

Dithiadiazolyls as heterocyclic chelators: a radical approach to coordination chemistry? ¹

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Abstract

The ability of heterocyclic compounds to act as chelating ligands via the cleavage of a heterocyclic E–E (or E–E') bond with concomitant formation of M–E (and M–E') bonds is described with particular reference to the 7π heterocyclic dithiadiazolyl radicals, RCN₂SSN. These electron-rich ring systems form a diversity of structural bonding types in which the heterocyclic ring can formally act as a $2e^-$, $3e^-$, $5e^-$ or $6e^-$ donor ligand. These structural bonding modes are described through examples in which the heterocyclic ring interacts with halide anions, N atoms and particularly metal centres, forming monometallic, dimetallic and trimetallic complexes. The structural features which determine which compounds are likely to act as cyclic chelators are discussed and examples of thiadiazole, diselenadiazolyl and dithiole rings acting as cyclic chelators are given. © 1998 Elsevier Science S.A.

Keywords: Sulfur; Nitrogen; Dithiadiazolyl; Chelate

1. Introduction

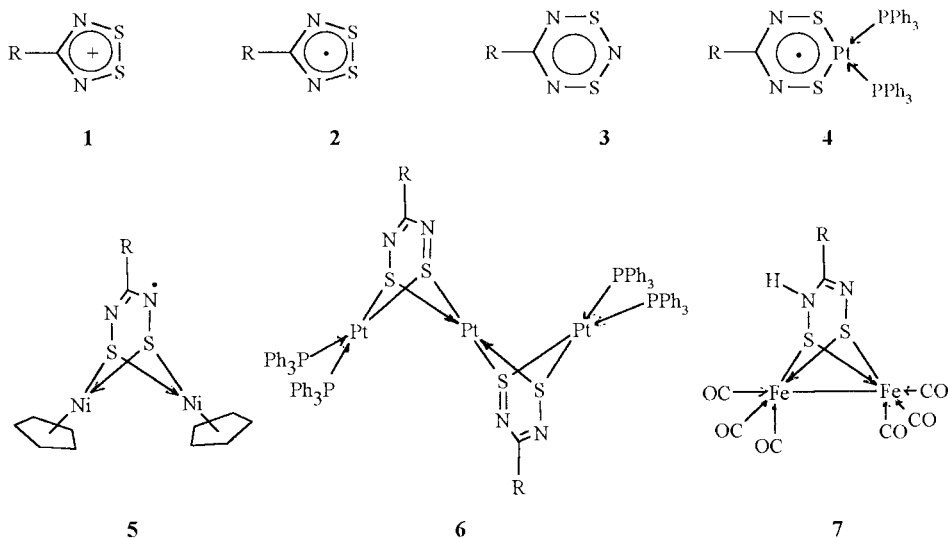
The coordination chemistry of simple sulfur–nitrogen compounds has produced a great diversity of complexes. The majority of these complexes have been prepared from the readily available starting materials S_4N_4 and $(NSCl)_3$ [1]. The ubiquitous S_4N_4 molecule has been shown to act as a source of a number of binary sulfur–nitrogen ligands [2,3] such as cyclic S_2N_2 , S_3N_2 and S_4N_4 amongst others. Thiazyl chloride, NSCl, has also been successfully used as a ligand [1,3], coordinating in a monodentate fashion via N. Three striking features of their coordination chemistries emerge. Firstly there is a propensity for both fragmentation and association to occur at metal centres, e.g., both S_4N_4 and NSCl can react with metal ions to form S_2N_2 adducts [4]. Secondly, these sulfur–nitrogen rings can undergo redox behaviour, for example S_2N_2 is known to coordinate to metals as the chelating $S_2N_2^{2-}$ dianion [2,3] but also in a neutral cyclic form [4]. Thirdly, these thiazyl ligands are able to coordinate to metals in a number of modes, either N or S-bound, monodentate, chelating or bridging [2–7]. In comparison, the coordination chemistry of carbon–sulfur–nitrogen ring systems has been less thoroughly examined, but we can anticipate similar chemical diversities both in reactivity and coordination mode. In this review article, we outline the coordination chemistry of one type of C–S–N ring system which we have begun to examine in recent years.

The syntheses and properties of the cationic dithiadiazolylum rings, **1**, and the related dithiadiazolyl radicals, **2**, have been studied by us [8] and several other research groups [9,10] and the patterns of their reactivity are gradually emerging. One of the most interesting properties is their capacity to act as chelating ligands, despite their cyclic nature. In this short review, we consider the ways in which this occurs.

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¹ This article is dedicated to Ken Wade, on the occasion of his 65th birthday, and is based on a lecture given by Dr. A.J. Banister at the 79th Canadian Annual Congress (Memorial University, Newfoundland, 1996).

In these heterocyclic compounds, the C and N atoms each contribute one electron to the π -system and each S supplies two such electrons, producing a 6π -aromatic dithiadiazolylium cation, **1**, or, in its neutral form, the 7π dithiadiazolyl radical, **2**. These radicals have attracted special attention because they can act as molecular building blocks in the preparation of both conducting materials [9] and ‘organic’ magnets [11]. A few reactions have been studied, e.g., with halogens [12], plasma nitrogen [13] and with some low oxidation state metal complexes [14–17],² and these results indicate that the 1,2,3,5-dithiadiazolyl radical exhibits a versatile coordination chemistry; both structurally, and in the variable number of electrons which can be utilised for ligand–metal bonding. In this short review we discuss the structure and bonding in the 6π dithiadiazolylium ring, **1**, the 7π dithiadiazolyl radical, **2**, and the N and metal insertion products **3** and **4**. We also examine other metal complexes in which the heterocyclic ring, **2**, bridges between two metal atoms to form the di- and tri-metallic complexes **5** and **6**, and the related complex **7** in which the heterocyclic ring becomes protonated.



