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Complexes of thiophenolate-containing Schiff-base macrocycles and their amine analogues

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Contents

Abstract

The complexes of thiophenolate-containing Schiff-base macrocycles, and of their amine analogues, are the subject of this review. In addition to discussing the structures and properties of these nickel, copper and zinc complexes, the routes to the required thiophenolate precursors are also reviewed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Macrocycle; Nickel; Copper; Zinc; Thiolate; Synthesis; Structure

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1. Introduction

1.1. Scope

This review covers the recent introduction of two closely related 'head units', 2,6-diformyl-4-methylthiophenolate **1** and 2,6-diformyl-4-*tert*-butylthiophenolate **2**, and the 'lateral unit', 2,6-bis(aminomethyl)-4-*tert*-butylthiophenolate **3**, into Schiff-base macrocyclic chemistry (Figs. 1 and 2). The reader is referred to earlier reviews on Schiff-base macrocycles for excellent introductions to this general area as well as reviews of the well-known pyridine and phenolate-based head units [1–6]. Schiff-base macrobicycles, or crypts, have also been comprehensively reviewed recently [7].

1.2. Reasons for interest in Schiff-base thiophenolate macrocycles

In the early 1990s a number of research groups independently initiated research aimed at introducing thiophenolate head units into Schiff-base macrocycles. There were many reasons for this convergence of ideas.

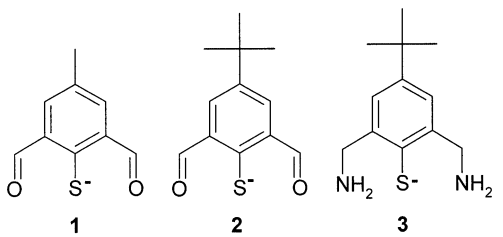


Fig. 1. The two thiophenolate head units (**1** and **2**) and the one thiophenolate lateral unit (**3**) used in macrocycles to date.

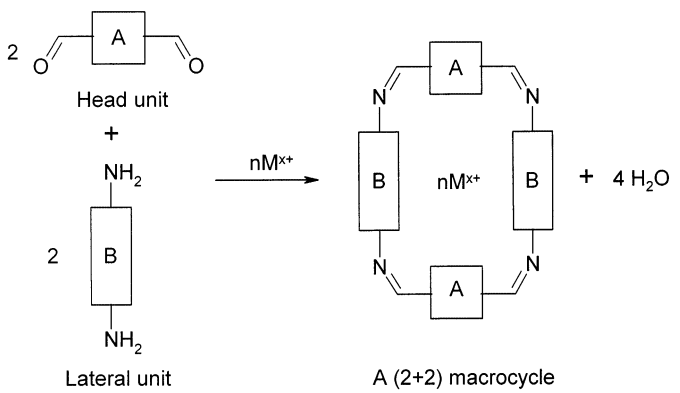


Fig. 2. Template synthesis of a (2 + 2) Schiff-base macrocycle from two head (dicarbonyl) units and two lateral (diamine) units.

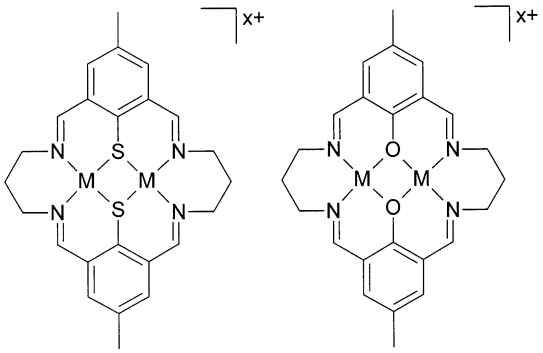


Fig. 3. Dimetallic complexes of a thiophenolate (2 + 2) Schiff-base macrocycle and of its phenolate analogue.

First, the possibility of comparing and contrasting the new generation of thiophenolate macrocyclic complexes with the analogous, extensively studied, phenolate macrocyclic complexes, the first of which had been described by Robson and co-workers in 1970 [8], was very attractive (Fig. 3). Like the phenolate-containing ligands, the thiophenolate-containing ligands provide bridges between the bound metal ions, facilitating communication between them, but the thiophenolate analogues are expected to reveal very different properties (e.g. redox and magnetic) due to the presence of the very polarisable thiophenolate donors.

Secondly, a suitable head unit, 2,6-diformyl-4-methylthiophenolate **1** (Fig. 1), was known as it had been prepared in the late 1970s by Robson and co-workers and used in a study of acyclic thiophenolate-bridged complexes (Section 2) [9–26]. An added bonus of utilising thiophenolates for initial thiolate studies is that they are expected to be easier to work with than, for example, alkyl thiolates.

Finally, added impetus to better understand and control thiolate coordination chemistry has come from the considerable, and rapidly growing, interest in thiolate-bridged metal active sites in biology. For example, the CuA site in cytochrome *c* oxidase [27,28], the active site of [NiFe]-hydrogenases, [29–33] and more recently the active site of Fe-only hydrogenases [34–36] are all novel entities which therefore provide us with considerable challenges. In these cases cysteine-derived thiolates bridge the metal ions so ideally alkyl thiolates should be employed in modelling these sites. The reader is referred to a review of the general approach taken to modelling biological active sites [37].

1.3. Challenges of working with thiolates

There are many difficulties traditionally associated with carrying out thiolate coordination chemistry which have tended to deter researchers from working with thiolates (see for example Ref. [38]). Firstly as thiolates are electron rich they have a strong tendency to bridge metal ions. If uncontrolled this can lead to the formation of aggregates or polymers of varying size which can be hard to study,

particularly in solution due to poor solubility and/or a lack of integrity of the clusters/polymers [39,40]. Traditionally control has been exerted by the use of steric factors and/or by the use of thiolates to which electron-withdrawing groups have been attached [40]. Control is achieved in the cases reviewed here by using a macrocyclic framework in combination with thiophenolate donor atoms. Careful positioning of the thiolate donor atoms within a macrocyclic framework neatly controls the thiolate coordination/bridging and consequently provides a significant degree of control over the nuclearity of the resulting complexes. This approach was nicely demonstrated by Lawrance and co-workers in the sole example of a dinickel complex of a thiolate-containing macrocycle which existed prior to the studies reviewed here [41]. The bridging tendency of thiolates is more easily controlled in the case of aromatic thiolate donors, such as thiophenolates, than in the case of alkyl thiolate donors, as they are less electron rich.

Another complication is the fact that the thiolates themselves can undergo redox processes. Hence the preparation of thiolate coordination complexes often requires careful Schlenk work, in particular avoiding the presence of oxygen which could lead to oxidation of the thiolates to disulphides or indeed to sulphenates or sulphinates as has been thoroughly investigated by Darensbourg and co-workers [42]. Even when coordinated this propensity to be redox active, that is to be potentially non-innocent ligands, complicates the interpretation of the observed redox properties of the metal complex [43]. However, this can and does add to our fundamental interest in such complexes [44], in part because such behaviour is highly relevant to the increasing numbers of examples of organic radicals and of delocalised electrons being important in various natural catalytic processes where the metal ions are bound to thiolate donors. Macrocyclic thiolate complexes have the advantage that the redox processes are often more reversible than in the acyclic analogues, indicating that the macrocyclic cavity helps to stabilise the redox products, at least on the cyclic voltammetry time scale (vide infra) [45,46].

Finally, there is also the unpleasant odour of thiols, but here again the choice of thiophenol head units should minimise this problem relative to, more volatile, alkyl thiols.

2. Access to the desired thiophenolate head and lateral units

Robson and co-workers earlier reported the synthesis and redox chemistry of a series of acyclic complexes derived from 2,6-diformyl-4-methylthiophenolate **1** (Fig. 1) [9–26]. For the synthesis of this head unit these papers refer to the method described in a seminal paper by Newman and Karnes, on the conversion of a series of related phenols to thiophenols [47]. The details of the synthesis of **1**, isolated and stored as the stable masked thiolate *S*-(2,6-diformyl-4-methylphenyl)-dimethylthiocarbamate, were published in 1996 [48]. Subsequently an improved synthesis of **1**, and of other related thiophenolate head units including the *tert*-butyl analogue **2** which is relevant here, has been developed and detailed in the literature by Brooker and co-workers (Fig. 4) [49]. The masking group is standardly

removed in situ by base hydrolysis. The macrocyclic complexes which have been prepared and characterised from **1** and **2** will be described in Sections 3 and 4.

