Inorganica Chimica Acta, 211 (1993) 47–54

Synthesis of 3-trimethylsilylpyridine-2-thione (3-$Me_3SipytH$) complexes of nickel, copper, zinc and cadmium: crystal and molecular structure of [Cd(3-$Me_3Sipyt)_2$]

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(Received March 1, 1993)

Abstract

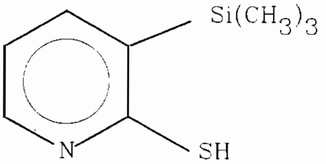
A series of complexes of Ni, Cu, Zn and Cd with 3-trimethylsilylpyridine-2-thione (3-$Me_3SipytH$) as ligand has been prepared. Complexes [M(3-$Me_3Sipyt)_2$] (M = Ni(II), Zn(II) and Cd(II)) and [Cu(3-Me_3Sipyt)] are obtained by electrochemical oxidation of the metal in an acetonitrile solution of the neutral ligand (3-$Me_3SipytH$). Adducts [Ni(3-$Me_3Sipyt)_2L$] (L = 2,2-bipyridine or 1,10-phenanthroline) were obtained by addition of the extra ligand to the electrolyte phase. Treatment of [Cu(3-Me_3Sipyt)] with 1,2-bis(diphenylphosphino)ethane (dppe) in acetone gave [Cu_2(3-$Me_3Sipyt)_2(dppe)_3$]. The X-ray structure of [Cd(3-$Me_3Sipyt)_2$] has been determined: monoclinic, space group $P2_1/n$, with $a = 11.818(1)$, $b = 13.649(1)$, $c = 13.218(1)$ Å, $\beta = 92.00(1)°$ and $Z = 4$. The structure was determined by direct methods and refined to $R = 0.030$ and $R_w = 0.031$. In the binuclear complex each cadmium(II) centre has a trigonal bipyramidal coordination sphere with an equatorial S_3 plane, involving two bridging sulfur and one terminal sulfur. The axial positions are occupied by the nitrogen atoms of two ligands. Vibrational, electronic and ^1H, ^{13}C and ^{31}P NMR spectral data are presented for all the compounds synthesized.

Introduction

The great current interest [1–3] in metal complexes of heterocyclic thione ligands stems in part from their wide ranging applications and also from the desire to use them as a reference when investigating the chemistry of metalloproteins.

However, the polymeric or oligomeric nature of neutral metal–thiolato compounds makes it difficult to obtain crystals suitable for X-ray diffraction studies. Recently, much effort has been made [4] to modify the thiolate ligand by introducing a solubilizing group or a bulky substituent that might modify the aggregation process. Pyridine-2-thione is one of the most versatile sulfur ligands, since it can behave either as a neutral ligand (through the sulfur atom) [5–7] or as a monoanionic S-monodentate [7, 8], N,S-bidentate [7–9] or as S-bridging [10] or N,S-bridging [6, 11] ligand.

As a part of our continuing interest in heterocyclic thione complexes [12, 13], we report in this paper the electrochemical synthesis of complexes of nickel, copper, zinc and cadmium with 3-trimethylsilylpyridine-2-thione, in which the bulky trimethylsilyl substituent close to the sulfur atom modifies the degree of aggregation of the thiolate complexes. Although the compounds [Ni(3-$Me_3Sipyt)_2$] [14], [Cu(3-Me_3Sipyt)] [15] and [Zn(3-$Me_3Sipyt)_2$] [16] are known and their structures have been described, the other compounds reported in this article have not been synthesized before.



Experimental

All solvents, pyridine-2-thione and other reagents are commercially available and were used without further purification. The metals (Ega Chemie) were used as *c.* 2×2 cm plates. 3-Trimethylsilylpyridine-2-thione was

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prepared following the method described by Block *et al.* [15].

Preparation of the complexes

The electrochemical method used was similar to that described previously [17]. The cell consisted of a tall-form beaker (100 cm^3), and the electrolyte phase was a solution of 3-trimethylsilylpyridine-2-thione (3-Me_3SipytH) in acetonitrile (50 cm^3) containing tetraethylammonium perchlorate (*c.* 20 mg). The anode was supported on a platinum wire. Direct current was obtained from a purpose-built d.c. power supply.

