Organometallic thiazenes. Oxidative addition of S_4N_4 to low-valent metals; electrochemistry and ^{15}N NMR of $CpCoS_2N_2$ and $Cp^*CoS_2N_2$ *

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Abstract

The reactions of S_4N_4 with $CpM(CO)_x$ and $Cp^*M(CO)_x$ (M = Mn, Fe, Co, Ni and Rh) result in tractable products only when M = Co. The electrochemical behaviour of the previously known complexes $CpCoS_2N_2$ and $Cp^*CoS_2N_2$ has been investigated by DC and AC cyclic voltammetry. Each has a single one-electron reduction process occurring at −0.65 V (Cp) and −0.99 V (Cp^*), *vs.* SCE, in CH_2Cl_2 solution. For the Cp complex, chemical reduction using cobaltocene has also been achieved. ^{15}N NMR spectra were recorded for 99% ^{15}N enriched samples: 550 (broad singlet) and 431 (singlet) for Cp, 518 (broad singlet) and 404 ppm (singlet) for Cp^*, referenced to liquid NH_3. The electronic absorption spectra are also reported, and interpreted in the light of EHMO calculations.

Key words: Cobalt; Thiazene; Oxidative addition; Electrochemistry; Extended Hückel calculations

1. Introduction

Heterocyclic thiazenes show great potential for the preparation of new materials with useful properties as conductors, superconductors, *etc.* [1,2]. Transition-metal containing heterothiazenes are a new potential source of such materials [3]. For example, some thiazyl complexes bear a striking similarity to metal dithiolenes, which have already received extensive consideration in the design of one-dimensional conductors [4].

A small number of organometallic thiazene heterocycles have been reported. These include the title compounds **1** and **2**, [5] as well as the iridium and platinum complexes **3** [6], **4** [7] and **5** [8], and the titanium complexes **6** and **7** [9]. Most of these compounds were prepared by the direct oxidative addition of S_4N_4 to a low valent organometallic compound. Only in **4** does this lead to insertion into a single S–N bond. In all other cases oxidative addition has been accompanied by some sort of extrusion process leading to complexes of (formally) $S_2N_2^{2-}$, $S_3N_2^{2-}$ and $S_3N_4^{2-}$. Reactions of binary metal carbonyls with S_4N_4 were explored many years ago [10]. Very few tractable products were obtained. Insoluble polymeric products were reported by most workers, some of which were explosive. Work-up of the initial solids from the reaction of $Ni(CO)_4$ with S_4N_4 in wet methanol yielded the product $Ni\{S_2N_2H\}_2$, which retained none of the carbonyl ligands [10c,d].

Edelmann has reported the preparation of the title compounds by reaction of CpCo(1,5-COD) or $Cp^*Co(CO)_2$ with S_4N_4 [5]. Our attempts to extend this chemistry to other mono-cyclopentadienides of the first-row transition elements have been singularly unsuccessful. Similar attempts to prepare Rh analogues to the title compounds using $CpRh(CO)_2$ also failed. Most of the material seems to end up as insoluble precipitates which are probably of a polymeric nature. Edelmann obtained similar results [11]. Thus the oxidative addition of S_4N_4 to monocyclopentadienyl complexes is similar to the binary metal carbonyls, except that we did not find any of the precipitated materials to be friction explosives [10].

Thus **1** and **2** are the only known examples of monocyclopentadienyl MS_2N_2 complexes which are isoelectronic to the well-characterized dithiolene derivatives. In this work we set out to make a detailed

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* In this paper: $Cp = \eta^5\text{-}C_5H_5$; $Cp^* = \eta^5\text{-}C_5Me_5$.