2. Dithiadiazolylium salts and dithiadiazolyl radicals

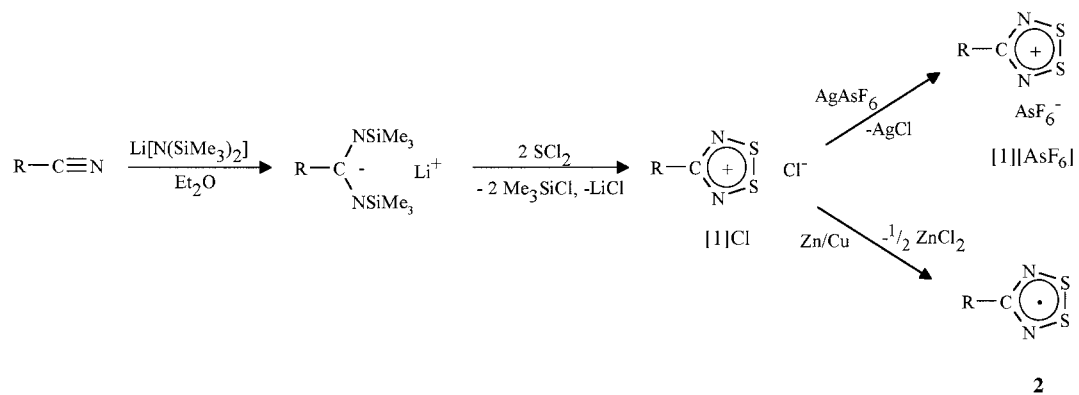
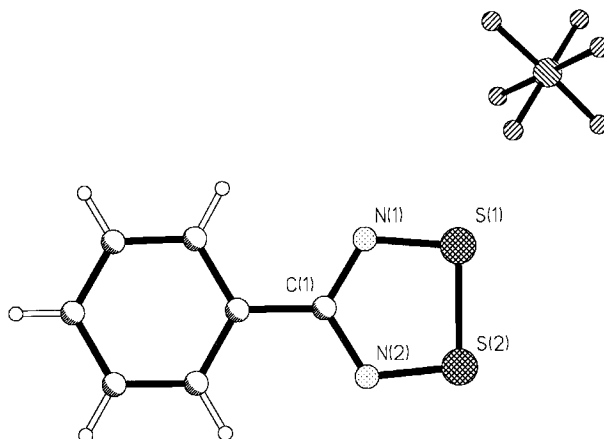
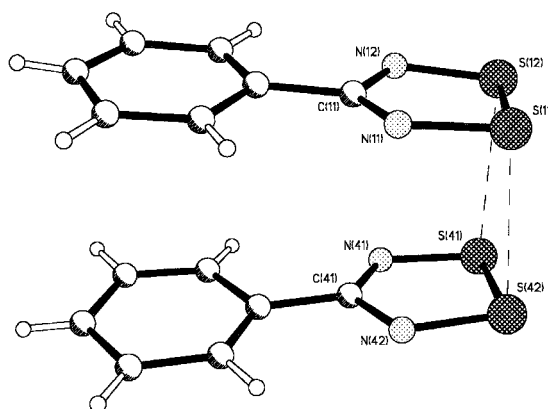
The majority of dithiadiazolylium salts, **1**, can be conveniently prepared [8] from the corresponding nitrile, RCN. The nitrile is converted to the silylated amidine by reaction with $\text{Li}[\text{N}(\text{SiMe}_3)_2]$, followed by condensation with SCl_2 to yield the dithiadiazolylium cation, **1**, as its chloride salt. Metathesis of this salt with AgAsF_6 yields the hexafluoroarsenate(V) salt, whereas its reduction with Zn–Cu couple yields the dithiadiazolyl radical, **2** (Scheme 1). The three steps involved in the preparation of **2** can be carried out as a one-pot reaction, and the product is typically recovered from the crude reaction mixture by vacuum sublimation. One of the easiest dithiadiazolyl radicals to prepare on a multi-gram scale is the simple phenyl derivative, **2** ($\text{R} = \text{Ph}$), which can be recovered [17] in ca. 50% yield (based on benzonitrile) and this has proved an ideal molecule with which to examine the chemistry of the dithiadiazolyl functional group. In the discussion that follows, $\text{R} = \text{Ph}$ unless otherwise specified.

2.1. Structure and bonding in **1** and **2**³

In discussing the structure of **1**, we refer to the AsF_6^- salt in which the anion can be regarded as non-interacting and the heterocyclic geometry is unperturbed. In both **1** and the corresponding radical **2**, the heterocyclic rings are planar, although the S–S bond in **2** is markedly longer [8] than in the cation **1**, cf. 2.023(2) Å in $[\mathbf{1}][\text{AsF}_6^-]$ and 2.089(5) Å in **2**. The structures of $[\mathbf{1}][\text{AsF}_6^-]$ and dimeric **2** ($\text{R} = \text{Ph}$) are shown in Fig. 1 and Fig. 2. Molecular orbital

² A.J. Banister, S.E. Lawrence, I. May, J.M. Rawson, unpublished work.

³ Published theoretical calculations are cited in the text. Additional calculations at the EHMO level [18] were carried out to aid comparisons between the metal and all non-metal containing molecules.

Scheme 1. General synthetic pathway for the preparation of **1** and **2**.Fig. 1. Molecular structure of $[\text{Ph}\overline{\text{C}}\overline{\text{N}}\overline{\text{S}}\overline{\text{S}}\overline{\text{N}}][\text{AsF}_6]$.Fig. 2. Molecular structure of $[\text{Ph}\overline{\text{C}}\overline{\text{N}}\overline{\text{S}}\overline{\text{S}}\overline{\text{N}}]_2$.

