen bonds with water molecules O(4A) and O(4B) (disordered) acting alternatively as either a donor or acceptor of protons (see Scheme 1).

In complex **2** the non-equivalence is due to the fact that one of the ligands, in the formation of the complex, loses only one proton from the carbazide fragment, whereas the second loses another proton from the pyridine nitrogen N'(4) (Fig. 2). This is confirmed by the fact that N'(4) accepts a hydrogen atom from O(2) (alcoholic) [O(2)–H(5)···N'(4) $(1-x, 1-y, -z)$ 2.80(1) Å; O(2)H(5)N'(4) 165.9°].

Although there is no imposed symmetry, inspection of the structures in Figs. 1 and 2 reveals that the complexes approach *C*2 symmetry. The bond distances in the pyridoxal rings agree well with those found in other compounds containing the same moiety.[10,22] The C'(6)–N'(4)–C'(5) angle of one pyridine ring in complex **2** [119.9(7)°] is typical of a deprotonated nitrogen.

The alcohol groups in all ligands adopt axial geometry, but different conformations as shown by the torsion angles. In **1** O(2) and O'(2) are −synclinal with regard to C(3) and C'(3) respectively [C(3)C(4)C(9)O(2) −64.3(9) and C'(3)C'(4)-C'(9)O'(2) −63.9(9)°], but the alcoholic hydrogen atoms, owing to disorder, are undetermined. In **2** O(2), O'(2) and H(5) are +synclinal to C(3), C'(3) and C(4) respectively while H'(5) is +anticlinal to C'(4) [C(3)C(4)C(9)O(2) 67.0(9), C'(3)C'(4)C'(9)O'(2) 64.6(1.0); C(4)C(9)O(2)H(5) 81.3(6), C'(4)C'(9)O'(2)H'(5) 179.8(6)°]. These conformations are probably realized in order to form intermolecular hydrogen bonds (Table 6). A comparison of the bond distances in the side chain either for the complexes in the present work or for other thiosemicarbazone structures[23–26] is shown in Table 5. In **2** a higher delocalization of the singly deprotonated ligand [N(3)–C(2) 1.323(10), N(2)–N(3) 1.371(7) Å] with respect to the doubly deprotonated one [N'(3)–C'(2) 1.266(10), N'(2)–N'(3) 1.405(9) Å] is observed, while in **1**, owing to the loss of regularity in the crystal due to the statistical distribution of protons in the pyridine groups, an average geometry is observed for both

Table 5 Comparison of bond distances (Å) and angles (°) for pyridoxal thiosemicarbazone (H_2L) and for some of its complexes

	$[Co^{III}(H_{0.5}L)_2]\cdot 3.5H_2O$[a]		$[Co^{III}(HL)L]\cdot 4.5H_2O$[a]		$[Mn^{II}(H_2L)(OH_2)Cl]Cl$[9]	$[Cu^{II}(HL)(OH_2)]Cl\cdot H_2O$[9]	H_2L[10]
M–S	2 206(2)	2.201(2)[b]	2.213(2)	2.230(3)[b]	2.477(4)	2.226(2)–3.066(2)	—
M–O(1)	1.958(4)	1.945(5)	1.946(3)	1.964(5)	2.002(7)	1.875(4)	—
M–O(w)	—	—	—	—	2.106(8)	1.941(5)	—
M–N(3)	1.901(6)	1.895(6)	1.891(7)	1.891(7)	2.269(9)	1.943(6)	—
M–Cl	—	—	—	—	2.408(4)	Cl(ionic)	—
S–C(1)	1.710(9)	1.736(7)	1.720(9)	1.745(9)	1.709(11)	1.719(7)	1.70(1)
C(1)–N(1)	1.347(10)	1.375(11)	1.344(7)	1.370(11)	1.301(14)	1.333(8)	1.33(1)
C(1)–N(2)	1.316(10)	1.299(9)	1.331(9)	1.301(11)	1.330(12)	1.324(8)	1.35(1)
N(2)–N(3)	1.374(8)	1.389(9)	1.371(7)	1.405(9)	1.362(11)	1.368(7)	1.40(1)
N(3)–C(2)	1.304(9)	1.275(9)	1.323(10)	1.266(10)	1.260(13)	1.298(8)	1.30(1)
C(2)–C(3)	1.444(11)	1.454(10)	1.429(8)	1.463(12)	1.458(14)	1.435(8)	1.45(1)
C(3)–C(4)	1.400(10)	1.421(9)	1.438(11)	1.379(10)	1.396(14)	1.432(8)	1.42(1)
C(4)–C(5)	1.384(12)	1.383(12)	1.352(8)	1.388(12)	1.334(15)	1.350(8)	1.37(1)
C(5)–N(4)	1.334(11)	1.352(9)	1.358(11)	1.359(12)	1.363(15)	1.338(9)	1.36(1)
C(6)–N(4)	1.340(10)	1.332(9)	1.355(10)	1.308(10)	1.320(14)	1.335(9)	1.34(1)
C(6)–C(8)	1.484(11)	1.491(11)	1.482(12)	1.497(13)	1.468(17)	1.463(10)	1.50(1)
C(6)–C(7)	1.422(10)	1.413(12)	1.398(8)	1.458(11)	1.424(14)	1.420(9)	1.42(1)
C(7)–C(3)	1.421(10)	1.420(10)	1.421(11)	1.430(12)	1.430(15)	1.396(9)	1.44(1)
C(7)–O(1)	1.294(9)	1.307(8)	1.311(10)	1.288(9)	1.269(13)	1.301(8)	1.29(1)
C(4)–C(9)	1.511(10)	1.493(11)	1.500(12)	1.503(13)	1.537(16)	1.497(10)	1.52(1)
C(9)–O(2)	1.416(10)	1.428(11)	1.460(9)	1.449(10)	1.302(19)	1.421(8)	1.43(1)
C(5)–N(4)–C(6)	123.4(7)	123.0(7)	122.5(6)	119.9(7)	124.0(10)	124.3(6)	124.1(5)