Kersting has prepared the diamine lateral unit, 2,6-bis(aminomethyl)-4-*tert*-butylthiophenolate **3**, via reduction of the dioxime (Fig. 5) [50]. A range of complexes of **3** have been reported [50–52] but, to date, no acyclic or macrocyclic ligands have been prepared from **3**. However, it is surely only a matter of time until this thiophenolate lateral unit is exploited in Schiff-base chemistry: having access to **3** considerably expands the interesting permutations possible in this area of chemistry, and, as it is stable in the unmasked form, it should be straightforward to prepare Schiff-base macrocycles from it.

Ligands which are effectively derived from the *tert*-butyl thiophenolate head unit **2** can also be accessed by a quite different route from that outlined in Fig. 4. The use of a *tert*-butyl moiety [Fig. 5 step (v)] results in the masked thiophenolate,

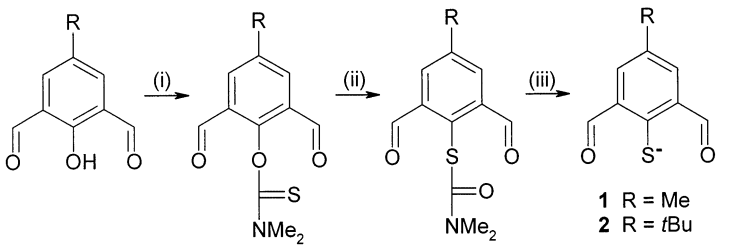


Fig. 4. Synthesis of the 2,6-diformyl-4-alkylthiophenolate head units (R = Me **1**, R = *tert*-Bu **2**) via the *S*-(2,6-diformyl-4-alkylphenyl)dimethylthiocarbamates (masked thiolates). Reagents: (i) DABCO [109], Cl–C(=S)NMe_2; (ii) BF_3OEt/toluene/85°C; and (iii) KOH [48,49].

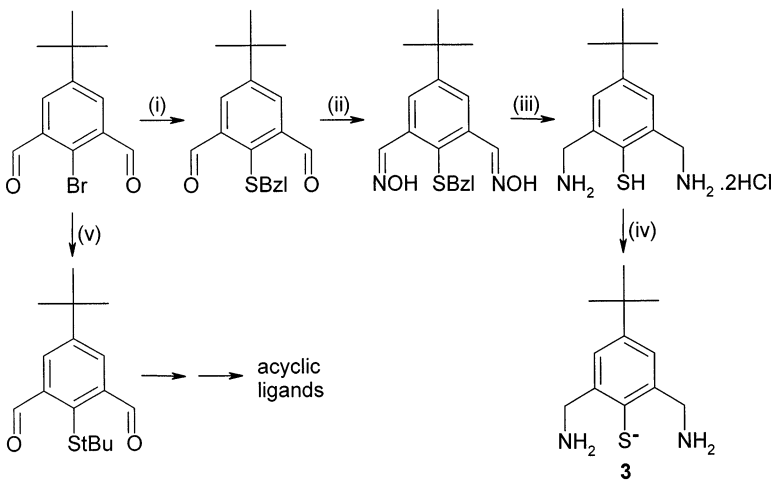


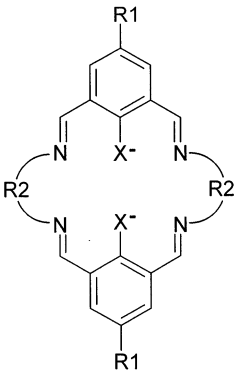
Fig. 5. Synthesis of the 2,6-bis(aminomethyl)-4-*tert*-butylthiophenolate lateral unit **3**: (i) $PhCH_2SH$/K_2CO_3; (ii) NH_2OH; (iii) 1. Na/NH_3 2. HCl; (iv) NaOMe [50] ; and (v) *tert*-BuSH/K_2CO_3.

tert-butyl(4-*tert*-butyl-2,6-diformylphenyl)sulphide, which can then be condensed with one equivalent of hydroxylamine and an appropriate amount of the amine of choice (monoamine or polyamine). The product is reduced in two stages: the Schiff-base and oxime bonds which were generated in situ are reduced to amines in the first stage and, under more vigorous reduction conditions, the thiolate is unmasked. The resulting thiophenolate ligands are therefore amines not Schiff-bases. To date, only acyclic ligands have been accessed by this route, so they will not be discussed further here [52–55].

In another extension of the synthesis outlined in Fig. 5, Kersting and co-workers have developed an elegant route to amine macrocycles which are effectively derived from the 2,6-diformyl-5-*tert*-butyl-thiophenolate head unit **2** (Section 4) [56]. Amine macrocycles have been produced by this route and will be further discussed in Section 4 (Fig. 18). Unless an alternative method of unmasking the thiophenolate can be developed it is unlikely that this approach can be used to access Schiff-base macrocycles.

3. Thiophenolate Schiff-base macrocycles

Schroder and co-workers reported the synthesis and structure of the first thiophenolate Schiff-base macrocyclic complex in a preliminary communication late in 1993 (Fig. 6, $LS1^{2-}$) [57]. Independently, Brooker and co-workers had also prepared this thiophenolate complex, with a different counter ion. They subsequently reported the full details of the synthesis, characterisation and rich redox properties of this dinickel(II) complex, as well as that of the very similar (somewhat more soluble) dinickel(II) complex of the *tert*-butyl analogue (Fig. 6, $LS2^{2-}$) [45,48,49]. The structures of the dinickel(II) complexes of $LS1^{2-}$, as PF_6^- and ClO_4^- salts, respectively, show the anticipated differences from the analogous phenolate complexes (Fig. 7) [45,48,57–59], the major difference being that the thiophenolate complex $[Ni_2(LS1)]^{2+}$ is bowed in dramatic contrast to the flat structures of the phenolate analogues, $[Ni_2(LO1)(MeCN)_4]^{2+}$ and $[Ni_2(LO8)(OH_2)_2(Cl)_2]$ (Figs. 6 and 7). The sulphur atoms adopt a pyramidal geometry whereas the oxygen atoms are trigonal. The Ni···Ni separations in these complexes are very similar {$[Ni_2(LS1)]^{2+}$ av. 3.151(2) Å; $[Ni_2(LO1)(MeCN)_4]^{2+}$ 3.1355(8) Å; $[Ni_2(LO8)(OH_2)_2(Cl)_2]$ 3.10 Å}. Another highly significant difference is that the nickel atoms in the phenolate complexes are octahedral (high spin) whereas in the thiophenolate complex the nickel atoms are square planar (low spin). Rich reversible redox is a feature of $[Ni_2(LS1)]^{2+}$, with four one-electron redox processes observed: the mixed valent Ni(II)Ni(III) thiophenolate complex has been isolated but is unstable even in the solid state [45]. The two reversible reduction processes and the two oxidation processes {$[Ni_2(LS1)]^{2+}$ in MeCN: -1.46^{R}, -1.01^{R}, $+0.63^{R}$, $+1.07^{QR}$ V vs 0.01 M $AgNO_3 \mid Ag$; Fc/Fc^+ occurred at $+0.13$ V in this system} occur more readily than in the analogous phenolate complex {$[Ni_2(LO1)(MeCN)_4]^{2+}$ in MeCN: -1.40^{I}, $+1.05^{QR}$, $+1.26^{I}$ V vs 0.01 M $AgNO_3 \mid Ag$; Fc/Fc^+ occurred at $+0.13$ V in this system} [45]. The oxidation waves are found to be sensitive to axial coordination by solvent molecules, as would be expected for Ni(III).



Ligand	X	R1	R2
$LS1^{2-}$	S	Me	$CH_2CH_2CH_2$
$LS2^{2-}$	S	*t*Bu	$CH_2CH_2CH_2$
$LS3^{2-}$	S	Me	$CH_2CH_2CH_2CH_2$
$LS4^{2-}$	S	Me	$CH_2CH_2NHCH_2CH_2$
$LS5^{2-}$	S	Me	$CH_2CH_2CH_2NHCH_2CH_2CH_2$
$LS6^{2-}$	S	Me	$CH_2CH_2NHCH_2CH_2CH_2CH_2NH$
$LS8^{2-}$	S	Me	$CH_2CH(OH)CH_2$
$LS9^{2-}$	S	Me	$CH_2CH_2CH(OH)CH_2CH_2$
$LO1^{2-}$	O	Me	$CH_2CH_2CH_2$
$LO8^{2-}$	O	Me	$CH_2CH(OH)CH_2$
$LO9^{2-}$	O	Me	$CH_2CH_2CH(OH)CH_2CH_2$
$LO12^{2-}$	O	Me	CH_2CH_2

Fig. 6. Thiophenolate (2 + 2) Schiff-base macrocycles prepared to date, and some phenolate analogues. For the sole example of a (4 + 4) Schiff-base see Fig. 13, and for other thiophenolate macrocycles see Figs. 14 and 18.

