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Electrochemical synthesis and structural characterisation of zinc, cadmium and mercury complexes of heterocyclic bidentate ligands (N, S)†

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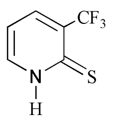
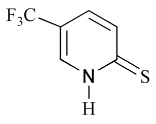
The electrochemical oxidation of anodic metal (zinc or cadmium) in acetonitrile solutions of 3-trifluoromethylpyridine-2-thione (3-CF_3-pySH) or 5-trifluoromethylpyridine-2-thione (5-CF_3-pySH) affords complexes [M(R-pyS)$_2$], M = Zn, Cd, R = 3-CF_3, 5-CF_3. Adducts of these compounds with 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen) were also obtained when the bidentate coligand was present in the cell. On the other hand, reaction of a methanol solution of mercury acetate with the corresponding pyridine-2-thione in the presence of triethylamine affords compounds of composition [Hg(R-pyS)$_2$]. All the compounds obtained have been characterised by microanalysis, IR spectroscopy and, in cases where the compound was sufficiently soluble, by ^{1}H, ^{13}C and ^{199}Hg NMR spectroscopy. The compounds [Zn(3-CF_3-pyS)$_2$(bipy)] (**1**), [Zn(3-CF_3-pyS)$_2$(phen)]·CH_3CN (**2**), [Zn(5-CF_3-pyS)$_2$(bipy)] (**3**), [Cd(3-CF_3-pyS)$_2$(DMF)]$_2$ (**4**), [Cd_2(5-CF_3-pyS)$_4$(DMF)]$_n$ (**5**), [Cd(3-CF_3-pyS)$_2$(bipy)]·CH_3CN (**6**), [Hg(3-CF_3-pyS)$_2$] (**7**) and [Hg(5-CF_3-pyS)$_2$] (**8**) were also characterised by X-ray diffraction.

Introduction

Much of the interest in metal–sulfur chemistry results from the potential relevance of resulting compounds to active sites in metalloenzymes and also to their ability to adopt various nuclearities of significant structural complexity.[1–5] However, in comparison with the coordination chemistry of transition metals, the chemistry of the main group metals with sulfur ligands remains much less developed.[6] In many cases, the interaction of toxic metals with biological systems involves bonding of the metal to the sulfhydryl groups present in enzymes. Hence, an insight into the chemistry of main group thiolate compounds is important in terms of understanding the aforementioned interaction and for the design of detoxifying agents.[7,8] In the case of zinc and cadmium, their neutral bischalcogenato complexes [M(ER)$_2$], M = Zn, Cd, E = S, Se, generally form infinite lattices with bridging ligands and tetrahedral metal centers.[9] The polymeric nature of these compounds renders them materials of low volatility. The volatility may be enhanced by modifying the degree of aggregation of these species through blocking some coordination sites, either with donor atoms from the thiolate ligand or from additional coligands. The aggregation phenomena may also be controlled by steric constraints produced by appropriate ligand design. In previous studies we have used this strategy for the synthesis of monomeric[10] and dimeric compounds[11] of zinc and cadmium with several trialkylsilylpyridine-2-thione ligands. These ligands show a wide versatility in their coordination forms, acting as neutral monodentate systems,[12] bridging through S,[13] anionic S-monodentate,[14] chelating[15] or bridging between two[16] or three metal atoms.[17] This versatility yields numerous complexes with unusual geometries, variable nuclearities and great structural diversity.[1] On the other hand, there is experimental evidence that the nature and location of the substituent in the heterocyclic ring is important in determining the structure of the metal–pyridinethionate complexes.[10,11,18] As a result of our continued interest in the coordination chemistry of thionate ligands, the work described here encompasses the synthesis and characterisation of zinc, cadmium and mercury complexes with 3-trifluoromethyl- and 5-trifluoromethylpyridine-2-thionato ligands.


3-CF_3-pySH


5-CF_3-pySH

Experimental

General considerations

All manipulations were carried out under an inert atmosphere of dry nitrogen. Zinc and cadmium (Aldrich Chemie) were used as plates (*ca.* 2 × 2 cm). 3-CF_3-pySH, 5-CF_3-pySH, 1,10-phenanthroline and 2,2′-bipyridine were commercial products and were used as supplied.

Elemental analysis was performed using a Carlo-Erba EA microanalyser. 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 MHz instrument using $CDCl_3$ as solvent. Chemical shifts were recorded against TMS as the internal standard. ^{119}Hg NMR spectra were recorded on a Bruker AMX500 spectrometer using $CDCl_3$ as solvent. The mass spectra (FAB) were recorded on Micromass Autospec spectrometer, with 3-nitrobenzyl alcohol as the matrix material.

Electrochemical synthesis

An acetonitrile solution of the ligand, containing about 15 mg of tetramethylammonium perchlorate as a current carrier, was electrolysed using a platinum wire as the cathode and a metal plate as the sacrificial anode. For the synthesis of mixed complexes, the corresponding coligand was also added to the solution. Applied voltages of 10–15 V allowed sufficient current flow for smooth solution of the metal. During electrolysis, nitrogen was bubbled through the solution to provide an inert atmosphere and also to stir the reaction mixture. The cell can be summarised as $Pt_{(-)}/CH_3CN + R\text{-pySH}/M_{(+)}$.

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† Dedicated to the memory of Professor C. A. McAuliffe, a good friend and a teacher.

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[Zn(3-CF$_3$-pyS)$_2$]. Electrochemical oxidation of a zinc anode in a solution of 3-CF$_3$-pySH (0.267 g, 1.492 mmol) in acetonitrile (50 cm^3) at 20 V and 20 mA for 2 h caused 44.4 mg of zinc to be dissolved, E_f = 0.46 mol F^{-1}. During the electrolysis process, hydrogen was evolved at the cathode and at the end of the reaction an insoluble yellow crystalline solid was observed at the bottom of the vessel. The solid was filtered off, washed with acetonitrile and diethyl ether, and dried under vacuum. Yield 0.236 g (75%). Anal. Calc. for $C_{12}H_6ZnF_6N_2S_2$: C, 34.2; H, 1.4; N, 6.7. Found: C, 34.5; H, 1.4; N, 6.8%. IR (cm^{-1}): 1600(s), 1530(m), 1450(m), 1420(s), 1170(s), 1140(s), 1125(s), 1110(s), 1008(m), 742(w), 720(m), 640(w). ^{1}H NMR (CDCl$_3$): δ 8.23 (d, 1H), 7.62 (t, 1H), 7.39 (d, 1H).

[Zn(5-CF$_3$-pyS)$_2$]. 5-CF$_3$-pySH (0.267 g, 1.492 mmol), 20 V, 20 mA, 2 h, 45.37 mg of metal dissolved, E_f = 0.47 mol F^{-1}. Yield 0.170 g (54%). Anal. Calc. for $C_{12}H_6ZnF_6N_2S_2$: C, 34.2; H, 1.4; N, 6.7. Found: C, 34.5; H, 1.4; N, 6.8%. IR (cm^{-1}): 1600(m), 1540(m), 1460(s), 1170(s), 1140(s), 1120(s), 1105(s), 1075(m), 1030(m), 740(w), 715(w), 660(w), 610(w). ^{1}H NMR (CDCl$_3$): δ 8.22 (s, 1H), 7.61 (d, 1H), 7.36 (d, 1H).

[Zn(3-CF$_3$-pyS)$_2$(bipy)]. The ligand (0.267 g, 1.492 mmol), 2,2′-bipyridine (0.233 g, 1.493 mmol), 20 mA, 20 V, 2 h, 45.87 mg of metal dissolved, E_f = 0.47 mol F^{-1}. Yield 0.244 g (57%). Anal. Calc. for $C_{22}H_{14}ZnF_6N_4S_2$: C, 45.7; H, 2.4; N, 9.7. Found: C, 45.5; H, 2.7; N, 10.1%. IR (cm^{-1}): 1580(s), 1540(s), 1480(w), 1460(m), 1430(m), 1155(s), 1130(s), 1120(s), 1100(m), 1060(m), 1015(m), 750(m) 720(m), 650(w), 630(w), 760(m), 730(m). ^{1}H NMR (CDCl$_3$): δ 8.22 (d, 1H), 7.50 (t, 1H), 7.40 (d, 1H), 8.89 (d, 1H), 8.68 (d, 1H), 8.29 (m, 1H), 8.02 (m, 1H). Crystals of [Zn(3-CF$_3$-pyS)$_2$(bipy)] (**1**) suitable for X-ray studies were obtained by crystallisation of the initial product from acetonitrile.

