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Metal complexes of 5-acetyl-2,2′-pyridylthiophene aroylhydrazones. Crystal structure of a cobalt(II) derivative

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Abstract

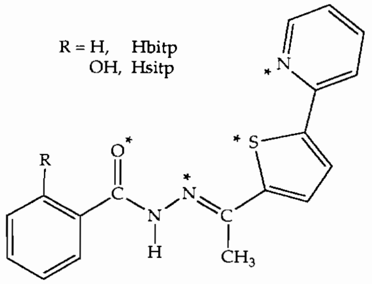
The new potentially tetradentate aroylhydrazone ligands, Hbitp and Hsitp, produced by condensation of 5-acetyl-2,2′-pyridylthiophene with benzoyl- and salicyloylhydrazine, respectively, have been reacted with several metal(II) acetates. Deprotonation at the amide nitrogen occurs and neutral complexes of the type $[M(bitp)_2L_2]$ and $[M(sitp)_2L_2]$ are obtained, where L is a solvent molecule. An X-ray crystal structure determination carried out on $[Co(bitp)_2(dmso)_2]$ (**I**) revealed that these ligands behave as bidentate through the –(O)C–N–N= hydrazide moiety, assuming the *Z* configuration around the C=N hydrazone bond. The coordination environment is distorted octahedral, the solvent molecules occupying the axial positions. The crystal structure of the ligand Hbitp (**II**) has also been determined for comparison.

Keywords: Crystal structures; Cobalt complexes; Multidentate ligand complexes; Hydrazone complexes; Chelate complexes

1. Introduction

N-Aroylhydrazones of heterocyclic aldehydes and ketones and of methyl pyruvate show considerable chelating ability towards metal species [1] and can be used in analytical chemistry to recover and selectively determine transition metals as hydrazone complexes [2]. Previous ^1H and ^{13}C NMR investigations [3] ascertained that these species (differently from the corresponding *N*-acylhydrazones) adopt preferentially in solution the *trans* conformation around the CO–NH amide bond and the *E* configuration around the C=N hydrazone double bond.

Continuing our investigations on the ligand behaviour of aroylhydrazones of aromatic aldehydes and ketones, we have focussed our attention on the coordination capability of a new class of hydrazones, obtained by condensation of 5-acetyl-2,2′-pyridylthiophene with benzoyl- and salicyloylhydrazine. Although, in the *E* configuration, they are potentially tetradentate planar ligands (through the starred atoms, as represented in the scheme below), however they have been found to assume the *Z* configuration, behaving as bidentate, owing to the inability of the thiophene ring to coordinate to metals in a planar fashion. Actually, in all the S-bound thiophene complexes structurally characterized [4,5], the metal lies out of the ring plane in such a way that the sulphur has a trigonal pyramidal environment.



2. Experimental

2.1. Syntheses and characterizations

Reagent grade metal acetates, 2,2′-thienylpyridine and acetyl chloride were commercial products and used

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as received. When necessary, analytical grade solvents were dried by standard techniques before use. Elemental analyses were performed on a Carlo Erba CHNS-O EA 1108 equipment; IR spectra were collected on a Nicolet 5PC FT spectrometer; UV–Vis spectra were recorded on a Kontron Uvikon 860 spectrophotometer; ^{1}H NMR spectra were obtained with a Bruker AC100 instrument; mass spectra were recorded on a Finnigan 1020 mass spectrometer at 70 eV ionizing voltage; thermogravimetric analyses (TGA) were performed with a Perkin-Elmer Delta Series TGA 7 equipment.

