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Crystal structures and physicochemical studies of some novel divalent and trivalent transition metal chelates of *N*-morpholine-*N*'-benzoylthiourea

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ABSTRACT

A series of Fe(III), Co(III), Ni(II), Cu(II), Zn(II) and In(III) *N*-morpholine-*N*'-benzoylthiourea complexes have been synthesised and characterised by elemental analysis, thermal analysis, infrared spectroscopy, ^{1}H nuclear magnetic resonance spectroscopy and single crystal X-ray crystallography. Thermogravimetric analysis shows that all the complexes undergo a two-step decomposition process except for the iron(III) complex and the indium(III) complexes, which show three-step and one-step decompositions, respectively. The complexes are thermally stable up to approximately 300 °C. The ligand coordinates the various metal ions in a bidentate (*L-kO,S*) chelating mode, facilitated by deprotonation of the acidic amide (–C(O) N'HC (S)) moiety. This mode of coordination allows for the facile formation of neutral bis/tris-6-membered chelates of type [M(*L-kS,O*)$_x$] where x = 2 or 3 for divalent or trivalent metal ions, respectively.

1. Introduction

Thiourea and thiobiuret/dithiobiuret compounds have recently generated interest among scientists due to their potential biological applications and their use in the fabrication of metal sulfide thin films and nanoparticles [1–4]. The main focus of the research into these compounds centres on their potential biological applications where they have been shown to possess antibacterial, antifungal, insecticidal, herbicidal, and plant-growth regulator properties [3–5] Thiourea compounds show great structural diversity and numerous derivatives can be prepared through facile modification of the starting materials. Examples of these compounds which include the *N,N*-dialkyl-*N*'-aroyl/acyl-thioureas (HL), are known in literature and are obtained through a simple one pot reaction which involves the addition of an acid chloride to KSCN followed by an amine [6–8]. The N–C–S moiety in thiourea is generally responsible for any biological properties, which may be further enhanced through the formation of metal complexes [9]. In addition to biological studies, thiourea compounds are also important in industrial applications, *i.e.* as corrosion inhibitors and as additives in lubricants [10–12].

The potential of thiourea and its derivatives to act as donor ligands for transition metal ions due to their carbonyl and thiocarbonyl groups means they are ubiquitous in the synthesis of metal sulfide nanomaterials from single-source precursors [13–15]. Thiourea ligands coordinate easily to a wide range of metal centres as either neutral, monoanionic or dianionic ligands [16]. The variability of donor atoms of thiourea-derived ligands including oxygen, nitrogen and sulfur provide a plethora of bonding modes, bidentate (*L-kO,S*) chelating groups are, however, dominant [17–19]. The presence of direct bonds between sulfur and the metal atom of interest results in better control over stoichiometry and the phase of nanomaterials. Ramasamy et al. described the synthesis of metal (Co, Cu, Ni) complexes of thiobiurets and dithiobiurets and their use as precursors for metal sulfide thin films by AACVD [1]. Akhtar et al. deposited CuS thin films by AACVD us-

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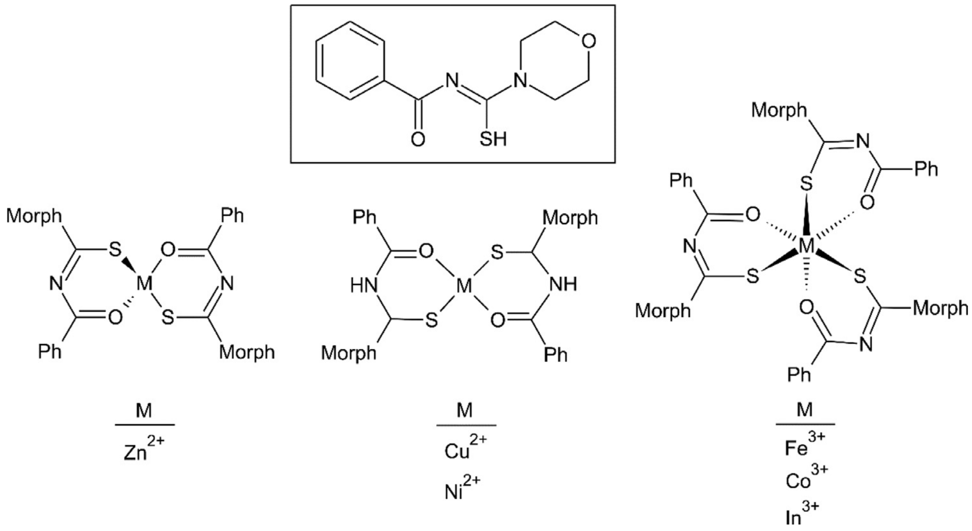

Fig. 1. Schematic Molecular diagrams of the ligand and metal complexes.

ing *N*,*N*-diethyl-*N*′-(1-naphthoyl)thiourea as a precursor [20]. They also synthesised a series of acyl thiourea complexes with different transition metals (Ni, Cu, Co, Zn) and investigated their suitability for the deposition of thin films by AACVD [21]. Revaprasadu et al. have similarly investigated the effects of surfactants on the phase of copper sulfide *via* colloidal synthesis and deposited thin films by AACVD using acyl thiourea copper complexes [22]. They also prepared PbS and PbS$_{1\text{-x}}$Se$_{\text{x}}$ solid solutions over wide range of compositions using chalcogeno urea complexes [23]. There are also reports of the Group congener of thiourea *i.e.* selenourea, for the synthesis of selenide based nanomaterials and thin films [23–25].

The versatile and flexible coordinating ability of thiourea has also resulted in formation of photo-induced isomers [26,27]. The photo-isomerisation occurs as a result of reversible protonation yielding a series of *cis*- or *trans*- isomers of Pt(II) and Pd(II) thiourea complexes. With such a variety of functions for thiourea-based, there is a need to investigate the structural features of a series of metal thiourea complexes with different oxidation states, coordination numbers and coordination geometries.