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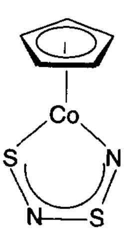

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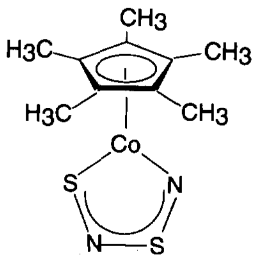

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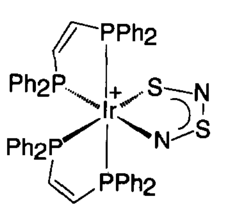

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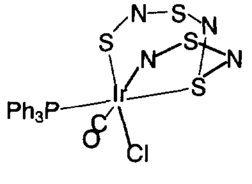

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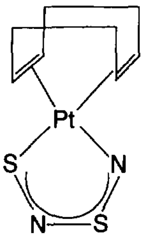

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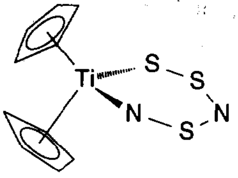

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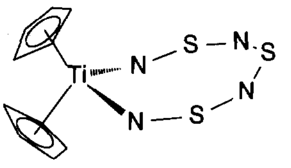

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comparison of the properties of the $S_2N_2^{2-}$ ligand in organometallic complexes with those of dithiolenes and the closely related tetrazabutadienes. We have studied the electrochemical behaviour of 1 and 2 by DC and AC cyclic voltammetry in order to probe the donor/acceptor character of the ligand. We have compared the orbital energies and topologies of model CpCo complexes of the three types of ligand and we have measured and assigned the electronic absorption spectra of 1 and 2.

We have also investigated the mechanism of the reaction of S_4N_4 with CpCoCOD which leads to the $S_2N_2^{2-}$ complex. Thus we have prepared ^{15}N enriched samples of these complexes, and have studied the reaction of CpCoCOD with $S_4{}^{15}N_4$ by *in situ* NMR methods. The ^{15}N NMR spectra of the two complexes are reported for the first time.

2. Experimental details

2.1. General

$CpCo(CO)_2$ [12], $Cp^*Co(CO)_2$ [13], CpCo(COD) [14] and S_4N_4 [15] were prepared by the literature methods. Cp_2Co (Strem) was sublimed *in vacuo* immediately before use. Cl_2 (Matheson) and $^{15}NH_4Cl$ (99% enriched, Merck, Sharpe and Dohme) were used as received. Solvents were Fisher reagent grade, and were distilled from sodium wire (toluene, THF). CH_3CN was double-distilled from P_2O_5 and CaH_2. CH_2Cl_2 for cyclic voltammetry was fractionated three times over P_2O_5 and stored over molecular sieves (4 Å). Unless otherwise indicated, all procedures were performed under an atmosphere of purified N_2 using a dry-box, Schlenk ware and vacuum-line techniques. Infrared spectra were recorded on a BOMEM MB102 Fourier transform spectrometer. Elemental analysis were performed by MHW Laboratories, Phoenix, AZ, USA. ^{15}N NMR spectra were recorded at 40.55 or 25.35 MHz on Bruker instruments. External neat CH_3NO_2 was used as the reference compound, but shifts are quoted with reference to liquid NH_3, using $\delta(CH_3NO_2) = 380.23$ ppm [16].

2.2. Preparation of $S_4{}^{15}N_4$

$S_3N_2Cl_2$ was prepared from $^{15}NH_4Cl$ by the published procedure [17]. Cl_2 was passed through the air condenser containing the crystalline product, effecting direct conversion to $S_3N_3Cl_3$. The yellow crystals (0.5 g, 2.0 mmol) were transferred in a glove box to a Schlenk tube, dissolved in 10 ml of warm acetonitrile and Ph_3Sb (1.2 g, 3.4 mmol) in 10 ml of acetonitrile was added dropwise. On cooling, small crystals of orange $S_4{}^{15}N_4$ were obtained, filtered, rinsed with a little hexanes, and dried. Yield 0.2 g (1.1 mmol, 71%).

2.3. Preparation of $CpCoS_2N_2$

This compound was prepared by a literature procedure from CpCo(COD) and S_4N_4 [5b]. An improvement in the general method was to concentrate the reaction mixture to a minimum volume, and then run it through a BioBeads SX-8 column swelled in toluene. S_4N_4 was the leading band. The deep purple band of product was separated, solvent evaporated, and the resulting solid recrystallized from toluene to give small black-purple plates. In a similar procedure, labelled material was prepared by the reaction of $S_4{}^{15}N_4$ (99% enriched), with CpCo(COD), followed by BioBeads chromatography.

