Preparation, Crystal Structure and Extended-Hückel Molecular-orbital Study of the Free-radical Complex $[Ni_2(cp)_2(PhCN_2S_2)](cp = \eta\text{-}C_5H_5)$†

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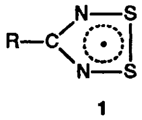
Dimeric 4-phenyl-1,2,3,5-dithiadiazole $(PhCN_2S_2)_2$ reacted with $[\{Ni(cp)(CO)\}_2]$ to give $[Ni_2(cp)_2(PhCN_2S_2)]$ (cp = η-C_5H_5). The X-ray structure was found to be based on an Ni_2S_2 tetrahedral core with Ni–Ni 2.441(1), S $\cdots$ S 2.905(2) and average Ni–S 2.172(1) Å. The relatively short nickel–nickel distance, indicating formally 19-electron nickel centres, and other structural features are discussed in relation to similar dinickel complexes and by means of extended-Hückel calculations.

The current interest in materials with interesting electronic and magnetic properties, *e.g.* molecular ferromagnetism[1] and low-dimensional conductivity,[2] has resulted in several recent publications on the 1,2,3,5-dithiadiazoles,[3,4] RCN_2S_2 **1**. These are stable, planar free radicals which are generally incompletely associated both in the solid state and in solution.



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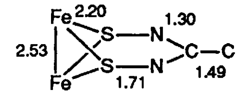

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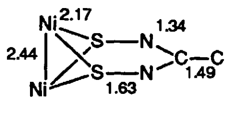

3

Distances in Å

We have recently reported[4] the formation of $[Fe_2(CO)_6(PhCN_2S_2)]$ **2** from $(PhCN_2S_2)_2$ and $[Fe_2(CO)_9]$ or $[Fe_3(CO)_{12}]$. Extended-Hückel molecular orbital (MO) calculations, supported by X-ray structural data, indicated that the ligand-based unpaired electron was responsible for the weak but significant interactions: intramolecular S $\cdots$ S and intermolecular N $\cdots$ N. The latter are responsible for the alignment of the iron complex molecules into chains. In the light of these results and a recent suggestion[5] that metal complexes containing free-radical ligands may exhibit ferromagnetism, we now report a new dithiadiazole nickel complex, $[Ni_2(cp)_2(PhCN_2S_2)]$ **3** (cp = η-C_5H_5), which contains a skeleton similar to that of $[Fe_2(CO)_6(PhCN_2S_2)]$.

Experimental

All manipulations of solids were carried out in a Vacuum Atmospheres HE43-2 glove-box fitted with an HE493 Dri-Train. Solutions were handled using standard Schlenk techniques. The dimer $(PhCN_2S_2)_2$ was prepared by zinc–copper reduction[6] of $[PhCN_2S_2]Cl$ in tetrahydrofuran, followed by sublimation. The compound $[\{Ni(cp)(CO)\}_2]$ was prepared using the literature method.[7] Toluene and light petroleum (b.p. 30–40 °C) were dried by refluxing over sodium–potassium alloy, followed by distillation under nitrogen. Tetrahydrofuran was dried by refluxing over potassium–diphenylketyl, followed by distillation under nitrogen. Infrared spectra were recorded as Nujol mulls between KBr plates or as solutions in a CaF_2 solution cell on a Perkin-Elmer 577 spectrophotometer, mass spectra on a VG Analytical 7070E spectrometer. Carbon, hydrogen and nitrogen were determined by microcombustion in a Carlo Erba 1106 elemental analyser. Nickel was determined using a Perkin-Elmer 5000 atomic absorption spectrophotometer.