Morpholine is an amino ether which is regarded as a versatile chemical with many important applications including optical brighteners and catalysts [28]. It is commonly used in dithiocarbamate metal-organic compounds, which exhibit desirable chemical stability under ambient conditions. It is for these reasons that morpholine was the preferred moiety in our study involving thiourea compounds. Herein, the ligand, *N*-morpholine-*N*'-benzoylthiourea is successfully coordinated to Cu(II), Co(III), Fe(III), In(III), Ni(II) and Zn(II). The metal chelate structures presented in this work have not been studied by single crystal X-ray crystallography previously, with the exception of the Co(III) and Ni(II) complexes (Fig. 1). In these cases, new polymorphs are presented. Our interest in these compounds stems from their potential use as precursors for the synthesis of metal sulfide nanomaterials.

2. Experimental

2.1. Chemicals

Benzoyl chloride 99%, potassium thiocyanate 99%, copper chloride dihydrate 99%, iron(III) chloride 97%, cobalt(III) chloride hexahydrate 98%, zinc nitrate hexahydrate 98%, nickel chloride 98%, indium(III) chloride 98%, hydrochloric acid 37%, ethanol 99.5%, acetone 99.5%, dichloromethane 99.9% (Sigma–Aldrich) and morpholine 99% (Merck) were all supplied from commercial sources and used as received. The ligand and metal complexes were prepared using a procedure reported in our previous work [29], with some modifications. Physical properties, elemental analysis results and IR data are summarised in Tables S1 and S2.

2.2. Synthesis of N-morpholine-N'-benzoylthiourea, [morthio] (HL)

Benzoyl chloride (2.0 mL; 17 mmol) was dissolved in 50 mL of acetone and added dropwise to a suspension of potassium thiocyanate (1.67 g; 17 mmol) in 30 mL of acetone. The reaction mixture was heated under reflux for 30 min, and then cooled to room temperature. A solution of morpholine (1.50 mL; 17 mmol) in 10 mL of acetone was added and the resulting mixture stirred for 2 h. Hydrochloric acid (300 mL, 0.1 M,) was added to the resultant solution and the solid product filtered off, washed with water and purified by recrystallization in ethanol: dichloromethane (1:1) mixture. ^{1}H NMR (400 MHz, acetone): δ 9.68 (s, 1H, NH), 8.02 (m, 2H, C_6H_5), 7.64 (d, 1H, C_6H_5), 7.61 (m, 2H, C_6H_5), 4.21 (s, 4H, CH_2), 3.77 (s, 4H, CH_2).

2.3. Synthesis of the complexes

2.3.1. Synthesis of tris(N-morpholine-N'-benzoylthioureato)iron(III), [Fe(morthio)$_3$] (1)

Under ambient conditions iron(III) chloride (0.44 g; 2.00 mmol) dissolved in water (20 mL) was added dropwise to a stirred suspension of *N*-morpholine-*N*'-benzoylthiourea ligand (1.50 g; 6.00 mmol) in acetone (50 mL). After 1 h of stirring, the resultant solution was filtered and crystals of suitable quality were grown from a mixture of ethanol and dichloromethane solvents.

2.3.2. Synthesis of tris(N-morpholine-N'-benzoylthioureato)cobalt(III), [Co(morthio)$_3$] (2)

Complex (**2**) was synthesised using the same method as compound (**1**) with cobalt(II) chloride hexahydrate (0.48 g, 2.00 mmol) used as the metal salt. The cobalt (II) is oxidised by atmospheric oxygen during the reaction process to cobalt(III). This is common practice in cobalt chemistry as the reaction kinetics of the d^6 cobalt(III) are slow.

2.3.3. Synthesis of bis(N-morpholine-N'-benzoylthioureato)nickel(II), [Ni(morthio)$_2$] (3)

Complex (**3**) was synthesized under identical conditions to complex (**1**) using 0.26 g; 2.00 mmol of nickel chloride and 1.00 g;

4.00 mmol of *N*-morpholine-*N'*-benzoylthiourea ligand in 50 mL of ethanol. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.13$ (m, 2H; 2-C_6H_5), 7.51 (d, 1H, 2-C_6H_5), 7.41 (m, 2H, 2-C_6H_5), 4.22 (m, 4H, 2-CH_2), 3.78 (m, 4H, 2-CH_2).

2.3.4. Synthesis of bis(N-morpholine-N'-benzoylthioureato)copper(II), [Cu(morthio)$_2$] (4)

Synthesis of complex (**4**) was carried out using the method for **(3)** with copper chloride dihydrate (0.27 g, 2.00 mmol) used as the metal salt.

2.3.5. Synthesis of bis(N-morpholine-N'-benzoylthioureato)zinc(II), [Zn(morthio)$_2$] (5)

Complex (**5**) was synthesised using the same procedure as for **(3)** with zinc nitrate hexahydrate (0.60 g, 2.0 mmol) used as the metal salt. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.17$ (m, 2H; 2-C_6H_5), 7.50 (d, 1H, 2-C_6H_5), 7.41 (t, 2H, 2-C_6H_5), 4.27 (m, 4H, 2-CH_2), 3.84 (m, 4H, 2-CH_2).

2.3.6. Synthesis of tris(N-morpholine-N'-benzoylthioureato)indium(III), [In(morthio)2] (6)

Complex (**6**) was synthesised using the procedure for (**1**) under the nitrogen with indium chloride (0.44 g, 2.00 mmol) used as metal salt. 1H NMR (400 MHz, $CDCl_3$): $\delta = 8.12$ (m, 2H; 3-C6H5), 7.47 (d, 1H, 3-C_6H_5), 7.36 (m, 2H, 3-C_6H_5), 4.16 (m, 4H, 3-CH_2), 3.75 (m, 4H, 3-CH_2).

2.4. Instrumentation

Elemental analysis (EA) using a Thermo Scientific Flash 2000 Organic Elemental analyser and thermal analysis by Mettler Toledo TGA/DSC1 star system were carried out at the Manchester University Microanalytical Laboratory. The thermal data points were collected at a ramp rate of 10 °C min^{-1} in a flowing N_2 stream. A 400 MHz Bruker Ascend Spectrometer was used to record NMR spectra at RT using $CDCl_3$ and D_2O as solvents.

