DALTON

Synthesis, structure and characterization of mixed cyclopentadienyl–dithiolene metal complexes, $[Co(\eta\text{-}C_5H_5)_2][Ni(C_3S_5)_2]_3{\cdot}2MeCN$ and $[Ni(\eta\text{-}C_5H_5)(C_3S_5)]$†

Christophe Faulmann,* Fabien Delpech, Isabelle Malfant and Patrick Cassoux

Equipe Précurseurs Moléculaires et Matériaux, LCC/CNRS, 205 Route de Narbonne,
31077 Toulouse Cédex, France

Two new compounds $[Co(\eta\text{-}C_5H_5)_2][Ni(C_3S_5)_2]_3{\cdot}2MeCN$ and $[Ni(\eta\text{-}C_5H_5)(C_3S_5)]$, both obtained by combination of the nickel complex anion $[Ni(C_3S_5)_2]^-$ (C_3S_5 = 4,5-disulfanyl-1,3-dithiole-2-thionate) and the metallocenium cation $[M(\eta\text{-}C_5H_5)_2]^+$ (M = Co or Ni), respectively, have been prepared and characterized crystallographically. The non-integral oxidation-state cobalt complex with the unusual 1 : 3 stoichiometry was obtained by electrochemical oxidation of $[NBu_4][Ni(C_3S_5)_2]$ in the presence of $[Co(\eta\text{-}C_5H_5)_2]PF_6$. It is semiconductive ($\sigma$ = 0.06 S cm^{-1} at room temperature, E_a = 0.18 eV between 300 and 250 K). The crystal structure shows that the asymmetric unit contains one $Ni(C_3S_5)_2$ unit, one $Ni(C_3S_5)$ entity, one Co $(\eta\text{-}C_5H_5)$ unit and one molecule of acetonitrile. The $Ni(C_3S_5)_2$ units are associated in triads stacked along the [101] direction. No significant differences are observed in the distances and angles within the two symmetry-unrelated $Ni(C_3S_5)_2$ units, indicating that the charges of both units are very similar. The cyclopentadienyl rings are staggered due to the location of the Co atoms on inversion centres. The average Co–C distance is comparable to those found in several cobaltocenium salts. The compound $[Ni(\eta\text{-}C_5H_5)(C_3S_5)]$ was obtained unexpectedly from the reaction of $[Ni(\eta\text{-}C_5H_5)_2]BF_4$ with $Na[Ni(C_3S_5)_2]$ and characterized by mass spectrometry, conductimetry and X-ray analysis. The crystal structure shows that the asymmetric unit consists of one $[Ni(\eta\text{-}C_5H_5)(C_3S_5)]$ entity. The C_5H_5 ring is disordered over two positions. The $Ni(C_3S_5)$ unit is planar and almost perpendicular to the C_5H_5 rings.

Since the discovery of superconductivity in $[ttf][Ni(C_3S_5)_2]_2$ [ttf = 2-(1,3-dithiol-2-ylidene)-1,3-dithiole(tetrathiafulvalene), C_3S_5 = 4,5-disulfanyl-1,3-dithiole-2-thionate][1] and related systems[2,3] a great deal of work has been devoted to the study of compounds derived from $M(C_3S_5)_2$ complexes. The principal aim of this work has been to extend the range of molecular conductors and superconductors based on transition-metal complexes in order more fully to understand the mechanism of conductivity and superconductivity in these systems. In the conducting non-integral oxidation-state (NIOS) compounds derived from $M(C_3S_5)_2$ complexes the counter cation may be a closed-shell cation (such as NMe_4)[4] or an open-shell radical cation such as ttf.[1] In the compounds with closed-shell cations only the $M(C_3S_5)_2$ entities are responsible for conduction. Their non-integral charge, x, may be directly inferred from the $[cation]_x[M(C_3S_5)_2]$ stoichiometry. By contrast, in the compounds with open-shell radical cations both the cation donor chain and the acceptor chain $[M(C_3S_5)_2]$ may contribute to the conduction process.[5–9] Partial charge transfer between the donor and acceptor in combination with the stoichiometry determines their non-integral charges.[10,11]