Preparation of $[Ni_2(cp)_2(PhCN_2S_2)]$.—A solution of $[\{Ni(cp)(CO)\}_2]$ (0.3 g, 1.0 mmol) and $(PhCN_2S_2)_2$ (0.18 g, 0.5 mmol) in toluene (25 cm^3) was stirred at room temperature for 14 h. Solution-phase IR spectroscopy showed that no carbonyl species were present after this time. The mixture was then filtered to give a black solid which was washed with toluene (3 × 2 cm^3) and pumped dry. This material (0.15 g) was insoluble in common organic solvents and was most probably polymeric (Found: Ni, 17.3; S, 9.1%. Ni:S 1:1). It was not investigated further. The dark red filtrate was pumped dry and the residue recrystallised from light petroleum–toluene (1:1, 25 cm^3) to give dark red crystals of $[Ni_2(cp)_2(PhCN_2S_2)]$ **3** (0.18 g, 42%) (Found: C, 48.5; H, 3.5; N, 6.8; Ni, 27.4. $C_{17}H_{15}N_2Ni_2S_2$ requires C, 47.6; H, 3.5; N, 6.5; Ni, 27.4%); ν_{max} 1410w, 1324m, 1338s, 1180(sh), 1172m, 1138w, 1070w, 1050w, 1030w, 1010m, 1000w, 840w, 816s, 803(sh), 795s, 775w, 762w, 731s, 705(sh), 698s, 672s and 432m cm^{-1}; m/z (EI) 427(M^+, 2), 278($M - PhCN_2S^+$, 3), 194(4), 189[$Ni(cp)_2^+$, 15], 186(6), 149($PhCN_2S^+$, 9), 130 [$(cp)_2^+$, 100], 121(14), 103($PhCN^+$, 66), 89(PhC^+, 7), 77(Ph^+, 12), 76(S_2N^+, 20), 65(cp^+, 35) and 64(S_2^+, 23%). Magnetic measurements were made at 21 °C on a laboratory-built vibrating sample magnetometer. The magnetisation curve was typical of that for a paramagnetic compound, *i.e.* a straight line, the slope of which gave a susceptibility of 0.022 J T^{-2} kg^{-1}. Crystals were grown by slow crystallisation from a saturated solution in toluene–light petroleum (1:1).

X-Ray Crystallography.—Crystal data. $C_{17}H_{15}N_2Ni_2S_2$, $M = 428.8$, monoclinic, space group $P2_1/n$, $a = 16.270(1)$, $b = 12.069(1)$, $c = 17.365(1)$ Å, $\beta = 93.863(7)°$, $U = 3402.1$ $Å^3$

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Non-SI unit employed: eV = 1.60×10^{-19} J.

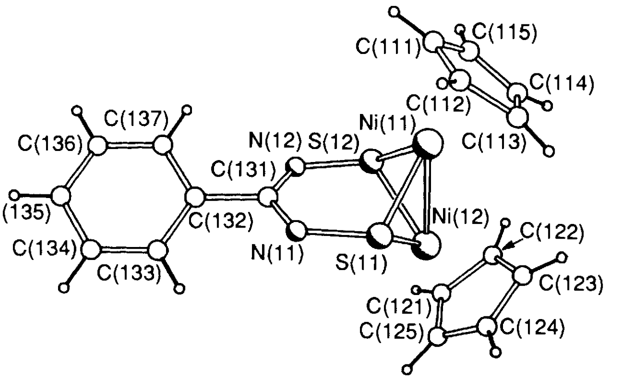


Fig. 1 Structure of one molecule of $[Ni_2(cp)_2(PhCN_2S_2)]$ **3** showing the numbering scheme. A corresponding scheme is adopted for the other molecule

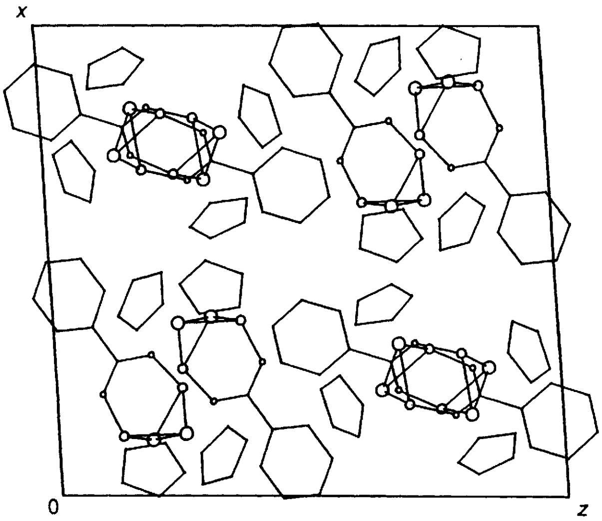


Fig. 2 Unit-cell contents of $[Ni_2(cp)_2(PhCN_2S_2)]$ **3** in projection along the *b* axis