5-Acetyl-2,2′-pyridylthiophene was prepared by the following procedure. 14.8 g (0.19 mmol) of acetyl chloride in dichloromethane (50 ml) were added dropwise to a stirred suspension of aluminium trichloride (50.5 g, 0.38 mol) in the same solvent (100 ml), under nitrogen atmosphere; most of the metal salt was dissolved and the temperature slightly raised. A dichloromethane (30 ml) solution of 2,2′-thienylpyridine (30.1 g, 0.19 mol) was then added by a dropping funnel and the resulting mixture was refluxed for 4 h. The reaction mixture was quenched by adding an aqueous solution of NaOH (10%); the organic layer was separated and the aqueous phase was extracted with ethyl ether. The pure product was recovered from the organic extracts by flash chromatography with silica as stationary phase and hexane–ethyl acetate (9:1) as mobile phase. 18.5 g of 5-acetyl-2,2′-pyridylthiophene were obtained, corresponding to a 50% yield; melting point, 121 °C. Mass spectrum, *m/z* (%): 202, M^+ (70), 188 (100), 160 (50). IR spectrum (KBr): 1653 cm^{-1} (CO stretch). UV spectrum (CHCl$_3$): λ(max) 327 nm, ϵ 27×10^3 l mol^{-1} cm^{-1}. ^{1}H NMR spectrum (CHCl$_3$-d$_1$), δ: 2.58 s (3H, Me), 7.24 m (1H), 7.59 d (1H), 7.69 d (1H), 7.73 m (2H), 8.60 m (1H).

The hydrazone ligand Hbitp (5-acetyl-2,2′-pyridylthiophene benzoylhydrazone) was prepared by refluxing in ethanol (50 ml) equimolar amounts of 5-acetyl-2,2′-pyridylthiophene (2.1 g) and benzoylhydrazine (1.4 g) in the presence of trifluoroacetic acid (one drop) as condensation catalyst. Pale yellow needles were obtained on cooling, which were filtered, washed with chilled ether and dried in vacuo (2.7 g, ~82%); Hbitp, m.p., 198 °C. Mass spectrum, *m/z* (%): 322, M^+ (35), 216 (20), 186 (20). IR spectrum (KBr): 1649 cm^{-1} (CO stretch). UV spectrum (CHCl$_3$): λ(max) 354 nm, ϵ 26.5×10^3 l mol^{-1} cm^{-1}. ^{1}H NMR spectrum (dmso-d$_6$), δ: 2.40 s (3H, Me), 7.20–7.90 m (10H, rings), 8.59 d (1H, 6-py), 10.85 s (1H, NH).

The other ligand Hsitp (5-acetyl-2,2′-pyridylthiophene salicyloylhydrazone) was prepared by the same procedure described for Hbitp; Hsitp, m.p. 252 °C. Mass spectrum, *m/z* (%): 337, M^+ (70), 217 (100), 121 (70). IR spectrum (KBr): 1644 cm^{-1} (CO stretch). UV spectrum (CHCl$_3$): λ (max) 362 nm, ϵ 29×10^3 l mol^{-1} cm^{-1}. ^{1}H NMR spectrum (dmso-d$_6$), δ: 2.36 s (3H, Me), 6.90–7.90 m (9H, rings), 8.61 d (1H, 6-py), 11.31 s (1H, NH), 11.79 s (1H, OH).

The divalent metal complexes were prepared by reaction of Hbitp or Hsitp with the corresponding metal acetates in refluxing water–methanol mixtures; coloured powdery precipitates, suddenly obtained on cooling, were filtered, washed and dried in vacuo (yields 70–90%). They gave satisfactory elemental C, H, N and S analyses, according to the proposed molecular formulae. Further evidence for the presence of solvent molecules came from TGA data: they were totally lost between 90 and 150 °C, at a rate of 20°/min, leaving the corresponding desolvated complexes. Characterization data along with major IR bands are given in Tables 1 and 2.

Further recrystallization of [Co(bitp)$_2$(H$_2$O)$_2$] in dimethyl sulfoxide afforded reddish brown prismatic crystals of [Co(bitp)$_2$(dmso)$_2$] (compound **I**) suitable for the X-ray analysis. Suitable crystals of the ligand Hbitp (compound **II**) were obtained by recrystallization in ethanol.