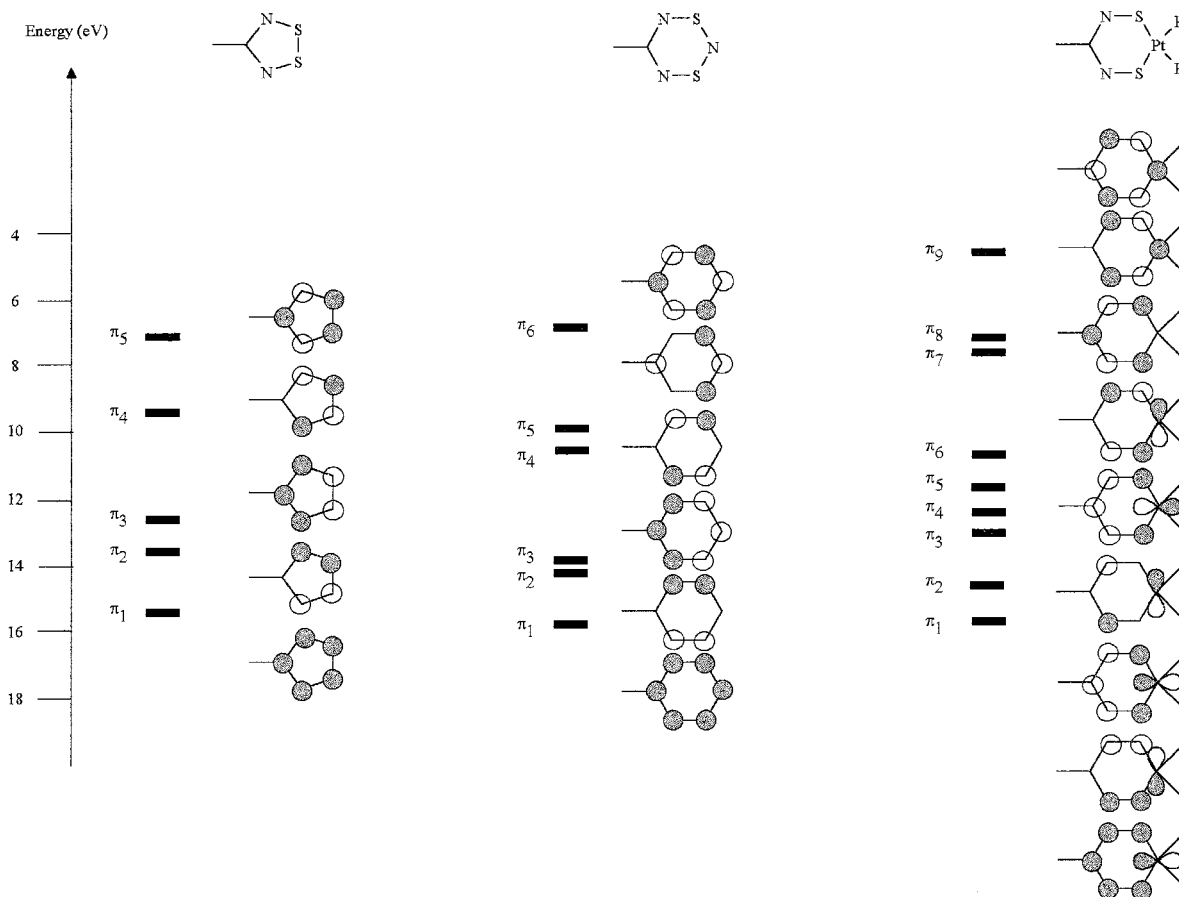


Fig. 3. Orbital energies and symmetries of the π -molecular orbitals in $[\text{H} \cdot \overline{\text{CNSSN}}]^+$, $[\text{H} \cdot \overline{\text{CNSNSN}}]$ and $[\text{H} \cdot \overline{\text{CNSNSN}}]\text{Pt}(\text{PH}_3)_2$.

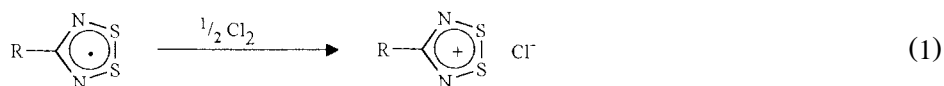
calculations show that three of the five π -molecular orbitals (Fig. 3) are fully-occupied and bonding, and in the radical, **2**, the SOMO (π_4) is π -antibonding. The antibonding nature of this semi-occupied π^* orbital (with respect to S–S) leads to the marked increase in $d_{\text{S-S}}$ on reduction of **1** to form **2**. The SOMO of **2** is nodal at carbon and the unpaired spin density is localised on the N_2S_2 portion of the heterocyclic ring. Because of the radical nature of **2**, ESR spectroscopy has proved a particularly convenient tool and provides a direct probe of the nature of the singly occupied molecular orbital. Solution ESR spectra of **2** typically exhibit a 1:2:3:2:1 pentet hyperfine structure due to coupling to two equivalent N nuclei ($I = 1$) and satellites due to the low abundance S^{33} isotope can also be observed [8].

With two notable exceptions [11,19] dithiadiazolyl radicals associate [8] in the solid state through a weak spin-paired dimerisation process ($\Delta H_{\text{dim}} \sim 35$ kJ/mol) although they readily dissociate in solution. This dimerisation process occurs through a SOMO–SOMO interaction [8] and a number of conformations are known (*cis*, *trans* and staggered) of which the *cis*-configuration (Fig. 2) is most common. The S...S separation between radicals is typically in the region 2.9 to 3.1 Å [8]. In the case of $p\text{-NC} \cdot \text{C}_6\text{F}_4 \cdot \overline{\text{CNSSN}}$, the in-plane CN...S interactions (see below), coupled with N...S and S...F electrostatic attractions, between molecules are sufficient to overcome the dimerisation energy and this derivative is monomeric in the solid state [11]. In the case of $[2,5\text{-F}_2\text{C}_6\text{H}_3 \cdot \overline{\text{CNSSN}}]$ the S...S separation between heterocycles is significantly longer [ca. 3.544(3) Å] than that normally observed for these radicals, but despite this marked increase the compound is still diamagnetic in the solid state [19].