Zinc and cadmium complexes

The oxidation of zinc in a solution of acetonitrile containing 0.21 g of 3-Me_3SipytH (3 h at 12 V and 10 mA) resulted in the loss of 33.6 mg of zinc from the anode ($E_f = 0.46$ mol F^{-1}). As electrolysis proceeded, hydrogen gas evolved at the cathode. Removal of solvent from the final yellow solution gave a yellow oil, which was dissolved in isopropanol. Concentration of the solution in a rotavapor gave a yellow solid identified as [Zn(3-Me_3Sipyt)$_2$]. *Anal.* Found: C, 44.3; H, 5.5; N, 6.8. Calc. for [Zn(3-Me_3Sipyt)$_2$]: C, 44.9; H, 5.6; N, 6.8%.

In the case of cadmium, electrolysis of 0.21 g of 3-Me_3SipytH in acetonitrile for 3 h at 13 V and 10 mA resulted in the dissolution of 64.7 mg of cadmium ($E_f = 0.51$ mol F^{-1}). By slow evaporation of the resulting yellow solution at room temperature, colourless crystals of [Cd(3-Me_3Sipyt)$_2$] suitable for X-ray studies were isolated. *Anal.* Found: C, 40.3; H, 4.9; N, 5.8. Calc. for [Cd(3-Me_3Sipyt)$_2$]: C, 40.3; H, 5.0; N, 5.9%.

The addition of 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen) to the solution phase before electrolysis caused no change in the nature of the product.

Copper complexes

Electrolysis of 3-Me_3SipytH (0.21 g) in acetonitrile for 3 h at 15 V and 10 mA dissolved 66.4 mg of copper ($E_f = 0.93$ mol F^{-1}). At the end of the experiment, small quantities of a black solid were removed by filtration, and the orange filtrate was slowly condensed at room temperature to give yellow–orange crystals of [Cu(3-Me_3Sipyt)]. *Anal.* Found: C, 37.8; H, 5.5; N, 5.9. Calc. for [Cu(3-Me_3Sipyt)]0.5H_2O: C, 37.8; H, 5.1; N, 5.5%.

Attempts to prepare adducts of [Cu(3-Me_3Sipyt)] by adding either bipy or phen to the electrolyte phase were unsuccessful, the compounds isolated still having the elemental formula [Cu(3-Me_3Sipyt)]. Reaction of this compound (0.13 g) with 1,2-bis(diphenylphosphino)ethane (0.31 g) in acetone (41 cm^3) yielded a yellow solution which upon slow evaporation of the solvent afforded yellow crystals identified as [Cu_2(3-Me_3Sipyt)$_2$(dppe)$_3$]. *Anal.* Found: C, 67.0; H, 5.7; N, 1.7. Calc. for [Cu_2(3-Me_3Sipyt)$_2$(dppe)$_3$]: C, 66.9; H, 5.7; N, 1.6%.

Nickel complexes

The electrochemical oxidation of nickel in a solution of 0.21 g of 3-Me_3SipytH occurred smoothly to afford first a yellow and finally a green solution. After *c.* 3 h at 34 V and 10 mA, 33.7 mg of nickel had been dissolved ($E_f = 0.51$ mol F^{-1}). The amber microcrystalline product which was precipitated as the oxidation proceeded was collected and recrystallized from acetone to give a crystalline solid identified as [Ni(3-Me_3Sipyt)$_2$]. *Anal.* Found: C, 45.3; H, 5.6; N, 6.7. Calc. for [Ni(3-Me_3Sipyt)$_2$]: C, 45.4; H, 5.7; N, 6.6%.

When a nickel anode was oxidized in a solution of 3-Me_3SipytH (0.21 g) and bipy (0.09 g) in acetonitrile (50 ml), an applied voltage of 28 V produced a current of 10 mA and after 3 h, 31.2 mg of nickel had been dissolved ($E_f = 0.47$ mol F^{-1}). After electrolysis, the orange–brown solution was allowed to stand in air at room temperature, and orange–brown crystals of [Ni(3-Me_3Sipyt)$_2$bipy] were isolated. *Anal.* Found: C, 53.4; H, 5.6; N, 9.7. Calc. for [Ni(3-Me_3Sipyt)$_2$bipy]: C, 53.9; H, 5.5; N, 9.7%.

The oxidation of nickel in the presence of phen (0.11 g) and 3-Me_3SipytH (0.21 g) in acetonitrile for 3 h at 12 V and 10 mA dissolved 35.8 mg of nickel ($E_f = 0.54$ mol F^{-1}). Slow evaporation of the orange–brown solution at room temperature produced orange–brown crystals of [Ni(3-Me_3Sipyt)$_2$phen]. *Anal.* Found: C, 53.3; H, 5.3; N, 8.5. Calc. for [Ni(3-Me_3Sipyt)$_2$phen]1.5H_2O: C, 53.3; H, 5.5; N, 8.9%.