2.2. X-ray data collections and structure refinements

The unit-cell dimensions and intensity data were measured at room temperature on a Philips PW-1100 diffractometer for compound **I** and on a Siemens AED diffractometer for compound **II**. Mo Kα radiation was used in both analyses. The results from automatic peak search, centring and indexing procedures were consistent with a monoclinic lattice in the case of **I** and with an orthorhombic lattice in the case of **II**. The systematic absences observed during the data collection identified the space group as $P2_1/n$ for I and as *Pbca* for **II**. Crystal data and details of intensity measurements and refinement are given in Table 3. No loss of intensity of standard reflections was detected during the X-ray experiment. Peak profile analysis was performed with a local modification of the Lehmann and Larsen method [6] and the data were corrected for Lorentz and polarization effects.

Both structures were solved by direct methods using the automatic multisolution routine in the SHELXS86 program package [7]. Refinement was by full-matrix least-squares procedures based upon *F* assuming anisotropic thermal parameters for all non-hydrogen atoms. For both compounds all the hydrogen atoms were located in inner-data difference maps and included in the refinement with individual isotropic thermal parameters, except those bonded to the methyl group which were placed in calculated positions. Rigid-group refinement was used for phenyl rings in **I**. Weights were derived from $w=k/[\sigma^2(F_o)+gF_o^2]$. In each case the final difference map showed no significant features.

Complex atom scattering factors were employed and anomalous dispersion corrections were applied to all

Table 1
Characterization data and main IR bands (cm^{-1}) of Hbitp and its complexes

Compound	Colour	Decomposition temperature (°C)	ν(N–H)	Amide I	Amide II	Ring	$\delta_s(CH_3)$
Hbitp	yellow	198[a]	3208w 3176w	1649s	1543s	1581m	1313s 1284s
$Co(bitp)_2 \cdot 2H_2O$	brown	>270		1502s	1368s	1585m	1302m
$Ni(bitp)_2 \cdot 2H_2O$	green	>270		1507vs	1372s	1587s	1302s
$Cu(bitp)_2$	green	267		1517s	1383s 1375sh	1588s	1303s
$Zn(bitp)_2 \cdot 2MeOH$	yellow	255		1503s	1380s	1585s	1303s
$Hg(bitp)_2 \cdot 2H_2O$	yellow	185		1496s	1384s 1359s	1584m	1314m 1301w

[a] Melting point.

Table 2
Characterization data and main IR bands (cm^{-1}) of Hsitp and its complexes

Compound	Colour	Decomposition temperature (°C)	ν(N–H)	Amide I	Amide II	Ring	$\delta_s(CH_3)$
Hsitp	yellow	252[a]	3269m	1644s 1621s 1607s	1545s 1529s	1565sh	1318s
$Co(sitp)_2 \cdot 2MeOH$	yellow	220		1590s	1374s	1538s	1300m
$Ni(sitp)_2 \cdot 2MeOH$	green	210		1589s	1362m 1347s	1560m	1303s
$Cu(sitp)_2$	brown	240		1591s	1371s	1565s	1308s
$Zn(sitp)_2 \cdot 2MeOH$	yellow	240		1587s	1371s	1565m	1305s
$Hg(sitp)_2 \cdot 4H_2O$	yellow	185		1585s	1359m	1558m	1312m

[a] Melting point.

Table 3
Crystallographic data, collection data and refinement procedures

Compound	**I**	**II**
Formula	$C_{40}H_{40}CoN_6O_4S_4$	$C_{18}H_{15}N_3OS$
MW	855.97	321.40
Crystal size (mm)	0.28×0.33×0.44	0.39×0.40×0.90
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$	*Pbca*
a (Å)	20.861(5)	20.034(6)
b (Å)	7.974(2)	8.282(2)
c (Å)	12.100(3)	19.502(6)
β (°)	93.62(2)	
V (Å^3)	2008.8(9)	3236(2)
Z	2	8
D_c (g cm^{-3})	1.415	1.320
μ (cm^{-1})	6.72	1.98
$F(000)$	890	1344
No. reflections measured	4007	3271
No. observed reflections	2156	1731
Parameters refined	310	236
Max. height in final ΔF map (e Å^{-3})	1.02	0.20
R, R_w	0.051, 0.064	0.037, 0.057

Details common to both analyses include the use of Mo Kα radiation (λ=0.71069 Å), the ϑ–2ϑ scan technique and the 2ϑ range (6–50°).

non-hydrogen atoms. All calculations were carried out on a GOULD 6040 computer using the SHELX76 [8], ABSORB [9], PARST [10] and ORTEP [11] program packages. The final atomic parameters for **I** and **II** are given in Table 4 and 5, respectively; selected bond distances and angles are in Table 6 and 7.