Brooker and co-workers had earlier reported that in ethanolic solvents acetal formation could lead to difficulties with this cyclisation reaction (Fig. 8) [60]. This resulted in the formation of an intriguing trinickel(II) complex, $[Ni_3(LS1^*)_2]^{2+}$, in which two different spin states are observed. The central nickel ion, which holds the two acyclic complexes together, is octahedral whereas the nickel ion in each acyclic ligand is square planar as would be expected. Subsequent to this discovery IPA and/or MeCN reaction solvents have been used in order to avoid this complication.

With this knowledge in hand, the lateral unit 1,4-diaminobutane was used in conjunction with **1** in order to explore the possibility of obtaining high-spin nickel centres in thiophenolate macrocycles by providing a larger cavity and hence a looser fit (Fig. 6, Table 1) [45,61]. The resulting complex, $[Ni_2(LS3)]^{2+}$, was diamagnetic in the solid state but did exhibit a greater tetrahedral distortion away from square planar than was the case for the $LS1^{2-}$ analogue {dihedral angle between NiN_2 and NiS_2 planes: 15.4–18.9° $[Ni_2(LS3)]^{2+}$; 2.3–6.1° $[Ni_2(LS1)]^{2+}$}. Consistent with this the $[Ni_2(LS3)]^{2+}$ complex did show an increased tendency to coordinate solvent molecules in the axial sites over that of the $[Ni_2(LS1)]^{2+}$

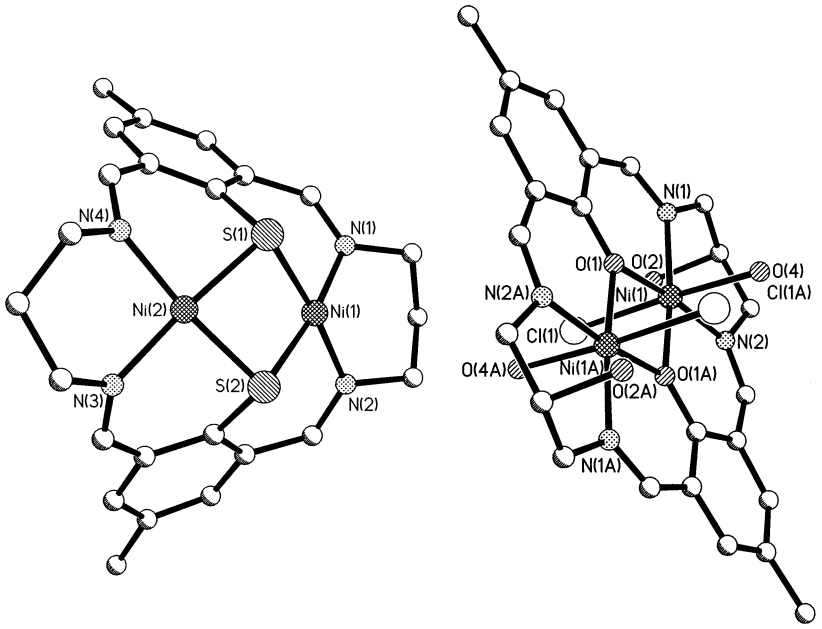


Fig. 7. Perspective view of $[Ni_2LS1]^{2+}$ (left) and of the phenolate analogue $[Ni_2(LO8)(OH_2)_2(Cl)_2]$ (right). The figure on the left is generated from the data reported originally in Ref. [48]. The figure on the right is generated from data downloaded from the Cambridge Crystallographic Database as published originally in Ref. [59].

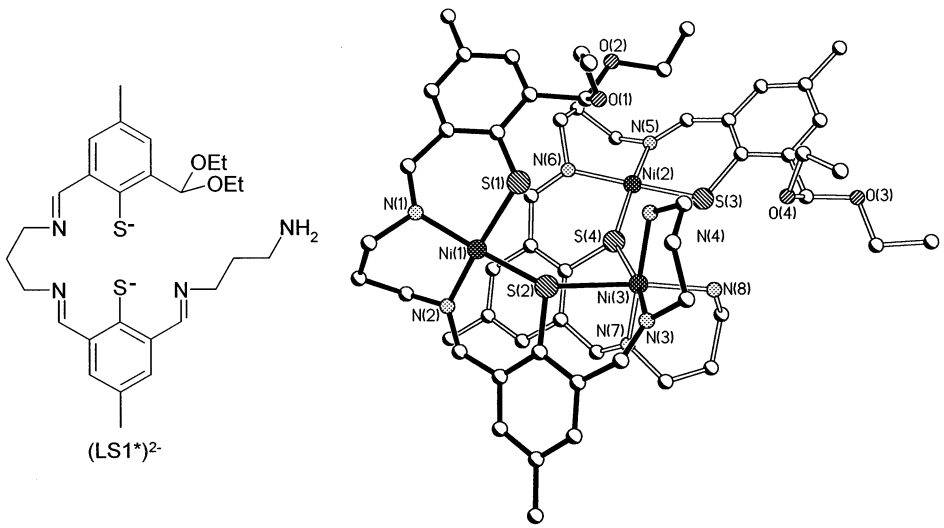


Fig. 8. Diagram of the acyclic acetal ligand $(LS1^*)^{2-}$ (left) and a perspective view of the structure of the resulting trinickel complex $[Ni_3(LS1^*)]^{2+}$ (right). The figure on the right is generated from data reported originally in Ref. [60].

Table 1
A selection of interatomic distances (Å) for all of the nickel thiophenolate-containing Schiff-base macrocycles and their amine analogues known to date, with the exception of the two structures for which only poor-quality X-ray data were obtained {$[Ni_2LS2]^{2+}$ and $[Ni_2(4+4)]$} [49,75]. Key: LS(Ni), low-spin nickel(II); HS(Ni), high-spin nickel(II). Only thiophenolate-bridged Ni···Ni interatomic distances are given. Only the S···S interatomic distances for bis(μ_2-thiophenolate) dinickel(II) moieties are given.

	LS(Ni)	References	HS(Ni)	References
$Ni–S_{thiophenolate}$	2.147–2.212	[45,48,49,56,57,80,99]	2.312–2.503	[45,56,63,80,90]
$Ni–O_{phenolate}$	1.952	[80]	2.090–2.121	[63,80]
$Ni–O_{alkoxide}$			1.973–2.124	[90]
$Ni–N_{imine}$	1.891–1.944	[45,48,49,57,80]	2.024–2.085	[45,63,80,90]
$Ni–N_{amine}$	1.935–1.963	[56,80,99]	2.035–2.167	[56,80]
$Ni–O_{acetate}$			2.002–2.111	[90]
$Ni–O_{dmf}$	2.575–2.644	[49,57]	2.102	[63]
$Ni–N_{MeCN}$			2.113–2.116	[80]
$Ni–N_{NCS}$			2.005–2.112	[45,56,63]
	Ni···Ni	S···S	$S···O_{phenolate}$	References
LS(Ni), LS(Ni)	3.02–3.214	2.74–2.872		[45,48,49,57,99]
LS(Ni), HS(Ni)	3.105–3.294	2.979–3.011	2.791	[45,56,80]
HS(Ni), HS(Ni)	2.910–3.172		3.036	[63,90]

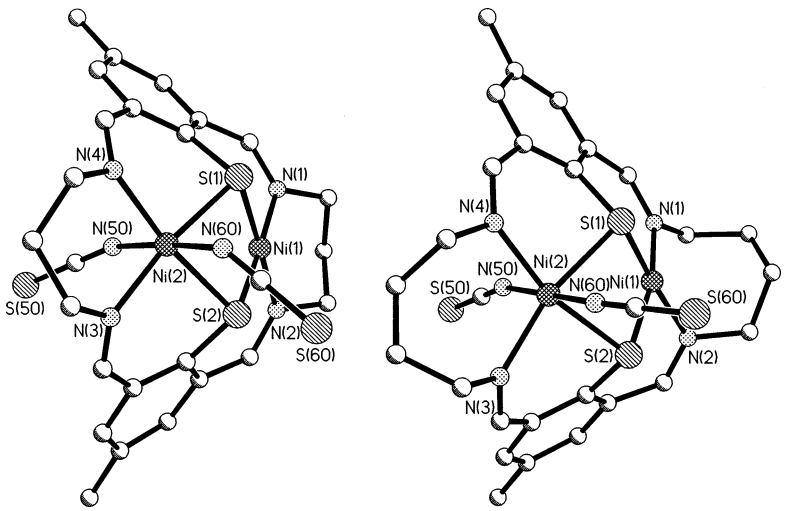


Fig. 9. Perspective views of $[Ni_2(LS1)(NCS)_2]$ (left) and $[Ni_2(LS3)(NCS)_2]$ (right). Both figures are generated from data reported originally in Ref. [45].