Physical measurements

Microanalyses were performed using a Carlo-Erba EA1108 microanalyser. IR spectra were recorded in KBr mulls on a Perkin-Elmer 180 spectrophotometer; ^{1}H, ^{13}C and ^{31}P NMR spectra were obtained with a Bruker WM 250 MHz instrument using DMSO or $CDCl_3$ as solvent. Solid reflectance spectra were recorded on a Perkin-Elmer Landa 9 spectrophotometer. Magnetic measurements were made using a SQUID.

X-ray data collection and reduction

A colorless prismatic crystal of [Cd(3-Me_3Sipyt)$_2$] was mounted on a glass fibre and used for data collection. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of the diffraction data from 25 reflections in the range of $9.48 < \theta < 21.27°$ in a ENRAF-NONIUS CAD4 four circle diffractometer [18]. Data were collected at 293 K using Mo Kα radiation ($\lambda = 0.70930$ Å) and the $\omega/2\theta$ scan technique and corrected for Lorentz and polarization effects. An empirical absorption correction

TABLE 1. Crystal data, data collection and structure refinement parameters of [Cd(3-Me_3Sipyt$)_2$]

Crystal shape	prismatic
Size (mm)	$0.30 \times 0.25 \times 0.30$
Chemical formula	$C_{16}H_{24}CdN_2S_2Si_2$
Formula weight	477.08
Crystal system	monoclinic
Space group	$P2_1/n$
Unit-cell dimensions	
a (Å)	11.818(1)
b (Å)	13.649(1)
c (Å)	13.218(1)
β (°)	92.00(1)
Volume of unit cell (Å^3)	2130.7(6)
Z	4
D_x (g cm^{-3})	1.487
F(000)	968
Linear absorption coefficient (cm^{-1})	13.201
Absorption correction: min., max., av.	0.694, 1.220, 0.991
Max. value of (sin θ)/λ reached in intensity measurement (Å^{-1})	0.660
Range of h, k, l	$0 \rightarrow 15$, $0 \rightarrow 18$, $-17 \rightarrow 17$
Standard reflections	$-2,3,-6$; $-1,2,-7$; $6,2,-2$
Interval standard reflections measured (s)	3600
Total no. reflections measured, θ range (°)	5576, 3–28
No. unique reflections, R_{int}	5086, 0.016
No. observed reflections	2865
Criterion for observed reflections	$I > 3\sigma(I)$
Weighting scheme	$1/\sigma^2(F)$
Parameters refined	281
Value of R	0.030
Value of R_w	0.031
Ratio of max. LS shift to e.s.d. (Δ/σ)	0.001
Max. $\Delta\rho$ in final difference electron density map (e Å^{-3})	0.312
Error in an observation of unit weight	1.465
Secondary-extinction coefficient	3.936×10^{-9}

was made [19]. A summary of the crystal data, experimental details and refinement results are listed in Table 1. See also 'Supplementary material'.

Structure solution and refinement

The structure was solved by direct methods [20] which revealed the position of all non-hydrogen atoms, and refined on F by a full-matrix least-squares procedure using anisotropic displacement parameters for all non-hydrogen atoms. The hydrogen atoms were located on a difference Fourier map and added to the structure factors calculations as fixed contributions ($B_{iso} = 4.0$ Å^2) and their positional parameters were refined isotropically. A secondary extinction correction was applied [21]. After all shift/e.s.d. ratios were less than 0.001, the refinement converged to the agreement factors listed in Table 1. Atomic scattering factors were taken from the International Tables for X-ray Crystallography [22]. Molecular graphics were obtained with the SCHAKAL program [23].

Results and discussion

The electrochemical oxidation of a sacrificial metal (zinc, cadmium, copper or nickel) anode in an acetonitrile solution of 3-trimethylsilylpyridine-2-thione proved to be a convenient one-step route to either [Cu(3-Me_3Sipyt)] or [M(3-Me_3Sipyt$)_2$] (M = Zn, Cd or Ni).

Attempts to prepare the corresponding adducts of these compounds by adding either bipy or phen to the electrolyte phase caused no change in the nature of the copper, zinc and cadmium complexes, but with nickel as anode, the reaction followed a different pathway and the mixed complexes [Ni(3-Me_3Sipyt$)_2$bipy] and [Ni(3-Me_3Sipyt$)_2$phen] were obtained. Reaction of the copper complex with 1,2-bis(diphenylphosphino)ethane (dppe) in acetone gave [Cu_2(3-Me_3Sipyt$)_2$(dppe$)_3$].