3. Dithiadiazolylum halides

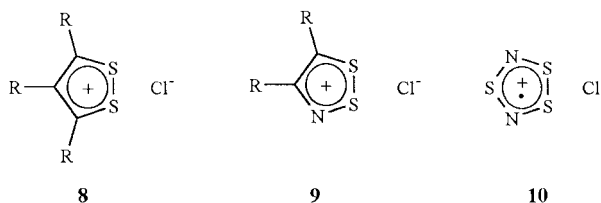
Dithiadiazolylum cations, particularly as their chloride salts, $[\mathbf{1}]\text{Cl}$, are formed as intermediates during the syntheses of the corresponding dithiadiazolyl radicals, **2** (Scheme 1). In these preparations, the dithiadiazolylum salts

are often contaminated with SCl_2 and other salts (usually LiCl), but can be prepared in high purity by re-oxidation of the dithiadiazolyl radical, **2**, with the corresponding halogen [12]. Chlorination of **2** (Eq. (1)) typically yields only the chloride salt [8], although a deficit of chlorine can lead to partial-oxidation states such as $[\text{R} \cdot \overline{\text{CNSSN}}]_3\text{Cl}$ [20]. Bromination and iodination lead to the formation of the corresponding bromide and iodide salts although the iodide salts are not all they may first appear to be [21], e.g., $[\text{Ph} \cdot \overline{\text{CNSSN}}]\text{I}$ turns out to be the tri-iodide salt, $[\text{Ph} \cdot \overline{\text{CNSSN}}]_3[\text{I}_3]$. In addition an excess of halogen [21] can also yield the polyhalides such as $[\text{Ph} \cdot \overline{\text{CNSSN}}][\text{I}_3]$. Some of these partially oxidized dithiadiazolyls have been found to be weakly conducting [9]. Indeed the affinity of the dithiadiazolyl radical for halogen is so great that $[\text{Ph} \cdot \overline{\text{CNSSN}}]_2$ can abstract Cl from Si–Cl, P–Cl and even activated C–Cl bonds [22]. For example, reaction of Ph_3SiBr with $[\text{Ph} \cdot \overline{\text{CNSSN}}]_2$ yields $\text{Ph}_3\text{Si-SiPh}_3$ and $[\text{Ph} \cdot \overline{\text{CNSSN}}]\text{Br}$. In this context, we can consider dithiadiazolyl radicals as organically soluble metals with an $E_{1/2}$ of ca. 0.6 V (vs. SSCE) [8].



3.1. Structure and bonding in dithiadiazolylum halides

In dithiadiazolylum halides, the halide ion lies in the plane of the heterocyclic ring and approaches closely to both sulfur atoms, such that the $\text{S} \dots \text{Cl}$ distance [8,23] (average 2.906(5) Å in **[1]Cl**) is significantly less than the sum of the van der Waal's radii [24] (ca. 3.3 Å). These three-centre disulfur–halogen interactions are a common feature in halide-containing salts of cationic 1,2-disulfur compounds such as the dithiolium (**8**), dithiazolium (**9**) and trithiadiazolylum (**10**) ions [24–26]. An analogous in-plane interaction is also observed in some dithiadiazolyl radicals bearing substituents with lone-pairs which lie in the molecular plane, e.g., the CN group of **1** ($\text{R} = p\text{-NC} \cdot \text{C}_6\text{F}_4$ and $p\text{-NC} \cdot \text{C}_6\text{H}_4$) [11,19,27].

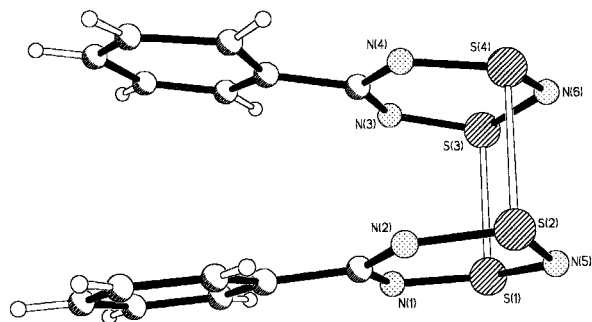


Despite the close approach of the halide anion, the length of the S–S bond is minimally changed [8] (cf. **[1][AsF₆]** and **[1]Cl** at 2.023(2) and 1.991(5) Å respectively). Calculations of the charge distribution close to the crystallographic $\text{S} \dots \text{Cl}$ separation³ indicate that less than 2% of the negative charge is transferred from the anion to the cationic ring, consistent with a predominantly ionic contribution to the bonding. Nevertheless, the closeness of approach, coupled with the coplanarity of the heterocyclic ring and chloride anion indicate some small degree of covalent character.

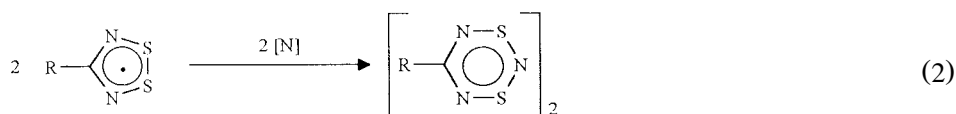
In **[1]Cl**, a three centre S_2Cl interaction is observed with retention of the S–S bond. When a nitrogen atom is incorporated into the structure (see below) it does so at the expense of the S–S σ -bond and this is described below.

4. Reaction of phenyl dithiadiazolyl with plasma nitrogen

When $[\text{Ph} \cdot \overline{\text{CNSSN}}]_2$ is reacted with plasma nitrogen in a discharge tube, a nitrogen atom inserts into the S–S bond, forming $[\text{Ph} \cdot \overline{\text{CNSNSN}}]_2$ (**3**) in good yield [13]. The proposed reaction mechanism is that electronically excited N atoms pass through the structure of $[\text{Ph} \cdot \overline{\text{CNSSN}}]_2$, followed by their sequential insertion into the S–S bonds of the dithiadiazolyl radical. It is fortuitous that $[\text{Ph} \cdot \overline{\text{CNSSN}}]_2$ possesses the necessary channels within its structure; some other derivatives which do not possess such molecular channels do not undergo this type of reaction. Phenyl dithiatiazine can also be prepared by more traditional chemical methods [28]. In the plasma nitrogen reaction, the S–S bond is broken and the dithiadiazolyl radical can perhaps be considered to be chelating a N atom and this

Fig. 4. Molecular structure of $[\text{Ph} \cdot \overline{\text{CNSNSN}}]_2$.

provides the first example of **2** acting as a *cyclic chelator*. The ability of dithiadiazolyls and related heterocyclic rings to act as cyclic chelators, particularly with metal ions, is discussed below.