[Zn(3-CF$_3$-pyS)$_2$(phen)]. 5-CF$_3$-pySH (0.267 g, 1.493 mmol), 1,10-phenanthroline (0.295 g, 1.63 mmol), 20 V, 20 mA, 2 h, 46.84 mg of metal dissolved, E_f = 0.48 mol F^{-1}. Yield 0.250 g (56%). Anal. Calc. for $C_{24}H_{14}ZnF_6N_4S_2$: C, 47.9; H, 2.3; N, 9.3. Found: C, 47.7; H, 2.2; N, 9.6%. IR (cm^{-1}): 1590(s), 1540(m), 1480(w), 1460(m), 1430(m), 1130(s), 1120(s), 1100(s), 1060(m), 1015(m), 750(m), 720(w), 650(w), 630(w), 1580(s), 821(m), 760(m). ^{1}H NMR (CDCl$_3$): δ 8.21 (d, 1H), 7.60 (t, 1H), 7.39 (d, 1H), 8.75 (d, 1H), 8.40 (d, 1H), 8.00 (s, 1H), 7.52 (m, 1H). Crystals of [Zn(3-CF$_3$-pyS)$_2$(phen)]·CH$_3$CN (**2**) suitable for X-ray studies were obtained by concentration of the solution.

[Zn(5-CF$_3$-pyS)$_2$(bipy)]. The ligand (0.267 g, 1.492 mmol), 2-2′-bipyridine (0.233 g, 1.493 mmol), 20 mA, 20 V, 2 h, 45.87 mg of metal dissolved, E_f = 0.47 mol F^{-1}. Yield 0.226 g (52%). Anal. Calc. for $C_{22}H_{14}ZnF_6N_4S_2$: C, 45.7; H, 2.4; N, 9.7. Found: C, 45.9; H, 2.6; N, 9.9%. IR (cm^{-1}): 1580(s), 1545(m), 1440(w), 1420(m), 1160(s), 1125(s), 1100(m), 1065(m), 1030(m), 745(m), 720(m), 660(w), 640(w), 780(m), 725(m). ^{1}H NMR (CDCl$_3$): δ 8.21 (s, 1H), 7.61 (d, 1H), 7.36 (d, 1H), 8.79 (d, 1H), 8.51 (d, 1H), 8.12 (m, 1H), 7.59 (m, 1H). Crystals of [Zn(5-CF$_3$-pyS)$_2$(bipy)] (**3**) suitable for X-ray studies were obtained directly from the cell.

[Zn(5-CF$_3$-pyS)$_2$(phen)]. The ligand (0.267 g, 1.492 mmol), 1,10-phenanthroline (0.295 g, 1.638 mmol), 20 mA, 20 V, 2 h, 45.86 mg of metal dissolved, E_f = 0.47 mol F^{-1}. Yield 0.290 g (65%). Anal. Calc. for $C_{24}H_{14}ZnF_6N_4S_2$: C, 47.9; H, 2.3; N, 9.3. Found: C, 48.1; H, 2.4; N, 9.5%. IR (cm^{-1}): 1590(s), 1545(m), 1460(m), 1420(w), 1150(s), 1130(s), 1110(s), 1070(s), 1020(m), 1010(m), 740(w), 715(w), 660(w), 620(w), 1500(m), 830(m), 730(m). ^{1}H NMR (CDCl$_3$): δ 8.20 (s, 1H), 7.60 (d, 1H), 7.38 (d, 1H), 8.90 (d, 1H), 8.29 (d, 1H), 8.08 (s, 1H), 7.88 (m, 1H).

[Cd(3-CF$_3$-pyS)$_2$]. The ligand (0.278 g, 1.553 mmol), 10 mA, 20 V, 2 h, 44.45 mg of metal dissolved, E_f = 0.53 mol F^{-1}. Yield 0.275 g (75%). Anal. Calc. for $C_{12}H_6CdF_6N_2S_2$: C, 30.7; H, 1.3; N, 6.0. Found: C, 31.0; H, 1.1; N, 6.0%. IR (cm^{-1}): 1580(m), 1555(m), 1440(w), 1400(s), 1160(m), 1130(s), 1110(m), 1065(m), 1035(m), 750(m), 720(m), 660(w). ^{1}H NMR (CDCl$_3$): δ 8.06 (d, 1H), 7.80 (d, 1H), 6.98 (m, 1H). Crystals of [Cd(3-CF$_3$-py)$_2$-(DMF)]$_2$ (**4**) suitable for X-ray studies were obtained by crystallisation of the initial product from dimethylformamide.

[Cd(5-CF$_3$-pyS)$_2$]. The ligand (0.278 g, 1.553 mmol), 10 mA, 20 V, 2 h, 42.6 mg of metal dissolved, E_f = 0.51 mol F^{-1}. Yield 0.262 g (72%). Anal. Calc. for $C_{12}H_6CdF_6N_2S_2$: C, 30.7; H, 1.3; N, 6.0. Found: C, 31.5; H, 1.3; N, 6.4%. IR (cm^{-1}): 1600(s), 1445(w), 1405(s), 1170(m), 1140(m), 1130(m), 1110(m), 1072(m), 745(w), 715(w), 650(w). ^{1}H NMR (CDCl$_3$): δ 8.10 (s, 1H), 7.63 (d, 1H), 7.40 (d, 1H). Crystals of [Cd$_2$(5-CF$_3$-pyS)$_4$-(DMF)] (**5**) suitable for X-ray studies were obtained by crystallisation of the initial product from dimethylformamide.

[Cd(3-CF$_3$-pyS)$_2$(bipy)]. The ligand (0.278 g, 1.553 mmol), 2,2′-bipyridine (0.243 g, 1.558 mmol), 20 mA, 20 V, 2 h, 104.0 mg of metal dissolved, E_f = 0.62 mol F^{-1}. Yield 0.320 g (66%). Anal. Calc. for $C_{22}H_{14}CdF_6N_4S_2$: C, 42.3; H, 2.2; N, 9.0. Found: C, 43.6; H, 2.2; N, 9.3%. IR (cm^{-1}): 1580(m), 1550(m), 1480(w), 1465(w), 1435(m), 1400(s), 1160(s), 1120(s), 1110(m), 1070(m), 1030(m), 1010(m), 750(m), 720(m), 650(w), 625(w), 760, 730. ^{1}H NMR (CDCl$_3$): δ 8.05 (d, 1H), 7.80 (d, 1H), 6.97 (m, 1H), 8.75 (d, 1H), 8.47 (d, 1H), 8.03 (m, 1H), 7.60 (m, 1H). Crystals of [Cd(3-CF$_3$-pyS)$_2$(bipy)]·CH$_3$CN (**6**) suitable for X-ray studies were obtained by crystallisation of the initial product from acetonitrile.

[Cd(3-CF$_3$-pyS)$_2$(phen)]. The ligand (0.278 g, 1.553 mmol), 1,10-phenanthroline (0.308 g, 1.711 mmol), 20 mA, 20 V, 2 h, 100.63 mg of metal dissolved, E_f = 0.60 mol F^{-1}. Yield 0.310 g (61%). Anal. Calc. for $C_{24}H_{14}CdF_6N_4S_2$: C, 44.4; H, 2.2; N, 8.6. Found: C, 44.4; H, 2.4; N, 8.5%. IR (cm^{-1}): 1610(s), 1540(m), 1505(m), 1440(w), 1420(m), 1160(s), 1125(s), 1100(m), 1065(m), 1020(m), 748(m), 718(m), 650(w), 638(w), 1580(m), 845(m), 730(m). ^{1}H NMR (CDCl$_3$): δ 8.10 (d, 1H), 7.80 (d, 1H), 6.93 (m, 1H), 9.19 (d, 1H), 8.80 (d, 1H), 8.22 (s, 1H), 8.03 (m, 1H).

[Cd(5-CF$_3$-pyS)$_2$(bipy)]. The ligand (0.278 g, 1.553 mmol), 2,2′-bipyridine (0.243 g, 1.558 mmol), 20 mA, 20 V, 2 h, 83.86 mg of metal dissolved, E_f = 0.50 mol F^{-1}. Yield 0.260 g (54%). Anal. Calc. for $C_{22}H_{14}CdF_6N_4S_2$: C, 42.3; H, 2.2; N, 9.0. Found: C, 42.5; H, 2.3; N, 9.3%. IR (cm^{-1}): 1595(s), 1570(m), 1530(m), 1480(w), 1460(m), 1162(m), 1140(m), 1110(s), 1060(m), 1040(w), 1010(m), 745(m), 732(m), 650(w), 785(m), 760(m). ^{1}H NMR (CDCl$_3$): δ 8.10 (s, 1H), 7.60 (d, 1H), 7.50 (d, 1H), 8.70 (d, 1H), 8.45 (d, 1H), 8.00 (m, 1H), 7.50 (m, 1H).