Table 4
Atomic coordinates (×10^4) and equivalent isotropic thermal parameters (Å^2) (one third trace of the diagonalized matrix) with e.s.d.s in parentheses for compound **I**

Atom	*x*	*y*	*z*	B_{eq}
Co	5000	0	0	2.50(2)
S(1)	7454(1)	1377(2)	−579(1)	3.20(4)
S(2)	4068(1)	3118(2)	−226(1)	3.90(4)
O(1)	5551(1)	130(5)	1451(3)	2.95(9)
O(2)	4738(2)	2552(5)	174(3)	3.71(10)
N(1)	6360(2)	1132(5)	414(3)	2.69(11)
N(2)	5924(2)	910(5)	−503(3)	2.56(11)
N(3)	9106(2)	2146(8)	−1973(5)	5.29(17)
C(1)	6111(2)	784(7)	1339(4)	2.66(13)
C(2)	6518(2)	1141(5)	2369(2)	2.77(13)
C(3)	6366(2)	394(5)	3362(2)	3.61(16)
C(4)	6730(2)	759(5)	4339(2)	4.69(19)
C(5)	7246(2)	1872(5)	4324(2)	4.57(19)
C(6)	7397(2)	2620(5)	3331(2)	4.64(19)
C(7)	7033(2)	2254(5)	2354(2)	3.73(16)
C(8)	6160(2)	1222(7)	−1433(4)	2.71(13)
C(9)	5715(3)	1300(11)	−2450(5)	4.08(18)
C(10)	6840(2)	1613(7)	−1590(4)	2.96(14)
C(11)	7078(3)	2097(9)	−2562(5)	4.08(18)
C(12)	7745(3)	2243(9)	−2515(5)	4.30(18)
C(13)	8023(2)	1852(8)	−1502(4)	3.52(15)
C(14)	8722(3)	1906(8)	−1148(5)	3.72(15)
C(15)	8932(3)	1790(11)	−74(6)	5.21(22)
C(16)	9588(3)	1955(13)	192(7)	6.32(26)
C(17)	9987(3)	2210(11)	−617(8)	6.37(26)
C(18)	9743(3)	2297(11)	−1681(8)	6.18(26)
C(19)	3935(3)	4951(8)	541(6)	4.78(18)
C(20)	4171(7)	4123(20)	−1506(9)	7.21(38)

Table 5
Atomic coordinates (×10^4) and equivalent isotropic thermal parameters (Å^2) (one third trace of the diagonalized matrix) with e.s.d.s in parentheses for compound **II**

Atom	*x*	*y*	*z*	B_{eq}
S	1628.6(4)	1344.6(9)	3429.3(4)	3.60(2)
O	3169(1)	3479(2)	2071(1)	3.77(5)
N(1)	2280(1)	5132(2)	2182(1)	2.84(5)
N(2)	1983(1)	4034(3)	2613(1)	2.91(5)
N(3)	690(1)	−1683(3)	4667(1)	4.30(7)
C(1)	2890(1)	4761(3)	1946(1)	2.85(6)
C(2)	3219(1)	6007(3)	1506(1)	2.93(6)
C(3)	3900(2)	6162(4)	1567(2)	3.78(7)
C(4)	4246(2)	7279(4)	1177(2)	4.90(9)
C(5)	3905(2)	8239(4)	722(2)	5.01(10)
C(6)	3231(2)	8080(4)	649(2)	4.52(9)
C(7)	2878(2)	6963(3)	1043(2)	3.59(7)
C(8)	1372(1)	4234(3)	2786(1)	3.01(6)
C(9)	911(2)	5554(4)	2559(2)	4.87(10)
C(10)	1115(1)	2938(3)	3229(1)	2.96(6)
C(11)	502(2)	2739(4)	3517(2)	4.27(9)
C(12)	433(2)	1287(4)	3905(2)	3.96(8)
C(13)	1018(1)	394(3)	3891(1)	2.99(7)
C(14)	1143(1)	−1210(3)	4201(1)	2.97(6)
C(15)	1673(2)	−2167(4)	4014(2)	4.48(9)
C(16)	1743(2)	−3672(4)	4316(2)	4.93(10)
C(17)	1294(2)	−4165(4)	4791(2)	5.03(10)
C(18)	783(2)	−3156(4)	4945(2)	5.19(10)