4.1. Structure and bonding in $(\text{Ph} \cdot \overline{\text{CNSNSN}})_2$

The structure of $(\text{Ph} \cdot \overline{\text{CNSNSN}})_2$ consists [28] of two six-membered rings held together through weak SS links between the rings (Fig. 4). The S...S separation between rings is 2.527(3) Å. Each six-membered ring is non-planar with the N inserted into the S–S bond lying out of the ring plane; the angle between the corresponding NS_2 and CN_2S_2 planes is ca. 16°. Within each ring the S–S bond has been broken, cf. d_{SS} in **2** and **3** at 2.089(5) Å and 2.764(3) Å respectively [28,29]. In addition to this increase in the S...S distance, the angles at both C and N atoms have opened considerably to accommodate the ring expansion; cf. average NCN and CNS angles in $[\text{Ph} \cdot \overline{\text{CNSSN}}]_2$ and $[\text{Ph} \cdot \overline{\text{CNSNSN}}]_2$ [Table 1].

In this compound the S–S bond is broken and the ‘chelating’ S atoms establish instead two SN σ -bonds. The N atom provides a further one electron to the π -cloud and, if the resultant π -system were planar, it would be anti-aromatic (8π). Theoretical calculations [28] at the Hückel level, using a planar C_{2v} symmetry approximation indicate that there are six π MOs with a pair of degenerate frontier orbitals, π_4 and π_5 , (Fig. 3). Further calculations [28] (at the MNDO level) indicate that of the two options (spin-paired singlet or paramagnetic triplet), the triplet state is preferred over the singlet by ca. 15 kcal/mol. However, puckering the heterocyclic ring by moving the inserted-nitrogen atom out of the molecular plane removes the C_{2v} symmetry and effectively splits the π_4 and π_5 orbitals, leading to a singlet ground state in which the π_4 orbital is completely filled and is the highest π molecular orbital. Similarly when **2** chelates or bridges metal atoms, the new bonds form at the expense of S–S and the new (metal) atom lies out of the ring plane.

5. Insertion of metal-fragments into the S–S bond: monometallic complexes

By far the most extensive studies of $[\text{Ph} \cdot \overline{\text{CNSSN}}]_2$ complexation chemistry have involved the reactivity of $[\text{Ph} \cdot \overline{\text{CNSSN}}]_2$ with zero-valent Pt and Pd phosphine complexes [16,17].¹ In these reactions, the dithiadiazolyl ligand undergoes an oxidative addition (Eq. (3)) to the metal forming a novel chelate complex of type **4**, in which the dithiadiazolyl radical is behaving as a *cyclic chelator*.

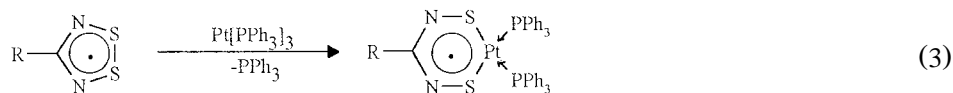


Table 1
Comparison of selected bond lengths and angles for compounds **1–6** (R = Ph)

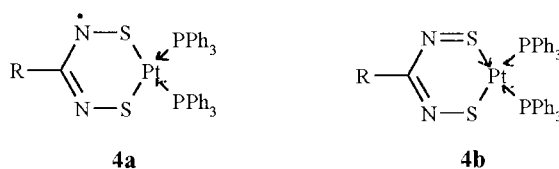
Compound	Bond distance (Å)				Bond angle (°)				Angle (τ) ^a
	C–N	N–S	S...S	S–E	NCN	CNS	NSE	SES	
[Ph·CNSSN] ₂	1.33	1.63	2.089(5)	–	121	116	–	–	–
[Ph·CNSSN][AsF ₆]	1.345(6)	1.568(5)	2.023(2)	–	117.4(4)	116.2(4)	–	–	–
[Ph·CNSSN]Cl	1.348(13)	1.592(10)	1.991(5)	2.906(5)	119.0(8)	114.7(7)	165.2(3)	40.1(1)	–
[Ph·CNSNSN] ₂	1.343(8)	1.593(5)	2.764(3)	1.625(6)	127.3(6)	122.8(5)	114.0(3)	116.5(3)	16
[Ph·CNSSN]Pt[PPh ₃] ₂	1.35(1)	1.638(7)	3.168(4)	2.302(2)	129.0(7)	128.2(6)	115.3(2)	86.78(8)	24
Cp ₂ Ni ₂ [PhCNSSN]	1.334(4)	1.634(3)	2.905(2)	2.172(1)	128.4(3)	124.8(2)	112.1(1)	83.9(1)	–
Pt ₃ [PhCNSSN] ₂ [PPh ₃] ₄	1.32(2)	1.65(1)	3.046(8)	2.358(5)	132.1	124.3	110.3(6)	78.8(2)	–
Fe ₂ (CO) ₆ [PhCNSSNH]	1.295(8)/1.348(7)	1.694(5)/1.716(5)	2.930(2)	2.226(2)	127.8(5)	123.6(4)/127.2(4)	110.5(2)	82.4(1)	–

^aThe angle τ is defined as that between the CN₂S₂ plane and S₂E plane where E is the heteroatom interaction with the CN₂S₂ ring.

5.1. Structure and bonding in $[\text{PhCNSSN}]\text{Pt}[\text{PPh}_3]_2$ and related complexes

$[\text{PhCNSSN}]\text{Pt}[\text{PPh}_3]_2$ (**4**) was the first [16] monometallic metal complex containing the dithiadiazolyl ligand. The analogous Pd compound could not be isolated due to rapid decomposition in solution with loss of PPh_3 (see later). This decomposition could be prevented² by using the chelating diphosphine (dppe). The three compounds **4**, $[\text{PhCNSSN}]\text{Pt}[\text{dppe}]$ and $[\text{PhCNSSN}]\text{Pd}[\text{dppe}]$ are structurally similar although there are some notable differences in geometries, and these are discussed below. Within the structure of **4** (Fig. 5) the S–S bond is formally broken ($d_{\text{S}\dots\text{S}} = 3.168(4)$ Å) [16] and the S atoms chelate to the Pt centre; as in **3**, $[\text{PhCNNSN}]$, the inserted atom is displaced from the CN_2S_2 ring plane: the angle between the CN_2S_2 and PtP_2S_2 mean planes is 24° . This deviation from planarity arises primarily from the bond angle imposed at Pt: a planar six-membered ring requires an average internal angle of 120° , and so the angle at square-planar Pt (86.8° for **4**) produces considerable ring strain within the metallo-heterocyclic framework. This ring strain is alleviated by a marked increase ($+12^\circ$) in the bond angle at nitrogen, a soft atom for angular distortion, and by displacement of the metal away from the heterocyclic plane. It is interesting to note that in the dppe analogues, $[\text{PhCNSSN}]\text{Pt}[\text{dppe}]$ and $[\text{PhCNSSN}]\text{Pd}[\text{dppe}]$, the chelating nature of the dppe ligand produces a slight increase in the SMS angle to approximately 90° for both Pt and Pd complexes. This leads to a small reduction in ring strain and the angle between the CN_2S_2 and MP_2S_2 planes is reduced to 11° . Despite its free-radical nature, **4** shows no tendency to dimerise in the solid state, e.g., through π – π interactions as in **2** and **3**.