2.4. Preparation of $Cp^*CoS_2N_2$

By the literature method from $Cp^*Co(CO)_2$ and S_4N_4 [5b], followed by Biobeads elution (toluene) and recrystallization from acetone. Labelled material was prepared by the same route using $S_4{}^{15}N_4$.

2.5. Preparation of $[Cp_2Co][CpCoS_2N_2]$

In an H-tube reaction vessel separated by a medium glass frit 0.27 g (1.35 mmol) of freshly sublimed Cp_2Co was placed in one arm, and 0.29 g (1.35 mmol) of recrystallized $CpCoS_2N_2$ was placed in the other arm. 50 ml of freshly distilled THF was condensed onto the $CpCoS_2N_2$, and subsequently degassed by three freeze–thaw cycles. About half of the solvent was vacuum transferred into the cobaltocene-containing arm, and the two reagents were carefully mixed by pouring the cobaltocene solution into the cobalt thiazene solution. Fibrous red-brown crystals precipitated, which were collected and washed with fresh solvent by vacuum transfer. 0.41 g (0.99 mmol, 73% yield), mp 130–140°C dec. Anal. Calc. for $C_{15}H_{15}Co_2S_2N_2$: C, 44.45; H, 3.73; N, 6.91%. Found: C, 44.32; H, 3.83; N, 6.69%. IR (1600–200 cm^{-1}): 1412 (w), 1109 (w), 1076 (w), 1013 (w), 991 (w), 864 (w), 848 (w), 723 (m), 770 (m), 723 (w), 677 (m), 604 (m), 588 (w), 575 (w), 502 (s), 459 (vs), 380 (s), 365 (vs), 320 (vs), 251 (m), 241 (w), 218 (w).

2.6. Electrochemistry

Electrochemical equipment: Princeton Applied Research (PAR) Model 173 Potentiostat and Model 175 Programmer in combination with Model 5208 Lock-in-Analyzer and Linseis X-Y-Y recorder. Cyclic voltammograms and alterning current voltammograms were obtained in a specially designed evacuable cell using platinum wire electrodes [18]. Electrochemical procedures: the cell was charged with **1** or **2** as well as ferrocene in separate break-seal side-arms, loaded with supporting electrolyte $[^nBu_4N][PF_6]$ in an argon-filled dry-box, evacuated, and dry CH_2Cl_2 transferred in on a vacuum line. $[^nBu_4N][PF_6]$ is prepared by neutralization of $[^nBu_4N]OH$ with HPF_6 (pH meter), recrystallized from ethanol/petroleum ether and dried at 80°C *in vacuo*. The measurements start with the IR-compensation and background scans, which were performed to determine the purity of solvent/electrolyte and the width of the electrochemical window. Then the $CpCoS_2N_2$ was introduced, and after acquiring DC cyclic voltammograms and AC voltammograms of these solutions, the second break-seal was opened and a small amount of ferrocene was introduced into the solution as an internal reference. The ferrocene/ferrocenium couple was determined in CH_2Cl_2 at +0.48 V *vs.* SCE.

2.7. Extended Hückel MO calculations

The program FORTICON8 [19] was employed using experimental geometries from X-ray crystal structures of **1**, $CpCoS_2C_2(CF_3)_2$ [20] and $CpCo(NC_6F_5)_2N_2$ [21]. Metal 4s and 4p exponents are the modified parameters introduced in ref. [22]. Sulfur d orbitals were included in all calculations as polarization functions, but are omitted from orbital sketches. d orbital exponents and coefficients are from ref. [23]. Cobalt H_{ii} were taken from ref. [24].

TABLE 1. Voltammetric data on $CpCoS_2N_2$ and $Cp^*CoS_2N_2$ [a]

	Cyclic voltammetry		A.c. voltammetry	
	$E_{1/2}$, V *vs.* SCE [b]	ΔE_p, mV [c]	$E_{1/2}$, V *vs.* SCE [b]	$W_{1/2}$ mV [d]
$CpCoS_2N_2$	−0.65	160	−0.66	220
$Cp^*CoS_2N_2$	−0.99	120	−1.02	160

[a] Supporting electrolyte: 0.4 M $[^nBu_4N][PF_6]$; solvent: CH_2Cl_2; working electrode: micro Pt.