(from 2θ values of 32 reflections in the range 20–25°, measured at $\pm\omega$), $Z = 8$, $D_c = 1.674$ g cm^{-3}, $F(000) = 1752$, $\mu = 2.46$ mm^{-1} for Mo-Kα radiation ($\lambda = 0.710\,73$ Å), $T = 295$ K.

Data collection and processing. Stoe-Siemens diffractometer, crystal size 0.15 × 0.4 × 0.4 mm, ω–θ scans with on-line profile fitting,[8] $2\theta_{max}$ 50°, index ranges *h* −19 to 19, *k* 0–14, *l* 0–20 and about half a set of equivalent reflections. No significant variation in intensity was observed for the three standard reflections. Semiempirical absorption corrections were applied; transmission factors ranged from 0.29 to 0.41. Of 10 227 measured data, 6002 were unique, and 4746 with $F > 4\sigma_c(F)$ (σ_c based on counting statistics only) were used for further analysis; $R_{int} = 0.017$.

Structure solution and refinement.[9] Atoms were located by direct methods and difference syntheses, and refined anisotropically to minimise $\Sigma w\Delta^2$ ($\Delta = |F_o| - |F_c|$), with weighting $w^{-1} = \sigma^2(F) = \sigma_c^2(F) + 12 - 112G + 468G^2 - 7H + 8H^2 - 90GH$ ($G = F_o/F_{max}$, $H = \sin\theta/\sin\theta_{max}$).[10] Hydrogen atoms were constrained to lie on ring-angle external bisectors with C–H 0.96 Å, $U(H) = 1.2\,U_{eq}(C)$. Scattering factors were taken from ref. 11. An isotropic extinction parameter *x* refined to $2.6(10) \times 10^{-7}$, whereby $F_c' = F_c/(1 + xF_c^2/\sin 2\theta)^{\frac{1}{4}}$. Final residuals: $R = 0.035$, $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}} = 0.028$, $S = 1.38$ for 416 parameters, maximum shift/estimated standard deviation = 0.031, mean 0.009, all features in a final difference map within ± 0.37 e Å^{-3}.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Table 1 Selected bond lengths (Å) and angles (°) in compound **3**

