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Electrochemical Synthesis and Characterization of Cobalt(II), Cobalt(III), and Nickel(II) Complexes with Pyrimidine-2-thionato Ligands

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Dedicated to Professor Joachim Strähle on the Occasion of his 70th Birthday

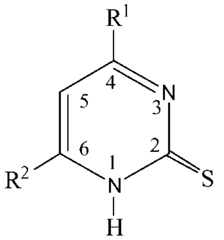
Abstract. The electrochemical oxidation of anodic metal (cobalt and nickel) in acetonitrile solutions of the appropriate pyrimidine-2-thione derivatives (RpymSH, where R = 4-CF_3, 4,6-CF_3Me, 4,6-MePh, 4,6-CF_3Ph, 4,6-Ph_2) afforded complexes of composition [M(RpymS)$_2$], M = Co, Ni or [Co(RpymS)$_3$]. When 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen) was added to the electrolytic cell, adducts of cobalt(II) and nickel(II) compounds with these coligands were obtained: [M(RpymS)$_2$bipy] and [M(RpymS)$_2$phen]. All of the compounds were characterized by microanalysis, electronic, vibrational spectroscopy and FAB mass spectrometry, and, in the cases of the compounds [Co(RpymS)$_3$], by ^{1}H and ^{13}C, NMR spectroscopy. The compound [Co(4-CF_3pymS)$_3$] was also characterized by X-ray diffraction. The crystal structure consists of monomeric molecules in which the central CoS_3N_3 unit has a slightly distorted octahedral coordination with the ligands adopting a meridional disposition.

Keywords: Electrochemical synthesis; Cobalt and Nickel complexes; Pyrimidine-thionate; Crystal structure

1 Introduction

Much of the interest in metal-sulfur chemistry results from the potential relevance of the resulting compounds to active sites in metalenzymes and also to their ability to adopt various nuclearities of significant structural complexity [1−3]. This latter characteristic is a consequence of the tendency of thiolates to bridge metal centres. However, the aggregation process may be limited by providing steric constraints through appropriate ligand design or the introduction of coligands to block a number of coordination sites [4].

As part of our continued interest in heterocyclic thione compounds, we report here the electrochemical synthesis of cobalt and nickel complexes with pyrimidine-2-thione ligands (Scheme 1) using an electrochemical procedure in which the metal is the anode of a cell containing the ligand in solution. The electrochemical procedure used in this work is a simple and successful route for the synthesis of metal complexes with heterocyclic thiones [5]. In a similar way to other heterocyclic thiones, such as pyridine-2-thione, these ligands are very versatile in terms of their coordination modes; they can act as neutral monodentate systems through sulfur (η^1-S) [6]; through one of the nitrogen atoms (η^1-N) [7]; as a neutral bridging ligand through sulfur (μ_2-S) [8]; a neutral −SN chelating ligand [9]; anionic S-monodentate (η^1-S) [10]; an −N,S chelating ligand [11]; a binuclear bridging ligand μ_2-(S,N)(η^1-S, η^1-N) [12] or μ_2-(S,N)(η^2-S) [13]; a binuclear triple bridging ligand μ_2-(S,N)(η^2-S, η^1-N) [14] or μ_2-(S,N)(η^2-N,S, N′, η^2-S) [15] or a trinuclear triple bridging ligand μ_3-(S,N)(η^2-S, η^1-N) [16]. Moreover, the presence in the ligands used in this work of different substituents on the pyrimidine ring (Scheme 1) allows the possibility of investigating whether the nature, position and number of substitutents has any influence on the coordinative behaviour of these ligands and, consequently, on the structure of the corresponding metal-heterocyclic thionate complexes. In addition, we are interested in incorporating coligands such as 1,10-phenanthroline and 2,2′-bipyridine into the coordination sphere of cobalt and nickel to assess whether its presence can lead to novel structures.



$R^1 = CF_3$; $R^2 = H, CH_3, Ph$
$R^1 = CH_3$; $R^2 = Ph$
$R^1 = Ph$; $R^2 = Ph$

Scheme 1

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Table 1 Analytical data for cobalt and nickel complexes. Theoretical values are given in brackets.