[Cd(5-CF$_3$-pyS)$_2$(phen)]. The ligand (0.278 g, 1.553 mmol), 1,10-phenanthroline (0.308 g, 1.711 mmol), 20 mA, 20 V, 2 h, 90.6 mg of metal dissolved, E_f = 0.54 mol F^{-1}. Yield 0.280 g (55%). Anal. Calc. for $C_{24}H_{14}CdF_6N_4S_2$: C, 44.4; H, 2.2; N, 8.6. Found: C, 45.6; H, 2.1; N, 9.0%. IR (cm^{-1}): 1602(s), 1537(m), 1462(m), 1425(s), 1130(m), 1112(s), 1073(m), 1009(m), 746(w), 638(w), 1513(m), 839(m), 726(m). ^{1}H NMR (CDCl$_3$): δ 8.20 (s, 1H), 8.05 (d, 1H), 7.75 (d, 1H), 9.20 (d, 1H), 8.80 (d, 1H), 8.00 (s, 1H), 7.70 (m, 1H).

[Hg(3-CF$_3$-pyS)$_2$]. A solution of 3-CF$_3$-pySH (0.200 g, 1.117 mmol) and NEt$_3$ (0.170 mL, 1.680 mmol) in methanol (10 mL) was heated under reflux and a solution of mercury acetate (0.178 g, 0.558 mmol) in methanol (10 mL) was added. A white solid formed immediately and the reaction mixture was stirred for 4 h. The solid was filtered off, washed with ethanol and diethyl ether and dried under vacuum. Yield 0.176 g (57%). Anal. Calc. for $C_{12}H_6HgF_6N_2S_2$: C, 25.9; H,1.1; N, 5.0; S, 11.5.

Found: C, 26.2; H, 1.1; N, 5.1; S 11.5%. Mass spectrum (FAB): *m*/*z* 557.0 (M^+). IR (cm^{-1}): 1584(m), 1551(m), 1404(s), 1314(s), 1173(s), 1129(s), 1010(s), 746(m), 646(m). ^1H NMR ($CDCl_3$): δ 8.27 (dd, 2H), 7.84 (dd, 2H), 7.12 (dd, 2H). ^{13}C NMR ($CDCl_3$): δ 163.0 (pyridine C^2); 150.3 (pyridine C^6); 135,3 (pyridine C^4); 128.8 (pyridine C^3); 125.6 (CF_3); 119.5 (pyridine C^5). ^{199}Hg NMR ($CDCl_3$), δ −1191. Crystals of [Hg(3-CF_3-pyS)$_2$] (**7**) suitable for X-ray studies were obtained from the mother liquor.

[Hg(5-CF_3-pyS)$_2$]. Similar procedure to that described for compound [Hg(3-CF_3-pyS)$_2$]: 5-CF_3-pySH (0.200 g, 1.117 mmol), NEt_3 (0.170 mL, 1.680 mmol) and mercury acetate (0.178 g, 0.558 mmol) in methanol gave a microcrystalline white solid. The solid was filtered off, washed with methanol and diethyl ether and dried under vacuum. Yield 0.166 g (54%). Anal. Calc. for $C_{12}H_6HgF_6N_2S_2$: C, 25.9; H, 1.1; N, 5.0; S, 11.5. Found: C, 26.9; H, 1.1; N, 5.2; S, 11.4%. Mass spectrum (FAB): *m*/*z* 557.0 (M^+). IR (cm^{-1}): 1597(s), 1553(m), 1464(m), 1379(m), 1327(s), 1168(m), 1112(s), 1075(m), 744(m), 638(m), 607(m). ^1H NMR ($CDCl_3$): δ 8.41 (s, 2H), 7.66 (dd, 2H), 7.41 (dd, 2H). ^{13}C NMR ($CDCl_3$): δ 168.1 (pyridine C^2; 144.8 (pyridine C^6); 133.6 (pyridine C^4); 125,5 (pyridine C^5); 123.0 (pyridine C^3); 121.9 (CF_3). ^{199}Hg NMR ($CDCl_3$), δ −1192. Crystals of [Hg-(5-CF_3-pyS)$_2$] (**8**) suitable for X-ray studies were obtained by crystallisation of the initial product from diethyl ether.

X-Ray crystallography

X-Ray data were collected on an Enraf Nonius CAD4 diffractometer for (**1**) and (**2**), and on a Smart-CCD-1000 Bruker diffractometer for (**3**)–(**8**), both with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The data were collected at 293 K for all structures. The ω scan technique was employed to measure intensities for all crystals. Decomposition of the crystals did not occur during data collection. Corrections were applied for Lorenz and polarisation effects and for absorption.

The structures were solved by direct methods, missing atoms were located in the difference Fourier maps and included in subsequent refinement cycles. The structures were refined by full-matrix least-squares refinement on F^2, using anisotropic displacement parameters for all non-hydrogen atoms. In all cases, hydrogen atoms were included using a riding model with C–H distances of 0.93–0.97 Å and fixed isotropic thermal parameters. A weighting scheme of the form $w = 1/\sigma^2(F)$ was introduced and the refinement proceeded smoothly to convergence.

Crystallographic programs used for the structure solutions and refinement were those included in SHELX97.[19] Atomic scattering factors and anomalous dispersion corrections for all atoms were taken from International Tables for X-ray Crystallography.[20] The crystal data and summary of data collection and structure refinement for these compounds are given in Table 1, and Ortep3 drawings,[21] along with the numbering scheme used, are shown in Figs. 1–5 and 7–9.

CCDC reference numbers 189578–189585.

See http://www.rsc.org/suppdata/dt/b3/b300133b/ for crystallographic data in CIF or other electronic format.

Results and discussion

Zinc and cadmium complexes of general formula [M(R-pyS)$_2$], R = 3-CF_3, 5-CF_3, and some adducts with 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen) (not all permutations were synthesised), were easily prepared in good yield by the simple one-step electrochemical procedure described above.

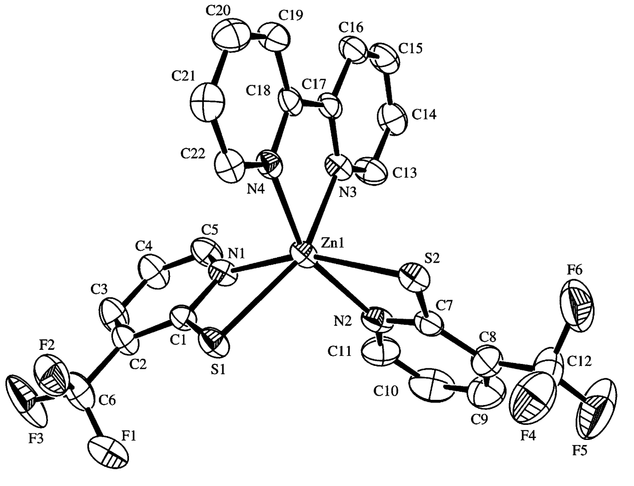

Fig. 1 The molecular structure of [Zn(3-CF_3-pyS)$_2$(bipy)] (**1**).

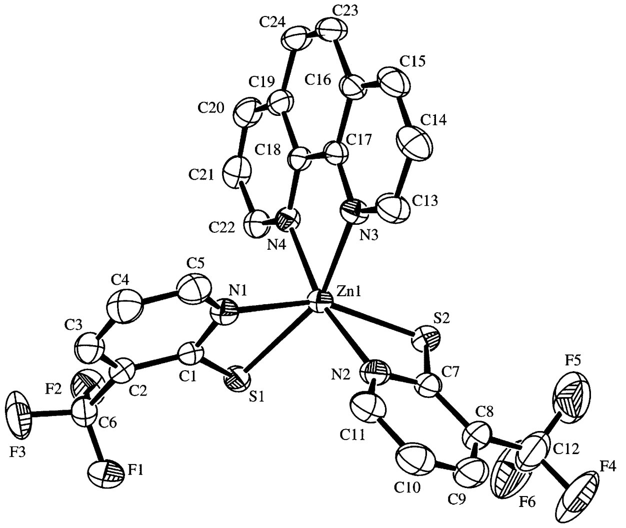

Fig. 2 The molecular structure of [Zn(3-CF_3-pyS)$_2$(phen)]·CH_3CN (**2**).