2.5. X-ray crystal structure analysis

Crystals suitable for single crystal X-ray diffraction studies were grown using vapour diffusion of a 1:1 solution mixture of dichloromethane and ethanol. X-ray data for all chelates, except the Cu(II) chelate, were collected on a dual source Rigaku FR-X rotating anode diffractometer using Cu Kα ($\lambda = 1.5418$ Å) radiation at 150 and 293 K, and reduced using CrysAlisPro 171.39.30c. All non-hydrogen atoms were located in the difference density map and refined anisotropically with SHELX-2016 [30]. Structures were solved by direct methods and subsequent refinement was carried out using SHELX-2016 (Olex2 v1.2.919–21). The Cu(II) chelate was analysed using a Bruker Apex Duo diffractometer equipped with an Oxford Instruments Cryojet operating at 100(2) K and an Incoatec microsource operating at 30 W power. The data were collected with Mo K_α ($\lambda = 0.71073$ Å) radiation by omega and phi scans with exposures taken at 30 W X-ray power and 0.50° frame widths using APEX2 [31]. The data reduction was performed using Bruker SAINT software [31] which corrects for Lorentz and polarisation effects. Absorption corrections for the reflection data were performed with semi-empirical and multi-scan techniques using SADABS. All structures were solved by direct methods, SHELX-2016 [32] and WinGX [33] packages. All hydrogen atoms were included as idealised contributors in the least squares refinement.

3. Results and discussion

3.1. Spectroscopic and gravimetric analysis

The *N*-morpholine-*N'*-benzoylthiourea ligand and its corresponding metal complexes synthesized from salts of Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and In(III) were obtained as high purity compounds in good yields, as confirmed by elemental analysis (ESI Table S1). The IR spectroscopy results (ESI Table S2) revealed that the medium peak observed at 3239 cm^{-1} for the ligand (**HL**) is attributed to the stretching of the N–H group adjacent to the carbonyl group. The disappearance of this band with the emergence of the bands observed at 1587-1585 cm^{-1} (attributed to the C=N functional group) in the complexes confirmed the deprotonation of the ligand facilitated by the addition of the base, *N*-morpholine. The deprotonation is also corroborated by ^{1}H NMR spectroscopy, where the peak observed at 9.68 ppm (attributed to the amide proton, N-H) for **HL** is absent in the spectra of the complexes. The strong band at 1663 cm^{-1} for **HL** is attributed to the vibration of the C=O carbonyl groups which shifts to lower wavenumbers upon complexation. This shift to lower frequencies is a result of the electron withdrawing nature of the ligands and the subsequent lowering of the C=O bond order. These data show that deprotonation involves delocalisation of the C=O stretching vibration, which is consistent with literature, [34,35] thus confirming coordination to the central metal ions through the oxygen atom from the carbonyl. The multiplet in the ^{1}H NMR spectra assigned to the aromatic protons, are observed in the 8.17-7.41 ppm range in both ligand and complexes. Two signals assigned to the methylene protons of morpholine are also observed in the 4.27-3.84 ppm range.

The thermal stability and decomposition profile of the synthesised complexes was investigated by TGA and DTA techniques as presented in Fig. 2 and Fig. S1, respectively. Merdivan et al. [36] studied the thermal decomposition of many thiourea complexes and suggested two decomposition steps. They proposed that the first step corresponds to the elimination of dialkylbenzamide, followed by the loss of SCN• and CN• radicals as a second step yielding either the metal sulfide or metal. Our complexes showed similar two-step TGA profiles, with the exception of complex **(1)** which showed three-step decomposition processes. In the case of the two step decomposition, the first step showed weight loss of 73.67% for **(4)**, 68.33% for **(3)**, 74.76% for **(5)**, 72.80% for **(2)** and 64.42% for **(6)** corresponding to the loss of 2 × MB (calcd: 68.03%), 2 × MB (calcd: 68.63%), 2 × MB+CN (calcd: 72.43%), 3 × MB (calcd: 71.11%) and 2 × MB+3 × CN (calcd: 56.86%) respectively,

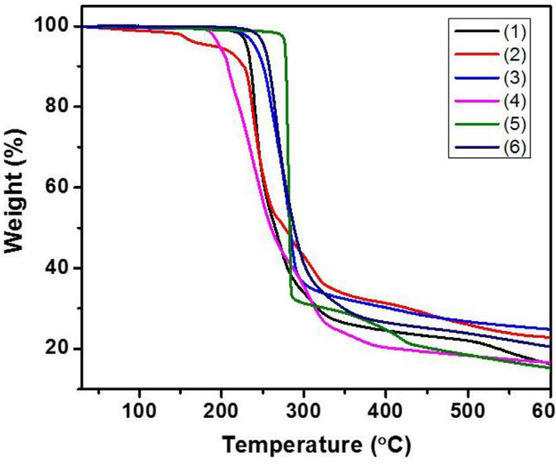

Fig. 2. TGA plots of complexes (**1** – **6**).

where MB = morpholinylbenzamide. The second step displayed a mass loss of 9.43%, 16.24%, 6.01%, 13.83% and 8.10% assigned to 2CN, SCN+CN, CN, 3CN+S and S (calcd: 9.26%, 15.09%, 4.62%, 13.65% and 8.62%), respectively. A similar trend in total weight loss is observed for complex (**1**). The masses of the final residue are 23.07% for **(1)**, 13.37% for **(2)**, 15.69% for **(3)**, 16.90% for **(4)**, 19.23% for **(5)**, and 23.40% for **(6)**, which are in good agreement with the theoretical values for Fe_2S_4 (calcd: 25.86%), CoS (calcd: 11.28%), NiS (calcd: 16.28%), CuS (calcd: 17.00%) and ZnS (calcd: 17.27%), respectively. The exception is compound **(6)** which did not correlate to either of the stable phases InS or In_2S_3. The latter can be attributed to carbon contamination and/or multiple-phase indium sulfide material. This indicates that the compounds are stable at ambient conditions, i.e. in air, moisture and at room temperature. In the DTA profiles (ESI Figure S1), a single endothermic peak is observed for complexes **(4), (2)** and **(1)** whereas two are observed for complexes **(3), (5)** and **(6)**. The value of the melting point of each complex is consistent with the value of the first endothermic peak in the DTA profiles which is in agreement with the work of Merdivan et al. [37]. The complete TGA and DTA data of the complexes are summarised in Table S3.