Complex	Colour	M. W.	%C (g/mol)	%N	%H	%S	Yield/%
$[Co(4\text{-}CF_3pymS)_3]$	Brown/Green	596.35	30.02(30.21)	13.91(14.09)	1.02(1.01)	15.98(16.13)	79
$[Co(4,6\text{-}CF_3MepymS)_3]$	Green	638.43	33.79(33.86)	13.02(13.16)	1.75(1.89)	15.27(15.07)	58
$[Co(4,6\text{-}MePhpymS)_2]$	Pale brown	461.46	56.79(57.26)	12.26(12.14)	3.97(3.97)	13.58(13.89)	61
$[Co(4,6\text{-}MePhpymS)_2bipy](H_2O)$	Brown	635.67	60.20(60.46)	13.52(13.22)	4.23(4.44)	9.81(10.09)	70
$[Co(4,6\text{-}MePhpymS)_2phen](H_2O)$	Pale brown	659.69	61.12(61.90)	12.46(12.74)	4.78(4.28)	9.82(9.72)	64
$[Co(4,6\text{-}CF_3PhpymS)_2]$	Grey	569.41	46.34(46.41)	10.16(9.84)	3.12(2.12)	11.16(11.26)	74
$[Co(4,6\text{-}CF_3PhpymS)_2bipy]$	Pale pink	725.59	52.06(52.97)	11.88(11.58)	3.51(2.78)	8.23(8.84)	63
$[Co(4,6\text{-}CF_3PhpymS)_2phen]$	Brown	749.04	53.91(54.47)	11.43(11.22)	2.27(2.69)	8.56(8.54)	70
$[Co(4,6\text{-}Ph_2pymS)_2]$	Orange	585.61	64.28(65.63)	9.38(9.57)	3.51(3.79)	10.82(10.95)	68
$[Co(4,6\text{-}Ph_2pymS)_2bipy](H_2O)$	Brown	759.81	66.09(66.39)	9.65(11.06)	4.79(4.25)	8.36(8.44)	70
$[Co(4,6\text{-}Ph_2pymS)_2phen]$	Brown	765.82	68.14(69.01)	10.94(10.97)	4.27(3.95)	8.36(8.37)	54
$[Ni(4,6\text{-}CF_3MepymS)_2]$	Brown	445.02	32.8(32.39)	11.72(12.59)	2.16(1.81)	14.17(14.41)	57
$[Ni(4,6\text{-}CF_3MepymS)_2bipy]$	Dark green	601.21	44.26(43.95)	14.10(13.98)	2.86(2.68)	10.37(10.67)	69
$[Ni(4,6\text{-}CF_3MepymS)_2phen]$	Brown	625.23	45.38(46.11)	12.90(13.44)	2.38(2.58)	10.08(10.26)	59
$[Ni(4,6\text{-}MePhpymS)_2]$	Brown	461.22	58.98(57.29)	13.10(12.15)	4.57(3.93)	13.70(13.90)	53
$[Ni(4,6\text{-}MePhpymS)_2bipy]$	Brown	617.10	62.60(62.23)	12.96(13.62)	4.12(4.25)	9.73(10.36)	55
$[Ni(4,6\text{-}MePhpymS)_2phen]$	Brown	641.10	63.24(63.64)	12.51(13.11)	4.00(4.09)	9.53(9.97)	67
$[Ni(4,6\text{-}CF_3PhpymS)_2]$	Green	569.16	47.42(46.43)	9.97(9.84)	3.39(2.13)	10.87(11.27)	79
$[Ni(4,6\text{-}CF_3PhpymS)_2bipy]$	Pale green	725.35	52.89(52.99)	11.06(11.59)	3.73(2.78)	8.72(8.84)	84
$[Ni(4,6\text{-}CF_3PhpymS)_2phen]$	Brown	749.37	53.31(54.50)	11.51(11.21)	3.71(2.69)	8.95(8.56)	93
$[Ni(4,6\text{-}Ph_2pymS)_2]$	Brown	587.08	65.08(65.41)	9.28(9.54)	3.97(4.12)	10.25(10.89)	76
$[Ni(4,6\text{-}Ph_2pymS)bipy]$	Brown	741.55	67,84(68.03)	10.27(11.33)	4.32(4.08)	8.31(8.65)	66
$[Ni(4,6\text{-}Ph_2pymS)_2phen]$	Brown	767.15	68.95(68.83)	10.85(10.95)	4.64(4.20)	8.51(8.34)	70

2 Results and Discussion

The anodic oxidation of cobalt and nickel in an electrochemical cell containing solutions of different ligands RpymSH in acetonitrile gave a series of complexes. The analytical data for these compounds are given in Table 1 and are consistent with the formulae $[M(RpymS)_2]$ (M = Co, Ni) or $[Co(RpymS)_3]$, depending on the nature of the ligand. In these formulae RpymS represents the anion of the corresponding heterocyclic thione. The compounds are air stable and moderately soluble in organic solvents such as dichloromethane and ethanol.

The presence in the pyrimidine ring of substituents that do not cause too great a steric impediment, e.g. 4-trifluoromethylpyrimidine-2-thione and 4,6-methyltrifluoromethylpyrimidine-2-thione, leads to Co^{III} complexes of the type $[Co(RpymS)_3]$. On the other hand, the use of ligands with greater steric hindrance, such as 4,6-methylphenylpyrimidine-2-thione, 4,6-phenyltrifluoromethylpyrimidine-2-thione and 4,6-diphenylpyrimidine-2-thione, gave Co^{II} complexes with the general formula $[Co(RpmyS)_2]$. This is probably due to the greater steric hindrance produced by the two substituents on the ligand in positions close to the donor atoms.

The presence in the electrochemical cell of additional nitrogen ligands like 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen) generally gave mixed Co^{II} and Ni^{II} complexes. The analytical data of these compounds (Table 1) are consistent with the formulae $[M(RpymS)_2bipy]$ and $[M(RpymS)_2phen]$, respectively. However, in some cases the presence of these additional ligands in the electrochemical cell did not lead to the formation of mixed complexes and the products had the composition $[Co(RpymS)_3]$ or $[M(RpymS)_2]$ (M = Co, Ni); in these compounds an additional neutral ligand is not incorporated into the coordination sphere of the metal atom.

The experimental conditions for the synthesis of these compounds are summarized in Table 2.

The Electrochemical Efficiency values (Table 2) − defined as the number of moles of metal dissolved per Faraday of charge − are approximately 0.5 mol.F^{-1} regardless of whether the metal atom in the complex is in oxidation state II or III. This observation indicates anodic oxidation processes leading to the production of Co^{II} or Ni^{II} species. This fact, along with the evolution of hydrogen at the cathode, is compatible with the following equations:

Cathode: $2\ RpymSH + 2e^- \rightarrow 2\ RpymS^- + H_2$

Anode: $M \rightarrow M^{2+} + 2e^-$

Overall $M + 2\ RpymSH \rightarrow [M(RpymS)_2] + H_2$

Overall $M + 2\ RpymSH + L \rightarrow [M(RpymS)_2L] + H_2$

L = bipy or phen

In those cases where the final product is a compound in which the cobalt atom is in oxidation state III, one can envisage a subsequent oxidation in solution of the initial cobalt(II) compound by another RpymSH molecule in order to generate the final species.

$[Co(RpymS)_2] + RpymSH \rightarrow [Co(RpymS)_3] + {}^1/_2\ H_2$

This type of behaviour has already been observed in the synthesis of cobalt(III) compounds with other ligands [17].

Table 2 Experimental conditions for the electrochemical synthesis of cobalt and nickel complexes.