The metal compounds are moderately soluble in the reaction medium and, in some cases, they are obtained as crystalline air-stable solids at the bottom of the cell. The compounds are insoluble in non-polar solvents but soluble in polar solvents such as dimethylsulfoxide or *N*,*N*′-dimethylformamide and, in some cases, crystallisation from these solvents provides crystals that are suitable for X-ray diffraction.

The electrochemical efficiency, defined as the amount of metal dissolved per Faraday of charge, was in all cases close to 0.5 mol F^{-1}. This is consistent with the following reaction schemes:

Cathode: $2\ \text{R-pySH} + 2e^- \rightarrow 2\ \text{R-pyS}^- + H_2$
Anode: $2\ \text{R-pyS}^- + M \rightarrow [M(\text{R-pyS})_2] + 2e^-$
or
$2\ \text{R-pyS}^- + M + L' \rightarrow [M(\text{R-pyS})_2L']$
(M = Zn, Cd; R = 3-CF_3, 5-CF_3; L' = bipy, phen)

The mercury thionates were readily prepared by reacting a methanol solution of mercury acetate with a solution of the pyridine-2-thione in the presence of triethylamine. The analytical data of the isolated complexes show them to have a formulation [Hg(R-pyS)$_2$].

Molecular structures of [Zn(3-CF_3-pyS)$_2$(bipy)] (1), [Zn(3-CF_3-pyS)$_2$(phen)]CH_3CN (2), [Zn(5-CF_3-pyS)$_2$(bipy)] (3) and [Cd(3-CF_3-pyS)$_2$(bipy)]CH_3CN (6).

Figs. 1–4 show perspective views of the molecular structures of **1**,**2**,**3** and **6** along with the atom labelling schemes used. Crystallographic data and a selection of bond distances and angles (with the estimated standard deviations) are given in Tables 1–3.

Table 1 Summary of crystal data and structure refinement

	(1)	**(2)**	**(3)**	**(4)**	**(5)**	**(6)**	**(7)**	**(8)**
Formula	$C_{22}H_{14}F_6N_4S_2Zn$	$C_{26}H_{17}F_6N_5S_2Zn$	$C_{11}H_7F_3N_2SZn_{0.5}$	$C_{15}H_{13}CdF_6N_3OS_2$	$C_{27}H_{19}Cd_2F_{12}N_5OS_4$	$C_{24}H_{17}CdF_6N_5S_2$	$C_{12}H_6HgF_6N_2S_2$	$C_{12}H_6HgF_6N_2S_2$
M	577.86	642.94	288.93	541.80	1010.51	665.95	556.90	556.90
Wavelength/Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Temperature/K	293(2)	295(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
Crystal symmetry	Triclinic	Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$Pbca$	$P2_1/c$
a/Å	8.261(4)	11.0734(17)	6.5755(11)	8.1086(17)	11.4195(16)	13.680(3)	7.5788(15)	14.639(6)
b/Å	13.050(7)	11.1806(17)	8.3861(14)	11.338(2)	12.4903(17)	9.7564(18)	18.800(4)	15.075(6)
c/Å	13.345(7)	11.8543(18)	20.4490(30)	12.460(3)	14.651(2)	20.410(4)	21.479(4)	6.934(6)
α/°	67.986(8)	92.975(2)	90	109.534(5)	64.648(4)	90	90	90
β/°	85.496(8)	108.253(2)	97.060(3)	105.748(5)	69.447(4)	90.684(3)	90	92.085(8)
γ/°	82.258(8)	102.908(2)	90	96.928(5)	77.377(4)	90	90	90
V/Å^3	1321.0(12)	1346.8(4)	1119.1(3)	1010.5(4)	1762.5(4)	2723.9(9)	3060.5(11)	1529.3(11)
Z	2	2	4	2	2	4	8	4
D_c/Mg m^{-3}	1.453	1.585	1.715	1.781	1.904	1.624	2.417	2.419
μ(Mo-Kα)/mm^{-1}	1.147	1.135	1.353	1.351	1.539	1.019	10.392	10.398
F(000)	580	648	580	532	984	1320	2064	1032
Crystal size/mm	0.51 × 0.24 × 0.05	0.62 × 0.38 × 0.22	0.26 × 0.15 × 0.14	0.32 × 0.16 × 0.05	0.52 × 0.29 × 0.20	0.54 × 0.33 × 0.32	0.37 × 0.19 × 0.11	0.64 × 0.12 × 0.04
θ Limits/°	1.65–24.71	1.82–28.31	2.01–26.41	1.84–30.65	1.81–30.58	1.78–28.25	1.90–26.39	1.94–26.43
Collected reflections	4500	6395	2287	18110	33971	6377	18043	6620
Unique reflections (R_{int})	4500 (0.000)	6395 (0.0000)	2287 (0.0000)	6166 (0.0647)	10697 (0.0352)	6377 (0.0000)	3136 (0.0699)	3124 (0.0362)
Observed reflections [$F_o > 2\sigma(F_o)$]	4500	6395	1667	3012	7627	6377	3136	3124
Goodness of fit on F^2	1.038	1.036	0.985	0.819	1.003	1.052	1.043	0.926
$R_1(F)$,[a] [$I > 2\sigma(I)$]	0.0539	0.0312	0.0291	0.0340	0.0319	0.0294	0.0284	0.0454
$wR_2(F^2)$,[b] [$I > 2\sigma(I)$]	0.1491	0.0766	0.0697	0.0551	0.0758	0.0693	0.0567	0.1218
Largest diff. peak, hole/e Å^{-3}	0.727, −0.518	0.381, −0.273	0.28, −0.29	0.52, −0.57	0.74, −0.56	0.245, −0.392	0.65, −0.87	1.85, −2.11

[a] $R_1 = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|]$. [b] $wR_2 = [\Sigma(F_o^2 - F_c^2)/\Sigma(F_o^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = (F_o^2 + 2F_c^2)/3$.

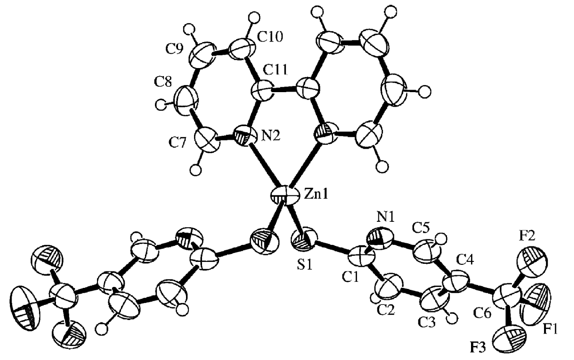

Fig. 3 The molecular structure of [Zn(5-CF_3-pyS)$_2$(bipy)] (**3**).

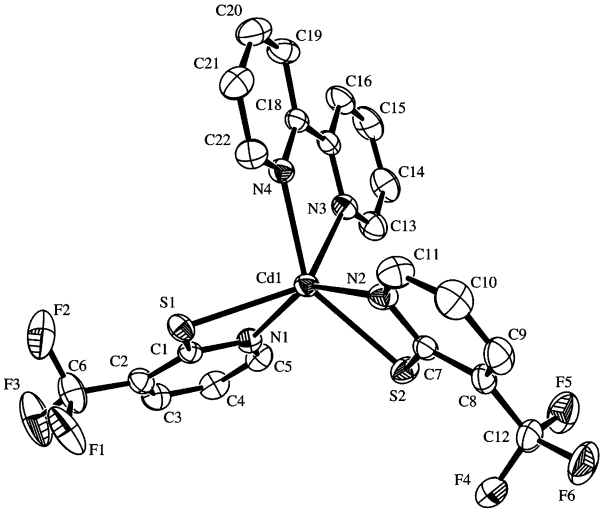

Fig. 4 The molecular structure of [Cd(3-CF_3-pyS)$_2$(bipy)]·CH_3CN (**6**).

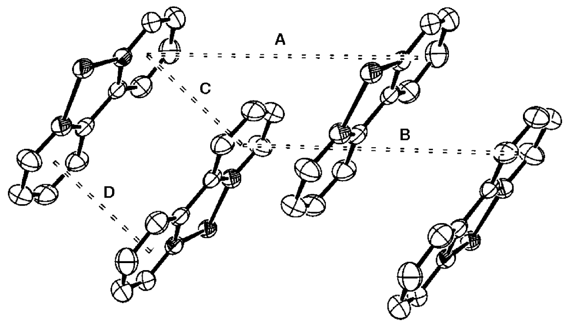

Fig. 5 Partial packing diagram of **1**, showing the interannular distances in the lattice.