For the zinc, cadmium and nickel complexes, the electrochemical efficiency E_f, defined as the amount of metal dissolved per Faraday of charge, was close to 0.5 mol F^{-1}, which is compatible with the following reaction schemes:

Cathode: $2(3\text{-Me}_3\text{SipytH}) + 2e^- \longrightarrow$

$\text{H}_2(\text{g}) + 2(3\text{-Me}_3\text{Sipyt}^-)$

Anode: $2(3\text{-Me}_3\text{Sipyt}^-) + \text{M} \longrightarrow$

$[\text{M}(3\text{-Me}_3\text{Sipyt})_2] + 2e^-$

M = Zn, Cd or Ni

or

$2(3\text{-Me}_3\text{Sipyt}^-) + \text{Ni} + \text{L} \longrightarrow$

$[\text{Ni}(3\text{-Me}_3\text{Sipyt})_2\text{L}] + 2e^-$

L = phen or bipy

For copper, E_f was close to 1.0 mol F^{-1}, corresponding to the process

Cathode: $3\text{-Me}_3\text{SipytH} + 1e^- \longrightarrow$

$1/2\ \text{H}_2\ (\text{g}) + 3\text{-Me}_3\text{Sipyt}^-$

Anode: $3\text{-Me}_3\text{Sipyt}^- + \text{Cu} \longrightarrow$

$[\text{Cu}(3\text{-Me}_3\text{Sipyt})] + 1e^-$

Structure of $[Cd(3\text{-}Me_3Sipyt)_2]$

A perspective view of the molecule is shown in Fig. 1 and a stereoview of the unit cell packing is shown in Fig. 2; the final atomic coordinates, bond lengths and angles are given in Tables 2 and 3, respectively. The compound consists of discrete neutral binuclear units with the Cd centres in $[\text{CdS}_3\text{N}_2]$ environments. Each Cd atom coordinates to the sulfur and nitrogen donors of one terminal 3-trimethylsilylpyridine-2-thiolate ligand, to the sulfur and nitrogen atoms of one bridging ligand and to the sulfur of a second bridging ligand. The cadmium and bridging sulfur atoms define a perfect plane, with two longer Cd–S bonds (2.667(2) Å) and two shorter ones (2.597(2) Å).

The geometry around each cadmium atom can be considered as a severely distorted trigonal bipyramid, with two nitrogen atoms in apical positions. The distortion is produced by the small chelating ligand angles S(1)–Cd–N(1), 62.06(9)° and S(2)–Cd–N(2), 64.84(9)°; the N(1)–Cd–N(2) angle, 158.1(1)°, is quite different from the ideal, 180°.

The Cd–S distances differ slightly, but significantly. As in other compounds with both bridging and terminal Cd–S bonds [24, 25], the bonds involving the sulfur bridges are longer, 2.597(2) and 2.667(2) Å, than the terminal bond, 2.495(1) Å. However, in this compound the Cd–S bond lengths are much shorter than those