3.2. Determination of crystal structures

The crystallographic refinement data for all crystal structures used in this work are presented in Table 1 and selected geometrical features of the complexes are summarised in Table 2. These ligands have been extensively studied by X-ray crystallography coordinated to a number of different metal ions, particularly heavy metal ions including, but not limited to: Pb(II) [29], Pt(II) [38], Hg(II) [39], Re(V), Tc(V) and Tc(III) [40,41]. The ligand has also reportedly been chelated to Co(III) [42–44], as well as Ni(II) [31,45,46]. The structures presented herein, with respect to the Co(III) and Ni(II) compounds, present new polymorphs of these known structures, the bulk of the compounds (four structures) are have not been previously reported. The Fe(III) complex (Fig. 3) crystallises in the monoclinic $P2_1/c$ space group. Three bidentate *S,O*-donor ligands surround the metal centre. This yields a distorted octahedral S_3O_3 environment with a stereochemical preference for a facial geometry common in closely related structures [47]. This geometry preference is common in related compounds, as shown by a search of the Cambridge Structural Database (CSD). The CSD shows that all structures with three bidentate ligands of the general structure S–C–N–C–O in the coordination sphere (as is the case for the compounds presented herein) have exclusively adopted a *fac*-configuration, irrespective of the moieties appended to the carbon atoms. Considering the ubiquitous nature of this configuration, it was further explored using DFT methods at the B3LYP/6-311G (dp) level of theory which showed, for a representative structure comprising three bidentate *S,O*-donor ligands coordinated to a metal(III) ion, that the *fac*-isomer is *ca.* 9 kJ mol^{-1} lower in energy than the meridional isomer. Further details on the computational method used are provided in the ESI.

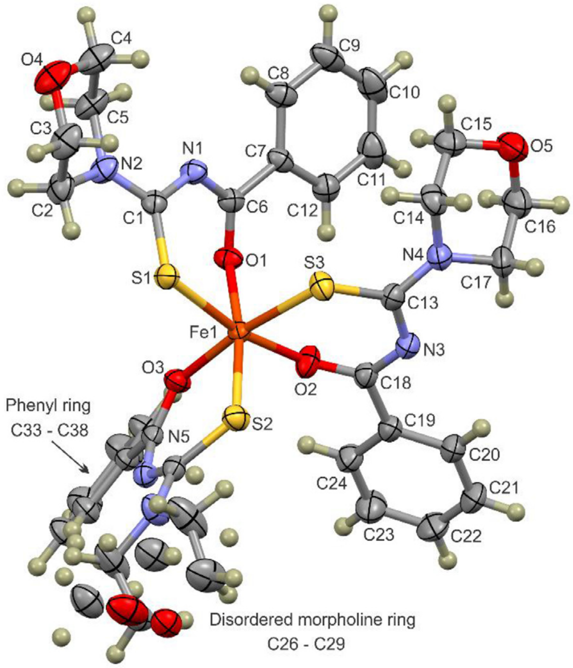

Fig. 3. The molecular structure of complex (**1**) showing the atom naming scheme. The sulfur and oxygen ligand donor atoms have adopted a *facial* (*fac*) coordination geometry. One of the three morpholine rings is disordered between a ring up and ring down orientation with a ratio of 53:47. Displacement ellipsoids are shown at the 50% probability level. Hydrogens are shown as spheres of arbitrary radius.

The ligand structure leads to three, six-membered *O,S* chelate rings (NC_2OS–Fe). The mean Fe–O bond distance (1.98(2) Å) is significantly shorter than the Fe–S bond length (2.43(1) Å). The phenyl rings of the benzoyl portion of the ligands are approxi-

Table 1
Crystallographic data of complexes (**1**–**6**).

Complexes	1	2	3	4	5	6
Formula	$C_{36}H_{39}FeN_6O_6S_3$, CH_2Cl_2	$C_{36}H_{39}CoN_6O_6S_3$	$C_{24}H_{26}N_4NiO_4S_2$	$C_{24}H_{26}CuN_4O_4S_2$	$C_{24}H_{26}N_4O_4S_2Zn$	$C_{36}H_{39}InN_6O_6S_3$, C_3H_6O
M g mol^{-1}	888.69	806.84	557.32	562.15		920.81
Space group	P 2_1/c	P 2_1/c	P -1	P -1	P -1	P 2_1/c
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic	Monoclinic
a (Å)	13.8376(2)	13.6419(2)	5.2078(1)	4.0786(3)	9.5245(2)	14.0804(1)
b (Å)	24.9520(3)	25.1576(4)	15.2193(2)	16.2842(10)	11.6012(3)	24.8811(2)
c (Å)	11.8570(2)	11.5569(2)	15.4417(2)	17.7096(11)	13.1616(3)	11.9042(1)
α (°)	90	90	90.374(1)	81.554(2)	110.724(2)	90
β (°)	98.865(1)	98.5570(10)	99.051(1)	86.833(3)	101.140(2)	98.172(1)
γ (°)	90	90	94.185(1)	83.113(3)	107.099(2)	90
V (Å^3)	4045.03(10)	3922.15(11)	1205.23(3)	1154.21(13)	1226.10(5)	4128.12(6)
T (K)	150	150.0(2)	150	100	293	150
Z	4	4	2	2	2	4
Dcalc (g cm^{-3})	1.459	1.366	1.536	1.617	1.528	1.482
F(000)	1844.0	1680.0	580.0	582.0	584.0	1896.0
R(F^2) (observed reflections)	0.0754(7686)	0.0390	0.0397(4609)	0.0301(3895)	0.0269 (4588)	0.0627(7203)
wR(F^2) (all reflns)	0.1865(8206)	0.0996	0.1058(4736)	0.0780(4951)	0.0711 (4771)	0.1677(7843)

Table 2
Selected geometrical parameters describing the coordination spheres of the compounds (**1**) – (**6**).