Ni(11)–Ni(12)	2.440(1)	Ni(21)–Ni(22)	2.441(1)
Ni(11)–S(11)	2.175(1)	Ni(21)–S(21)	2.171(1)
Ni(11)–S(12)	2.168(1)	Ni(21)–S(22)	2.172(1)
Ni(12)–S(11)	2.174(1)	Ni(22)–S(21)	2.169(1)
Ni(12)–S(12)	2.180(1)	Ni(22)–S(22)	2.170(1)
S(11)–N(11)	1.640(2)	S(21)–N(21)	1.634(3)
S(12)–N(12)	1.634(3)	S(22)–N(22)	1.627(3)
N(11)–C(131)	1.336(4)	N(21)–C(231)	1.325(4)
N(12)–C(131)	1.324(4)	N(22)–C(231)	1.327(4)
C(131)–C(132)	1.485(4)	C(231)–C(232)	1.488(4)
Ni(12)–Ni(11)–S(11)	55.9(1)	Ni(22)–Ni(21)–S(21)	55.7(1)
Ni(12)–Ni(11)–S(12)	56.1(1)	Ni(22)–Ni(21)–S(22)	55.7(1)
S(11)–Ni(11)–S(12)	84.5(1)	S(21)–Ni(21)–S(22)	83.4(1)
Ni(11)–Ni(12)–S(11)	55.9(1)	Ni(21)–Ni(22)–S(21)	55.8(1)
Ni(11)–Ni(12)–S(12)	55.6(1)	Ni(21)–Ni(22)–S(22)	55.8(1)
S(11)–Ni(12)–S(12)	84.2(1)	S(21)–Ni(22)–S(22)	83.5(1)
Ni(11)–S(11)–Ni(12)	68.3(1)	Ni(21)–S(21)–Ni(22)	68.5(1)
Ni(11)–S(11)–N(11)	111.8(1)	Ni(21)–S(21)–N(21)	110.9(1)
Ni(12)–S(11)–N(11)	112.1(1)	Ni(22)–S(21)–N(21)	113.4(1)
Ni(11)–S(12)–Ni(12)	68.3(1)	Ni(21)–S(22)–Ni(22)	68.4(1)
Ni(11)–S(12)–N(12)	110.2(1)	Ni(21)–S(22)–N(22)	112.1(1)
Ni(12)–S(12)–N(12)	113.0(1)	Ni(22)–S(22)–N(22)	113.0(1)
S(11)–N(11)–C(131)	124.0(2)	S(21)–N(21)–C(231)	125.2(2)
S(12)–N(12)–C(131)	125.1(2)	S(22)–N(22)–C(231)	125.0(2)
N(11)–C(131)–N(12)	129.0(3)	N(21)–C(231)–N(22)	127.7(3)
N(11)–C(131)–C(132)	115.7(2)	N(21)–C(231)–C(232)	115.7(2)
N(12)–C(131)–C(132)	115.2(2)	N(22)–C(231)–C(232)	116.6(2)

Results and Discussion

Reaction of $(PhCN_2S_2)_2$ with $[\{Ni(cp)(CO)\}_2]$ in toluene gave the dark red crystalline paramagnetic complex $[Ni_2(cp)_2(PhCN_2S_2)]$ **3**. The structure of **3** was determined by X-ray crystallography and is shown in Figs. 1 and 2. Table 1 contains selected bond lengths and angles. Atomic coordinates are given in Table 2. There are two crystallographically independent molecules and the distances used in this discussion are averages of these values, which do not differ significantly.

The Ni_2S_2 units are in the same tetrahedral array adopted by the Fe_2S_2 unit[4] in $[Fe_2(CO)_6(PhCN_2S_2)]$ **2** and are similar to the Ni_2S_2 units in $[Ni_2(cp)_2(C_{10}Cl_4S_4)]$[12] (although in this compound, population of the Ni–Ni antibonding orbital opens out the Ni_2S_2 fragment so that the Ni–S–Ni angle is 15° higher than in **3**) and $[\{Ni_2(cp)_2S_2\}_2Ni]$.[13] The most interesting structural feature of **3** is the Ni–Ni distance at 2.441(1) Å. This value is rather longer than that observed in other cyclopentadienenickel complexes, *e.g.* 2.3217(8) Å in $[\{Ni(cp)(MeNC)\}_2]$[14] and 2.345(3) Å in $[Ni_2(cp)_2(HC\equiv CH)]$[15] but is shorter than a previously reported 'short' non-bonding Ni–Ni distance, *i.e.* 2.880 Å in $[Ni_2(cp)_2(C_{10}Cl_4S_4)]$.[12] Some relevant structural parameters are given in Table 3.

Since a Ni–Ni bond does seem to be present in compound **3**, this implies that each of the nickel atoms possesses a 19-electron configuration. It should also be noted that the average Ni–Ni and Ni–S distances in **3** are shorter than the Fe–Fe and average Fe–S distances in **2** [2.441(1) and 2.172(1) *vs.* 2.553(2) and 2.225(10) Å, respectively] in spite of the higher electron count in the former.