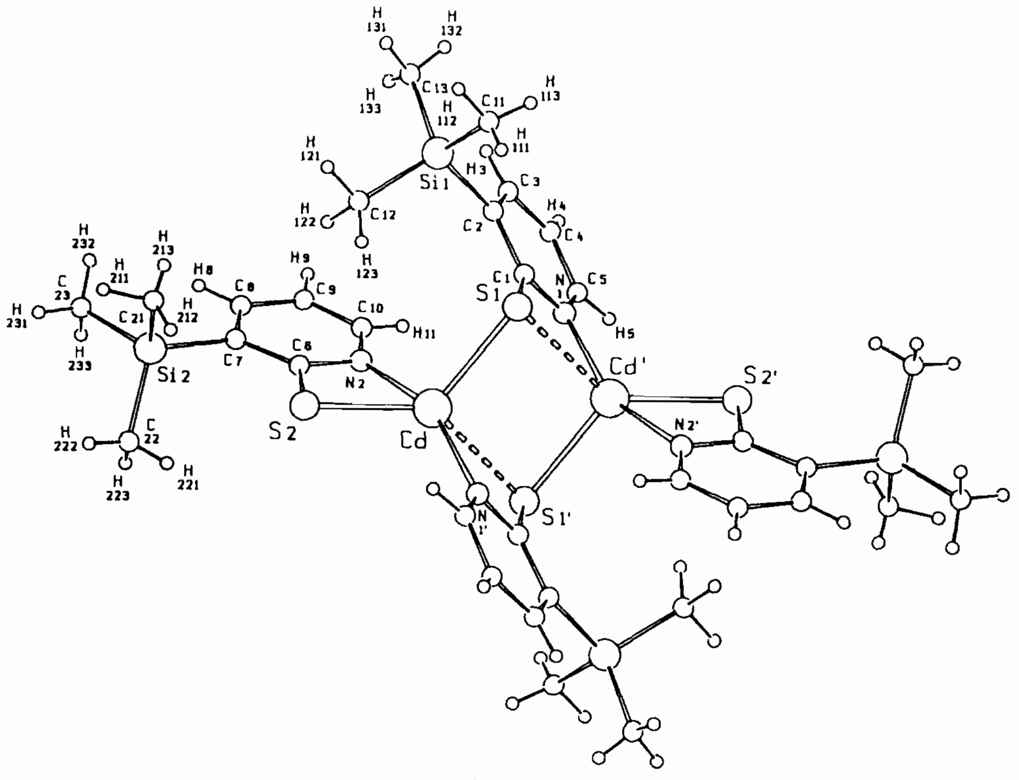

Fig. 1. Perspective view showing the atom numbering scheme and the coordination geometry about the cadmium atoms in the dimer. Symmetry code is: $-1-x,\ 1-y,\ 1-z$.

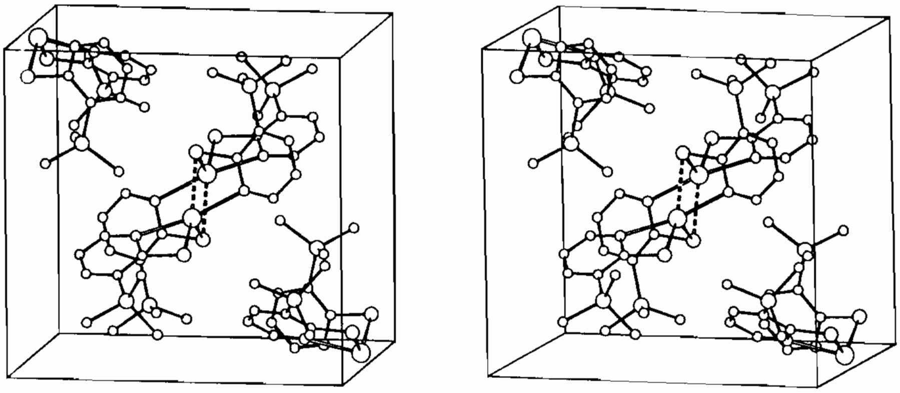

Fig. 2. Stereoview of the unit cell packing. The origin of the unit cell lies at the lower right corner, with *a* pointing toward the rear part, *b* from right to left, and *c* upwards.

TABLE 2. Atomical positional parameters and isotropic thermal parameters (Å^2) for [Cd(3-Me$_3$Sipyt)$_2$]

Atom	*x*	*y*	*z*	B_{iso}
Cd	−0.36354(3)	0.49873(3)	0.54943(2)	3.686(5)
S(1)	−0.55432(9)	0.5004(1)	0.64102(7)	3.34(2)
S(2)	−0.17312(9)	0.5034(1)	0.6370(1)	4.26(2)
Si(1)	−0.5315(1)	0.3441(1)	0.84522(9)	4.07(3)
Si(2)	0.0212(1)	0.3622(1)	0.7580(1)	3.45(2)
N(1)	−0.3764(3)	0.3480(3)	0.4637(3)	3.17(7)
N(2)	−0.2880(3)	0.3433(3)	0.5978(3)	3.31(7)
C(1)	−0.5871(3)	0.3742(3)	0.6306(3)	2.90(8)
C(2)	−0.5804(4)	0.3089(3)	0.7124(3)	3.27(8)
C(3)	−0.6164(4)	0.2135(4)	0.6902(4)	4.4(1)
C(4)	−0.6557(5)	0.1869(4)	0.5943(4)	4.7(1)
C(5)	−0.3431(4)	0.2559(4)	0.4805(4)	4.1(1)
C(6)	−0.1920(3)	0.3767(3)	0.6447(3)	3.00(8)
C(7)	−0.1139(3)	0.3151(3)	0.6963(3)	3.00(8)
C(8)	−0.1440(4)	0.2163(3)	0.6992(4)	3.79(9)
C(9)	−0.2432(4)	0.1815(3)	0.6529(4)	4.3(1)
C(10)	−0.3118(4)	0.2470(4)	0.6034(4)	4.0(1)
C(11)	−0.6250(5)	0.4391(5)	0.8963(4)	5.8(1)
C(12)	−0.3830(5)	0.3873(5)	0.8469(4)	5.9(1)
C(13)	−0.5387(6)	0.2330(5)	0.9259(4)	7.1(2)
C(21)	−0.0118(5)	0.4490(4)	0.8615(4)	5.4(1)
C(22)	0.1115(4)	0.4215(5)	0.6647(4)	5.5(1)
C(23)	0.0976(5)	0.2555(4)	0.8156(5)	5.6(1)