(1)				(2)			
Bond	Length	Bond	Angle	Bond	Length	Bond	Angle
Fe–S1	2.448(1)	S1–Fe–O2	168.8(1)	Co–S1	2.2153(6)	S1–Co–O5	176.61(5)
Fe–S2	2.414(1)	S2–Fe–O1	171.34(8)	Co–S2	2.2066(7)	S2–Co–O1	176.25(5)
Fe–S3	2.428(1)	S3–Fe–O3	171.86(8)	Co–S3	2.2085(7)	S3–Co–O3	176.60(5)
Fe–O1	1.998(1)	O1–Fe–S1	86.19(8)	Co–O1	1.917(2)	O1–Co–S1	94.98(5)
Fe–O2	1.976(1)	O2–Fe–S3	86.6(1)	Co–O3	1.941(2	O3–Co–S2	95.04(5)
Fe–O3	1.972(1)	O3–Fe–S2	86.31(8)	Co–O5	1.922(1)	O5–Co–S3	94.84(5)

(3)				(4)			
Bond	Length	Bond	Angle	Bond	Length	Bond	Angle
Ni1–S1	1.833	O1–Ni1–S1[a]	95.48	Cu1–S1	1.906	O1–Cu1–S1[a]	93.77
Ni1–O1	2.1733	O1–Ni1–S1[b]	84.52	Cu1–O1	2.2812	O1–Cu1–S1[b]	86.23
Ni2–S2	2.1817	S2–Ni2–O3[a]	95.06	Cu2–S2	2.2790	S2–Cu2–O3[a]	93.51
Ni2–O3	1.827	S2–Ni2–O3[b]	84.94	Cu2–O3	1.909	S2–Cu2–O3[b]	86.49

(5)				(6)			
Bond	Length	Bond	Angle	Bond	Length	Bond	Angle
Zn–S1	2.2730(6)	O1–Zn–S1[a]	98.14(5)	In–S1	2.526(1)	O1–In–S2	171.1(1
Zn–O1	1.959(1)	S2–Zn–O3[a]	98.99(4)	In–S2	2.544(1)	O2–In–S3	165.5(1)
Zn–S2	2.2700(5)	O1–Zn–O3[b]	101.36(6)	In–S3	2.550(1)	O3–In–S1	169.50(8)
Zn–O3	1.955(2)	O1–Zn–S2[b]	116.82(5)	In–O1	2.140(3)	S1–In–O1	85.4(1)
		S1–Zn–S2[b]	122.25(2)	In–O2	2.167(3)	S2–In–O2	85.9(1)
		S1–Zn–O3[b]	118.32(5)	In–O3	2.169(3)	S3–In–O3	84.54(8)

[a] intraligand bond angle.
[b] interligand bond angle.

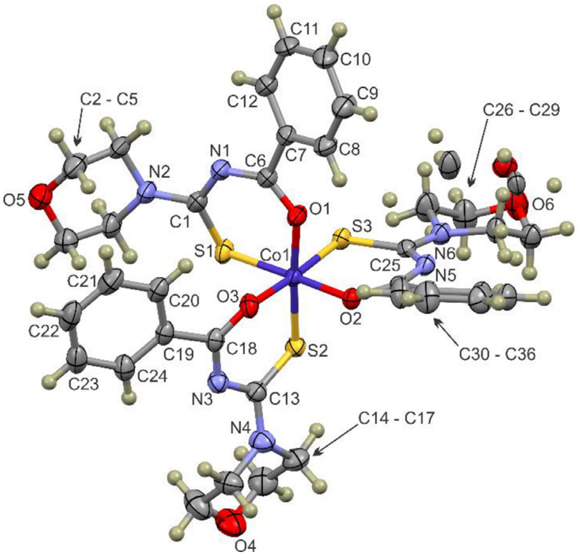

Fig. 4. The molecular structure of complex **(2)** showing the atom naming scheme. The sulfur and oxygen ligand donor atoms have adopted a *facial* (*fac*) coordination geometry. One of the three morpholine rings is disordered between a ring up and ring down orientation with a ratio of 78:23. Displacement ellipsoids are shown at the 50% probability level. Hydrogens are shown as spheres of arbitrary radius.

mately coplanar with the OCNCS–Fe chelate ring. This conformation allows for extended π-conjugation from the phenyl ring to the carbonyl group. The relatively long C–S and short C–O average bond lengths of 1.737(4) and 1.267(5) Å for (**1**), respectively highlight the single- and double-bond character of these groups. This pattern of bond lengths in all three ligands of (**1**) suggests that the formal negative charge is predominantly localised on the S atom. The structure crystallised with a disordered dichloromethane molecule in the asymmetric unit, which was removed in silico leaving a solvent-accessible void of 174 Å [3].

The single crystal X-ray structure of the cobalt complex (Fig. 4) shows that the cobalt(III) ion has a nominally octahedral coordination geometry with an S_3O_3 environment similar to that of complex **(1)**. This structure is a polymorph of one previously reported [42–44]. The previously reported structure crystallised in the *P*-1 Space Group; similarly with a single molecule in the asymmetric unit [42,44]. The two structures show comparable molecular geometries in terms of both bond lengths and bond angles [42,44]. Similar to compound (**1**), three thiourea ligands coordinate the metal ion to form three six-membered chelate rings (NC_2OS–Co) and a neutral metal complex. The Co–S bond distances of the present structure range from 2.2066(7) to 2.2153(6) Å and the Co–O bond distances range from 1.917(2) to 1.941(2) Å. The structure shows the same ligand geometry with respect to the coplanar nature of the phenyl rings and carbonyl groups. Closely related ligands with fluorine on the phenyl ring have also been coordinated to the Co(III) ion as well as ligands with piperidine in place of morpholine [43]. It is interesting to note that when the Co(II) ion is prevented from oxidizing, it forms a nominally tetrahedral complex with two ligand molecules (both with fluorine substitution on the phenyl ring, but the same morpholine moiety) [43]. When the reaction mixture is allowed to oxidize, the same fluorine- substituted ligand forms a tri-ligated species with Co(III) which consequently has an octahedral geometry. In both cases the metal chelates are neutral overall [43]. Despite the strongly electron withdrawing effect of the fluorine group, the geometric parameters compare favourably with those of complex (**2**) reported herein. Seemingly, the fluorine substituent is too remote from the coordination sphere to have any significant impact on the geometric parameters.