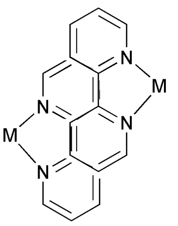

Fig. 6 Overlapping between bipyridine rings of two neighbouring molecules of **1**.

Table 2 Selected bond distances (Å) and angles (°) for [Zn(3-CF_3-pyS)$_2$(bipy)] (**1**), [Zn(3-CF_3-pyS)$_2$(phen)]·CH_3CN (**2**) and [Cd(3-CF_3-pyS)$_2$(bipy)]·CH_3CN (**6**)

	(**1**)	(**2**)	(**6**)
M(1)–S(1)	2.5602(19)	2.5602(7)	2.5875(8)
M(1)–S(2)	2.4770(19)	2.4781(7)	2.5311(8)
M(1)–N(1)	2.138(4)	2.1934(17)	2.517(2)
M(1)–N(2)	2.241(5)	2.2111(17)	2.576(2)
M(1)–N(3)	2.209(4)	2.1913(16)	2.366(2)
M(1)–N(4)	2.144(4)	2.1603(16)	2.353(2)
S(1)–C(1)	1.719(5)	1.718(2)	1.738(3)
S(2)–C(7)	1.727(6)	1.724(2)	1.724(3)
S(2)–M(1)–S(1)	105.15(5)	103.669(19)	119.89(3)
N(1)–M(1)–S(1)	65.97(12)	65.52(4)	61.61(5)
N(1)–M(1)–S(2)	158.59(13)	154.62(5)	93.94(5)
N(2)–M(1)–S(2)	65.96(13)	66.63(5)	61.50(5)
N(2)–M(1)–S(1)	102.90(12)	100.15(5)	111.82(6)
N(4)–M((1)–N(1)	103.56(16)	95.66(6)	123.73(7)
N(4)–M(1)–S(1)	97.29(12)	93.55(4)	93.63(5)
N(3)–M(1)–S(2)	98.25(12)	100.11(5)	101.68(6)
N(3)–M(1)–S(1)	156.15(12)	156.05(5)	127.75(6)
N(3)–M(1)–N(2)	90.67(16)	91.79(6)	115.43(8)
N(4)–M(1)–S(2)	96.78(11)	108.25(4)	139.37(5)
N(1)–M(1)–N(2)	96.16(17)	91.88(7)	148.61(7)
N(4)–M(1)–N(2)	156.20(16)	166.15(6)	86.13(7)
N(3)–M(1)–N(1)	93.42(16)	93.63(6)	87.05(7)
N(4)–M(1)–N(3)	75.13(16)	76.18(6)	69.10(8)

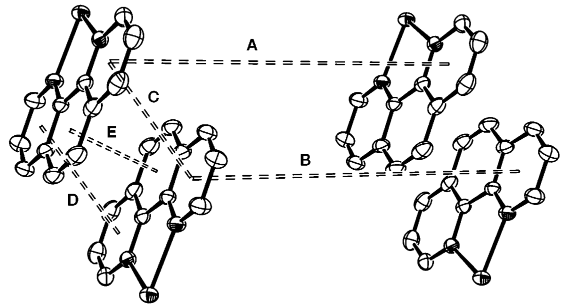

Fig. 7 Partial packing diagram of **2**, showing the interannular distances in the lattice.

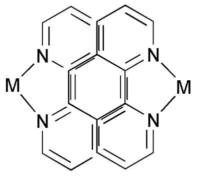

Fig. 8 Overlapping between phenanthroline rings of two neighbouring molecules of **2**.

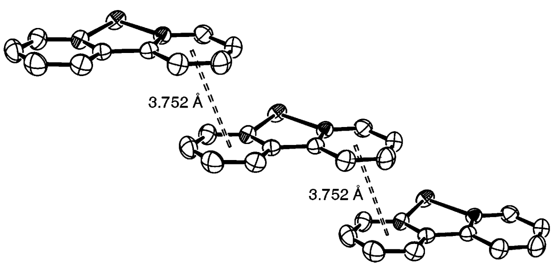

Fig. 9 Partial packing diagram of **3**, showing the interannular distances in the lattice.

In all four cases the crystal structure consists of discrete molecular species. This fact shows that the presence of an additional bidentate coligand inhibits the polymerisation of the compound. Despite the similarities between the ligands, the three compounds have different structures depending on the position of the trifluoromethyl group in the heterocyclic ring. For example, in the cases of compounds **1**, **2** and **6**, all of which contain a trifluoromethyl group in the 3-position, the metal atom is hexacoordinated by the chelating nitrogen ligand (bipy or phen) and two anionic pyridine-2-thionate ligands, which also act in a bidentate manner (S,N). In this way the metal atom is in an [S_2N_4] distorted octahedral environment. These two

Table 3 Selected bond distances (Å) and angles (°) for [Zn(5-CF$_3$-pyS)$_2$(bipy)] (**3**)

Zn(1)–S(1)	2.3117(6)	Zn(1)–N(2)	2.1023(17)
S(1)–C(1)	1.731(2)	N(1)–C(5)	1.330(3)
N(2)–Zn(1)–N(2)[a]	77.58(9)	N(2)–Zn(1)–S(1)	103.45(5)
N(2)–Zn(1)–S(1)[a]	124.94(5)	S(1)–Zn(1)–S(1)[a]	117.80(5)

[a] Symmetry transformation used to generate equivalent atoms: $-x + 2$, y, $-z + 1/2$.

compounds differ in the disposition of the thiolate sulfur atoms, which are *cis* in complexes **1** and **6** but *trans* in **2**.

In complex **3** the trifluoromethyl group is in the 5-position of the heterocyclic ring and, in this case, the metal is in a distorted tetrahedral [S$_2$N$_2$] environment. The metal is coordinated by one bipyridine molecule, which acts in a bidentate manner, and by two anionic pyridine-2-thionate ligands, which in this case act in a monodentate fashion and coordinate to the metal through the sulfur atom only. The pyridine nitrogen atom of this ligand is 2.8143(19) Å from the zinc centre, a distance that is significantly longer than the sum of the covalent radii of zinc and nitrogen. It is worth noting that the different coordinative behaviour observed in the thiolate ligands in these two cases is also observed in the cadmium complexes to be discussed later.

At this moment it is not possible to provide an explanation for the different coordination behaviours observed in these complexes upon changing the position of the trifluoromethyl group.

The four complexes discussed above all show significant deviations from regular geometries and the main causes of this are the small angles of the chelate rings. In the hexacoordinated complexes the values of the four-membered chelate ring bond angles, S–Zn–N, are in the range 65.97–65.52° and the bond angles S–Cd–N are 61.50(5) and 61.61(5)°. Similarly, the bond angles N–M–N (five-membered rings) are 75.13(16), 76.18(6), 77.58(9) and 69.10(8)° in **1**, **2**, **3** and **6**, respectively. These values are in the expected range for zinc or cadmium complexes containing this type of chelating nitrogen ligand.[22]

The metal–ligand bond distances are dependent on the coordination number of the metal as a consequence of the monodentate or chelating nature of the thiolate ligand. The Zn–S bond distance in **3** [2.3117(6) Å] is significantly shorter than the average values [2.5186(19) and 2.5192(7) Å, respectively] found for the corresponding distances in the hexacoordinated complexes **1** and **2**. This observation is undoubtedly due to the lower coordination number in the former complex. In all cases, however, the distances found are within the ranges reported for tetracoordinated (2.25–2.36 Å)[23] or hexacoordinated (2.54–2.67 Å)[22,24] zinc complexes with thiolate ligands. Similar effects are seen on considering the bond distances between the zinc and the nitrogen atoms of the chelating ligands. In all cases the bond distances are close to the value (2.085–2.291 Å) found in zinc complexes with ligands derived from pyridine.[22,25]

The Cd–S bond distances [2.5875(8) and 2.5311(8) Å] are essentially the same as those found in cadmium complexes with terminal thiolates [2.549–2.588 Å].[11,26] The Cd–N bond distances [2.353(2), 2.366(2), 2.517(2) and 2.576(2) Å] are clearly different and the Cd–N distances corresponding to the nitrogen atoms of the thionate ligand are markedly longer. This situation is probably due to the fact that the chelate coordination gives rise to a four-membered ring, which causes an elongation of the C–N bond because the interaction with sulfur is more favourable and the thiolate ligand is rigid.