[a] Present work. [b] The second set of values are for the ligands with primed labels.

Table 6 Relevant hydrogen bonds

Compound **1**[a]			Compound **2**[b]		
Bond	Distance/Å	Angle/°	Bond	Distance/Å	Angle/°
D–H ··· A	D ··· A	D–H ··· A	D–H ··· A	D ··· A	D–H ··· A
N(1)–H(11) ··· $O(2^{V})$	2.93(1)	134.3(4)	N(1)–H(11) ··· $O'(1^{I})$	3.26(1)	160.7(4)
$N'(1)–H'(21) \cdots O(1^{II})$	3.08(1)	156.5(4)	N(1)–H(21) ··· $O(2^{I})$	3.13(1)	167.6(5)
$N(4)–H(4) \cdots O(4B^{IV})$	2.91(2)	169.7(8)	$N'(1)–H'(11) \cdots O(1^{IV})$	3.29(1)	154.2(4)
$N'(4)–H'(4) \cdots N'(4^{I})$	2.69(1)	179.8(4)	$N'(1)–H'(21) \cdots O'(2^{IV})$	3.06(1)	152.4(4)
$O(2) \cdots O(4A^{VI})$	2.69(2)		$N(4)–H(4) \cdots O(4^{II})$	2.76(1)	127.1(4)
$O'(2)–H'(5) \cdots O(3^{II})$	2.66(1)	152.9(5)	$O(2)–H(5) \cdots N'(4^{III})$	2.80(1)	165.9(4)
$O'(2)–H''(5) \cdots O'(2^{III})$	2.70(1)	126.6(4)	O'(2)–H'(5) ··· O(3)	2.68(1)	163.6(4)
O(3)–H(13) ··· N'(2)	2.90(1)	170.6(4)	O(3)–H(23) ··· $O(4^{IV})$	2.79(1)	119.1(6)
O(3) ··· O(5)	2.61(2)		$O(3)–H(13) \cdots N(2^{VI})$	2.75(1)	169.0(4)
$O(4A) \cdots N(4^{VII})$	2.69(1)		$O(4)–H(14) \cdots O(3^{VII})$	2.76(1)	163.8(4)
$O(4B) \cdots O(6A^{II})$	2.64(3)		O(4)–H(24) ··· O(6)	2.90(1)	165.2(6)
$O(4B) \cdots O(4A^{II})$	2.90(2)		O(5)–H(15) ··· O(6)	2.81(2)	173.5(6)
O(5) ··· O(4B)	2.49(3)		$O(5)–H(25) \cdots O'(2^{II})$	2.74(1)	113.7(5)
$O(6A) \cdots O'(1^{VI})$	2.92(2)		O(6)–H(16) ··· O(7)	2.80(2)	124.8(9)
$O(6B) \cdots N(2^{VI})$	2.78(2)		$O(7) \cdots O(2^{VIII})$	2.80(2)	
			$O(7) \cdots O(2^{V})$	2.85(2)	

[a] Symmetry operations: I $-x, y, -z-\frac{1}{2}$; II $-x, y, \frac{1}{2}-z$; III $-x-\frac{1}{2}, \frac{1}{2}-y, -z$; IV $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$; V $1-x, -y, -z$; VI $\frac{1}{2}-x, \frac{1}{2}-y, -z$; VII $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$. [b] Symmetry operations: I $-x, -y, -z$; II $1-x, 1-y, 1-z$; III $1-x, 1-y, -z$; IV $-x, 1-y, 1-z$; V $1-x, -y, 1-z$; VI $x, 1+y, z$; VII $x, y-1, z$; VIII $x, y, z+1$.