The Ni(II) chelate has been previously reported by Zhou et al., Del Campo et al., and Richter et al. [31,45,46]. Despite the numerous reports of the structure, the present compound is a new polymorph, differing in both the unit cell parameters and contents of the unit cell. The present structure is the only example with inversion symmetry about the divalent metal ion. Two of the previously reported compounds also have solvent in the lattice; either toluene or dichloromethane [45,46]. The Ni(II) and Cu(II) chelates, compounds (**3**) and (**4**), respectively, are isostructural from a crystallographic perspective and will be discussed together. Both compounds crystallise in the triclinic Space Group *P*-1 with two half-

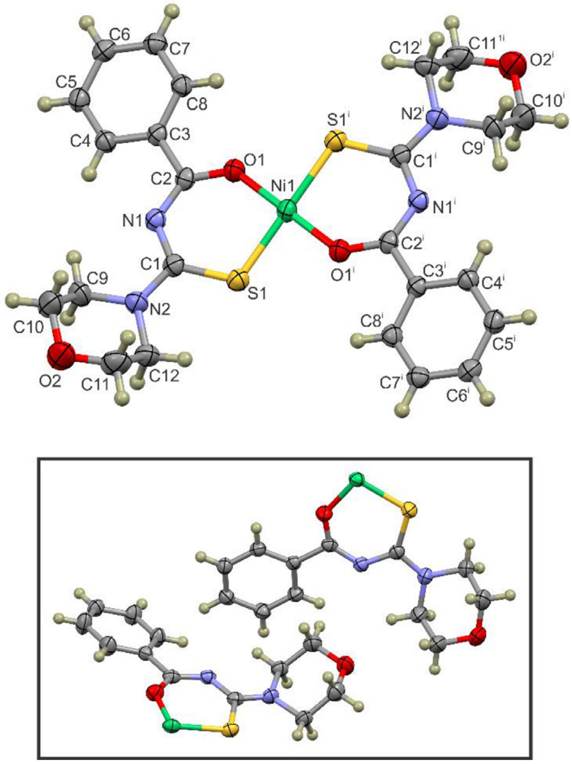

Fig. 5. [Main] The symmetry-completed structure of a single molecule of complex **(3)** showing the atom naming scheme. [Inset] The contents of the asymmetric unit of complex (3) comprising two half molecules with inversion symmetry on the metal centre. Displacement ellipsoids are shown at the 50% probability level. Hydrogens are shown as spheres of arbitrary radius. Symmetry code: i = -x, -y, -z.

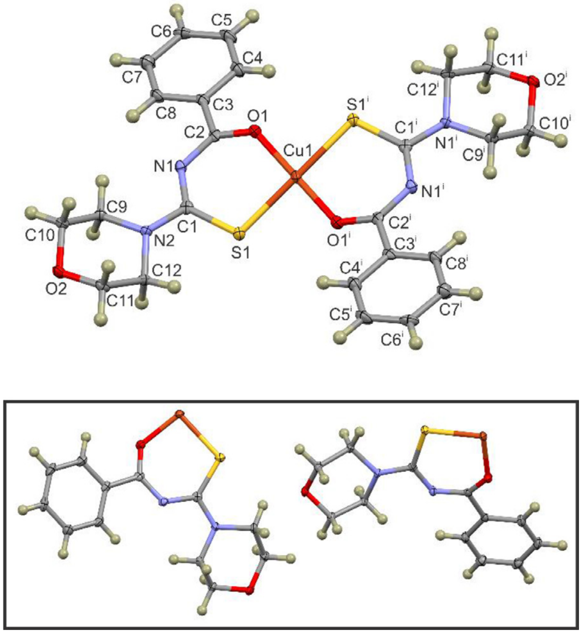

Fig. 6. [Main] The symmetry-completed structure of a single molecule of complex **(4)** showing the atom naming scheme. [Inset] The contents of the asymmetric unit of complex (**4**) comprising two half molecules with inversion symmetry on the copper(II) metal centre. Displacement ellipsoids are shown at the 50% probability level. Hydrogens are shown as spheres of arbitrary radius. Symmetry code: i = -x, -y, -z.

molecules in the asymmetric unit and inversion symmetry at the metal centre; as shown in Figs. 5 and 6, respectively. The divalent nickel and copper ions are each coordinated by two bidentate ligands giving an approximate square planar geometry. In both cases the S–M–O intraligand bond angles are obtuse measuring *ca.* 95° and 94° for (**3**) and (**4**), respectively. This is a consequence of the ligand bite and resulting six-membered chelate ring. Subsequently, the interligand S–M–O bond angles are acute, measuring *ca.* 85° and 86° for (**3**) and (**4**), respectively. The inversion symmetry of the molecule necessitates that the interligand S–M–S and S–M–O bond angles measure 180°.

Despite the different coordination geometries compared to compounds (**1**) and (**2**), the ligands still show relatively long C–S and short C–O mean bond lengths of 1.730(4) Å and 1.266(5) Å, respectively. These are consistent with predominantly single (C–S) and double- (C=O) bond character and suggest that the negative charge of the ligand is located predominantly on the sulfur atom. Although the Ni(II) chelate is a new polymorph, as with the Co(III) chelate, the geometric parameters describing the coordination sphere are comparable to the previously reported divalent nickel chelates [31,45,46].

A least squares fit of a selection of the non-hydrogen atoms for the two molecules in the asymmetric unit of (**3**) shows that the key difference is the relative orientation of the morpholine rings (ring up versus ring down). In the case of compound (**4**), the difference is again the orientation of the morpholine rings, but the difference is not as stark as the ring up/ring down orientations of the half-molecules in (**3**). These fits are shown in Fig. 7.