Reaction	Ligand (mg)	Coligand (mg)[a]	Metal dissolved (mg)	Time (h)	Initial Voltaje(V)[b]	Electrochemical Efficiency (Ef)
Co + 4-CF_3pymSH	150	−	17	1.48	10	0.52
Co + 4,6-CF_3MepymSH	200	−	25	2.09	15	0.54
Co + 4,6-MePhpymSH	150	−	21	1.90	8	0.50
Co + 4,6-MePhpymSH + bipy	150	57	20	1.90	24	0.48
Co + 4,6-MePhpymSH + phen	150	73	20	1.90	8	0.48
Co + 4,6-CF_3PhpymSH	100	−	12	1.05	8	0.52
Co + 4,6-CF_3PhpymSH + bipy	100	30	11	1.05	10	0.46
Co + 4,6-CF_3PhpymSH + phen	100	35	11	1.05	8	0.46
Co + 4,6-Ph_2pymSH	150	−	17	1.52	5	0.51
Co + 4,6-Ph_2pymSH + bipy	150	45	15	1.52	6	0.45
Co + 4,6-Ph_2pymSH + phen	150	56	16	1.52	7	0.48
Ni + 4,6-CF_3MepymSH	200	−	32	2.76	23	0.53
Ni + 4,6-CF_3MepymSH + bipy	200	60	28	2.50	37	0.51
Ni + 4,6-CF_3MepymSH + phen2	007	50	27	2.50	29	0.49
Ni + 4,6-MePhpymSH	150	−	19	1.90	5	0.46
Ni + 4,6-MePhpymSH + bipy	150	57	21	1.90	10	0.50
Ni + 4,6-MePhpymSH + phen	150	73	22	1.90	7	0.52
Ni + 4,6-CF_3PhpymSH	100	−	12	1.05	8	0.51
Ni + 4,6-CF_3PhpymSH + bipy	100	30	11	1.05	8	0.48
Ni + 4,6-CF_3PhpymSH + phen	100	35	11	1.05	8	0.47
Ni + 4,6-Ph_2pymSH	150	−	17	1.50	5	0.51
Ni + 4,6-Ph_2pymSH + bipy	150	44	18	1.52	7	0.54
Ni + 4,6-Ph_2pymSH + phen	150	56	11	1.05	6	0.48

[a] Plus $[NEt_4]ClO_4$ (ca. 20 mg).
[b] Voltage to produce current of 10 mA.

2.1 Description of the molecular structure of [Co(4-CF_3-pymS)$_3$]

The crystal structure of the complex [Co(4-CF_3-pymS)$_3$] is shown in Figure 1 along with the atom numbering scheme. Crystallographic data and a selection of bond angles and distances for this complex are given in Tables 3 and 4.

There are three independent molecules in the asymmetric unit and the angles and distances differ slightly between these three molecules (Table 4).

It can be seen from Figure 1 that the compound consists of discrete molecules in which the metal atom is coordinated to three monoanionic ligands in a chelate fashion through one of the nitrogen atoms and the sulfur atom to give an octahedral CoN_3S_3 environment around the cobalt centre.

The arrangement of the nitrogen and sulfur atoms around the metal atom is such that the meridional isomer is obtained. It can be seen that this disposition is maintained in solution, a situation confirmed by ^1H and ^{13}C NMR spectroscopy. This isomer is also found in other metal trischelates described in the literature, e.g. the pyridine-2-thionates [Co(pyS)$_3$] [18] and [Co(3-Me_3SipyS)$_3$] [19], but is different to that observed for the pyrimidine derivative [Co(4,6-Me_2-pymS)$_3$] [20] in which a facial conformation is found.

In molecule 1, as in the other two molecules, the equatorial plane is formed by one of the nitrogen atoms from one of the heterocyclic thiones and three sulfur atoms from the three pyrimidine-2-thionate ligands − although these four atoms are not exactly coplanar. If we consider the best plane that includes these four atoms, N(31) and S(11) occupy *trans* positions and are located below the plane at −0.1548 and −0.2314 Å, respectively, while the S(12) and S(13) atoms are located above the plane by +0.1677 and +0.2185 Å, respectively. The cobalt atom is very close to the aforementioned plane and is only 0.005 Å below it.

Table 3 Summary of Crystal Data for [Co(4-CF_3pymS)$_3$].

Empirical Formula	$C_{15}H_6CoF_9N_6S_3$
Formula weight	596,37
Temperature	293.10 K
Colour; Habit	green, prismatic
Crystal System	monoclinic
Space Group	$P2_1/c$
Unit Cell Dimensions	a = 23.0701(12) Å b = 11.1850(6) Å c = 25, 8817(13) Å β = 96.8860(10)°
Volume, Å^3	6630.3(6)
Z	12
d_{calc}, g cm^{-3}	1.792 g cm^{-3}
Absorption coefficient	1.152 mm^{-1}
F(000)	3528
Crystal size /mm	0.54 x 0.37 x 0.17
λ, Å (MoKα radiation)	0.71073
ν (MoKα), mm^{-1}	4.871
Theta range for data collection	1.72 to 28.00 deg.
Index ranges	$-30 \le h \le 23$ $-14 \le k \le 14$ $-34 \le l \le 26$
Reflections collected	35543
Independent reflections	14569 (R_{int} = 0.0133)
Max. and min. Transmission	0.8283 and 0.5752
Data/ restraints / parameters	14569/ 0 / 919
Goodness of fit on F^2	0.883
Final R indices [I >2sigma(I)]	R_1 = 0.0571, wR_2 = 0.1253
R indices (all data)	R_1 = 0.1404, wR_2 = 0.1478
Largest diff.peak and hole	0.860 and −0.579 e.Å^{-3}

These deviations from planarity are evident in the bond angles around the metal atom; N(31)−Co−S(11),

Table 4 Bond lengths and angles for [Co(4-CF_3pymS)$_3$]