complex (NMR in coordinating vs non-coordinating solvents). Therefore $[Ni_2(LS1)]^{2+}$ and $[Ni_2(LS3)]^{2+}$ were reacted with a source of good donor atoms, sodium thiocyanate: both formed complexes with two thiocyanate ions on just one of the two nickel ions (Fig. 9). These di-thiocyanate complexes form even when

four equivalents of sodium thiocyanate are used. The fact that a neutral complex is generated appears to be important as it is a feature which is common to related literature complexes (e.g. Figs. 15 and 19, vide infra) [53,62,63]. Here this may well lead to reduced solubility and consequent crystallisation from the reaction mixture which is useful from the point of view of facile isolation of the complex but has the disadvantage that it prevents solution studies such as redox characterisation. The observation of juxtaposed high and low-spin nickel(II) ions is unusual: these two examples are even more unusual as this occurs despite the provision of potentially equivalent macrocycle binding sites. Given that high-spin nickel ions make bonds which are typically about 0.15–0.20 Å longer than low-spin nickel ions [64–66] it is not surprising that the smaller of the two macrocycles, $LS1^{2-}$, struggles to accommodate the single high-spin nickel atom as is evidenced by the low yield (19%) of $[Ni_2(LS1)(NCS)_2]$ and the formation of significant amounts of a ring-opened byproduct (Table 1). In contrast, the yield of $[Ni_2(LS3)(NCS)_2]$ is very good (83%) and there was no evidence of the formation of any ring opened byproduct.

Interestingly, two different zinc(II) complexes of $LS1^{2-}$ can be isolated and have been characterised [48,58,67]. In $[Zn_2(LS1)(H_2O)_2]^{2+}$ the dizinc(II) complex has two bound water molecules, whilst in $[Zn_2(LS1)(OH)]_2^{2+}$, formed under more basic conditions, the coordinated water molecules have deprotonated and bridge two dizinc(II) macrocycles (Figs. 6 and 10). The zinc(II) coordination geometry in the former complex is distorted trigonal bipyramidal [48] whereas in the latter, two zinc ions have a geometry intermediate between square pyramidal and trigonal bipyramidal whilst the other two zinc ions are square pyramidal [67]. Square-pyramidal geometry of the zinc ions is also observed in one of the two forms (the other geometry observed in the asymmetric unit is distorted octahedral, due to weak coordination of two of the perchlorate counter ions) of the analogous phenolate

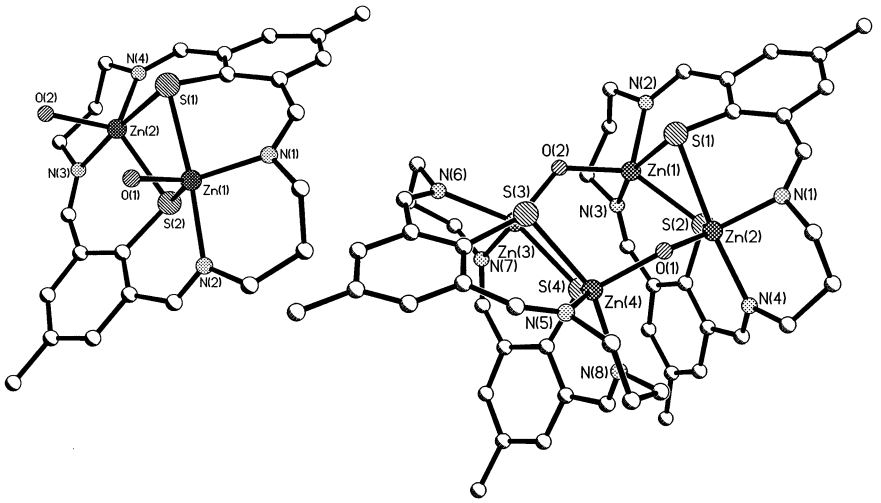


Fig. 10. Perspective views of $[Zn_2(LS1)(H_2O)_2]^{2+}$ (left) and $[Zn_2(LS1)(OH)]_2^{2+}$ (right). The figure on the left is generated from the data reported originally in Ref. [48]. The figure on the right is generated from data downloaded from the Cambridge Crystallographic Database as published originally in Ref. [67].

complex, $[Zn_2(LO1)(H_2O)_2]^{2+}$, described by Fenton and co-workers [68]. Both forms of the phenolate complex, cleverly prepared by transmetallation of the disodium complex, have very flat macrocycle conformations, in contrast to the thiophenolate analogues (Fig. 10). Zinc(II) is a redox inactive metal ion so it is expected to be a good template ion for these thiophenolate-containing macrocycles. The resulting macrocyclic complexes are expected to be useful both as redox 'blanks', to check for ligand redox, and because in principle the zinc(II) ions can subsequently be replaced by other, redox active, transition metal ions which are of interest.

Brooker and co-workers investigated the redox chemistry of the zinc complex with coordinated water and found an irreversible, approximately two-electron oxidation redox process, in acetonitrile, at $+1.30$ V vs SCE [48]. This may be due to either oxidation of coordinated water [69] or to disulphide formation [70]. To our knowledge, the redox chemistry of the phenolate analogue has not been reported, with studies focussing instead on their ability to catalyse the hydrolysis of phosphate esters [68]. The dinickel(II) complex, $[Ni_2(LS1)]^{2+}$ (Figs. 6 and 7), was prepared by transmetallation of the dizinc complex, $[Zn_2(LS1)(H_2O)_2]^{2+}$ [48]. Likewise Schroder and co-workers isolated a dicopper(II) complex of $LS1^{2-}$ by transmetallation of the dizinc complex (Fig. 11) [58,67]. The $[Cu_2(LS1)(MeOH)_2]^{2+}$

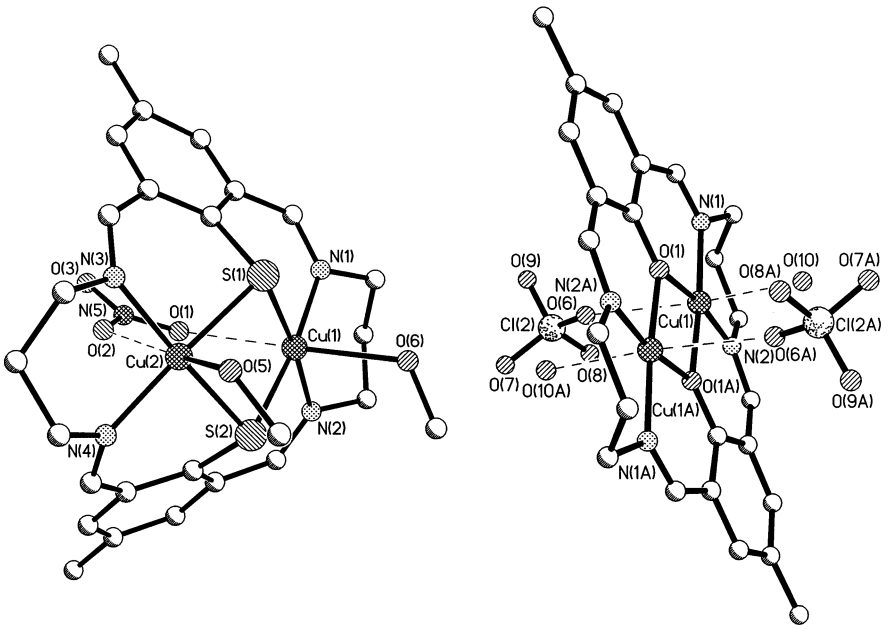


Fig. 11. Perspective view of $\{[Cu_2(LS1)(MeOH)_2][NO_3)]\}^+$ (left), selected interatomic distances (Å): Cu(1)–O(6) = 2.359(4); Cu(2)–O(5) 2.386(4); Cu(1)···O(1) 2.703(4); Cu(2)···O(2) 2.659(4); and of $[Cu_2LO1(H_2O)_2(ClO_4)_2]$ (right), selected interatomic distances (Å): Cu(1)···O(10) 2.451(9) and Cu(1)···O(6) 2.589(10). Both figures are generated from data downloaded from the Cambridge Crystallographic Database as published originally in Ref. [58] (left) and Ref. [71] (right).

complex contains two distorted square-pyramidal copper(II) ions (they also interact with the nitrate counter ion), which is reported to undergo two reversible one-electron metal-centred reductions, at $E_{1/2} = -0.61^{R}$ and -0.81^{R} V, and one quasi-reversible oxidation, at $E_{1/2} = +0.59^{QR}$ V vs Fc/Fc^{+} [67]. The dicopper complexes of the analogous phenolate macrocycle $LO1^{2-}$ (Figs. 6 and 11) have been extensively studied by a number of research groups over the years, in particular with regard to magnetic and redox behaviour [8,71]. Strong antiferromagnetic exchange, and two well-separated one-electron reductions, at ca. -0.8 and -1.4 Vs Fc/Fc^{+} in MeCN, are features of the dicopper(II) phenolate complexes. The Class II (Robin and Day) [72] mixed valent Cu(I)Cu(II) phenolate complex has been isolated and characterised so, on the basis of redox potential, it would appear that it should be possible to isolate the thiophenolate analogue [67]. The latter complex would be of considerable interest, in particular with regard to the degree of electron delocalisation between the two copper centres (cf. the CuA site, Section 1.2).