[b] $E_{1/2}$ = half-wave potential *vs.* SCE using the ferrocene/ferrocenium redox couple as internal reference standard ($E_{1/2}$ = 0.48 V *vs.* SCE).

[c] ΔE_p = peak separation for oxidation and reduction peak potentials.

[d] $W_{1/2}$ = width at half-wave height.

3. Results and discussion

3.1. Electrochemistry

The results of our electrochemical investigation of **1** and **2** are presented in Table 1 and Fig. 1. Only a single one-electron reduction step was observed for each compound under conditions of cyclic voltammetry and AC voltammetry. An oxidation process was not observed. The reduction occurred for **1** at a half-wave potential $E_{1/2} = -0.65$ V and for **2** at $E_{1/2} = -0.99$ V *vs.* SCE. The voltammograms in Fig. 1 show the superposition of the ferrocene/ferrocenium redox couple, added as an internal standard, with that of **1** and **2**. In order to assess the reversibility of the two processes given the noticeable difference in the appearance of the anodic return waves of **1** and **2**, we have also studied their alternating current voltammograms. There we find the width at half-height, $w_{1/2}$, to be 220 mV for **1** and 160 mV for **2**. These values are comparable to the width in the same solution for the reversible $Cp_2Fe^{0/+1}$ redox couple. (Although the theoretical value for a reversible one-electron alternating current

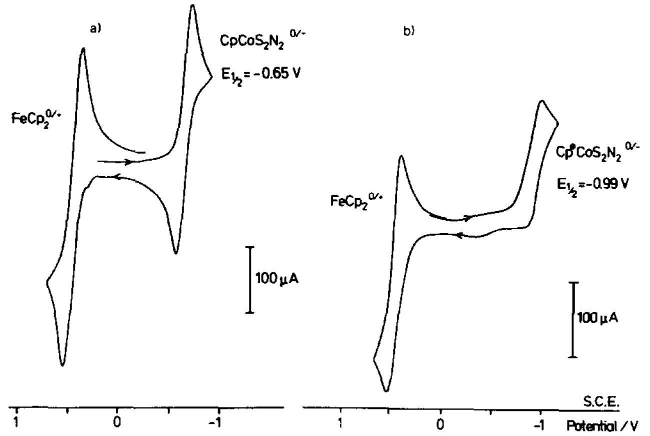


Fig. 1. Cyclic voltammograms of solutions containing mixtures of ferrocene and **1** or **2** in CH_2Cl_2, 0.4 mol l^{-1} $[^nBu_4N][PF_6]$.

AC process is 90 mV [25], larger values can be explained by the high internal resistance of the non-aqueous solutions.) Thus despite the appearance of the DC cyclic voltammograms, there is no ground to distinguish the reversibility of the processes in **1** and **2**, and we judge them both to be at least quasi-reversible. Further evidence for the stability of the anion of **1** is afforded by its chemical generation (see below).

The difference observed between the reduction potentials of **1** and **2** is entirely consistent with substitution of Cp* for Cp in similar complexes. For example, the potentials for the reduction of cobaltocenium to cobaltocene is −0.91 V, while that for the $Cp^*{}_2Co^{0/+}$ couple is −1.47 V (*vs.* SCE) [26]. The lower reduction potential of the Cp* compound is attributed to the electron donating ability of the methyl groups, which raises the energy of the antibonding orbitals into which the extra electron is accepted.

3.2. Chemical reduction

Since the electrochemistry showed reversible reduction of **1** at −0.65 V, and the oxidation of cobaltocene occurs at −0.91 V, we reasoned that Cp_2Co should be capable of reducing **1** chemically. The reaction of cobaltocene with **1** in THF affords a fine needle-like burgundy solid which analyses for $[Cp_2Co][CpCoS_2N_2]$ (eqn. (1)).

$$Cp_2Co + CpCoS_2N_2 \longrightarrow [Cp_2Co][CpCoS_2N_2] \quad (1)$$

We were unable to grow crystals suitable for X-ray crystallography.

3.3. UV-Vis spectra

Although the ultra-violet photoelectron spectra of **1** and **2** have been reported [6b], the electronic absorption spectra have not. Table 2 presents the data for these intensely purple-coloured complexes, and comparative data on related organometallic heterocycles.