We shall discuss the bonding in **4** as representative of this group of complexes. The Pt–S distances $2.302(2)$ Å, normal for single bonds (usually ca. 2.3 Å²) indicate a typical square-planar 16 electron Pt(II) complex with **2** acting as a $2e^-$ donor and the unpaired electron localised on the N atoms (**4a**). The structure can also be rationalised as a 17 electron Pt(I) complex (structure **4b**) with **2** acting as a three-electron donor resulting in a metal-based unpaired electron. Solution ESR spectra [16] of **4** exhibit hyperfine coupling to two N nuclei and possess Pt^{195} satellites indicating a state intermediate between **4a** and **4b**. In addition further hyperfine coupling was also observed to two P nuclei.



A molecular orbital approach [17] also indicates a situation intermediate between these two extremes. Assuming planar C_{2v} symmetry, the Pt complex can provide three d-orbitals (d_{xz} , d_{yz} and d_{z^2}) and a p-orbital for π -bonding. Of the nine π -molecular orbitals, five are fully-occupied and the sixth is singly occupied. The SOMO has contributions from N,S and Pt but is nodal at C and this is in agreement with the ESR data. The hyperfine coupling to P presumably arises through the availability of d orbitals on P which are of the correct symmetry to interact with the SOMO of **4**. The SOMOs of **2** and **4** are related and electrochemical studies on both compounds have shown a reversible one-electron reduction [8].² The complete filling of the SOMO produces a HOMO related to that of **3**, although it should be noted that the HOMO of **3** is nodal at the N-inserted atom whereas d-orbitals on Pt allow more extended delocalisation onto the metal in the SOMO of **4**.

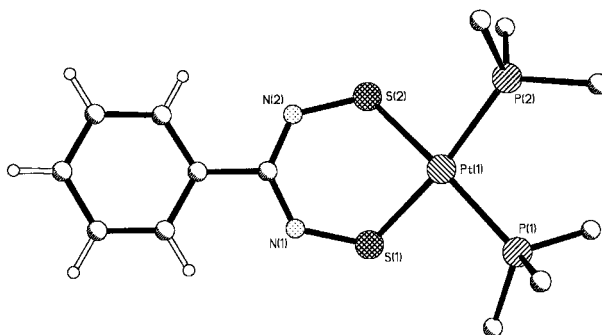
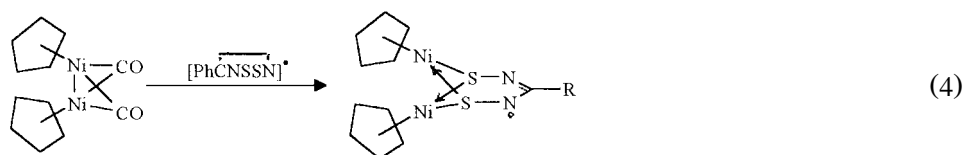


Fig. 5. Molecular structure of $[\text{PhCNSSN}]\text{Pt}[\text{PPh}_3]_2$.

The square-planar Pt(II) complex *cis*-platin is one of the worlds best-selling anti-cancer drugs, and numerous other square-planar Pt(II) complexes have been tested for biological activity [30]. Within **4**, not only do we have a square-planar Pt(II) coordination geometry, but there is an additional biologically active free-radical bound in close proximity to the square-planar Pt centre. Biological studies have shown that **4** is extremely potent towards a number of cell lines, although its high activity is also accompanied with a high toxicity [17].

6. Insertion of metal-fragments into the S–S bond: dimetallic complexes

So far we have seen examples in which **2** interacts with a single atom (Cl or N) or a metal fragment. However as well as chelating, the dithiadiazolyl ring can also act as a bridging ligand, linking two metals together. The first dithiadiazolyl-metal complexes to be reported [14,15] were $[\text{Fe}_2(\text{CO})_6(\text{PhCNSSN})]$ and $[\text{Cp}_2\text{Ni}_2(\text{PhCNSSN})]$, both of which contain a dimetallic framework, in which the metal–metal vector is bridged by the dithiadiazolyl ring. It has since transpired [10] that the iron compound is in fact a protonated analogue in which one of the heterocyclic nitrogen atoms is H-bound, i.e., $[\text{Fe}_2(\text{CO})_6(\text{PhCN}(\text{H})\text{SSN})]$. This compound is discussed later. As with the monometallic complexes, containing a chelating dithiadiazolyl unit, $[\text{Cp}_2\text{Ni}_2(\text{PhCNSSN})]$ was prepared [10,15] by an oxidative addition reaction of **2** to a low-valent transition metal complex; reaction of $[\text{CpNi}(\text{CO})]_2$ with **2** yielded $[\text{Cp}_2\text{Ni}_2(\text{PhCNSSN})]$, **5**, as a deep red solid.



6.1. Structure and bonding in $[\text{Cp}_2\text{Ni}_2(\text{PhCNSSN})]$

In **5** the sulfur atoms of the dithiadiazolyl ring bridge between the two metal atoms [15] (Fig. 6). This metal–ligand bonding interaction is accompanied by a breaking of the S–S bond, with the S...S distance increasing from 2.089(5) Å in **2** to a non-bonding 2.905(2) Å in **5**. This distance is a little larger than that observed for **3** but somewhat shorter than observed in **4** (see Table 1) consistent with the intermediate size of the Ni atom (cf. covalent radii of N, Ni and Pt at 0.74, 1.15 and 1.29 Å respectively). The Ni–Ni distance opens up from 2.3569(9) Å [31] in $[\text{CpNi}(\text{CO})]_2$ to 2.441(1) Å in **5**, associated with the weakening of the Ni–Ni bond. As with complexes **3** and **4**, the necessity for the ring to open is accommodated by an increase in bond angles at the heterocyclic C and to a greater extent at N (+7° and +9° respectively).