Co(1)-N(11)	1.907(4)	Co(1)-N(21)	1.910(4)
Co(1)-N(31)	1.951(4)	Co(1)-S(11)	2.283(2)
Co(1)-S(13)	2.2990(14)	Co(1)-S(12)	2.302(2)
S(11)-C(11)	1.714(5)	S(12)-C(21)	1.719(5)
S(13)-C(31)	1.724(5)	N(11)-C(15)	1.308(6)
Co(2)-N(41)	1.897(4)	Co(2)-N(51)	1.917(4)
Co(2)-N(61)	1.943(4)	Co(2)-S(21)	2.281(2)
Co(2)-S(23)	2.293(2)	Co(2)-S(22)	2.304(2)
S(21)-C(41)	1.720(5)	S(22)-C(51)	1.726(5)
S(23)-C(61)	1.709(5)	Co(3)-N(91)	1.904(4)
Co(3)-N(71)	1.916(4)	Co(3)-N(81)	1.936(4)
Co(3)-S(31)	2.264(2)	Co(3)-S(32)	2.2813(14)
Co(3)-S(33)	2.303(2)	S(31)-C(91)	1.719(5)
S(32)-C(71)	1.712(5)	S(33)-C(81)	1.716(5)
N(71)-C(75)	1.326(6)		
N(11)-Co(1)-N(21)	168.6(2)	N(11)-Co(1)-N(31)	95.3(2)
N(21)-Co(1)-N(31)	94.3(2)	N(11)-Co(1)-S(11)	72.68(13)
N(21)-Co(1)-S(11)	99.38(12)	N(31)-Co(1)-S(11)	161.54(12)
N(11)-Co(1)-S(13)	91.83(12)	N(21)-Co(1)-S(13)	96.92(13)
N(31)-Co(1)-S(13)	72.42(12)	S(11)-Co(1)-S(13)	93.58(6)
N(11)-Co(1)-S(12)	100.29(12)	N(21)-Co(1)-S(12)	72.25(12)
N(31)-Co(1)-S(12)	97.99(12)	S(11)-Co(1)-S(12)	97.93(6)
S(13)-Co(1)-S(12)	165.30(6)	N(41)-Co(2)-N(51)	167.7(2)
N(41)-Co(2)-N(61)	94.9(2)	N(51)-Co(2)-N(61)	95.3(2)
N(41)-Co(2)-S(21)	73.12(12)	N(51)-Co(2)-S(21)	97.74(11)
N(61)-Co(2)-S(21)	164.77(12)	N(41)-Co(2)-S(23)	93.15(12)
N(51)-Co(2)-S(23)	96.41(12)	N(61)-Co(2)-S(23)	72.36(12)
S(21)-Co(2)-S(23)	98.38(6)	N(41)-Co(2)-S(22)	99.78(13)
N(51)-Co(2)-S(22)	72.47(12)	N(61)-Co(2)-S(22)	95.60(12)
S(21)-Co(2)-S(22)	95.74(6)	S(23)-Co(2)-S(22)	163.13(6)
C(41)-S(21)-Co(2)	77.5(2)	N(91)-Co(3)-N(71)	165.0(2)
N(91)-Co(3)-N(81)	97.5(2)	N(71)-Co(3)-N(81)	93.8(2)
N(91)-Co(3)-S(31)	73.06(13)	N(71)-Co(3)-S(31)	97.48(14)
N(81)-Co(3)-S(31)	165.64(12)	N(91)-Co(3)-S(32)	96.09(12)
N(71)-Co(3)-S(32)	72.87(13)	N(81)-Co(3)-S(32)	95.97(12)
S(31)-Co(3)-S(32)	95.80(6)	N(91)-Co(3)-S(33)	96.08(12)
N(71)-Co(3)-S(33)	96.71(13)	N(81)-Co(3)-S(33)	72.48(12)
S(31)-Co(3)-S(33)	97.33(6)	S(32)-Co(3)-S(33)	164.22(6)

S(12)−Co−S(13) and N(11)−Co−N(21) have values that are significantly different to the ideal value of 180° [161.54(13), 165.30(6) and 168.6(2)°, respectively]. One of the main causes of this distortion from the regular geometry is undoubtedly the small size of the chelate angle, which influences coordination of the different ligands to the cobalt atom. The average value of the chelate angles N−Co−S is 72.45(13)°. This value is similar to that found in other complexes in which the ligand coordinates in a bidentate fashion to give a five-membered ring.

The values of the three Co−N bond distances for each of the molecules are slightly different [1.907(4), 1.910(4) and 1.951(4) Å], with the longest distance corresponding to the Co−N(31) bond, which is in the *trans* position with respect to the Co−S(11) bond. The average value for this bond, 1.923(4) Å, is very similar to those found in a series of Co^{III} complexes that are octahedrally coordinated by the heterocyclic thiones pyridine-2-thione and pyrimidine-2-thione. The value described above is very similar to those found in [Co(pyS)$_3$], 1.912(6)−1.923(6) Å, [Co(3-Me_3SipyS)$_3$], 1.86(1)−1.91(1) Å and [Co(4,6-pymS)$_3$], 1.975(5)−1.986(5) Å (pyS = pyridine-2-thionate; 3-Me_3SipyS = 3-trimethylsilylpyridine-2-thionate).

The Co−S bond distances are also different to one another and are in the range 2.283(2)−2.302(2) Å, with the shortest distance in each molecule corresponding to the bond *trans* with respect to the nitrogen atom. However, these values are similar to those observed in the aforementioned trischelates; 2.292(3)−2.313(3) Å in [Co(pyS)$_3$], 2.241(8)−2.315(8) Å in [Co(3-Me_3SipyS)$_3$] and 2.252(2)−2.269(2) Å in [Co(4,6-pymS)$_3$].