3.4. ^{15}N NMR data

The ^{15}N NMR spectra of **1** and **2** were obtained in $CDCl_3$ solution at 40.55 and 25.35 MHz. The results are shown in Fig. 2. For each compound, there are two singlets, with little evidence of N–N coupling. The downfield singlets in both spectra are significantly broadened with reference to the upfield ones. The effect is much more dramatic for **2**. We attribute this line-broadening to coupling with ^{59}Co (spin 7/2). (In the inset to the figure, fine structure is evident on the 518 ppm signal of **2**.) On the basis of this effect, we assign the 520–550 ppm resonances to the nitrogen attached to the metal, and the 400–430 ppm resonances to the SNS nitrogen. The increased line-broadening for **2**, and the rather large differences in chemical shift between the two compounds are both indicative of a large degree of electronic interaction between the organometallic and the sulfur–nitrogen rings, which is consistent with the results obtained from MO calculations showing the high degree of covalency in these compounds.

The ^{15}N shifts in **1** and **2** can be compared to ^{14}N shifts reported for several d^8 MS_2N_2 complexes of Pd and Pt [27]. All the resonances in **1** and **2** occur further downfield than any observed for the latter, for which the signals occur in the range 220–360 ppm. Since ^{14}N and ^{15}N chemical shifts are normally more-or-less interchangeable, this suggests that the differences are real, and are caused by significant differences in the electronic structures of the metallacycles. This is not surprising. Thiazyl rings of this type have delocalized

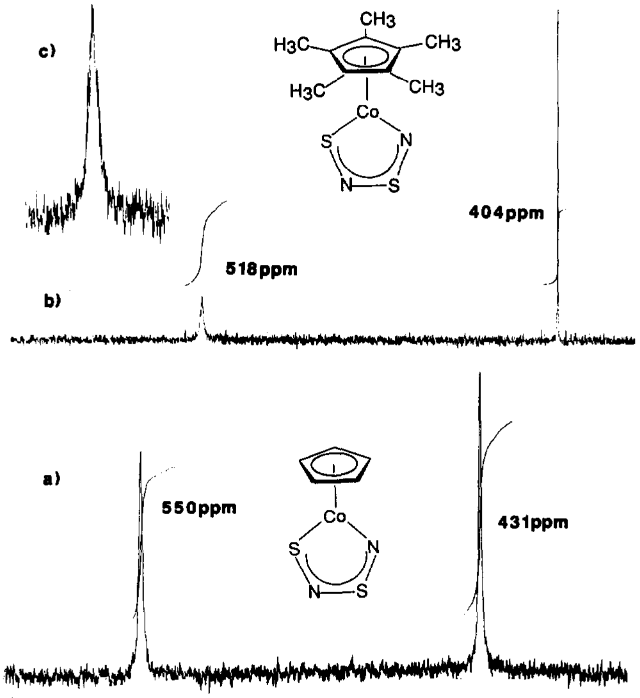


Fig. 2. 40.55 MHz ^{15}N NMR spectra of (a) **1**; (b) **2** in $CDCl_3$ solution at r.t. Inset (c) is an enlargement of the 518 ppm signal for **2**.

TABLE 2. Electronic spectral data on $CpCoS_2N_2$, $Cp^*CoS_2N_2$ and related compounds [a]

$CpCo(S_2N_2)$ [b]	278 (25000)	376 (5000)	504 (2900)	750 (sh)
$Cp^*(S_2N_2)$ [b]	286 (19000)	383 (4200)	518 (2500)	
$CpCo(MeN_4Me)$ [c]	230 (22200)	338 (1860)	428 (7650)	623 (246)
$CpCo(PhN_4Ph)$ [c]	270 (20900)	390 (sh)	471 (7520)	669 (860)
$CpCo(R_FN_4R_F)_2$ [c,d]	255 (sh)	342 (3520)	467 (6740)	656 (523)

[a] Absorption maxima in nm (molar absorptivity).

[b] Recorded in 10 mm cells in CH_2Cl_2; no marked solvent dependence was observed (toluene, CH_3CN).