Table 6
Selected bond distances (Å) and angles (°) for compound **I**

Co–O(1)	2.039(3)	C(10)–C(11)	1.362(8)
Co–N(2)	2.183(4)	C(11)–C(12)	1.395(8)
Co–O(2)	2.121(4)	C(12)–C(13)	1.359(8)
O(1)–C(1)	1.294(6)	C(13)–S(1)	1.723(6)
C(1)–N(1)	1.294(7)	S(1)–C(10)	1.725(5)
N(1)–N(2)	1.401(5)	C(13)–C(14)	1.493(7)
N(2)–C(8)	1.280(6)	O(2)–S(2)	1.518(4)
C(8)–C(9)	1.495(8)	S(2)–C(19)	1.763(7)
C(8)–C(10)	1.477(7)	S(2)–C(20)	1.768(12)
O(1)–Co–N(2)	76.3(1)	C(8)–C(10)–C(11)	125.2(5)
O(1)–Co–O(2)	90.0(1)	S(1)–C(10)–C(11)	110.4(4)
N(2)–Co–O(2)	86.9(1)	C(10)–C(11)–C(12)	113.9(5)
Co–O(1)–C(1)	113.2(3)	C(11)–C(12)–C(13)	112.7(5)
O(1)–C(1)–N(1)	126.3(4)	C(12)–C(13)–S(1)	111.3(4)
C(1)–N(1)–N(2)	112.4(4)	C(12)–C(13)–C(14)	127.3(5)
N(1)–N(2)–Co	111.2(3)	S(1)–C(13)–C(14)	121.3(4)
N(1)–N(2)–C(8)	114.0(4)	C(10)–S(1)–C(13)	91.6(2)
Co–N(2)–C(8)	134.8(3)	Co–O(2)–S(2)	119.4(2)
N(2)–C(8)–C(9)	118.6(5)	O(2)–S(2)–C(19)	104.5(3)
N(2)–C(8)–C(10)	125.4(4)	O(2)–S(2)–C(20)	104.7(5)
C(9)–C(8)–C(10)	115.9(4)	C(19)–S(2)–C(20)	96.7(5)
C(8)–C(10)–S(1)	124.3(4)		

3. Results and discussion

The reaction of the new potentially tetradentate aroylhydrazone ligands Hbitp and Hsitp with some first-row transition metal acetates, in water–methanol mixtures, gives the corresponding complexes of general formula $[M(bitp)_2L_2]$ and $[M(sitp)_2L_2]$, where L is a solvent molecule. The choice between water or methanol is probably driven by crystal packing requirements. They are coloured, high-temperature decomposing solids, poorly soluble in all common solvents (chiefly sitp complexes), but soluble in dimethyl sulfoxide. In Tables 1 and 2 the main IR bands of Hbitp and Hsitp are given, respectively, along with their colours and decomposition points.