TABLE 3. Selected bond distances (Å) and angles (°) for [Cd(3-Me$_3$Sipyt)$_2$]

Cd–S(1)	2.597(2)	N(1)–C(1)	1.352(5)
Cd–S(1)^{i}	2.667(2)	N(1)–C(5)	1.335(7)
Cd–S(2)	2.495(1)	N(2)–C(6)	1.353(5)
Cd–N(1)	2.380(4)	N(2)–C(10)	1.345(6)
Cd–N(2)	2.381(4)	C(1)–C(2)	1.401(6)
S(1)–C(1)	1.770(4)	C(2)–C(3)	1.398(6)
S(2)–C(6)	1.749(4)	C(3)–C(4)	1.384(8)
Si(1)–C(2)	1.891(4)	C(4)–C(5)	1.364(8)
Si(1)–C(11)	1.847(6)	C(6)–C(7)	1.407(6)
Si(1)–C(12)	1.850(6)	C(7)–C(8)	1.395(6)
Si(1)–C(13)	1.857(7)	C(8)–C(9)	1.387(7)
Si2–C(7)	1.881(4)	C(9)–C(10)	1.360(7)
Si2–C(21)	1.861(6)	Cd–Cd	3.4374(5)
Si(2)–C(22)	1.845(6)	S(1)–S(1)	3.985(1)
Si(2)–C(23)	1.863(6)		
S(1)–Cd–S(1)^{i}	98.45(3)	C(1)–N(1)–C(5)	119.0(4)
S(1)–Cd–S(2)	124.57(4)	C(6)–N(2)–C(10)	118.6(4)
S(1)–Cd–N(1)	99.92(9)	C(8)–C(9)–C(10)	117.9(4)
S(1)^{i}–Cd–N(2)	101.90(9)	N(2)–C(10)–C(9)	123.1(4)
S(1)^{i}–Cd–S(2)	136.93(4)	S(1)–C(1)–N(1)	113.0(3)
S(1)^{i}–Cd–N(1)	62.06(9)	S(1)–C(1)–C(2)	123.6(4)
S(1)–Cd–N(2)	112.21(9)	N(1)–C(1)–C(2)	123.5(4)
S(2)–Cd–N(1)	103.88(9)	Si(1)–C(2)–C(1)	124.2(3)
S(2)–Cd–N(2)	64.84(9)	Si(1)–C(2)–C(3)	120.9(3)
N(1)–Cd–N(2)	158.1(1)	C(1)–C(2)–C(3)	114.9(4)
C(2)–Si(1)–C(11)	110.5(2)	C(2)–C(3)–C(4)	121.8(4)
C(2)–Si(1)–C(12)	110.6(2)	C(3)–C(4)–C(5)	118.5(5)
C(2)–Si(1)–C(13)	107.9(2)	N(1)–C(5)–C(4)	122.3(4)
C(11)–Si(1)–C(12)	110.5(3)	S(2)–C(6)–N(2)	114.4(4)
C(11)–Si(1)–C(13)	108.9(3)	S(2)–C(6)–C(7)	122.5(4)
C(12)–Si(1)–C(13)	108.4(4)	N(2)–C(6)–C(7)	123.1(4)
C(7)–Si(2)–C(21)	110.0(2)	Si(2)–C(7)–C(6)	122.5(3)
C(7)–Si(2)–C(22)	111.3(2)	Si(2)–C(7)–C(8)	122.2(3)
C(7)–Si(2)–C(23)	107.5(2)	C(6)–C(7)–C(8)	115.3(4)
C(21)–Si(2)–C(22)	110.7(3)	C(7)–C(8)–C(9)	122.1(4)
C(21)–Si(2)–C(23)	107.9(3)	Cd–S(1)–Cd	81.56(4)
C(22)–Si(2)–C(23)	109.4(3)		

$^{i} = -x-1,\ 1-y,\ 1-z$.

found in other dimeric cadmium complexes with pentacoordinate environments around cadmium: in {$Cd_2[S_2CN(C_2H_5)]_4$} [24] and {$Cd_2[S_2CN(CH_2)_6]_4$} [25], the Cd–S(bridging) and Cd–S(terminal) bond lengths are in the ranges 2.80–2.87 and 2.53–2.64 Å, respectively.