Other, bigger, Schiff-base macrocycles have been prepared by using zinc(II) ions to template the reaction of **1** with larger lateral units. When diethylenetriamine, dipropylenetriamine and triethylenetetramine are used as lateral units, the result is the formation of dizinc(II) complexes of the macrocycles $LS4^{2-}$, $LS5^{2-}$ and $LS6^{2-}$, respectively (Figs. 6 and 12). X-ray crystal structure determinations of $[Zn_2(LS5)]^{2+}$ and $[Zn_2(LS6)]^{2+}$ revealed that these are the first examples of non-bridging thiophenolate head units (Fig. 12) [70,73]. Indeed, the $[Zn_2LS5]^{2+}$ complex is also the first, and only example to date, of a tetrahedral geometry within a thiophenolate Schiff-base macrocycle [73]. A distorted tetrahedral geometry is also observed for one of the four copper(I) ions in a dimer-of-dimers complex of a related acyclic thiophenolate ligand [the other three copper(I) centres are trigonal planar] [74]. Intramolecular π–π stacking of the thiophenolate rings is a feature of these zinc(II) and copper(I) complexes [70,73,74]. The earlier report of an irreversible, approximately two-electron, oxidation process at $+1.03$ V vs 0.01 M $AgNO_3 \mid Ag$, for $[Zn_2(LS5)]^{2+}$ in MeCN [73], was subsequently shown to arise as a result of insufficient drying of the sample: rigorously dried samples of this complex were found to be redox inactive out to the solvent limits [70]. To date, no other metal ions have been inserted into these larger ring systems, by transmetallation or otherwise.

McKenzie, McKee and co-workers reported that by judicious choice of reaction conditions an acyclic nickel(II) complex (Fig. 13) can be isolated. The 'three-quarter' acyclic ligand is one diaminopropane lateral unit short of being the $LS1^{2-}$ macrocycle, and can be isolated from the reaction mixture because it is relatively insoluble and therefore precipitates [75]. In a similar manner the ethylene analogue has also been prepared. These two acyclic complexes each contain two aldehyde moieties, so they should be excellent precursors complexes for the preparation of unsymmetrical and mixed metal, complexes: both symmetrical and unsymmetrical ligands should be readily accessed by subsequent reaction with the amine of choice. That this principle is sound was demonstrated by the isolation of an unsymmetrical acyclic complex, and of two symmetrical Schiff-base macrocycles of differing sizes, from the propylene precursor complex (Figs. 6 and 13) [75]. Depending on the

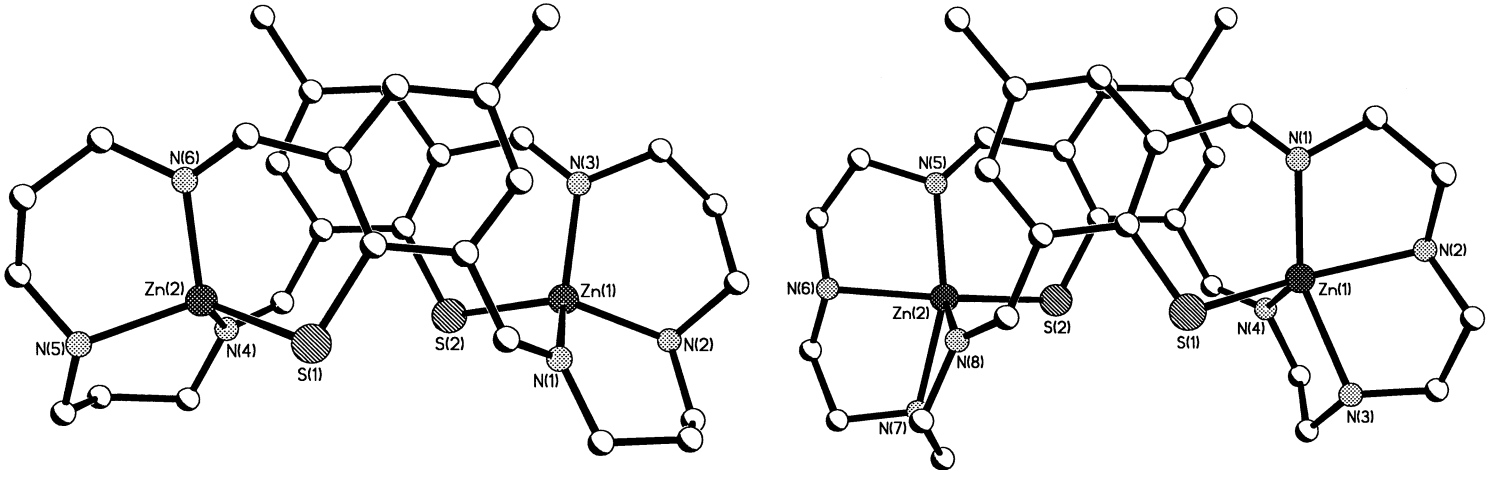


Fig. 12. Perspective views of $[Zn_2(LS5)]^{2+}$ (left) and $[Zn_2(LS6)]^{2+}$ (right). In both cases the view is that obtained by taking a mean plane through the six carbon atoms of the phenyl ring attached to S(1). Both figures are generated from data reported originally in Ref. [73] (left) and Ref. [70] (right).

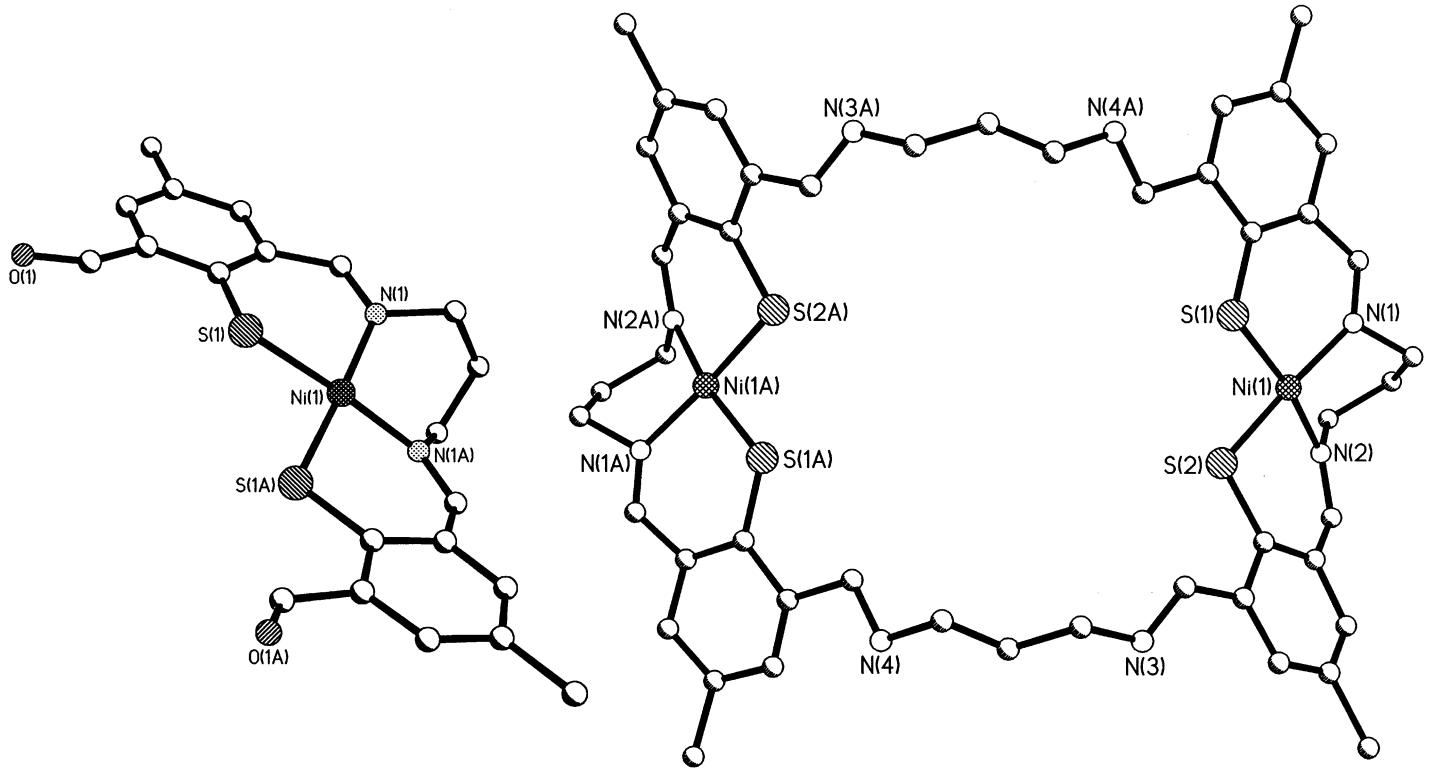


Fig. 13. Perspective views of the 'three-quarter' acyclic precursor complex (left) and of a Schiff-base macrocyclic complex derived from it, $[Ni_2(4+4)]$ (right), where $(4+4)^{4-}$ is the Schiff-base macrocycle which is twice the size of $LS1^{2-}$. Both figures are generated from data downloaded from the Cambridge Crystallographic Database as published originally in Ref. [75].