In the cyclic chelates **3** and **4**, each S provides one electron for σ -bonding to N or Pt respectively, two electrons for the π -system and retains a non-bonding lone-pair. In **5**, the lone-pair on each sulfur becomes involved in bonding, i.e., each Ni atom forms a σ -bond with one sulfur and a dative bond with the second sulfur. The dithiadiazolyl radical, **2**, now acts as a $6e^-$ donor ligand. This leads to each Ni having an 18 electron configuration and the Ni–Ni bond is formally cleaved. However, some modification of this valence bond description is necessary. This VB approach

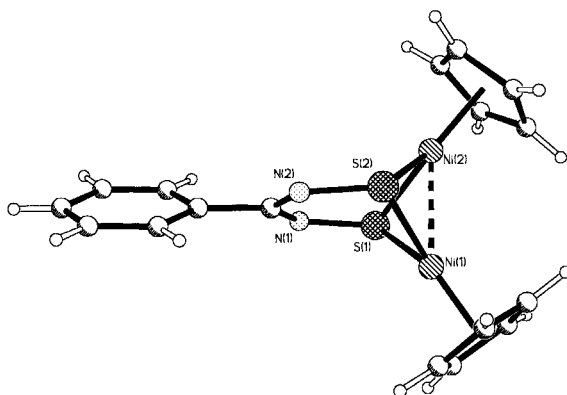


Fig. 6. Molecular structure of the nickel complex, $\text{Cp}_2\text{Ni}_2[\text{PhCNSSN}]$.

assumes that the unpaired electron is retained on the ring N which is in direct conflict with both experimental observations (ESR) and MO studies. MO calculations [10,15] at the EHMO level indicate that the SOMO of **2** (Fig. 2) is nodal at C but on coordination the unpaired electron becomes delocalised onto the metal-framework and there is a depopulation of the SOMO of **2** which now contributes to the LUMO of **5**. The SOMO of **5** now lies in a molecular orbital based on the Ni, S and C atoms and is nodal at N. This is in complete agreement with ESR studies which show only a singlet resonance in solution with no hyperfine coupling [10] (Ni, S and C all have high-abundance $I = 0$ nuclei).

7. Attachment of a further metal-fragment to the S–S bond: trimetallic complexes

If a dichloromethane solution of the monometallic complex, **4**, is allowed to stand, the blue-green colouration associated with **4** is dissipated to be replaced by a murky brown solution over an orange precipitate [16]. The precipitate was found to be a trimetallic complex, $\text{Pt}_3[\text{PhCNSSN}]_2[\text{PPh}_3]_4$, **6**, of a new type. A combination of NMR and ESR studies [17] showed that the brown solution contained paramagnetic **2**, also **6** and PPh_3 . Further work ¹ has indicated that the decomposition of the kinetic product, **4**, to give **6** occurs via loss of phosphine ligand, and we can consider that the S lone-pairs available on **4** successfully displace the PPh_3 ligand. This process is thermodynamically favoured through the chelating nature of the S atoms of the dithiadiazolyl ligand. However the use of chelating phosphine ligands can retard or prevent the decomposition process, e.g., the dppe analogue of **4** does not decompose in the same manner. ¹



7.1. Structure and bonding in $\text{Pt}_3[\text{PhCNSSN}]_2[\text{PPh}_3]_4$

The structure of $\text{Pt}_3[\text{PhCNSSN}]_2[\text{PPh}_3]_4$, **6**, (Fig. 7) can be considered [17] as two molecules of **4** sandwiching a naked Pt atom. As with other metal complexes, the S–S bond is formally broken ($d_{\text{S} \dots \text{S}} = 3.046(8)$ Å) and the increase in ring size is accommodated by an increase in the hinge angles at C and N ($+11^\circ$ and $+8^\circ$ respectively). The structure of **6** contains two distinct Pt environments; the terminal Pt atoms have a P_2S_2 coordination in which each P is a two electron donor and each S is a one-electron donor, identical to the bonding we described in **4**. This donor set provides six electrons giving the terminal Pt a $16e^-$ square-planar geometry. The central Pt has an S_4 donor set which provides six electrons as two lone pairs and two σ -bonds. In this way we can envisage **6** as being built up of a Pt atom bonded to two molecules of **4** in which each molecule of **4** provides a σ -bonding electron (the unpaired electron associated with **4**) and one of the sulfur atoms on each ring donates a lone pair. In this complex each dithiadiazolyl ligand provides a total of $5e^-$ for metal-bonding.

Incorporation of the unpaired electron associated with **4** into the metal-bonding framework is associated with depopulation of the SOMO of **4** and EHMO calculations show that the SOMO of **4** contributes to the LUMO of **6**. Since the SOMO of **1** contributes to the SOMO of **4**, then this is entirely analogous to the dimetallic nickel complex in which depopulation of the SOMO of **1** is also observed. This involvement of the unpaired electrons in bonding within the trimetallic structure is confirmed by magnetic and ESR spectroscopic measurements which show the compound to be diamagnetic.

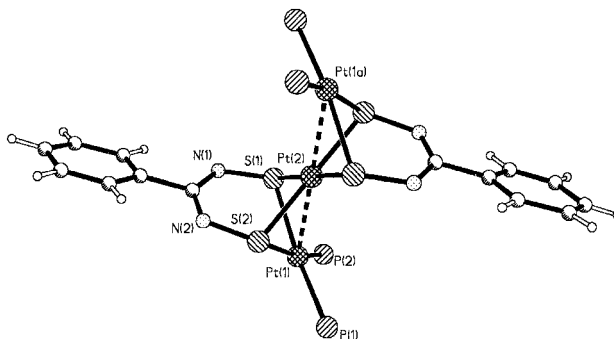
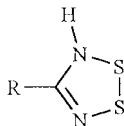


Fig. 7. Molecular structure of the trimetallic platinum complex, $\text{Pt}_3[\text{PhCNSSN}]_2(\text{PPh}_3)_4$.