The Cd–N distances are identical to within experimental error, 2.381(4) Å, but are slightly longer than those found in octahedral cadmium complexes with heterocyclic ligands with a nitrogen donor. For example, Cd–N is 2.310(3) Å in bis(*N*-isonicotinato)tetraaquo cadmium(II) [26], 2.336(5) Å in diformatodiaquobis(nicotinamide) cadmium(II) [27], 2.35 Å in $CdCl_2 \cdot 2py$ [28] and 2.343 Å in [Cd(pyt)$_2$]$_n$ [29].

The pyridine rings are essentially planar, but the sulfur atoms lie out of the plane of the pyridine to which they are bound (by 0.1079 Å for S(1) and 0.0771 Å for S(2)). The mean S–C distance, 1.760(4) Å, is longer than the 1.68 Å found in free pyridine-2-thione [30], which in the solid state is in the thione form. This suggests that in the cadmium complex the ligand is in thiolate form.

The above structure is different from that of $[Cd(pyt)_2]_n$ [29], a polymer with octahedral $[CdS_4N_2]$ cadmium centres and N,S-bridging pyridine-2-thiolato ligands. The difference can be ascribed to the presence of the bulky $SiMe_3$ substituent in 3-trimethylsilylpyridine-2-thione, which prevents a coordination number six around each cadmium in $[Cd(Me_3Sipyt)_2]_2$. $[Cd(Me_3Sipyt)_2]_2$ also differs from $[Zn(Me_3Sipyt)_2]_2$ [16] which consists of discrete neutral binuclear units with distorted tetrahedral $[ZnS_2N_2]$ zinc centres in which each Zn atom coordinates to the sulfur and nitrogen donors of a terminal 3-trimethylsilylpyridine-2-thiolate ligand and to the sulfur of one bridging ligand and the nitrogen of another. The bridging ligands thus act as 3-electron donors in the Zn complex and as 5-electron donors in the Cd complex.

IR spectra

The IR spectra of the complexes (Table 4) lack the weak band for ν(N–H) which appears at 3140 cm^{-1} in the spectrum of the free ligand. The strong bands for νC=C and νC=N at 1600 and 1570 cm^{-1} in the ligand spectrum are shifted to smaller wavenumbers in the complexes; this is the behaviour expected for aromatic vibrations tension, and it supports the notion that the ligand is coordinated in thiolate form. All the IR spectra show a strong band at 840 cm^{-1} which is attributed to ν(Si–C) [31].

The mixed complexes $[Ni(3\text{-}Me_3Sipyt)_2L]$ (L = bipy, phen) and $[Cu_2(3\text{-}Me_3Sipyt)_2dppe_3]$ show IR absorptions typical of coordinated 2,2′-bipyridine [32] (*c.* 780 and 730 cm^{-1}), phenanthroline [32, 33] (*c.* 1512, 850 and 725 cm^{-1}) and 1,2-bis(diphenylphosphine)ethane [34] (*c.* 1705, 1480, 1170 and 1030 cm^{-1}).

NMR studies

The ^1H NMR spectra of $[M(3\text{-}Me_3Sipyt)_2]$ (M = Ni, Zn and Cd), $[Cu(3\text{-}Me_3Sipyt)]$ and $[Cu_2(3\text{-}Me_3Sipyt)_2\text{-}dppe_3]$ show four signals corresponding to the hydrogen atoms of the $3\text{-}Me_3Sipyt^-$ ligands (Table 5), but not the broad signal of the NH proton shown at 13.37 ppm by the free ligand spectrum. This confirms that in the complexes the ligands are deprotonated and coordinate in thiolate form. As in the corresponding pyridine-2-thione complexes [35], coordination simplifies the H_6 signal, and shifts it downfield; this may be interpreted as due to the loss of the NH proton and the N-coordination observed by X-ray diffraction in the case of $[Cd(3\text{-}Me_3Sipyt)_2]$.