In the IR spectra of the complexes, the disappearance of the ν(NH) band and the significant shift of the amide I and II bands indicate deprotonation of the ligands and suggest the chelating behaviour of the aroylhydrazone moiety. The deprotonation of the ligands is also confirmed by the absence of the NH peak in the proton NMR spectrum of the Zn–bitp complex. The so-called amide I and II bands, which in the free ligands result from the interaction between ν(CN) and δ(NH), in the complexes are probably due to the stretching of the coordinated $-O-C=N-N=C$ system. The stoichiometry of these chelates, particularly the presence of oxygen-donor solvent molecules, and the IR spectra strongly suggest a bidentate behaviour of the ligands and hexacoordination for the metals (with the exception of the Cu(II) complexes), as was confirmed

Table 7
Selected bond distances (Å) and angles (°) for compound **II**

C(1)–O	1.224(3)	C(10)–C(11)	1.362(4)
C(1)–N(1)	1.341(3)	C(11)–C(12)	1.427(5)
N(1)–N(2)	1.374(3)	C(12)–C(13)	1.386(4)
N(2)–C(8)	1.280(4)	C(13)–S	1.711(3)
C(8)–C(9)	1.499(4)	S–C(10)	1.718(3)
C(8)–C(10)	1.472(4)	C(13)–C(14)	1.481(4)
C(2)–C(1)–O	120.7(2)	C(8)–C(10)–S	119.0(2)
C(2)–C(1)–N(1)	116.1(2)	C(8)–C(10)–C(11)	130.3(3)
O–C(1)–N(1)	123.2(2)	S–C(10)–C(11)	110.7(2)
C(1)–N(1)–N(2)	116.9(2)	C(10)–C(11)–C(12)	114.0(3)
N(1)–N(2)–C(8)	119.3(2)	C(11)–C(12)–C(13)	111.0(3)
N(2)–C(8)–C(9)	127.3(3)	C(12)–C(13)–S	111.6(2)
N(2)–C(8)–C(10)	113.3(2)	C(12)–C(13)–C(14)	127.9(3)
C(9)–C(8)–C(10)	119.3(3)	S–C(13)–C(14)	120.5(2)
		C(10)–S–C(13)	92.6(1)

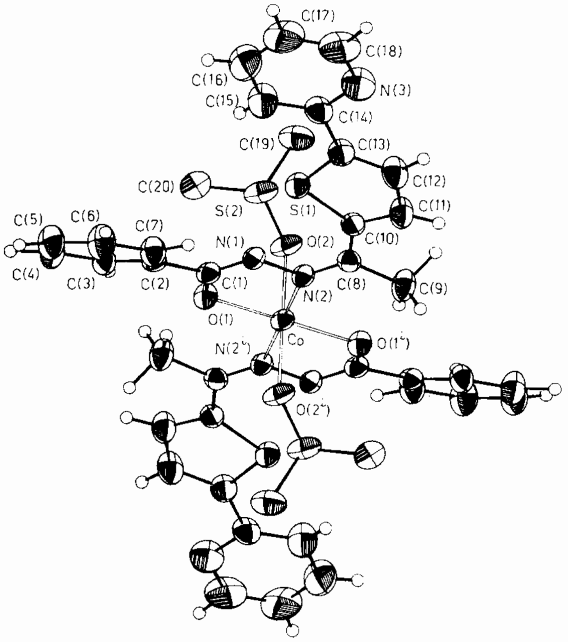

Fig. 1. ORTEP drawing of compound **I** with thermal ellipsoids at the 50% probability level.

by the X-ray structural analysis carried out on $[Co(bitp)_2(dmso)_2]$ (**I**) and described below.

The crystal structure of **I** consists of monomeric units of the complex, one of which is depicted in the ORTEP diagram of Fig. 1, which also shows the atomic labelling scheme employed (the primed atoms are related to the unprimed ones by the symmetry operation $1-x$, $-y$, $-z$). The space group $P2_1/n$ has four general positions which require that the two molecules per unit cell be constrained at special positions. Accordingly, the cobalt atom is located on a crystallographically imposed centre of symmetry and coordination about it is distorted octahedral with two O and two N atoms from two ligand molecules occupying the equatorial plane and two O atoms from two dmso molecules in the axial sites.