The bidentate 4-trifluoropyrimidine-2-thionate ligands are planar, within the margins of error, with a maximum deviation of 0.03 Å. However, as mentioned above, the three independent molecules in the unit cell are not completely equivalent. For example, the sulfur atoms in molecule 1 are essentially in the plane of the pyrimidine ring to which they are bonded, with the maximum deviation of the sulfur atoms from the best plane of the pyrimidine being 0.028(6) Å. The cobalt atom is in the plane of one of these

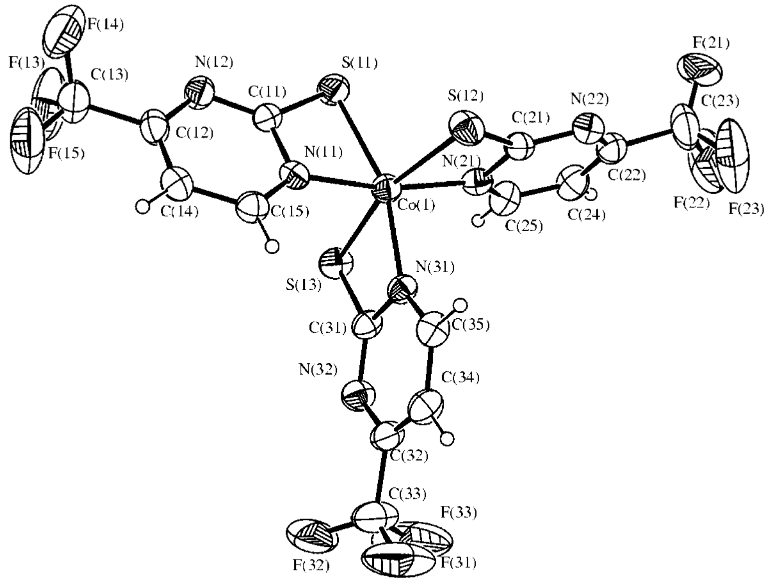

Figure 1 Molecular structure of [Co(4-CF_3-pymS)$_3$]

rings [0.011(6) Å] but is out of the planes of the other two rings, with deviations of +0.273(6) and −0.124(6) Å. The planes of these rings are almost perpendicular to one another, with interplanar angles of 82.2(1), 82.8(1) and 77.2(1)°. However, in the case of molecule 2 only one of the sulfur atoms is located in the plane of the pyrimidine ring to which it is bonded [0.025(6) Å], with the other two sulfur atoms displaced from the plane of the ring to which they are bonded [0.081(7) and 0.104(6) Å]. The cobalt centre, in a similar way to that in molecule 1, is in the plane of one of the rings [0.043(6) Å] and out of the planes of the other two [−0.077(7) and 0.124(6) Å]. The interplanar angles are closer to perpendicular than those in molecule 1, with values of 85.3(1), 79.9(1) and 89.4(1)°. In molecule 3, two of the sulfur atoms are in the plane of the ring to which they are bonded [−0.001(1) and −0.021(7) Å] and the other is out of the plane [0.070(7) Å]. The Co(3) atom is in the plane of one of the ligands [0.043(6) Å] and out of the planes of the other two [−0.065(7) and 0.099(7) Å]. The angles between these planes are 82.9(2), 84.2(2) and 87.1(1)°. In all three molecules the four-membered chelate rings (Co, S, N and C) are essentially planar, with the maximum deviation with respect to the best plane being 0.042(2) Å.

The S−C [1.709(5)−1.726(5) Å] bond distances in the pyrimidine-2-thionate ligands are intermediate between the values observed in the free ligands 4,6-dimethylpyrimidine-2-thione [21] and 1-phenyl-4,6-dimethylpyrimidine-2-thione [22] [1.692(2) Å and 1.686(4) Å, respectively], which exist in the thione form in the solid state, and the values of 1.781(2) Å and 1.782(3) Å found in the bis-pyrimidyl-2-2′-disulfide [23] and bis-(4,6-dimethylpyrimidyl)-2,2′-disulfide [24], which possess a simple C−S bond; this suggests that the ligand is coordinated in a form that is closer to the pyrimidine-2-thionate than to the thione form.

2.2 Spectroscopic data

IR Spectra

The IR spectra of the complexes do not contain bands due to ν(N−H), which in the free ligands appear between 3200 and 3100 cm^{-1}. This fact shows that deprotonation of the NH group has occurred during the synthesis and, therefore, that the ligand is coordinated in the thionato form.

This conclusion is supported by the shift to lower wavenumbers of the strong bands for ν(C=C) and ν(C=N), which appear at 1600−1550 and 1570−1525 cm^{-1} in the free ligands, on going from the free ligands to the complexes. In addition, bands attributable to the ring breathing vibration at ca. 1000 and 630 cm^{-1} are observed. These shifts provide evidence that the nitrogen atom is bound to the metal atom [25, 26]. In addition, the mixed complexes show bands that are typical for coordinated 2,2′-bipyridine [27] (770 and 730 cm^{-1}) and 1,10-phenanthroline [27, 28] (1530−1505, 840 and 720 cm^{-1}).

Table 5 Magnetic and UV-Vis. Spectroscopic data for Co^{II} single complexes.

Complex	$^4A_2 \rightarrow {}^4T_1$ (F) ν_2 (cm^{-1})	$^4A_2 \rightarrow {}^4T_1$ (P) ν_3 (cm^{-1})	$^4A_2 \rightarrow {}^4T_2$ ν_1 (calc.)(cm^{-1})	μ (BM)
$[Co(4,6\text{-}Me_2,5\text{-}EtpymS)_2]$	8650, 9852	14880	5835	4.45
$[Co(4,6\text{-}Ph_2pymS)_2]$	9671	15720	6046	4.35
$[Co(4,6\text{-}PhMepymS)_2]$	8665, 9940	15150	5827	4.16
$[Co(4,6\text{-}CF_3PhpymS)_2]$	9140	16390	5463	4.65

Table 6 Magnetic and UV-Vis. Spectroscopic data for Co^{II} mixed complexes.