The Zn(II) complex, compound (**5**), is shown in Fig. 8. This compound is also four-coordinate with two bidentate ligands and crys-

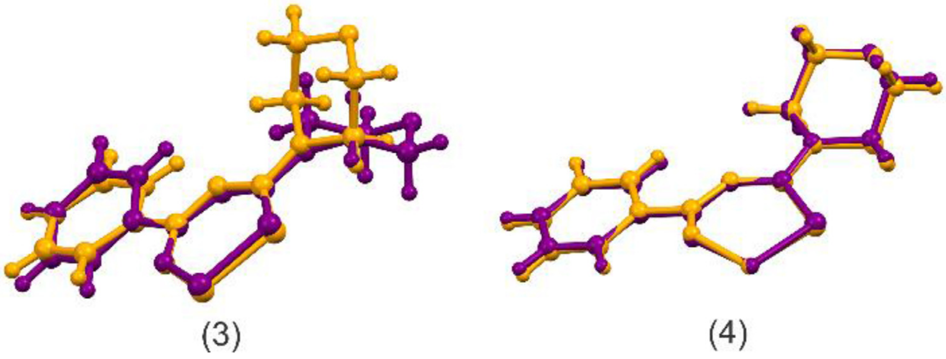

Fig. 7. Least-squares fits of the two half-molecules in the asymmetric units of (**3**) and (**4**) showing the main structural differences. For (**3**), the half-molecules in the asymmetric unit differ by the relative orientation of the morpholine ring. A least-square fit of the benzoyl thiourea portion of the molecule (i.e. excluding the morpholine ring) gives an RMSD of 0.198 Å for the 13 atoms used in the structure overlay (molecule A in purple and B in yellow). The half molecules of (**4**) are more similar as illustrated by an RMSD of 0.0765 Å for the same 13 non-H atoms.

Table 3
Selected bonds lengths (Å) and bonds angles (°) for the complexes with some known structures made from benzoylthiourea (diethyl amine and piperidine used as secondary amine).

Secondary amine ([a]piperidine)	Cis-[Ni]	Trans-[Ni]	Cu	Cis-[Zn]
Bond	**Length (Å)**	1.835(2)	1.905(3)	1.949(2)
M-O1	1.853(2)			
M-O2	1.861(2)			1.968(2)
M-S1	2.133(1)	2.172(1)	2.244(8)	2.291(1)
M-S2	2.140(1)			2.286(1)
S1-C8	1.728(4)	1.716(4)	1.732(4)	1.742(3)
S2-C21	1.719(4)			1.743(3)
O1-C1	1.264(4)	1.268(4)	1.268(5)	1.277(3)
O2-C14	1.257(4)			1.271(3)
N1-C1	1.320(4)	1.316(4)	1.313(5)	1.305(4)
N3-C14	1.325(4)			1.310(3)
N1-C8	1.336(4)	1.341(4)	1.349(5)	1.341(4)
N3-C21	1.342(4)			1.344(4)
N2-C8	1.339(4)	1.344(4)	1.339(5)	1.329(4)
N4-C21	1.340(4)	94.4(8)	93.8(1)	1.326(4)
Bond	**Angle (°)**	85.6(8)	86.2(1)	108.4(9)
O1-M-O2	85.4(1)	**[Fe]**	1.986(2)	98.7(7)
O1-M-S1	95.6(8)	Fe-O1	2.4221(8)	117.8(7)
O1-M-S2	168.9(1)	Fe-S1	1.726(3)	118.1(7)
O2-M-S1	169.9(9)	S1-C8	1.353(3)	97.7(6)
O2-M-S2	94.9(8)	N1-C8	1.319(3)	118.1(4)
S1-M-S2	86.0(4)	C7-N1	1.247(3)	
([b]diethylamine)	**[Cu]**	C7-O1	87.52(9)	
Bond	**Lenght (Å)**	O1-Fe-O1#	85.55(6)	
Cu1-O1	1.918(4)	O1#-Fe-S1	99.77(7)	
Cu1-O2	1.929(4)	O1-Fe-S1*	169.70(7)	
Cu1-S1	2.221(2)	O1-Fe-S1#	88.13(3)	
Cu1-S2	2.233(2)	S1-Fe-S1*	125.2(2)	
O2-C19	1.261(5)	C7-N1-C8		
N3-C20	1.339(6)			
S2-C20	1.742(4)			
S1-C8	1.740(5)			
O1-C7	1.265(6)			
N1-C8	1.338(6)			
N1-C7	1.324(6)			
N3-C19	1.318(6)			
Bond	**Angle (°)**			
O1-Cu1-O2	86.40(16)			
O1-Cu1-S1	93.32(12)			
O2-Cu1-S2	93.87(11)			
S1-Cu1-S2	86.39(6)			
O2-Cu1-S1	179.71(13)			
O1-Cu1-S2	173.04(15)			
C8-N1-C7	125.4(4)			
C19-N3-C20	125.8(4)			

Symmetry code: * = (1-y, x-y, -1+z) and # = (1-x+y, 1-x, -1+z).

[a] Data are taken from Xie *et al.* [49].

[b] Data are taken from Mandal *et al.* [42].

tallises in the triclinic *P*-1 Space Group. The molecular structure of (**5**), however, adopts approximately tetrahedral coordination geometry as opposed to the square planar configuration of (**3**) and (**4**). The tetrahedron is defined by angles around the Zn(II) ion ranging from 98.14(5)–122.25(2)°. The more acute angles of 98.14(5)° and 98.99(4)° are associated with the intraligand S1−Zn1−O1 and S2−Zn1−O3 bonds, respectively. These angles are in good agreement with the comparable intraligand bond angles of (**3**) and (**4**) as they are constrained by the ligand bite and associated six-membered chelate rings. The interligand bond angles, which are not constrained by the ligand geometry, range from 101.36(6) to 122.25(2). The details of these bond angles are available in Table 2. The C−N bonds lengths observed for the ligands in this work may suggest a process of imine–enamine tautomerism [48]. The C−S and C−O bond lengths (1.745(2) and 1.270(2) follow the same trend as the other compounds in this study and suggest the negative charge is predominantly located on the sulfur atom.