Table 7 Comparison of dihedral angles (°) between planes[a]

	Planes									
Complex	1–2	1–3	2–3	1–4	1–5	4–5	2–4	2–5	3–4	3–5
$[Co^{III}(H_{0.5}L)_2]\cdot 3.5H_2O$[b]	16.5	30.3	14.6	30.2	23.1	8.6	17.0	14.1	7.1	13.3
	155.7	139.4	17.9	141.0	149.2	8.7	21.4	17.3	10.9	15.9
$[Co^{III}(HL)L]\cdot 4.5H_2O$[b]	17.2	30.5	14.7	29.6	23.0	7.7	17.4	14.8	7.9	13.2
	20.8	35.3	15.8	26.0	35.0	9.5	19.2	14.3	8.7	14.0
$[Mn^{II}(H_2L)(OH_2)Cl]Cl$[b]	14.6	17.5	22.7	6.1	11.3	5.9	14.7	13.0	11.6	9.7
$[Cu^{II}(HL)(OH_2)]Cl\cdot H_2O$[b]	5.7	5.5	1.8	5.9	5.7	1.4	1.7	3.0	0.5	1.1
$[Cu^{II}(H_2L)(OH_2)Cl]Cl$[c]	8.3	6.9	10.2	4.6	6.3	2.2	3.9	4.1	6.7	6.1
$[Fe^{III}(HL)Cl_2]$[c]	17.1	19.0	15.6	4.9	5.9	5.5	19.3	17.1	14.2	14.3

[a] 1 = Pyridine ring, 2 = six-membered chelate ring, 3 = five-membered chelate ring, 4 = thiourea moiety, 5 = hydrazine chain. [b] This work. [c] M. Belicchi Ferrari, G. Gaspari Fava, M. Lanfranchi, C. Pelizzi and P. Tarasconi, unpublished work.

ligands. However, small differences in bond lengths may be perturbed by the different hydrogen-bonding patterns. The ligands in both compounds deviate considerably from planarity and this fact can be illustrated by considering one of the ligands.