Complex	$^4T_{1g}(F) \rightarrow {}^4T_{2g}$ (ν_1) (cm^{-1})	$^4T_{1g}(F) \rightarrow {}^4A_{2g}$ (ν_2) (cm^{-1})	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) (cm^{-1})	μ (MB)
$[Co(4,6\text{-}Ph_2pymS)_2bipy]$	9520	15625	21230	4.98
$[Co(4,6Ph_2pymS)_2phen]$	8900	15528	20790	4.64
$[Co(4,6\text{-}PhMepymS)_2bipy]$	10000	15625	21413	5.02
$[Co(4,6\text{-}PhMepymS)_2phen]$	9750	15430	21230	4.92
$[Co(4,6\text{-}CF_3PhpymS)bipy]$	78901592318	832,	20534	5.33
$[Co(4,6\text{-}CF_3PhpymS)phen]$	8820		21270	4.70

Electronic spectra and magnetic moments

The diffuse electronic reflectance spectra of the Co^{III} complexes contain bands at 15150 cm^{-1} and 20870 cm^{-1} for $[Co(4\text{-}CF_3pymS)_3]$ and at 15870 and 20080 cm^{-1} for $[Co(4,6\text{-}MeCF_3pymS)_3]$. These bands are characteristic of low spin Co^{III} complexes in which the metal is in an octahedral environment [29]. The first of these bands is attributed to the transition $^1A_{1g} \rightarrow {}^1T_{1g}$ and the second to the $A_{1g} \rightarrow {}^1T_{1g}$ transition. The magnetic moments of the $[CoL_3]$ complexes show that these compounds are essentially diamagnetic and are consistent with their being low spin d^6 octahedral complexes.

The diffuse electronic reflectance spectra of complexes (Table 5) with the formula $[Co(RpymS)_2]$ are characteristic of species with the metal atom in a distorted tetrahedral environment [29]. The spectra show two d-d bands, one close to 15000 cm^{-1} and the other a broad multiplet between 8600−9950 cm^{-1}. The band in the visible region was assigned to the transition $^4A_2 \rightarrow {}^4T_1(P)$ (ν_3) and the multicomponent band in the infrared region to the transition $^4A_2 \rightarrow {}^4T_1(F)$ (ν_2). The transition $^4A_2 \rightarrow {}^4T_2$ (ν_1) was not observed but its position was calculated (ca. 5800 cm^{-1}) on the basis of the band assigned as ν_3 and taking ν_2 as the centre of the multiple band according to the procedure described by *Lever* [29]. The magnetic moments of these compounds are between 4.16 and 4.65 BM and this is in the expected range for Co^{II} complexes with tetrahedral environments.

In the mixed Co(II) complexes $[Co(RpymS)_2L]$ the solid state ultraviolet spectra are characteristic of species with distorted octahedral environments around the metal atom [29]. The complexes show three bands (Table 6). One of these bands is in the region 9000 cm^{-1} and this can be assigned to the transition $^4T_{1g}(F) \rightarrow {}^4T_{2g}$ (ν_1). Another band is observed between 15000 and 16000 cm^{-1} [due to the $^4T_{1g}(F) \rightarrow {}^4A_{2g}$ transition (ν_2)] and a third band is seen

Table 7 Magnetic and UV-Vis. Spectroscopic data for Ni^{II} single complexes.

Complex	$^3T_1(F) \rightarrow {}^3A_2$ (ν_2)/cm^{-1}	$^3T_1(F) \rightarrow {}^3T_1(P)$ (ν_3)/cm^{-1}	$^3T_1(F) \rightarrow {}^3T_2$ (ν_1)/calc. cm^{-1}	μ (MB)
[Ni(4,6-CF$_3$MepymS)$_2$]	8780, 9960	15390	4320	3.39
[Ni(4,6-PhMepymS)$_2$]	8800, 9900	15150	4306	3.0
[Ni(4,6-CF$_3$PhpymS)$_2$]	8626	15674, 17513	3957	
[Ni(4,6-Ph$_2$pymS)$_2$]	7645, 8779, 9794	13220, 14750	4030	3.27

Table 8 Magnetic andUV-Vis. Spectroscopic data or Ni^{II} mixed complexes.

Complex	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (ν_1)/cm^{-1}	$^3A_{2g} \rightarrow {}^3T_{2g}$ (ν_2)/cm^{-1}	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (ν_3)/cm^{-1}	μ (MB)
[Ni(4,6-CF$_3$MepymS)$_2$bipy]	10504	16340	21050	
[Ni(4,6-CF$_3$MepymS)$_2$phen]	10406	16103	22173	2.98
[Ni(4,6-Ph$_2$pymS)$_2$bipy]	10000	15060	23000	3.17
[Ni(4,6-Ph$_2$pymS)$_2$phen]	10780	16100	24875	2.98
[Ni(4,6-PhMepymS)$_2$bipy]	10764	15923	21050	2.93
[(Ni(4,6-PhMepymS)$_2$phen]	10406	15640	22170	3.05
[Ni(4,6-CF$_3$PhpymS)$_2$bipy]	9940	15430	23860	
[Ni(4,6-CF$_3$PhpymS)$_2$phen]	10000	15620	19900	3.03

between 20500 and 21500 cm^{-1} [assigned to the transition $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3)]. These bands are all consistent with the metal atom being in an octahedral environment. The magnetic moments of these complexes at room temperature are in the range 4.64−5.33 BM. These values are as expected for octahedral Co^{II} complexes (4.70−5.20 BM).

The diffuse reflectance spectra of all the homoleptic complexes of nickel^{II} (Table 7), [Ni(RpymS)$_2$], are very similar and show bands at around 9000 cm^{-1} (ν_2) and 15000 cm^{-1} (ν_3). These bands are in the ranges expected for pseudotetrahedral Ni^{II} complexes [29] and can be assigned to the transitions $^3T_1(F) \rightarrow {}^3A_2$ (ν_2) and $^3T_1(F) \rightarrow {}^3T_1(P)$ (ν_3), respectively. The spin allowed d-d transition of lowest energy, $^3T_1(F) \rightarrow {}^3T_2$ (ν_1), was not observed. However, the position of this band was calculated and gave a value of 4030 to 4320 cm^{-1}, which is consistent with the range expected for tetrahedral nickel(II) complexes. The magnetic moments of these complexes, measured at room temperature, are between 3.00 and 3.43 BM and these are characteristic of Ni^{2+} complexes with a tetrahedral geometry.