The anionic ligand bitp adopts the *Z* configuration and acts as a bidentate N,O-donor giving rise to a nearly planar five-membered Co–N–N–C–O chelate ring (max. deviation 0.06 Å). The Co–O and Co–N distances of 2.039(3) and 2.183(4) Å, respectively, agree very well with the corresponding ones found in related hexacoordinated cobalt(II) complexes having the same chelation ring (Co–O 2.018–2.113 Å; Co–N 2.171–2.224 Å) [12–16]. As far as we are aware, there is only one cobalt(II)–dmso complex characterized by X-ray diffractometry, namely the hexacoordinate *catena*-tetrakis(μ-thiocyanato)bis(dimethyl sulfoxide)-cobalt–mercury [17], where the Co–O distances are 2.079 and 2.108 Å, only slightly shorter than the value (2.121 Å) found here.

The coordination geometry appears to promote a weak hydrogen bond interaction between the coordinated oxygen atom O(1) and the methyl carbon C(9) belonging to the centrosymmetrically related molecule, the distance being 3.18(1) Å. The same interaction is expected to be present also in solution; actually the NMR spectrum of the Zn–bitp complex in dimethyl sulfoxide confirms this hypothesis, as the resonance due to the methyl protons is shifted lowfield (2.64 ppm) with respect to the free ligand (2.40 ppm).

An analysis of the crystal packing reveals that van der Waals interactions are the dominant stabilizing forces in the crystal lattice of **I**, the closest approach between neighbouring molecules being 3.247(8) Å between C(8) and C(19) at $1-x$, $1-y$, $-z$.

As can be seen by comparing the structural parameters of the coordinated *Z*-bitp in **I** (Table 6) with the corresponding ones found in the neutral uncoordinated *E*-Hbitp (**II**) (Table 7), whose structure is illustrated in Fig. 2, the major difference involves the O–C–N–N moiety as a direct consequence of the coordination to metal. In particular, the C–O carbonyl distance in **I** is significantly longer than in **II**, whilst the C–N distance is shorter. Furthermore, the *Z* configuration of the

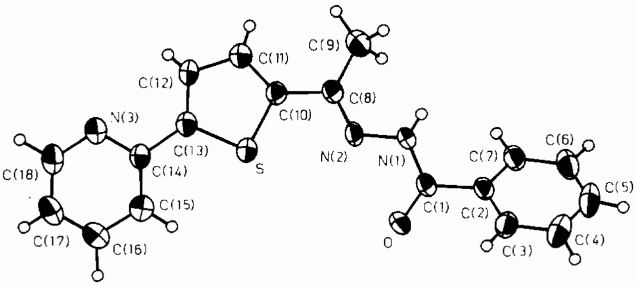

Fig. 2. ORTEP drawing of compound **II** with thermal ellipsoids at the 50% probability level.

ligand in **I** causes a rather short intramolecular contact between the thiophene sulfur and the hydrazone nitrogen N(1). The distance (2.653(4) Å) is shorter than the sum of the van der Waals radii and suggests a polar interaction.

Other differences occur in the dihedral angles involving the four essentially planar parts of the two molecules (i.e. the three aromatic rings and the C(1)O(1)N(1)N(2)C(8) moiety, the values being:

	I	**II**
C(2)...C(7) ∧ C(1)O(1)N(1)N(2)C(8)	18.7(2)°	35.7(1)°
C(1)O(1)N(1)N(2)C(8) ∧ S(1)...C(13)	18.7(2)	6.6(1)
S(1)...C(13) ∧ N(3)...C(18)	9.2(2)	15.8(1)

The molecular packing in **II** is mainly determined by intermolecular hydrogen bonds occurring between N(1) and O N(1)···O^{i} 2.923(3) Å, (N(1)−H···O^{i} 170(3)°, i = $\frac{1}{2}-x, \frac{1}{2}+y, z$) which link the molecules leading to a polymeric structure.

4. Conclusion

The main result of this investigation is that the inability of the thiophene ring to coordinate to metals in a planar fashion forces the potentially tetradentate planar ligands Hbitp and Hsitp to behave as bidentate assuming the *Z* configuration around the C=N hydrazone bond.

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