The solid state structure of the In(III) chelate, compound (**6**), depicted in Fig. 9 shows the indium(III) ion to have a slightly distorted octahedral coordination geometry with a *fac*-S_3O_3 coordination environment similar to that of complexes **(1)** and **(2)**. It similarly crystallises in the monoclinic $P2_1/c$ space group with three monoanionic, bidentate ligands coordinated. This leads to three six-membered chelation rings (NC_2OS–In) with In–S bond lengths ranging from 2.526(1) to 2.550(1) Å and In–O bonds lengths ranging from 2.140(3) to 2.169(3) Å. The compound crystallised as the acetone monosolvate. The absence of formal hydrogen bond donors in the ligand structure precludes any intermolecular hydrogen bonding. All the structures do, however, show numerous weakly stabilising C–H•••O and C–H•••N interactions in the solid state.

The data in Table 2 show that the interligand S–M–O *trans* bond angles describing the nominally octahedral geometry of the metal ion are more acute than the ideal bond angle of 180°. The intraligand S–M–O bond angles vary in magnitude which is somewhat unexpected considering the limitations imposed by the ligand bite. The most notable difference is evident in the three octahedral chelates, Fe(III), Co(III) and In(III). The intraligand bond angles of the Fe(III) and In(III) chelates are all slightly acute. In all other complexes (whether octahedral, tetrahedral or square pla-

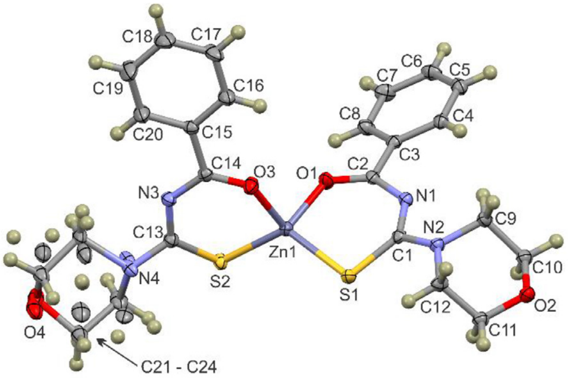

Fig. 8. The structure of complex (**5**) showing the atom naming scheme. Displacement ellipsoids are shown at the 50% probability level. One of the morpholine rings is disordered over two positions with a 1:1 ratio of the two positions. Hydrogens are shown as spheres of arbitrary radius.

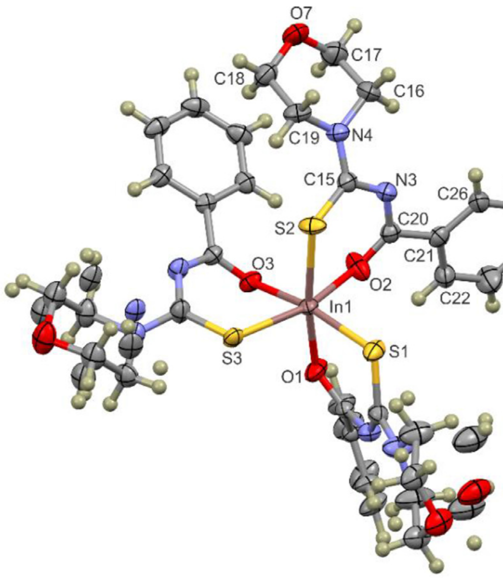

Fig. 9. The molecular structure of complex (**6**) showing the atom naming scheme. The sulfur and oxygen ligand donor atoms have adopted a *facial* (*fac*) coordination geometry. Two of the three morpholine rings are disordered between a ring up and ring down orientation with ratios of 76:24 and 69:31. Displacement ellipsoids are shown at the 50% probability level. Hydrogens are shown as spheres of arbitrary radius.

nar), the 6-membered chelate rings and the associated bite of the ligand leads to obtuse intraligand S–M–O bond angles. The trivalent iron and indium chelates are also the only solvated compounds, although the reason is not immediately apparent, it is possible that there is a relationship between the solvation of these compounds and the acute intraligand bond angles.

A comparative study of selected bond lengths and bond angles for the compounds synthesised herein with those of similar structures (diethyl amine and piperidine used as secondary amine) is presented in Table 3. In general, it is observed that the bond lengths and bond angles of Cu(II) and Fe(III) complexes of *N*-piperidine-*N'*-benzoylthiourea and those of Cu(II), Zn(II) and Ni(II) complexes of *N, N-diethyl-N'*-benzoylthiourea are larger than those of the corresponding morpholine complexes. This is likely attributable to inductive effects, as morpholine contains a more electronegative oxygen atom and piperidine is more electron donating as it is a heterocyclic amine, in comparison to diethyl amine, which is a secondary amine.

4. Conclusion

N-morpholine-*N'*-benzoylthiourea and its novel complexes of Fe(III), Co(III), Ni(II), Cu(II), Zn(II) and In(III) were synthesized and characterised using various techniques including single crystal X-ray diffraction studies. The trivalent compounds all adopt comparable octahedral structures comprising three monoanionic bidentate ligands coordinated to the metal centre. The octahedral complexes all showed a preference for an S_3O_3 facial arrangement of coordinating atoms. This ubiquitous geometry was found to be *ca.* 9 kJ.mol^{-1} lower in energy than the comparable meridional isomer using DFT methods. The divalent metal chelates are square planar in the case of Cu(II) and Ni(II), but tetrahedral for Zn(II). The coordination sphere of the divalent compounds is completed by two of the *S,O*-donor bidentate ligands. From the TGA and unpublished data, the complexes have shown a potential usefulness as single source molecular precursors for the preparation of metal sulfide nanomaterials.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Kevin I.Y. Ketchemen: Data curation, Writing - original draft. **Malik Dilshad Khan:** Conceptualization, Supervision, Writing - original draft. **Sixberth Mlowe:** Conceptualization, Supervision, Writing - original draft. **Matthew P. Akerman:** Data curation, Formal analysis, Writing - review & editing. **Inigo Vitorica-Yrezabal:** Data curation. **George Whitehead:** Data curation. **Linda D. Nyamen:** Supervision, Writing - original draft. **Peter T. Ndifon:** Supervision, Funding acquisition, Writing - review & editing. **Neerish Revaprasadu:** Conceptualization, Supervision, Funding acquisition, Writing - review & editing. **Paul O'Brien:** Supervision, Funding acquisition.

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Supplementary data

CCDC 2021576, 2021575, 2021578, 1569168, 2021579 and 2021577 contains the crystallographic data for compounds (**1**) – (**6**), respectively.

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