reaction conditions, either a (2 + 2) complex identical to that described above ($LS1^{2-}$, Figs. 6 and 7) or a very small amount (insufficient for elemental analysis etc.) of a (4 + 4) macrocycle is isolated (Fig. 13). Interestingly both macrocyclic complexes are dimetallic, containing two, square planar, nickel(II) ions despite the (4 + 4) macrocycle, in principle, having room to bind four metal ions. This is only the third structurally characterised example of a (4 + 4) Schiff-base macrocycle [76–79]. A general lack of solubility has restricted further physical and reactivity studies on this series of complexes so the incorporation of solubilising groups is therefore being investigated [75].

Mixtures of thiophenolate and RO^- bridging have been observed in two distinct families of Schiff-base macrocycles to date. Brooker and co-workers described the first such complex, $[Ni_2(LS7)(MeCN)_2]^{2+}$, which contains bridging thiophenolate and phenolate moieties, in 1995 (Fig. 14) [46,63,80]. Two differing spin states {as noted for $[Ni_3(LS1^*)_2]^{2+}$} [60] are observed for the nickel(II) ions in the $[Ni_2(LS7)(MeCN)_2]^{2+}$ complex (Fig. 15) [80]. Despite the provision of two potentially equivalent macrocycle binding sites one nickel ion is square planar whilst the other is octahedral having coordinated two acetonitrile solvent molecules. The replacement of one thiophenolate diimine moiety of $LS1^{2-}$ by a phenolate diamine moiety ($LS7^{2-}$) has clearly significantly reduced the ligand field strength of the resulting macrocycle as, in the absence of coordinating counter ions, the dinickel(II) complexes of $LS1^{2-}$ are square planar (diamagnetic). As with the axial binding study on the $LS1^{2-}$ complexes (Figs. 7 and 9) [45,48,60] an attempt was made to produce a complex in which both nickel(II) centres were high spin, using sodium thiocyanate as a source of good donor atoms. This was successful and the resulting complex remains the only example of a dinickel(II) thiophenolate-containing macrocycle in which both nickel(II) centres are high spin (Fig. 15) [63]†. As in the case of the $LS1^{2-}$ complexes the dinickel(II) complex coordinates just two thiocyanate ions (even when four equivalents are used), forming a neutral complex

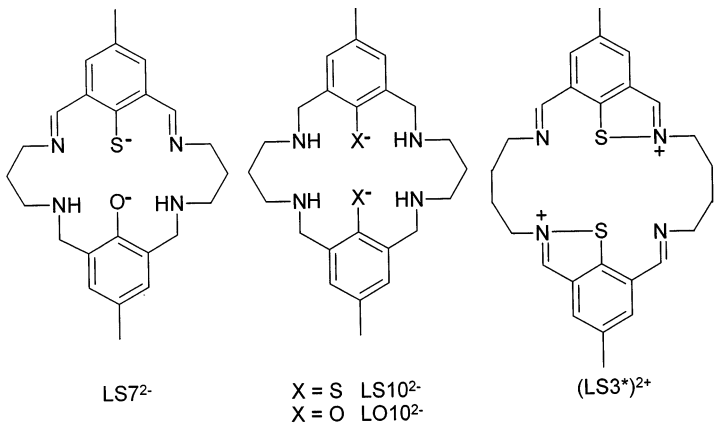


Fig. 14. The mixed thiophenolate/phenolate macrocycle $LS7^{2-}$ (left), the amine thiophenolate macrocycle $LS10^{2-}$ and the phenolate analogue $LO10^{2-}$ (centre), and the oxidised macrocycle $(LS3^*)^{2+}$ (right).

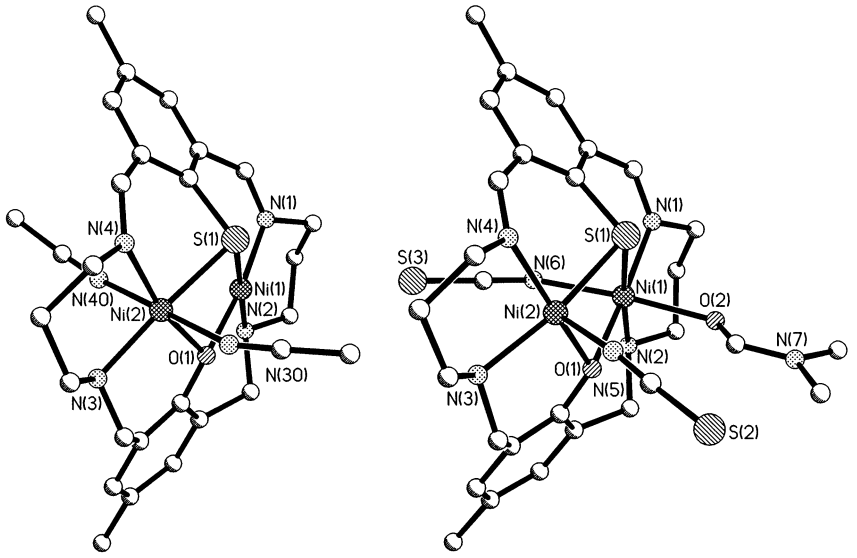


Fig. 15. Perspective view of $[Ni_2(LS7)(MeCN)_2]^{2+}$ (left) and $[Ni_2(LS7)(NCS)_2(dmf)]$ (right). Both figures are generated from data reported originally in Ref. [80] (left) and Ref. [63] (right).

which precipitates from solution. In this case, however, rather than both anions binding to the same nickel ion (Fig. 9) [45], here one anion binds to each of the two nickel ions (Fig. 15) as is seen for the phenolate amine analogue $[Ni_2(LO10)(NCS)_2(OH_2)_2]$ ($LO10^{2-}$, Fig. 14) [62]. One of the two nickel ions is therefore square pyramidal, whilst the other is octahedral as it also coordinates a dimethylformamide (dmf) solvent molecule. The square-pyramidal nickel(II) ion is readily established to be high spin by examination of the structural information [81] and this was confirmed by a magnetic moment determination [46,63]. This is a rare example of a high-spin square-pyramidal thiolate-coordinated nickel(II) ion [82]. Nag and co-workers studied the axial binding ability of dinickel(II) complexes of the related phenolate macrocycle, $LO10^{2-}$ (Fig. 14), and found a delicate balance to exist between high-spin square-pyramidal and octahedral (high spin) geometries, with the outcome depending on the choice of axial ligand [65,83–85]. The ligand field strength of the $LO10^{2-}$ ligand was insufficient to result in any examples of spin pairing, however, reducing the ring size of this phenolate macrocycle, by replacing one propylene lateral unit by an ethylene lateral unit, does result in the observation of square-planar (diamagnetic) nickel ions in the smaller compartment [65]. Likewise, with the Schiff-base analogues, changing from two propylene ($LO1^{2-}$, Fig. 6) to two ethylene lateral units ($LO12^{2-}$, Fig. 6), results in a change from high-spin to low-spin dinickel(II) complexes as was first reported by Okawa in 1972 [8,45,58,59,86,87]. The redox potentials for the perchlorate complex, $[Ni_2(LS7)(MeCN)_2]^{2+}$ in MeCN (-1.50^{I}, -1.23^{QR}, $+0.65^{I}$, $+1.00^{R}$ V vs 0.01 M $AgNO_3 \mid Ag$), do not simply fall in between those obtained for the dinickel(II) complexes of the $LS1^{2-}$ and $LO1^{2-}$ macrocycles [46]. The two oxidation waves

occur at similar potentials to those observed for the $LS1^{2-}$ analogue, whilst the reductions, which are expected to be more sensitive to changes to the macrocyclic donors, are quite different. The first reduction process occurs at a potential similar to that of the tetraamine analogue of $LS1^{2-}$ ($LS10^{2-}$, Fig. 14, vide infra). The synthetic chemistry involved in the final stages of the stepwise synthesis of these macrocyclic complexes was far from easy, with many oily products obtained from these complexation studies, so further exploitation of this fascinating system has not been pursued.