The dithiadiazole ring structural data for compounds **1**–**3** are given in Table 4. These data reveal some other interesting structural features: the S–N bond lengths in **3** are shorter than those in **2**, while the C–N bond lengths in **2** are slightly shorter than those in **3**. Also, the S–S distance in **3** is slightly shorter than that in **2**; both values indicate little, if any, S–S bonding. The expansion in the ring angles observed in **2** and **3** has been explained previously.[4]

There are two molecules of compound **3** in the asymmetric unit. The major difference between them is in the dihedral angle between the phenyl groups and the dithiadiazole rings. These

Table 2 Atomic coordinates (× 10^4) for compound **3**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ni(11)	6 743.4(2)	2 883.6(3)	3 179.6(2)	Ni(21)	6 176.0(2)	3 441.6(3)	6 856.8(2)
Ni(12)	7 751.1(2)	4 309.4(3)	3 567.8(2)	Ni(22)	6 314.3(2)	1 658.7(3)	7 517.0(2)
S(11)	8 058.2(4)	2 740.3(6)	3 043.1(4)	S(21)	6 252.6(4)	1 857.8(7)	6 273.0(4)
S(12)	6 852.6(5)	4 449.3(6)	2 583.2(4)	S(22)	7 295.0(5)	2 873.3(7)	7 488.3(4)
C(111)	5 721(3)	1 887(4)	2 849(2)	C(211)	5 974(3)	4 983(3)	6 288(3)
C(112)	6 239(3)	1 303(3)	3 281(4)	C(212)	5 269(3)	4 317(4)	6 175(3)
C(113)	6 345(3)	1 828(6)	4 011(3)	C(213)	4 986(3)	4 114(4)	6 891(4)
C(114)	5 824(3)	2 735(5)	3 929(3)	C(214)	5 490(4)	4 615(4)	7 429(3)
C(115)	5 476(2)	2 726(4)	3 239(3)	C(215)	6 114(3)	5 166(3)	7 080(3)
C(121)	8 074(2)	5 928(3)	3 965(2)	C(221)	6 469(3)	363(3)	8 340(2)
C(122)	7 429(2)	5 486(3)	4 387(2)	C(222)	6 178(3)	1 328(4)	8 694(2)
C(123)	7 732(3)	4 526(3)	4 778(2)	C(223)	5 407(2)	1 572(3)	8 340(3)
C(124)	8 537(2)	4 380(3)	4 580(2)	C(224)	5 240(2)	807(3)	7 766(3)
C(125)	8 747(2)	5 248(3)	4 095(2)	C(225)	5 908(3)	44(3)	7 782(2)
N(11)	8 274(1)	2 888(2)	2 140(1)	N(21)	7 143(1)	1 715(2)	5 902(1)
N(12)	7 255(1)	4 254(2)	1 756(1)	N(22)	8 002(1)	2 524(2)	6 915(1)
C(131)	7 862(2)	3 558(2)	1 638(2)	C(231)	7 862(2)	2 028(2)	6 237(2)
C(132)	8 137(2)	3 547(2)	840(2)	C(232)	8 592(2)	1 821(2)	5 785(2)
C(133)	8 952(2)	3 356(4)	700(2)	C(233)	8 510(2)	1 329(3)	5 069(2)
C(134)	9 186(3)	3 376(5)	−36(3)	C(234)	9 200(2)	1 153(3)	4 639(2)
C(135)	8 623(3)	3 544(5)	−645(2)	C(235)	9 965(2)	1 448(3)	4 946(2)
C(136)	7 829(3)	3 745(4)	−518(2)	C(236)	10 048(2)	1 941(4)	5 643(3)
C(137)	7 576(2)	3 748(3)	215(2)	C(237)	9 370(2)	2 127(4)	6 076(2)

Table 3 Comparison of structural data (in Å and °)

Compound	Ni–S	Ni–Ni	S···S	Ni–S–Ni	Ref.
$[Ni_2(cp)_2(PhCN_2S_2)]$	2.172(1)	2.441(1)	2.905(2)	68.4(1)	This work
$[Ni_2(cp)_2(C_{10}Cl_4S_4)]$	2.167(4)	2.880(4)	2.955(8)	83.4(2)	12
$[\{Ni_2(cp)_2S_2\}_2Ni]$	2.18(1)	2.495(3)		70.0(1)	13

Table 4 Structural parameters (in Å and °) for some dithiadiazole systems

Compound	S–S	S–N	C–N	N–C–N	C–N–S	Ref.
$(PhCN_2S_2)_2$	2.09	1.63	1.33	121	115	16
2 $[Fe_2(CO)_6(PhCN_2S_2)]$	2.930(2)	1.705(5)	1.322(8)	127.8(5)	125.4(4)	4
3 $[Ni_2(cp)_2(PhCN_2S_2)]$	2.905(2)	1.634(3)	1.334(4)	128.4(3)	124.8(2)	This work

have values of 33.1 and 1.9°, the difference presumably being due to packing forces. There are no significant intermolecular interactions.