The electronic spectra of the mixed nickel(II) complexes are shown in Table 8 and are consistent with systems having an octahedral symmetry [29]. The solid state electronic spectra of these complexes show three bands in the ranges 9940−10780, 15430−16340 and 19900−24875 cm^{-1}. These bands are consistent with octahedral Ni^{2+} complexes and can be assigned to the following transitions: $^3A_{2g} \rightarrow {}^3T_{2g}$ (ν_1), $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (ν_2) and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (ν_3), respectively. The magnetic moments (2.93 to 3.17 MB) are also indicative of octahedral nickel(II) complexes. All of the data suggest that these complexes are monomeric and the coordination number six is achieved through the chelate N,S thionate ligands, with the bipyridine or phenanthroline ligands also acting in a chelate fashion. Analogous octahedral structures to those proposed here have also been found by X-ray diffraction on the complexes [Ni(pyS)$_2$bipy] [30] and [Ni(pymS)$_2$bipy] [31].

NMR Spectra

The diamagnetic nature of the complexes [Co(RpymS)$_3$] allowed nuclear magnetic resonance spectra to be acquired (both ^{1}H and ^{13}C). The ^{1}H NMR spectra of the complexes do not contain a signal for the NH proton of the free ligand, which shows that the ligands are deprotonated in the complexes. The ^{1}H and ^{13}C spectra of these complexes show three signals for each proton and carbon atom, one for each ligand. This demonstrates that the ligands in the complexes are not equivalent. This situation suggests that these complexes have the same structure in solution as they do in the solid state, i.e. an octahedral environment around the metal centre with the ligands arranged in such a way that the meridional isomer is formed − as found by X-ray diffraction for the complex [Co(4-CF$_3$pymS)$_3$].

Mass Spectra

The cobalt and nickel complexes were also characterized by mass spectrometry using the positive ion FAB technique (*m*/*z*) in 3-nitrobenzyl alcohol (NBA) as matrix. The FAB spectra of the cobalt(III) compounds show the molecular ion with the appropriate isotope distribution, e.g. at *m*/*z* 638 for [Co(4-Me,6-CF$_3$pymS)$_3$], along with peaks due to the fragments produced by the loss of one (*m*/*z* 445) and two thionate ligands (*m*/*z* 252). For the [CoL$_2$] complexes the FAB spectra contain peaks due to the molecular ions and, in some cases, peaks corresponding to the loss of one ligand molecule.

In the majority of the mass spectra of the mixed complexes [Co(RpymS)$_2$bipy] and [Co(RpymS)$_2$phen], the molecular ion peak was not observed. However, peaks due to lower mass species were observed and these correspond to fragments formed by the loss of different groups. For example, it is worth highlighting the peak arising from the loss of one of the thiolate ligands and the peak corresponding to [CoL].

In some cases the spectra of the complexes [Ni(RpymS)$_2$] contain the expected molecular ion peak [M$^+$] along with other lower mass peaks due to fragments resulting from the loss of different groups. Of these peaks it is worth highlighting the one due to the loss of one ligand molecule from the molecular ion.

The spectra of the mixed complexes [Ni(RpymS)$_2$bipy] and [Ni(RpymS)$_2$phen] contain a molecular ion peak along with peaks corresponding to the loss of one [Ni(RpymS)L] and two [NiL] of the thionate ligands.

3 Experimental Section

Acetonitrile, 1,1,1-trifluoro-2,4-pentanedione, thiourea, benzoylacetone, *trans*-benzylideneacetophenone, 1,1,1-trifluoroacetone, benzaldehyde, sodium, 4-trifluoromethylpyrimidine-2-thione, 1,10-phenanthroline, 2,2′-bipyridine, ethanol and methanol were commercial products and were used as supplied. Cobalt and nickel (Aldrich) were used as 2 × 2 cm plates.

Preparation of ligands

[4,6-CF_3MepymSH]. This compound was obtained by reacting thiourea (2.428 g, 32 mmol) and 1,1,1-trifluoro-2,4-pentanedione (5 g, 32 mmol) in ethanol. Concentrated hydrochloric acid (1 mL) was added in order to catalyse the reaction. The mixture was heated under reflux for 2 h and the resulting yellow solid was filtered off. Anal.: C: 36.39; N: 14.26; H: 2.60, S: 16.08 %. Calc. for $C_6F_3H_5N_2S$: C 37.11; N 14.43; H 2.60; S 16.51 %.

IR (KBr/cm^{-1}): 1615 ($\nu_{C=N}$), 3100−3400 ($\nu_{C=N}$, $\nu_{C\text{-}H}$). **^{1}H NMR** ($CDCl_3$, ppm): δ = 14.40 (s, 1H, NH), H_5, 7.19 (s, 1H, H_5); Me, 2.39 (s, 3H, CH_3); − **^{13}C NMR** (300 MHz, DMSO-d^6): δ = 181.00 and 172.13 (s, C_2); 155.86 and 153.72 [q, C_4; $^2J(^{13}C\text{-}^{19}F)$ = 35 Hz]; 104.89 (s, C_5); 163.61 (s, C_6); 119.27 and 119.67 [q, CF_3; $^1J(^{13}C\text{-}^{19}F)$ = 275 Hz]; 23.45 and 18.46 (s, CH_3) ppm. **Mass spectrum** (FAB): MS (*m*/*z*): 195 (M^+), 124 ($M^+ - CF_3$).

[4,6-PhMepymSH]. This ligand was obtained using a similar method to the previous compound. The precursors were benzoylacetone (15 g, 92.5 mmol) and thiourea (11.01 g, 144 mmol). Concentrated hydrochloric acid (30 mL) was added to the reaction mixture. The product was a yellow dusty solid. Anal.: C, 66.94; N, 15.24, H, 5.35, S, 16.01 %. Calc. for $C_{11}H_{10}N_2S$: C, 65.34; N, 13.86; H, 4.95, N: 15.84 %.

IR (KBr/cm^{-1}): 3000−3100 ($\nu_{N\text{-}H}$); 1650 ($\nu_{C=N}$). **^{1}H NMR** (DMSO-d^6, ppm): 2.37 (s, 3 H, CH_3); Ph, 7.4−8 (m); 7.3 (s, 1H, H_5), 13.7 (s, 1H, NH). **MS** (*m*/*z*): 203 (M^+), 403 (M_2^+), 187 ($M^+ - Me$).