[c] Ref. 30.

[d] $R_F = C_6F_5$.

π-electrons (see below), and these π-electrons are known to be easily polarized. Thus the ^{15}N shifts are sensitive to the difference in electronic structure imparted by substituents on the cyclopentadienyl rings. Nitrogen NMR is thus a sensitive probe of electronic structure in thiazyl metallacycles.

We have tried to follow the mechanism of the reaction of CpCoCOD with enriched S_4N_4 by an *in situ* ^{15}N NMR study. CpCoCOD and S_4N_4 were allowed to react in $CDCl_3$ solution in a 10 mm NMR tube. Sequential spectra show the slow disappearance of the S_4N_4 signal (123.2 ppm) [28] with concomitant growth of the two signals of **1**. The reaction is essentially complete after 3 h at r.t., with no sign of long-lived reaction intermediates in the ^{15}N spectra. Only trace amounts of soluble side products could be detected, although some dark-coloured precipitates formed during the reaction. We can therefore neither confirm nor refute the postulate that prior coordination of the S_4N_4 cage is followed by cleavage to S_2N_2 and subsequently by oxidative addition [3a]. While this is an entirely plausible view in terms of the known conversion of S_4N_4 to S_2N_2 by Lewis acids in solution or in solid-state reactions, the isolation of Ir complex **4** suggests that it is equally likely that S_4N_4 oxidatively adds intact to the metal centre, which could be followed by extrusion of S_2N_2 from the resultant complex. According to this view, in **4**, further coordination of the intact S_4N_4 stabilizes the ring against such an extrusion process. In **1** and **2**, where the additional site is blocked by the cyclopentadienyl ligand, extrusion follows immediately. Our results indicate that none of the intermediates in this process have a long lifetime in solution.

3.5. MO calculations

The similarity in the electronic structure of **1** and **2** with analogous dithiolene and tetrazabutadiene complexes has been suggested [5b]. We have performed extended Hückel calculations on model complexes **1**, **8** and **9**. The relative orbital energies are presented in Fig. 3. The complexes are arranged from left to right in the order of the increasing electronegativity of the ligand atoms. The calculated orbital energies of the dithiolene and the model S_2N_2 complex are very similar. By contrast the tetrazabutadiene has a significantly higher-lying LUMO and consequently has a greater HOMO–LUMO separation.

3.6. Electronic structure

The striking similarity in the orbital energies and orbital topologies between the model complexes **1**, **8** and **9** suggest that these complexes should have very similar electronic structures. Although these are all highly mixed MOs, it is possible to generalize and say that in each case there is a low lying π_3 component from a metal-ring π bonding interaction, followed by three essentially metal-based orbitals corresponding to the t_{2g} set of an octahedral complex, one of which is the HOMO, followed by the LUMO as a π_3^* orbital which is metal–ring π antibonding. This is a unique pattern which distinguishes these metallacycles from main group inorganic heterocycles. Thus there are empty and filled π orbitals in this complex, but in contrast to analogous main group rings, the HOMO of the molecule is not a π orbital.

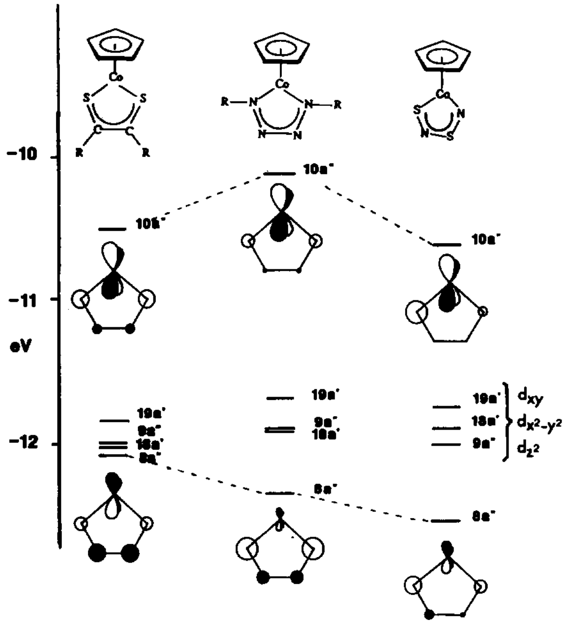
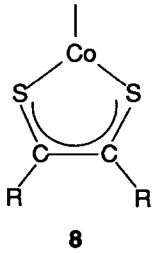


Fig. 3. Orbital energy and topology for three related model CpCo complexes of **1**, **8** and **9** by the extended Hückel method.