In an attempt to shed some light on the structure of compound **3**, especially the short Ni–Ni bond length, we have performed a series of extended-Hückel calculations.[17] We now discuss the electronic structure of **3** on the basis of these calculations and in terms of the fragment MO formalism.[18] Several theoretical investigations have dealt with the interactions of the M(cp) (M = transition metal) fragment with an attached ligand,[19] and Fig. 3 shows an interaction diagram between RCN_2S_2 to the left and $Ni_2(cp)_2$ to the right leading to compound **3**. Only significant interactions are shown, and HOMO refers to the highest *doubly* occupied MO.

The frontier orbitals of RCN_2S_2 to the left show the expected ordering with the singly occupied molecular orbital (SOMO) of p_x character and the two doubly occupied MOs of p_x and a combination of s, p_y and p_z character, respectively. These are located close in energy about 2 eV below the SOMO (they reverse in **2** largely due to longer metal–metal and sulphur–sulphur distances[4]). For the $Ni_2(cp)_2$ fragment the HOMO (mainly the antibonding d_{xy}-d_{yz} combination on the metal atoms) and the lowest unoccupied molecular orbital, LUMO (mainly the antibonding combination of p_z, d_{z^2} and $d_{x^2-y^2}$ on the metal atoms), are almost degenerate. The second HOMO is the bonding counterpart of the HOMO; the slightly lower energy MO (*i.e.* the third HOMO) is mainly of d_{z^2} character. The second LUMO is a combination of Ni s, p_x, $d_{x^2-y^2}$ and d_{z^2}. Fig. 3 also shows that the LUMO of RCN_2S_2 interacts with the second HOMO of $Ni_2(cp)_2$ and the SOMO of RCN_2S_2 interacts with the HOMO of $Ni_2(cp)_2$. The latter interaction leads to a crossing of orbitals in the middle of Fig. 3, and one of the three electrons transfers to the SOMO of **3**. The HOMO of RCN_2S_2 interacts with the LUMO of $Ni_2(cp)_2$; lower occupied orbitals of both fragments are also involved. This interaction also leads to a crossing of orbitals. The second HOMO of RCN_2S_2 interacts with both the second LUMO and the third HOMO of $Ni_2(cp)_2$.

If we now focus attention on the structural differences between $[Ni_2(cp)_2(PhCN_2S_2)]$ and $[Fe_2(CO)_6(PhCN_2S_2)]$ we see that a major difference between $Fe_2(CO)_6$ and $Ni_2(cp)_2$ is that two more electrons are located in the latter fragment. These are found in the HOMO and their interaction with the ring SOMO results in Ni–S bonding and some Ni–Ni antibonding. The interaction (mentioned above) of the second HOMO of RCN_2S_2 with the second LUMO and the third HOMO of the $Ni_2(cp)_2$ fragment leads to a population of the Ni–Ni bonding MO (see below), **I**, by 0.73e in **3**. This interaction is responsible for the short Ni–Ni distance in **3**.