[4,6-Ph_2pymSH]. The synthesis of this ligand was performed using a different route [32]. Sodium (8.83 g, 3.84 mmol) was added to dry ethanol (300 ml). Thiourea (7.31 g, 96 mmol) was added to the reaction mixture and, after stirring for 15 min, *trans*-benzylideneacetophenone (20 g, 96 mmol) was added. The mixture was heated under reflux under an inert atmosphere for 24 h. The solvent was removed under vacuum and the resulting solid was treated with water and filtered. The solution was adjusted to pH = 6 with acetic acid to give a yellow solid. The solid was purified by column chromatography. Anal.: C, 72.30, N, 10.47; H, 4.47; S, 12.73 %. Calc. for $C_{16}H_{12}N_2S$; C, 72.72; N, 10.44; H, 4.11; S, 11.94 %.

IR (KBr/cm^{-1}): 3400−3500 ($\nu_{N\text{-}H}$), 1600 ($\nu_{C=N}$). **^{1}H NMR** (DMSO-d^6, ppm): 13.5 (broad singlet, 1 H, NH); 8.4 (s, 1H, H_5), Ph, 6.90−7.20 (m). **MS** (*m*/*z*): 265 (M^+), 527 (M_2^+).

[4,6-CF_3PhpymSH]. This compound was prepared using a similar synthetic route, but in this case the precursor 1,1,1-trifluoro-4-phenyl-3-buten-2-one was not a commercial product. NaOH (9.93 g) was dissolved in water and the mixture was cooled to 0 °C. Benzaldehyde (5.22 g, 49 mmol) and 1,1,1-trifluoroacetone (5.21 g, 49 mmol) were added to the reaction mixture. The mixture was allowed to warm up to room temperature and stirred for 6 h. The mixture was then heated to 65 °C for 12 h and allowed to cool down to room temperature. The organic compounds were removed by extraction with CH_2Cl_2. The combined organic layers were dried ($MgSO_4$) and the solvent was removed under reduced pressure to give a colourless liquid. ^{1}H NMR ($CDCl_3$, ppm): olefinic protons: 6.8 (dd), 6.9 (dd); Ph, 7.3 (m).

The ligand [4,6-CF_3PhpymSH] was obtained by reacting thiourea (0.38 g, 4.99 mmol) and sodium (0.459 g, 19.9 mmol) in ethanol (40 mL). The reaction mixture was heated under refluxes and 1,1,1-trifluoro-4-phenyl-3-buten-2-one (1 g, 5 mmol) was added. The mixture was heated under reflux for a further 24 h. The solvent was removed and the resulting solid was added to water (50 mL). The solution was acidified with AcOH and the resulting orange solid was filtered off. Anal.: C, 51.40; N, 11.02; H, 2.81; S, 12.39 %. Calc. for $C_{11}F_3H_7N_2S$: C, 51.50; N, 10.93; H, 2.75; S, 12.51 %.

IR (KBr/cm^{-1}): 3450−3500 ($\nu_{N\text{-}H}$), 1650 ($\nu_{C=N}$). **^{1}H NMR** (300 MHz, DMSO-d^6): δ = 13.0 (s, 1H, NH); 7.8 (s, 1H, H_5); 7.6 (m, Ph) ppm. **^{13}C NMR** (300 MHz, DMSO-d^6): 169.30 (s, C_2); 167.31 (q, C_4); 110.42 (s, C_5); 163.85 (s, C_6); 118.54 (q, CF_3); 122.98−135.32 (phenyl ring) ppm. **MS** (*m*/*z*): 257.2 (M^+); 511 (M_2^+).

Preparation of complexes

The complexes were obtained using an electrochemical method [33]. The cell was a 100 ml tall-form beaker fitted with a rubber bung through which the electrochemical leads entered. An acetonitrile solution of the ligand containing about 20 mg of tetraethylammonium perchlorate as a current carrier was electrolysed using a platinum wire as the cathode and the cobalt plate as the sacrificial anode. Direct current was obtained from a purpose-built d.c. power supply. Applied voltages of 5−15 volts allowed sufficient current flow for smooth dissolution of the metal. The current was kept at 10 mA for the time previously calculated. Hydrogen was evolved at the cathode. The cell can be summarized as:

$$M_{(+)} \,/\, CH_3CN + RpymSH/Pt_{(-)}.$$

After electrolysis, the solutions were filtered and dusty solids or brown solutions were obtained. The solids were washed with acetonitrile and diethyl ether and dried at room temperature. The solutions were allowed to evaporate at room temperature. Dark green crystals suitable for X-ray diffraction studies were obtained for [Co(4-CF_3pymS)$_3$] by recrystallization from a dichloromethane/ethanol mixture.

Physical measurements

The C, H, N and S contents of the compounds were determined on Carlo Erba EA 1108 and LECO CHNS-932 microanalysers. IR spectra were recorded as KBr mulls on a Bruker IFS-66V spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX 300 spectrometer using $CDCl_3$ or DMSO-d_6 as solvents. UV-Vis spectra were recorded in the solid state on a Hitachi-4-3200 spectrophotometer Determination of magnetic susceptibility was carried out on a Manics DSMS magnetometer at room temperature. FAB mass spectra were recorded on a Kratos-MS-50 using m-NBA as matrix.

Crystal structure determination

The data collection was taken on a SIEMENS Smart CCD area-detector diffractometer with graphite-monochromated Mo-K_α radiation. Absorption corrections were carried out using SADABS [34]. The structure was solved by direct methods and refined by a full matrix least squares based on F^2 [35]. Hydrogen atoms were also included in idealised positions and refined with isotropic displacement parameters. Atomic scattering factors and anomalous dispersion corrections for all atoms were taken from International Tables for X-ray Crystallography [36]. Details of crystal data and structural refinement are given in Table 3. ORTEP3 drawings [37], along with the numbering schemes used, are shown in Figure 1.

Crystallographic data for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC- 631154 for Co(4-CF_3pymS)$_3$]. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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