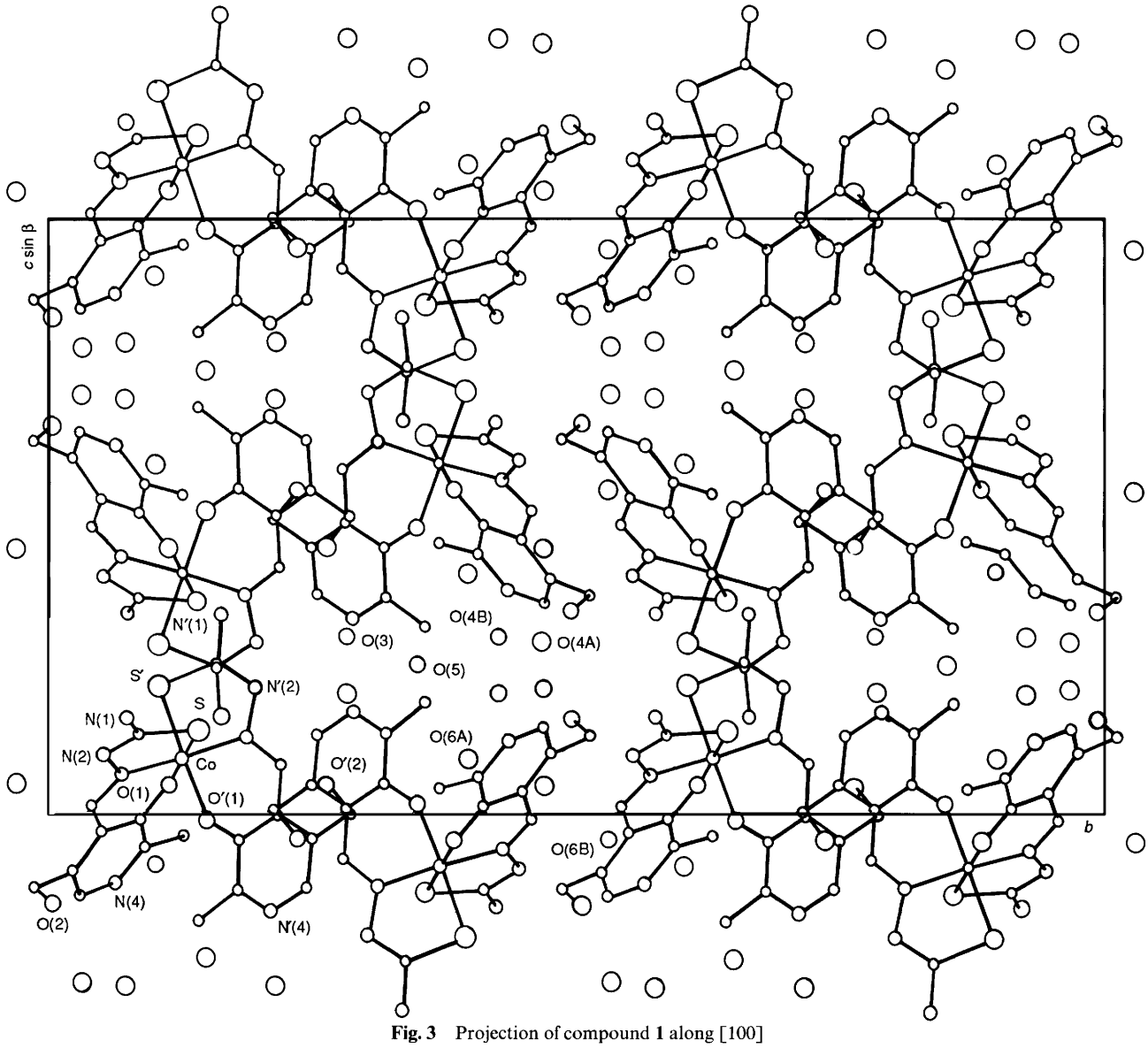


Fig. 3 Projection of compound **1** along [100]

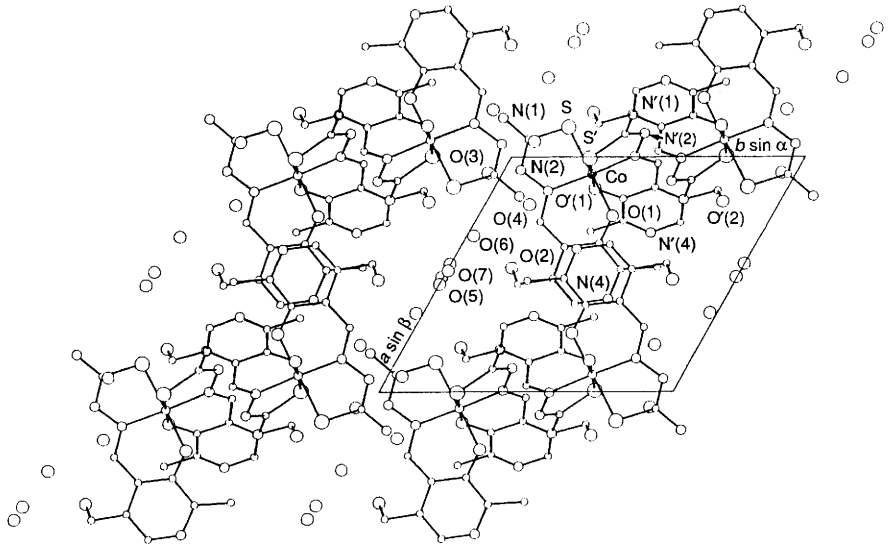


Fig. 4 Projection of complex **2** along [001] showing a channel filled with water molecules

For example, for the 'unprimed' ligand in complex **2** the heterocyclic ring is planar with deviations ranging between 0.003(6) and 0.018(6) Å and the thiourea moiety is also planar, but the hydrazinic chain gives a curvature to the whole ligand which assumes a boat-like conformation. A similar situation also exists for the other ligands. In **1** the pyridine ring of the 'primed' ligand is perfectly planar [the largest deviation from the best plane being 0.002(7) Å for C′(3)], probably owing to the strong hydrogen bond between the nitrogen atoms. The chelate rings are non-planar and in both compounds the six- and five-membered rings show 'twist-boat' and 'envelope' conformations respectively. The dihedral angles between the planes are reported in Table 7.

In complex **1** the packing is governed by hydrogen bonds involving the water molecules distributed statistically and in Fig. 3 a possible scheme for these hydrogen bonds is illustrated. The statistical behaviour of the pyridine atom N(4), acting as either a donor or acceptor of protons, is also shown. In **2** (Fig. 4) hydrogen bonds between N(1), N′(1) and N′(4) and alcoholic or phenolic oxygen atoms of neighbouring molecules form, in the three-dimensional structure, polar channels along the *z* axis, which are full of water molecules.

Extensive use of the Cambridge Crystallographic Data Files has been made for the bibliography search.[27]

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