The use of 1,3-diaminopropan-2-ol as a lateral unit, in combination with **1**, results in a dinickel(II) complex of the $LS8^{2-}$ Schiff-base macrocycle (Fig. 6). This complex is very similar structurally to that obtained when 1,3-diaminopropane is employed as the lateral unit to form $LS1^{2-}$ (Fig. 6) as the alcohol groups are not coordinated [58]. In contrast, McKee and Kruger have reported that the (2 + 2) condensation of **1** with 1,5-diaminopentan-3-ol [88,89], using nickel(II) template ions, does result in a combination of thiophenolate and RO^- bridging (Figs. 6 and 16) [90]. The large Schiff-base macrocycle, $LS9^{4-}$, provides two bridging thiophenolate and alkoxy moieties, and encircles four nickel(II) ions. A μ_4-OH^- group bridges the four metal ions, as has been seen by Robson and by McKee in a number of tetrametallic complexes of various phenolate analogues of the $LS9^{4-}$ macrocycle, such as the tetracopper(II) complexes of $LO9^{4-}$ [91–95]. The neutral complex is asymmetric in the sense that the nickel ions, whilst all six-coordinate, have differing environments, largely due to the mixture of acetate ions and acetic acid molecules which differentiate the two faces of the planar Ni_4 array. The nickel(II) ions in this complex are high spin as was observed in the dinickel(II) thiocyanate complex of $LS7^{2-}$ (Figs. 14 and 15) and in the tetranickel complexes of the tetraphenolate analogues of $LS9^{4-}$ [46,63,91,93,95]. Detailed magnetic studies are underway on this complex in which there are five different bridging groups (Fig. 16) [90].

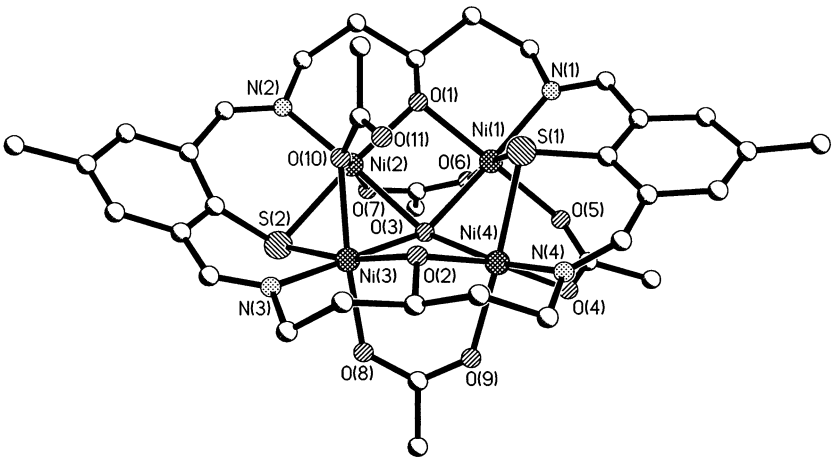


Fig. 16. Perspective view of $[Ni_4(LS9)(OH)(MeCO_2)_3(MeCO_2H)]$. The figure is generated from data downloaded from the Cambridge Crystallographic Database as published originally in Ref. [90].

Despite the stabilisation of both the reduced and oxidised forms of many of the complexes described above, as established by electrochemistry, to date there are no structurally characterised examples of metal-centred redox products. Reported examples of isolated redox products are few. These include the one-electron oxidation product of $[Ni_2^{(II)}(LS1)]^{2+}$, the black complex $Ni_2(LS1)Ce(NO_3)_6$, in which the oxidation is believed to be primarily metal centred, and the macrocyclic ligand oxidation product obtained in low yields from the oxidation of $[Ni_2^{(II)}LS3]^{2+}$ with iodine (Figs. 6, 14 and 17) [45,46,49].

4. Amine analogues of the thiophenolate Schiff-base macrocycles

In general, the amine analogues of Schiff-base macrocycles are more robust than the parent Schiff-bases. Schiff-base macrocycles are susceptible to nucleophilic attack leading to hydrolysis (water as the nucleophile) or addition products (other nucleophiles, e.g. amines and alcohols) [1,96–98]. The first tetra-amine analogue of any of these thiophenolate Schiff-base macrocycles was reported by Brooker and co-workers in 1998 (Figs. 14 and 17) [99]. They used the now well-established route of sodium borohydride reduction of the appropriate Schiff-base macrocyclic complex, as described by Curtis in 1965 [100], which had in turn been prepared by metal ion template methods ($LS1^{2-}$ Figs. 6 and 7). Interestingly, despite the acid workup, the nickel(II) ions remain bound, and in the $+2$ oxidation state, presumably due

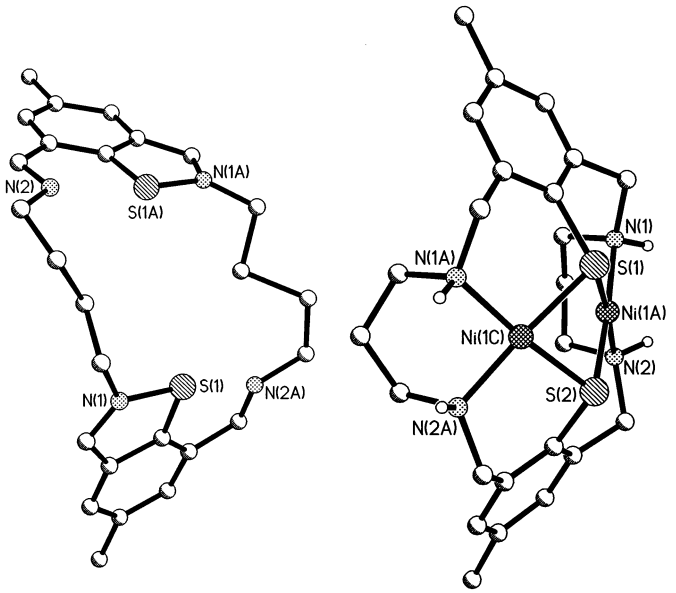


Fig. 17. Perspective view of the product of iodine oxidation of $[Ni_2(LS3)]^{2+}$, $(LS3^*)^{2+}$ (left), and of the dinickel(II) complex of the amine macrocycle, $LS10^{2-}$, derived from reduction of $[Ni_2LS1]^{2+}$ (right). Both figures are generated from data reported originally in Ref. [49] (left) and Ref. [99] (right).

to the experiment being carried out in air (Fig. 17). As for the complexes of $LS1^{2-}$ the macrocycle is bowed and the nickel(II) ions square planar. However, in this case a bowl is formed with the 'walls' provided by the phenyl rings and the alkyl lateral chains. The latter is facilitated by the greater flexibility of the amine bonds in $LS10^{2-}$ (cf. the Schiff-base bonds in $LS1^{2-}$). The bowl effectively distinguishes the two faces of the macrocyclic complex, providing an 'inside' and an 'outside' face, a feature that might become important in future reactivity studies. As expected, electrochemical experiments show that this dinickel(II) complex is harder to reduce than that of the Schiff-base counterpart (-1.86^{QR}, -1.18^{R} V vs 0.01 M $AgNO_3 \mid Ag$, in MeCN) [45,99]. Based on a comparison with related mononickel(II) thiophenolate analogues [101–103], one would expect that the oxidation processes would also move to less positive potentials. This is not observed ($+0.69^{R}$ and $+1.10^{QR}$ V). The potentials for the two oxidation processes occur at the same values as those observed for the imine analogue indicating the influence of the thiophenolate-bridged dinickel(II) centre [45,99].

Having made a wide range of interesting acyclic complexes from the two *tert*-butyl thiophenolates available to them [50–55,104–107], Kersting and co-workers reported their first macrocyclic thiophenolate complex in 1999, by a new, very elegant, and potentially very versatile, synthetic approach (Fig. 18) [56]. Initially two 4-*tert*-butyl-2,6-diformylbromobenzene molecules are linked together by reaction with 1,2-ethanedithiolate, and this link then acts as a template for the cyclisation of this air-stable masked thiophenolate with an appropriate diamine, for example 1,2-diaminoethane or 1,3-diaminopropane, under medium to high dilution conditions. The reaction mixture is then reduced in two steps, analogous to those described above (Section 2), which results in the reduction of the Schiff-base bonds to amine bonds and in the unmasking of the thiolate. The products of these reactions are effectively (4 + 4) amine macrocycles [NB. they are actually formed by a (2 + 4) condensation]: no (2 + 2) amine macrocycles are formed [56].