TABLE 4. Selected IR spectroscopic data for compounds (cm^{-1})

Compounds	ν(C=C)	ν(C=N)	ν(Si–C)
$[Ni(3\text{-}Me_3Sipyt)_2]$	1560(s)	1540(m)	845(br, vs)
$[Ni(3\text{-}Me_3Sipyt)_2bipy]$	1555(s)	1530(s)	835(br, vs)
$[Ni(3\text{-}Me_3Sipyt)_2phen]\cdot 1.5H_2O$	1560(s)	1540(s)	845(br, vs)
$[Cu(3\text{-}Me_3Sipyt)]\cdot 0.5H_2O$	1560(s)	1540(s)	840(br, vs)
$[Cu_2(3\text{-}Me_3Sipyt)_2dppe_3]$	1555(s)	1535(s)	850(br, vs)
$[Zn(3\text{-}Me_3Sipyt)_2]$	1575(s)	1540(s)	845)br, vs)
$[Cd(3\text{-}Me_3Sipyt)_2]$	1565(s)	1540(s)	840(br, vs)

The ^1H NMR spectrum of $[Cu_2(3\text{-}Me_3Sipyt)_2(dppe)_3]$ contains a multiplet at 7.43–7.25 ppm for the diphosphine phenolic protons and a broad singlet at 2.18 ppm for the methylene protons. Due to partial masking by the more intense dppe signals, the only clearly distinguishable $3\text{-}Me_3Sipyt$ signals are those of H_5 and the methyl groups.

In the ^{13}C NMR spectra of the complexes, the upfield shift of the C_2 signal is probably due to a reduction in the order of the C–S bond [36], and is thus further evidence of the predominance of the thiolate form of the ligands in these complexes.

The ^{13}C NMR spectrum of $[Cu_2(3\text{-}Me_3Sipyt)_2dppe_3]$ shows signals at 135.0–128.6 ppm, for the aromatic dppe carbon atoms, and a multiplet at 25.8 ppm, attributed to the methylene carbons. The ^{31}P NMR spectrum shows a broad signal at −10.86 ppm which has shifted downfield from its position in the free ligand spectrum (−12.5 ppm) [37]. This shift is characteristic of bridging dppe [38], which suggests that the two copper atoms are linked by the dppe molecules.

Since further Cu(I) tends to have trigonal or tetrahedral environments, it is suggested that each copper atom coordinates tetrahedrally to three bridging dppe molecules and a single S-monodentate pyridine thiolato ligand.

Magnetic moments and electronic spectra

The diffuse reflectance spectrum of $[Ni(3\text{-}Me_3Sipyt)_2]$ has three bands (Table 5) attributable to the transitions $^1A_{1g} \rightarrow {}^1B_{1g}$ (15 750 cm^{-1}), $^1A_{1g} \rightarrow {}^1E_{1g}$ (20 830 cm^{-1}) and $^1A_{1g} \rightarrow {}^1A_{2g}$ (23 250 cm^{-1}), and exhibits diamagnetic behaviour. These findings suggest a square planar environment for the nickel atom, in agreement with X-ray diffraction results [14].

The effective magnetic moments at room temperature, μ_{eff} (2.8 for $[Ni(3\text{-}Me_3Sipyt)_2bipy]$ and 2.9 for $[Ni(3\text{-}Me_3Sipyt)_2phen]$) are compatible with an octahedral geometry around the nickel(II) centre. This interpretation is supported by the diffuse reflectance spectra of $[Ni(3\text{-}Me_3Sipyt)_2bipy]$ and $[Ni(3\text{-}Me_3Sipyt)_2phen]$, which display two bands at 10 500 and 17 000 cm^{-1} and a shoulder at 7000 cm^{-1}; these data are very similar to those of the mixed pyridine-2-thione/bipy complex $[Ni(pyt)_2bipy]$, the pseudo-octahedral structure of which has been confirmed by X-ray diffraction [12]. The lower

TABLE 5. NMR (^{1}H and ^{13}C) data for complexes

Compound	^{1}H				^{13}C					
	H_6	H_4	H_5	CH_3	C_2	C_6	C_3	C_4	C_5	CH_3
3-Me_3SipytH	7.62td	7.50dd	6.73t	0.31s	182.0	144.2	142.0	138.5	112.5	−1.3
[Zn(3-Me_3Sipyt)$_2$]	7.90d	7.55dd	6.89t	0.33s					116.3	−1.7
[Cd(3-Me_3Sipyt)2]	7.80dd	7.45dd	6.82dd	0.32s	177.7	147.3	142.7	133.3	116.1	−1.4

^{a}In DMSO-d_6 as solvent.

energy band may be attributed to the transition, $^{3}A_{2g} \rightarrow {}^{3}T_{2g}$ (ν_1), the higher to $^{3}A_{2g} \rightarrow {}^{3}T_{1g}$ (F) (ν_2), and the shoulder to the splitting of ν_1, as a consequence of the distortion of the octahedral geometry [39].

Supplementary material

Crystallographic data have been deposited as Supplementary Publication No. CSD 57022. Copies can be obtained through the Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen, Germany.

Acknowledgement

We thank the Xunta de Galicia (XUGA20306B91), Spain, for financial support.

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