The structural characteristics of the thiolate ligand and the bipyridine unit are as one would expect and do not warrant further discussion. The acetonitrile molecules in **2** and **6** are not incorporated within the coordination sphere of the metal atom and abnormally short intermolecular contacts are not observed.

Crystal packing and intermolecular interactions. Fig. 5 shows the crystal structure of compound **1**.

It can be seen that the bipyridine rings form chains along axis *a* and in this arrangement the rings on the same side are completely superimposed (distance between centroids, $A = B =$ 8.216 Å). These rings are intercalated with another chain formed by bipyridine rings that are situated on the other side. Distances C and D between the centroids of the neighbouring bipyridines in two different chains are 3.896 Å. This distance is greater than that proposed by Janiack[27] for the existence of π–π stacking interaction. In addition, these two rings are displaced with respect to the ideal situation for "perfect facial alignment" to such an extent that only the outer carbon atoms from each bipyridine unit are overlapped (Fig. 6).

In compound **2** (Fig. 7) the formation of chains within the crystal network is similar to that for compound **1** but in this case with phenanthroline rings rather than bipyridine systems along axis *a*. The interanular distances are: $A = B = 11.073$; $C = D = 4.142$; $E = 3.492$ Å. Of the interactions outlined above, only E can be considered as real. In addition, it can be seen from Fig. 8 that the alignment of the faces is perfect, a situation described by Janiak as a 'rare phenomenon'.

The situation in compound **3** (Fig. 9) is completely different to that described above in that the interactions between the rings of different neighbouring bipyridine ligands are different.

In this case the interanular distance is less than 3.8 Å, with the rings slightly displaced in comparison to "perfect facial alignment". This situation is confirmed by considering the C–C bond distances (3.626, 3.738 and 3.902 Å), which show that the rings are not completely parallel. Given this situation, it is reasonable to believe that π–π stacking interactions are present in this case.

The crystal structure of compound **6** is similar to that of **1**, *i.e.* a parallel-displaced structure, but in this case the distances between centroids are longer (Fig. 10).

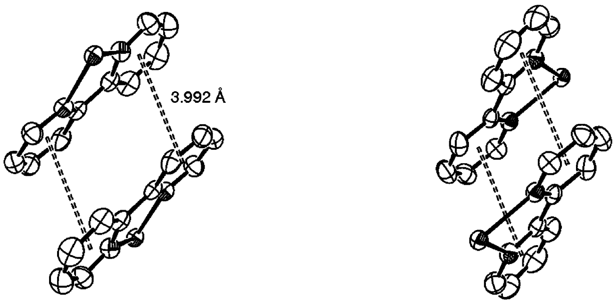

Fig. 10 Partial packing diagram of **6** showing the interannular distances in the lattice.

The nature of the chain propagation in compound **6** is also different to that in compound **1**. In **6** the bipyridine rings do not form chains but are arranged in pairs that are intercalated with other groups.

Crystal structures of [Cd(3-CF$_3$-pyS)$_2$(DMF)]$_2$ (4) and [Cd$_2$(5-CF$_3$-pyS)$_4$(DMF)]$_n$ (5)

Figs. 11 and 12 show perspective views of the molecular structures of **4** and **5** along with the atom labelling schemes used. Crystallographic data and a selection of bond distances and angles (with the estimated standard deviations) are given in Tables 1, 4 and 5. Once again, the structural differences between these complexes are dictated by the position of the trifluoromethyl group.

Complex **4** contains dimeric molecular species in which the two cadmium atoms are related by a center of inversion situated

Table 4 Selected bond distances (Å) and angles (°) for [Cd(3-CF_3-pyS)$_2$(DMF)]$_2$ –(**4**)

Cd(1)–S(1)	2.5336(10)	Cd(1)–S(2)	2.8746(10)
Cd(1)–S(2)^a	2.6204(10)	Cd(1)–N(1)	2.455(3)
Cd(1)–N(2)	2.305(3)	Cd(1)–O(1)	2.341(2)
S(1)–C(1)	1.723(3)	S(2)–C(7)	1.748(3)
N(1)–Cd(1)–S(2)^a	167.55(7)	S(1)–Cd(1)–S(2)^a	106.17(3)
N(1)–Cd(1)–S(1)	62.57(7)	S(2)–Cd(1)–S(2)^a	93.39(3)
N(2)–Cd(1)–S(2)	59.24(7)	S(1)–Cd(1)–S(2)	103.65(3)
N(1)–Cd(1)–S(2)	94.56(6)	N(2)–Cd(1)–S(1)	148.99(7)
N(2)–Cd(1)–S(2)^a	100.83(6)	N(1)–Cd(1)–N(2)	91.48(9)
O(1)–Cd(1)–N(1)	89.33(9)	O(1)–Cd(1)–N(2)	86.41(9)
O(1)–Cd(1)–S(1)	108.51(7)	O(1)–Cd(1)–S(2)	145.47(7)
O(1)–Cd(1)–S(2)^a	89.55(7)		

^{a} Symmetry transformation used to generate equivalent atoms: $-x + 2$, $-y + 2$, $-z + 1$.

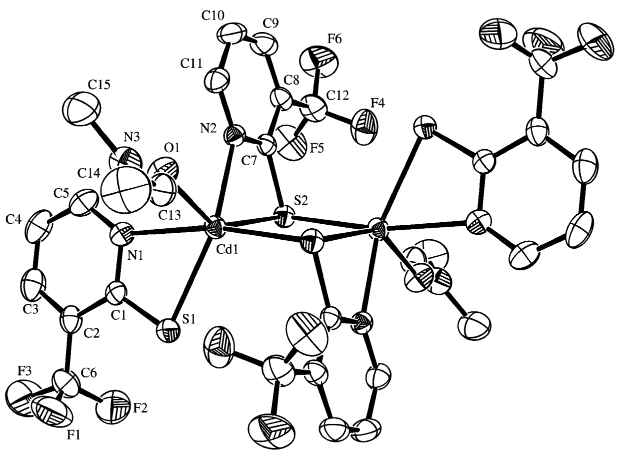

Fig. 11 The molecular structure of [Cd(3-CF_3-pyS)$_2$(DMF)]$_2$ (**4**).

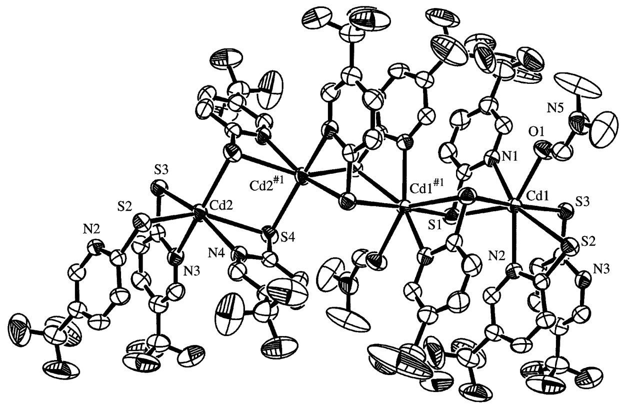

Fig. 12 The molecular structure of [Cd$_2$(5-CF_3-pyS)$_4$(DMF)]$_n$ (**5**).

at the mid-point of the line between the two metal centers. In both cases the metal is hexacoordinated by two anionic ligands that coordinate in different ways. One of the ligands acts as a terminal chelating system (N,S) while the other behaves as both a chelate and a bridge through the sulfur [N,(μ-S)] and donates five electrons. The coordination sphere of the metal in both complexes is completed by an oxygen atom from an additional molecule of dimethylformamide, the solvent used in the crystallisation of the complexes. The metal is therefore in an [S_3N_2O] distorted octahedral environment, with the small values of the bond angles of the four-membered chelate rings being responsible for the distortion from the ideal geometry.