Using this approach to produce the large, metal-free, amine macrocycle, $H_4LS11 \cdot 8HCl$, three nickel(II) complexes were then prepared by neutralising in situ with NEt_3 and adding an appropriate amount of a suitable nickel(II) salt. A purple, diamagnetic, neutral dinickel(II) complex and a tetranickel(II) perchlorate complex were prepared [56]. Presumably the dinickel complex has a structure similar to that of the related complex reported by McKenzie, McKee and co-workers (Fig. 13) [75], as the effect of the shorter ethylene (vs propylene) chains is probably offset to a significant extent by the increased flexibility of the amine (vs imine) macrocycle. The tetranickel(II) complex was converted to the neutral thiocyanate salt and structurally characterised (Fig. 19) [56]. Reminiscent of the acyclic trinickel(II) complex of $(LS1^*)^{2-}$ complex and of the thiocyanate complexes of the dinickel(II) complexes of $LS1^{2-}$, $LS3^{2-}$ and $LS7^{2-}$ [45,46,60,63], here also a mixture of square planar (low-spin) and octahedral (high-spin) nickel(II) ions is observed. The asymmetric unit consists of half of the macrocyclic complex. Indeed the structure looks rather like two independent dinickel complexes linked together. This is due to the way that pairs of thiophenolate sulphurs have doubly bridged pairs of nickel centres rather than connecting all of the nickel centres together as is seen in the

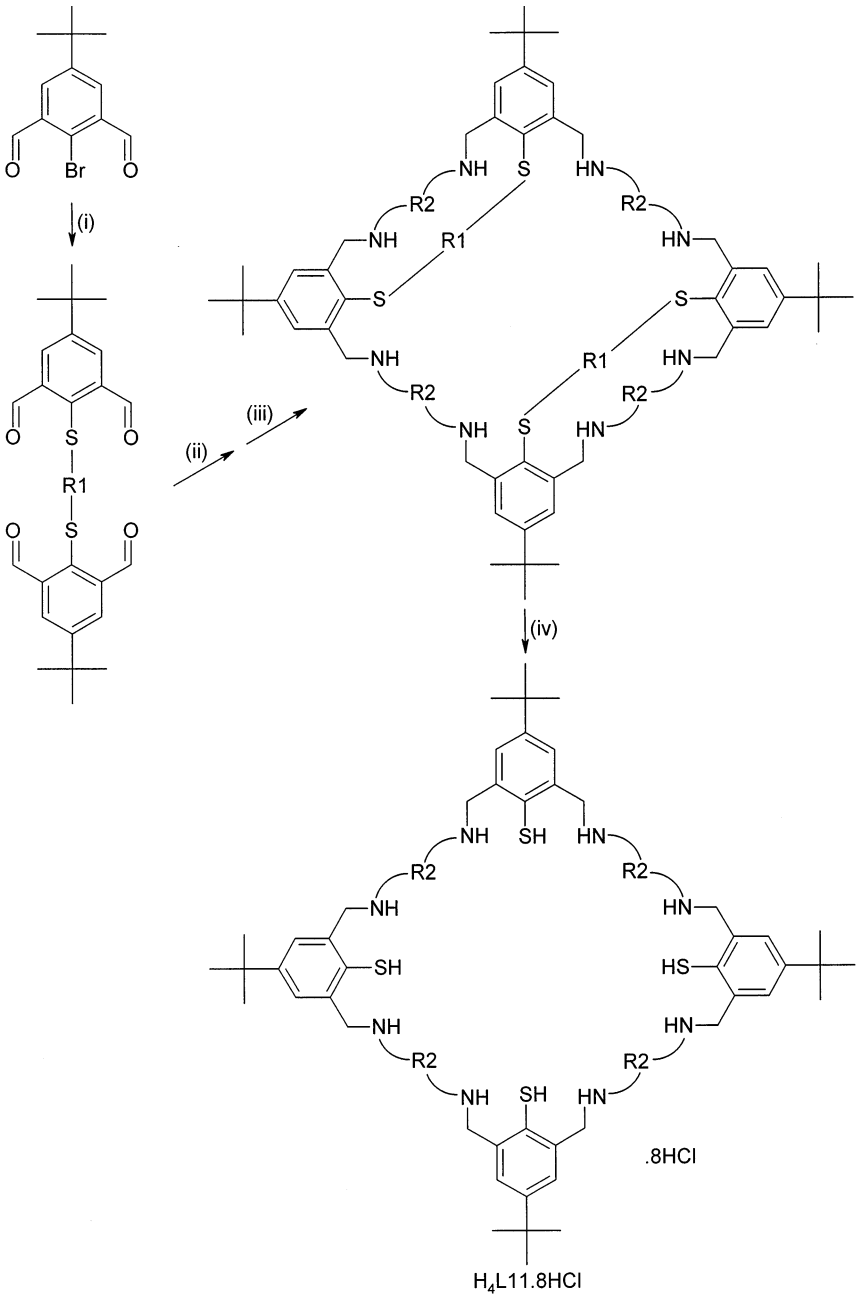


Fig. 18. Use of an organic linker as a template for thiophenolate-containing amine macrocycles: (i) K_2CO_3/HS(R1)SH, where R1 = CH_2CH_2; (ii) 1. $H_2N(R2)NH_2$ [where R2 = $(CH_2)_n$ and $n = 2$ or 3]; (iii) $NaBH_4$; (iv) 1. Na/NH_3, 2. HCl [56].

phenolate and $LS9^{4-}$ analogues (e.g. Fig. 16) [90–95]. The square-planar nickel centre, Ni(2), is less tetrahedrally distorted away from square planar (dihedral angle between NiN_2 and NiS_2 planes 1.7°] than was observed for the $[Ni_2(LS1)]^{2+}$ complex (Fig. 7). The octahedral centre, Ni(1), has bound two thiocyanate ions, in *cis* positions which is a first for these complexes [56].

In establishing this new, organic template, approach to macrocycle formation Kersting has opened up many exciting possibilities [56]. For example, he has already mentioned that it is possible to link together more than just two 4-*tert*-butyl-2,6-diformylbromobenzene molecules, so all sorts of new ligand architectures can be envisioned [108].

5. Conclusions

There is a major drive to further understand the coordination chemistry of thiolate-containing ligands, which represent an under-exploited class of donors. The relevance of the systems reviewed above, as models for biological systems, will be improved considerably by the development of a new generation of alkyl thiolate head units, using the knowledge built up from these first generation studies. Once the synthetic challenges are met such studies need to move on to consider the reactivity and possible catalytic activity of these complexes.

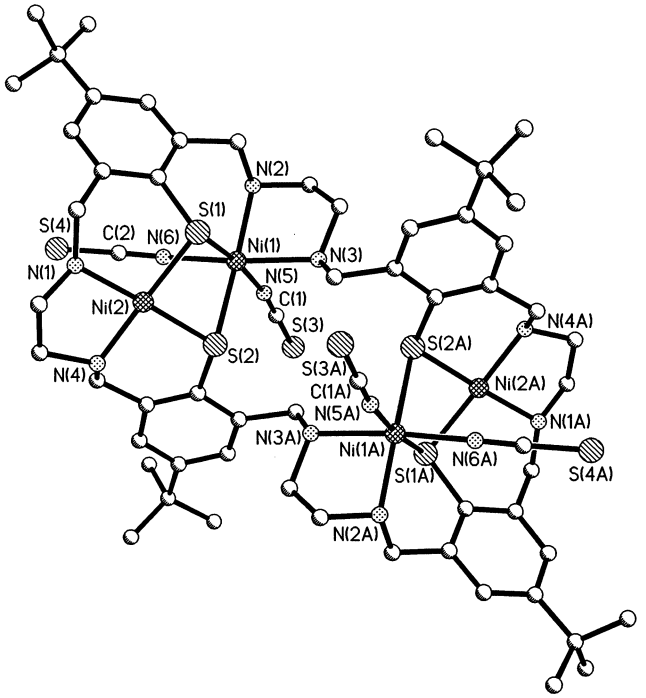


Fig. 19. Perspective view of $[Ni_4(LS11)(NCS)_4]$. The figure is generated from data downloaded from the Cambridge Crystallographic Database as published originally in Ref. [56].

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† Just prior to the publication of this review, a second example appeared in the literature: B. Kersting, G. Steinfeld, Chem. Commun. (2001) 1376.