This similarity is substantiated by the similar electronic spectra and electrochemical properties of these three classes of complexes. Trogler has suggested an assignment of the visible spectra of tetrazabutadiene complexes of type **9** [29]. By analogy with his postulates, the HOMO–LUMO transition in **1** is probably the shoulder observed at 750 nm. (The HOMO–LUMO



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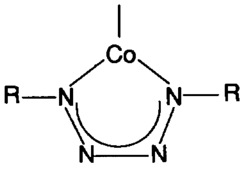

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gap obtained in DV-Xα calculations on **1** corresponds to a wavelength of 815 nm [5b].) The larger HOMO–LUMO gap calculated for complexes of type **9** are substantiated by the data in Table 2. The lower-lying metal-*d* centred orbitals 18a′ and 9a″ contribute to the intense 504 nm band. The 376 nm band may involve transitions to the second unoccupied orbital 11a″. In contrast to the RN_4R complexes, this transition is allowed for S_2N_2. Support for this assignment comes from the data for **2**. The red-shift of the 504 nm band on pentamethylation is double that for the 376 nm band. This makes sense if the former represents excitation to 10a″, the latter to 11a″, since 11a″ is a S–N ring-centred π^* orbital, and should be less affected by the electron-donating methyl groups.

All three types of complex are resistant to electrochemical oxidation [29,30]. Typically they show one-electron reductions to the corresponding 19 e^- anions at comparable potentials. It is difficult to make an exact comparison of the redox potentials, since for $CpCo(RN_4R)$ complexes, there is more than half a volt difference depending on the nature of R [29]. The observed range is -0.71 ($R = C_6F_5$) to -1.53 ($R = CH_3$) V *vs.* SCE. The reduction potentials of dithiolene complexes are also substituent-dependent, although only the electrochemistry of the complexes with the more electron withdrawing R groups has been reported [31]. Astruc has argued persuasively that these metallacyclic anions have a great deal of metal–ligand covalency, and that the added electron is effectively shared between the metal and the ligands [32]. This explains the large dependence of the reduction potential on substituent effects. Similar arguments can be put forward regarding the 19 e^- thiazene complexes. Accordingly, DV-Xα calculations divide the LUMO 10 a″ orbital of $CpCoS_2N_2$ 41% Co; 39% S_2N_2 and 19% Cp [5b].

4. Conclusions

This work has extended the knowledge of the electronic structure of organometallic thiazenes, and has demonstrated that the best way to understand MS_2N_2 compounds is by analogy with other heterometallacycle complexes, such as the 1,2-dithiolenes or 1,4-tetrazabutadienes. There is a strong similarity in the orbital energy and topologies of the CpCo complexes of these three types of ligands. S_2N_2 is definitely a non-innocent ligand, and in these complexes the metal is more oxidized than it is in any of the several dithiolene or tetrazabutadiene complexes whose electrochemistry has been investigated. Thus it is more effective as a π-acceptor ligand and less effective as a σ-donor ligand than either the dithiolene or tetrazabutadiene, although the contribution of ring substituents to the bonding of the latter two should not be underestimated. This serves to consolidate comments that have previously been made regarding the high effective orbital electronegativity of sulfur in unsaturated thiazenes [1].

S_4N_4 and presumably S_2N_2 as well are readily reduced by low valent metal complexes. Despite being formally electron rich, they are good electron acceptors, and the resulting metal complexes are more oxidized than analogous RN_4R complexes, even those with electron-withdrawing fluorocarbon substituents. However, direct reaction with S_4N_4 is not a generally suitable synthetic route to MS_2N_2 complexes, and most low-valent organometallic compounds give insoluble, dark, presumably polymeric products on reaction with S_4N_4.

5. Supplementary material available

Figure 4 presents the UV-Vis spectra of **1** and **2**, and is available from the authors.

Acknowledgments

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