In contrast to the above, complex **5** is an infinite polymeric species in which the cadmium atoms are coordinated to two anionic pyridine-2-thionate ligands, which both act as bridging chelate ligands [N,(μ-S)] that donate five electrons. In addition, a dimethylformamide molecule is associated, in an alternating manner, with one of the cadmium atoms in such a way that two types of cadmium exist within the polymeric species. The system contains hexacoordinated cadmium atoms with an [S_4N_2] coordination sphere and also cadmium atoms with a coordination number of seven, in which the metal is in an [S_4N_2O] distorted pentagonal bipyramidal environment. The propagation of the polymer is based on a basic dimeric unit that contains both types of metal center and is established by an inversion of this unit followed by a translation in such a way that two units containing the hexacoordinated cadmium alternate with two units containing the heptacoordinated cadmium (see Fig. 13). The octahedral environment of the hexacoordinated cadmium centers is highly distorted, as demonstrated by the low values for the bond angles involving the metal centers and the donor atoms in the *trans* positions [151.94(2), 156.98(6) and 159.47(6)°]. These values are significantly different from those expected for the ideal geometry. Despite this situation, the pentagonal bypyrimidal environment corresponding to the atoms around the heptacoordinated cadmium atoms is reasonably regular, with an S(3)–Cd–S(1)^a bond angle of 173.85(2)° and bond angles between the metal and donor atoms in the equatorial plane of the bipyramid close to the 72° expected for a regular geometry. Further evidence for this arrangement comes from the dihedral angle [89.24(4)°] formed between the equatorial plane of the bipyramid and the plane containing the metal and the axial sulfur atoms, an angle that is very close to the 90° expected for a regular geometry.

Table 5 Selected bond distances (Å) and angles (°) for [Cd$_2$(5-CF_3-pyS)$_4$(DMF)]$_n$ (**5**)

Cd(1)–S(1)	2.9041(8)	Cd(2)–S(2)	2.6370(8)
Cd(1)–S(1)^a	2.6627(8)	Cd(2)–S(3)	2.6350(8)
Cd(1)–S(2)	2.9975(8)	Cd(2)–S(4)	2.9150(9)
Cd(1)–S(3)	2.7284(8)	Cd(2)–S(4)^b	2.6170(8)
Cd(1)–N(1)	2.378(2)	Cd(2)–N(3)	2.473(2)
Cd(1)–N(2)	2.371(2)	Cd(2)–N(4)	2.331(2)
Cd(1)–O(1)	2.444(2)	S(1)–C(1)	1.739(3)
S(2)–C(7)	1.731(3)	S(3)–C(13)	1.747(3)
S(4)–C(19)	1.745(3)		
S(1)–Cd(1)–S(1)^a	88.52(2)	N(4)–Cd(2)–S(4)	59.04(6)
S(1)–Cd(1)–S(2)	142.90(2)	N(4)–Cd(2)–S(4)^b	94.77(6)
S(1)–Cd(1)–S(3)	97.29(2)	N(3)–Cd(2)–N(4)	96.58(8)
S(2)–Cd(1)–S(1)^a	91.07(2)	O(1)–Cd(1)–S(1)^a	82.93(6)
S(2)–Cd(1)–S(3)	85.49(2)	O(1)–Cd(1)–S(3)	91.60(6)
S(2)–Cd(2)–S(3)	95.15(3)	O(1)–Cd(1)–S(1)	133.10(6)
S(2)–Cd(2)–S(4)	151.94(2)	O(1)–Cd(1)–S(2)	83.51(6)
S(2)–Cd(2)–S(4)^b	102.30(2)	S(3)–Cd(2)–S(4)	107.24(2)
S(3)–Cd(1)–S(1)^a	173.85(2)	S(3)–Cd(2)–S(4)^b	103.78(3)
S(4)–Cd(2)–S(4)^b	88.82(2)	N(1)–Cd(1)–S(1)	58.61(6)
N(1)–Cd(1)–S(1)^a	98.21(6)	N(1)–Cd(1)–O(1)	77.09(8)
N(1)–Cd(1)–S(2)	157.21(6)	N(2)–Cd(1)–O(1)	140.59(8)
N(1)–Cd(1)–S(3)	83.24(6)	N(3)–Cd(2)–S(2)	93.91(6)
N(2)–Cd(1)–S(1)	85.60(6)	N(3)–Cd(2)–S(3)	61.78(5)
N(2)–Cd(1)–S(1)^a	92.57(6)	N(3)–Cd(2)–S(4)	82.47(5)
N(2)–Cd(1)–S(2)	57.35(6)	N(3)–Cd(2)–S(4)^b	159.47(6)
N(2)–Cd(1)–S(3)	89.87(6)	N(4)–Cd(2)–S(2)	94.06(6)
N(1)–Cd(1)–N(2)	142.05(8)	N(4)–Cd(2)–S(3)	156.98(6)

^{a} Symmetry transformation used to generate equivalent atoms: $-x + 2$, $-y + 1$, $-z$. ^{b} $-x + 1$, $-y + 1$, $-z + 1$.

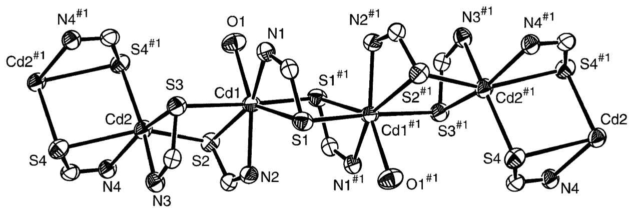

Fig. 13 Perspective view of the coordination sphere of the metals in [Cd$_2$(5-CF_3-pyS)$_4$(DMF)]$_n$ (**5**).

The Cd–S bond distances in each of the complexes are different depending on the way in which the ligand is coordinated. In the dimeric species **4**, the shortest value [2.5336(10) Å] corresponds to the bond distance Cd(1)–S(1), which involves the sulfur atom in the terminal chelate ligand. This distance is very similar to the average bond length found previously between cadmium and terminal thiolate sulfur (2.549–2.588 Å).[11,26] In the case where the ligand acts as a bridge, the two distances for the Cd–S bond are different and fall in the range 2.6170(8)–2.9975(8) Å. This fact shows that the bridge is not symmetrical. In all cases the bond length values are higher in complexes where the sulfur atom forms part of a four-membered chelate ring, in conjunction with a nitrogen atom, and the Cd–S associations are stronger in the cases where the sulfur does not form part of the chelate ring.

The Cd–N bond distances found in both complexes are in the range 2.305(3)–2.473(2) Å, which is not dissimilar to the average value [2.365–2.53 Å] found in hexacoordinated cadmium complexes containing different pyridine derivatives as ligands.[11,28] Similarly, the Cd–O bond distances in complexes **4** and **5** have values of 2.341(2) and 2.444(2) Å, respectively, with a higher value observed in the polymeric species where the metal has a higher coordination number. Once again these bond distances are similar to those found in other cadmium complexes that contain dimethylformamide as a ligand.[29]

The pyridine-2-thionato ligands in the complexes are essentially planar. The values of the structural parameters for these ligands, as well as those of the DMF, are not unusual and do not warrant further discussion

Molecular structures of [Hg(3-CF$_3$-pyS)$_2$] (7) and [Hg(5-CF$_3$-pyS)$_2$] (8)

Figs. 14 and 15 show perspective views of the crystal structures of **7** and **8** along with the atom labelling schemes used. Crystallographic data and a selection of bond distances and angles (with the estimated standard deviations) are given in Tables 1 and 6.

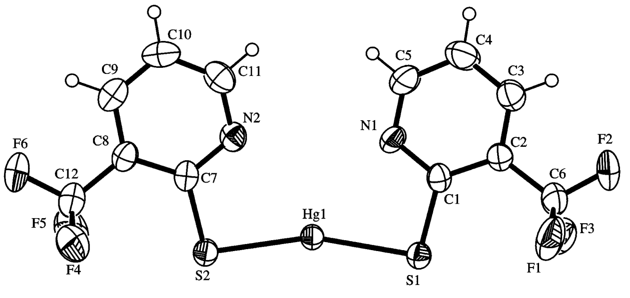

Fig. 14 The molecular structure of [Hg(3-CF$_3$-pyS)$_2$] (**7**).

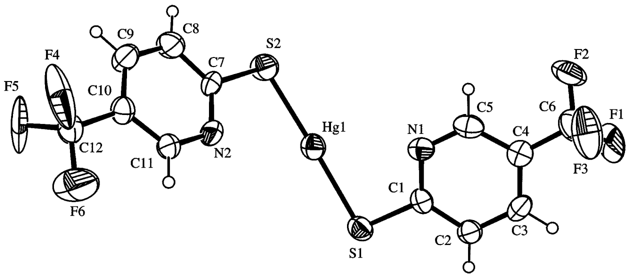

Fig. 15 The molecular structure of [Hg(5-CF$_3$-pyS)$_2$] (**8**).