8. Protonated dithiadiazolyl complexes

Although the N-protonated dithiadiazolyl compound, $\text{Ph}\overline{\text{CNSSNH}}$, **12**, is not known in its isolated form, a complex has been prepared in which the heterocyclic ring is protonated; A recent re-investigation [10] showed that this compound is diamagnetic and possesses an N–H stretch in the IR consistent with N-protonation and formulation $\text{Fe}_2(\text{CO})_6[\text{PhCNSSNH}]$. It was prepared from $\text{Fe}_2(\text{CO})_9$ with **1**, in the presence of adventitious moisture.



(12)

8.1. Structure of $\text{Fe}_2(\text{CO})_6(\text{PhCNSSNH})$ and effect of protonation on bonding

Within the structure of $\text{Fe}_2(\text{CO})_6(\text{PhCNSSNH})$, (Fig. 8) the S–S bond is cleaved ($d_{\text{S}\dots\text{S}} = 2.930(2) \text{ \AA}$) and there are the normal increases in hinge angles associated with the heterocyclic C and N atoms in order to accommodate the additional atoms within the structure. Notably (Table 1) there are marked differences in bond lengths and angles at the two heterocyclic N atoms. If we assign the NH group to the N with the longest C–N bond (consistent with the formulation of **12**) then there is a marked increase in the hinge angle at the protonated N ($+11^\circ$) whereas the changes in bond angles at C and second ring N are less marked ($+7^\circ$ and $+8^\circ$ respectively).

The tendency for some complexes such as $\text{Fe}_2(\text{CO})_6(\text{PhCNSSN})$ to become protonated, whereas $\text{Cp}_2\text{Ni}_2(\text{PhCNSSN})$ does not, can be rationalised [10] through the number of electrons within the cluster and the orbitals which they occupy. In $\text{Fe}_2(\text{CO})_6(\text{PhCNSSN})$ the unpaired electron is accommodated in a ring σ^* orbital based on the $\text{M}_2(\text{PhCNSSN})$ framework. This electronic configuration is highly reactive and leads to protonation in the presence of water. In contrast, the $\text{M}_2(\text{PhCNSSN})$ core of the dimetallic nickel complex possesses a further two electrons and the unpaired electron is now located in a π -based MO on the heterocyclic ring, with extensive delocalisation onto the metal framework. Notably the unpaired electron in the monometallic Pt complex, **4**, is also in a π -based MO.

9. Other cyclic chelators

There are two key features for compounds to act as efficient cyclic chelators. Firstly there must, of course, be a heterocyclic bond susceptible to cleavage. In the case of **2**, there is also a partially occupied S–S antibonding π orbital (π_4) which weakens the S–S bond. Secondly there must be an efficient hinge atom where the ring strain (introduced by increasing the ring size) can be accommodated. In the case of **2**, N provides a particularly efficient hinge, i.e. there is a low energy cost to expand the angle at nitrogen (the inversion of NH_3 occurs at 2000 cm^{-1} or ca. 25 kJ/mol) [32]. Since there is a limit to the extent to which hinge atoms can accommodate the ring strain, some degree of non-planarity can also be anticipated.

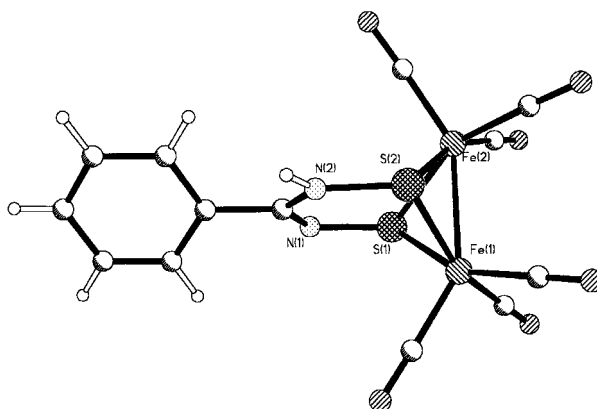
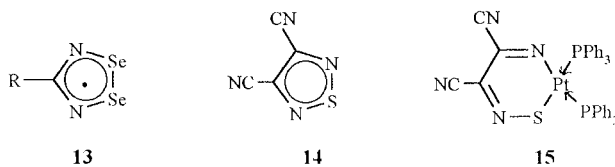


Fig. 8. Molecular structure of the protonated iron complex, $\text{Fe}_2(\text{CO})_6[\text{PhCN}(\text{H})\text{SSN}]$.

Given these factors we can anticipate other types of compounds which might act as efficient cyclic chelators, and we shall highlight these with a few literature examples; replacement of S by Se leads to a family of diselenadiazolyl rings, **13**, and ESR studies have indicated [33] that they should exhibit similar coordination chemistries to the dithiadiazolyl radicals, **2**. Dithiadiazolyl salts, **1**, are structurally related to dithiolium salts, **8**, and we would expect the latter compounds to exhibit similar coordination geometries. Indeed complexes of **8**⁻ are well known [34] and are analogous to β -diketonates such as acac^- . The thiadiazole ring system, $(\text{RC})_2\text{N}_2\text{S}$, **14**, has also been shown [35] to act as cyclic chelator through cleavage of an N–S bond. Its complex **15**, has planar $\text{C}_2\text{N}_2\text{S}$ and P_2NS geometries but ring buckling is again observed with an angle between the two planes at the Pt centre of 12.8° .



10. Conclusions

This work has shown that the dithiadiazolyl radical, **2**, is a versatile ligand in coordination chemistry. It can form chelating complexes in which it can donate two to three electrons, or as a bridging ligand in which it can either donate five or six electrons. This versatility arises through the ability of the ligand to either retain or utilise both the unpaired electron and a lone pair on each sulfur atom in metal bonding. The ability of this ligand to become involved in metal bonding is promoted by two factors: the weakness of the S–S bond (facilitated by the S–S antibonding contribution in the SOMO) and the ability of the N atom to act as an efficient hinge. We have indicated other compounds which might act as efficient cyclic chelators, but of these the dithiadiazolyl ring is particularly important as its free-radical nature provides us with a direct ESR probe of the bonding.

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