The iron complex, **2**, has two fewer electrons and so the HOMO of **3** [derived in part from orbital **I** of $Ni_2(cp)_2$] becomes the SOMO of **2**. Thus, for the iron complex, the orbital similar to **I** contributes less to the bonding, so giving the longer Fe–Fe distance. The unpaired electron in **3** is located at Ni, S and C in

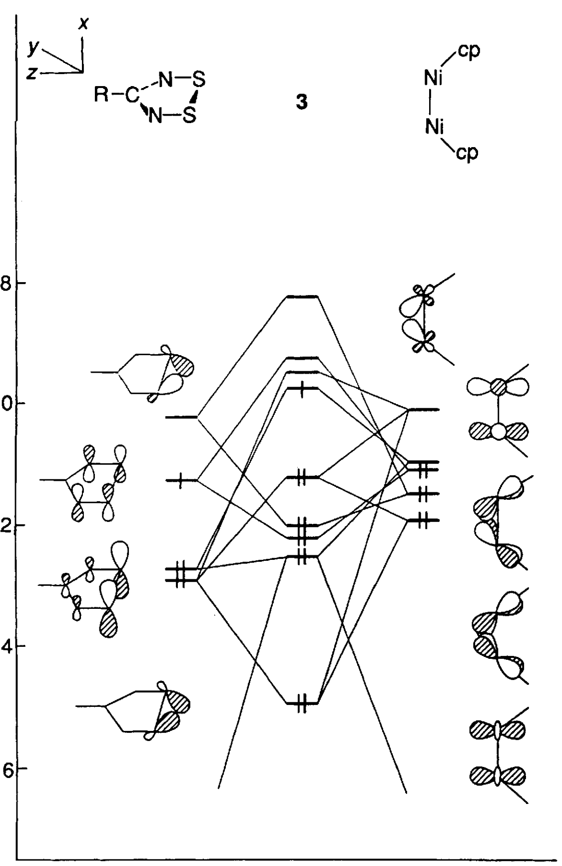
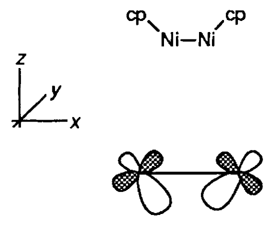


Fig. 3 Molecular-orbital diagram for $[Ni_2(cp)_2(PhCN_2S_2)]$ **3**



I

Table A1 Atomic parameters used in extended-Hückel calculations

Atom	Orbital	H_{ij}/eV	ζ_1
Ni	4s	–10.95	2.10
	4p	–6.27	2.10
	3d	–13.30	6.27*
N	2s	–26.00	1.95
	2p	–13.40	1.95
S	3s	–20.00	1.82
	3p	–13.30	1.82
C	2s	–21.40	1.63
	2p	–11.40	1.63
H	1s	–13.60	1.30

* ζ_2 5.75. Coefficients used in the double-zeta expansion of the metal d orbitals: c_1 0.5683, c_2 0.6292.

the $Ni_2S_2N_2CR$ core, with the following amplitudes: Ni, 0.51; S, 0.26; and C, 0.22.

The shortening of the S–N bond in **3** compared with the same bond in **2** can also be traced to orbital interactions. Comparison of those orbitals of $Ni_2(cp)_2$ and $Fe_2(CO)_6$ which are of appropriate symmetry for overlap with the SOMO and HOMO orbitals of RCN_2S_2 shows that the nickel orbitals are of lower energy.[20] Consequently, in the nickel complex there is greater loss of electronic charge from the SOMO and HOMO of RCN_2S_2 and since these orbitals are SN antibonding the bonds are shorter. The longer C–N bond length in **3** compared with **2** might also be accounted for by the HOMO of the RCN_2S_2 fragment, as this orbital is C–N bonding; donation of electron density from this orbital into the metal fragment leads to a weakening of this particular bond. This donation is greater for **3** compared with **2**, and the C–N bond is longer in this complex.

We have shown that 4-phenyl-1,2,3,5-dithiadiazole forms a free-radical complex $[Ni_2(cp)_2(PhCN_2S_2)]$ based on a butterfly-shaped Ni_2S_2 core. The unpaired electron is located predominantly at nickel, sulphur and carbon. The absence of significant intermolecular attractions is presumably due to steric hindrance by the cp groups and is to the detriment of possible ferromagnetic effects.

Appendix

The orbital parameters together with the H_{ij} values are given in Table A1. The bond lengths and angles used were taken from the X-ray data but the phenyl group was replaced by hydrogen.

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