Table 6 Selected bond distances (Å) and angles (°) for [Hg(3-CF$_3$-pyS)$_2$] (**7**) and [Hg(5-CF$_3$-pyS)$_2$] (**8**)

	(**7**)	(**8**)
Hg(1)–S(2)	2.3642(18)	2.319(3)
Hg(1)–S(1)	2.3761(17)	2.348(3)
Hg(1)–N(2)	2.808(6)	3.027(9)
Hg(1)–N(1)	2.786(6)	2.805(10)
S(1)–C(1)	1.760(7)	1.750(11)
S(2)–C(7)	1.752(7)	1.756(11)
N(1)–C(1)	1.324(8)	1.347(14)
N(1)–C(5)	1.333(8)	1.317(15)
N(2)–C(7)	1.333(7)	1.333(13)
N(2)–C(11)	1.345(9)	1.324(13)
S(2)–Hg(1)–S(1)	161.41(6)	178.36(11)
S(2)–Hg(1)–N(1)	137.70(13)	120.1(2)
S(1)–Hg(1)–N(1)	60.21(12)	61.2(2)
S(2)–Hg(1)–N(2)	60.26(11)	58.38(19)
S(1)–Hg(1)–N(2)	136.60(11)	120.18(19)
N(1)–Hg(1)–N(2)	77.54(16)	123.8(3)

In both cases, the crystal structure consists of discrete centrosymmetric molecules with the mercury atom coordinated to the sulfur atoms of two thionate ligands in a digonal geometry. However, the relative dispositions of the ligands in the two complexes are different. In **7** both ligands are situated on the same side of the line defined by the bonds S–Hg–S and the pyridine rings are in an eclipsed conformation; dihedral angle between the two rings 19.08(35)°. In complex **8**, however, the two ligands are on different sides of the aforementioned line and the heterocyclic rings are in a staggered conformation; dihedral angles between rings 60.65(36) and 55.51(14)°, respectively. Once more, the presence of the CF$_3$ group in position 3 of the heterocycle produces a different structural arrangement.

The Hg–S bond distances are in the range 2.319(3)–2.3761(17) Å, *i.e.* similar to the range (2.321–2.374 Å) typically found in other mercury thionato complexes with a linear geometry.[30] The Hg–N bond distances are 2.786(6) and 2.808(6) for **7** and 2.805(10) and 3.027(9) for **8**. These distances are longer than the sum of the covalent radii of mercury and nitrogen (2.25 Å) and longer than the Hg–N distances observed in other mercury complexes involving heterocyclic nitrogen donor ligands, for example 2.210 Å in [Hg(pyS)(OAc)][31] 2.210 and 2.23 Å in [MeHg(py)]NO$_3$.[32] However, they are shorter than the sum of the van der Waals radii of nitrogen (1.55 Å)[33] and mercury (1.73 Å),[34] *i.e.* a total of 3.23 Å, and are comparable to distances characteristic of weak intramolecular Hg–N interactions in other mercury thiolate complexes (2.798–2.980 Å).[35]

The S–Hg–S bond angles are 161.41(6) and 178.36(11)° for **7** and **8**, respectively. In the case of **8** the value is close to those expected for a regular geometry. However, in the case of **7** the value is much lower, most probably as a result of the steric hindrance produced by the heterocyclic rings.

Spectroscopic studies

The ν(N–H) bands of the ligands, which appear at 3200–3100 cm^{-1}, are absent in the thiolato complexes, indicating that the ligand in the complexes is in the deprotonated form. The strong ligand bands in the range 1640–1660 cm^{-1} are due to the ν(C=N) and ν(C=C) vibrations but are not caused by an aromatic ring.[36] The aromatic bands for the complexes appear in the region 1590–1545 cm^{-1}, which is characteristic of vibrations of tension due to an aromatic group, thus confirming the presence of thiolate in the complexes.

Bands assigned to ring deformation modes are observed in the region 1110–990 and 750–620 cm^{-1}, which are at higher wavelengths in comparison to the corresponding bands in the free ligands. This shift in wavelength provides evidence for coordination of the ligands through the nitrogen atoms.[37]

In the mixed complexes that contain additional nitrogen ligands, bands are observed at 780 and 730 cm^{-1}, which is characteristic of bipyridine or 1,10-phenanthroline coordinated to the metal.[38]

In the ^{1}H NMR spectra of the thiolate complexes, the main change brought about by complexation is the disappearance of the broad signal of the N–H proton, which appears at about 14 ppm in the free ligands. This change confirms that, in this

Table 7

Compound	Environment around the metal atom
[Zn(3-CF_3-pyS)$_2$(bipy)]	*cis*-(S,S) [ZnS_2N_4]
[Zn(3-CF_3-pyS)$_2$(phen)]	*trans*-(S,S) [ZnS_2N_4]
[Zn(5-CF_3-pyS)$_2$(bipy)]	[ZnS_2N_2]
[Cd(3-CF_3-pyS)$_2$(DMF)]$_2$	[CdS_3N_2O]
[Cd_2(5-CF_3-pyS)$_4$(DMF)]$_n$	[CdS_4N_2] and [CdS_4N_2O]
[Cd(3-CF_3-pyS)$_2$(bipy)]	*cis*-(S,S) [S_2CdN_4)]
[Hg(3-CF_3-pyS)$_2$]	S_2
[Hg(5-CF_3-pyS)$_2$]	S_2

instance, the ligand is in the deprotonated thiolate form in the complexes. The spectra also show all the signals due to the pyridine ring and these are shifted with respect to those in the free ligand. This change in shift is more marked for the H(6) signal due to coordination by the nitrogen of the heterocycle.[39]

The ^{1}H NMR spectra of the mixed complexes contain signals due to the protons of the coligands (2,2′-bipyridine or 1,10-phenanthroline), which appear as four groups of signals in the aromatic region. The most representative of these signals are those corresponding to the protons *ortho* to the nitrogen atoms and these signals appear at lowest field. These signals are slightly shifted to lower field in comparison to the corresponding signals in the free coligands. These changes in chemical shift again provide evidence of coordination of the coligands to the metal atom through the nitrogens.[40]

The mercury thiolate complexes exhibit $\delta(^{199}Hg)$ values in the range −1168 to −1192 ppm. These values are close to those found in other mercury(II) complexes that contain thione ligands.[41]

Conclusions

This paper describes the synthesis and structural characterisation of a series of zinc, cadmium and mercury complexes with trifluoromethyl derivatives of pyridine-2-thione, which differ in the location of the substituent in the heterocyclic ring. Table 7 summarises the results described.

As can be seen, the structure of the compounds depends on the location of the CF_3 group. In the cases of [Zn(3-CF_3-pyS)$_2$(bipy)] and [Zn(3-CF_3-pyS)$_2$(phen)], the metal atom is in an [S_2N_4] octahedral environment, while for [Zn(5-CF_3-pyS)$_2$(bipy)] it is in an [S_2N_2] tetrahedral geometry. This is most remarkable as the ligand with higher steric hindrance produces the complexes with the higher coordination number. The same happens in the case of cadmium. The compound [Cd(3-CF_3-pyS)$_2$(DMF)]$_2$ is a dimer while [Cd_2(5-CF_3-pyS)$_4$(DMF)]$_n$ is a linear polymer. Again, the most congested structure is produced by the 3-CF_3 ligand. Unfortunately, all the attempts to obtain single crystals of the homoleptic compounds [ML_2] were unsuccessful; consequently, to this moment we can not tell if the location of the CF_3 group affects their structure. However, in view of the structures of [Cd(3-CF_3-pyS)$_2$(DMF)]$_2$ and [Cd_2(5-CF_3-pyS)$_4$(DMF)]$_n$ we tentatively propose that [Cd(3-CF_3-pyS)$_2$] has a dimer structure and [Cd(5-CF_3-pyS)] a polymeric structure. In this sense, it is of note that [Cd(pyS)$_2$]$_n$ is a polymer,[42] but [Cd(3-$SiMe_3$-pyS)$_2$]$_2$ is a dimer.[11]

In the case of mercury, both ligands produce the same environment around the metal. However, the relative dispositions of the ligands in the two complexes are different. In [Hg(3-CF_3-pyS)$_2$] both ligands are situated on the same side of the line defined by the bonds S–Hg–S and the pyridine rings are in an eclipsed conformation. In [Hg(5-CF_3-pyS)$_2$], however, the two ligands are on different sides of the aforementioned line and the heterocyclic rings are in a staggered conformation.

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