In addition to the above work, metallocenes have been extensively studied with the particular aim of preparing ferromagnetically ordered molecule-based charge-transfer salts.[12–15] In some of these salts the decamethylferrocenium cation, $[Fe(\eta\text{-}C_5Me_5)_2]^+$, has been combined with metal complex anions of 1,2-dithiolate ligands. Typical examples are $[Fe(\eta\text{-}C_5Me_5)_2][M\{S_2C_2(CN)_2\}_2]$ (M = Ni or Pt) and $[Fe(\eta\text{-}C_5Me_5)_2][Ni\{S_2C_2(CF_3)_2\}_2]$,[16] $[Fe(\eta\text{-}C_5Me_5)_2][NiL_2]$ with L = $C_3S_5^{2-}$ or benzene-1,2-diselenolate,[17] and $[Fe(\eta\text{-}C_5Me_5)_2][M(C_3S_5)_2]$ (M = Au or Fe).[18,19] Recently, the synthesis of salts combining $[Fe(\eta\text{-}C_5Me_5)_2]^+$ and $[M\{S_2C_2(CN)_2\}_2]$ anions (M = Cu, Co or Fe) has been reported.[20] The cobaltocenium cation has been also used in the preparation of $[Co(\eta\text{-}C_5H_5)_2]_n[M(C_3S_5)_2]$ salts (M = Ni or Pd, n = 2 or 1).[21]

The preparation of molecular conductors exhibiting interactions between conduction electrons and localized magnetic moments is of interest as it could allow the observation of previously unknown conductivity mechanisms. Several systems have been studied along this line, including CuL_2 (L = 2-X,5-Y-substituted *N,N′*-dicyano-*p*-benzoquinone diimine; X, Y = Me, Cl or Br),[22] $[C_{20}H_{12}]_2[M\{S_2C_2(CN)_2\}_2]$ ($C_{20}H_{12}$ = perylene)[23] and $[ttf][M\{X_2C_2(CF_3)_2\}_2]$ (M = Cu or Au; X = S or Se).[24] Several bettf-based conductors [bettf = bis(ethylenedithio)tetrathiafulvalene] incorporating magnetic anions have been reported,[25] and recently the first molecular superconductor in this series, β''-$[bettf]_4[Fe(C_2O_4)_3(H_2O)]{\cdot}PhCN$ (T_c = 8.5 K) has been characterized.[26] Interaction between conduction electrons and localized magnetic moments has been evidenced in the λ-$[betsf]_2[FeCl_4]$ compound [betsf = bis(ethylenedithio)tetraselenafulvalene].[27]

A logical step is therefore to use metallocenium cations in combination with complexes of 1,2-dithiolate ligands, and especially of $C_3S_5^{2-}$. However, high, and possibly metal-like, conductivity can only be achieved provided that there is a non-integral oxidation state in the $M(C_3S_5)_2$ chain.[3] To our knowledge, very few NIOS compounds involving a metallocenium cation, $[Fe(\eta\text{-}C_5Me_5)_2]^+$ or $[Fe(\eta\text{-}C_5H_5)_2]^+$, and a metal complex anion (M = Au or Fe) of 1,2-dithiolate ligands [$C_3S_5^{2-}$ or $C_3Se_5^{2-}$ (4,5-diselanyl-1,3-diselenole-2-selenonate)] have been reported and even these have not been fully characterized.[18,19,28] We report in this work the preparation and full characterization by crystal structure determination of $[Co(\eta\text{-}C_5H_5)_2][Ni(C_3S_5)_2]_3{\cdot}2MeCN$, *i.e.*, a NIOS $M(C_3S_5)_2$ complex involving a metallocenium counter cation.

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

The combination of metallocenes and sulfur-based ligands in one single metal complex molecular unit has been previously reported.[29-33] The most recent studies have centred on such mixed-ligand complexes with the hope of preparing materials with novel electrical conduction, optical and magnetic properties.[34-36] Also contained in this report are the preparation and crystal structure of a new member of this series, $[\mathrm{Ni}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{C_3S_5})]$, which was unexpectedly obtained while attempting to prepare $[\mathrm{Ni}(\eta\text{-}\mathrm{C_5H_5})_2][\mathrm{Ni}(\mathrm{C_3S_5})_2]$.

Experimental

Syntheses

The compounds $[\mathrm{Co}(\eta\text{-}\mathrm{C_5H_5})_2]\mathrm{PF_6}$ and $[\mathrm{Ni}(\eta\text{-}\mathrm{C_5H_5})_2]$ (Aldrich) were used as received. 4,5-Bis(benzoylsulfanyl)-1,3-dithiole-2-thione and $[\mathrm{NBu_4}][\mathrm{Ni}(\mathrm{C_3S_5})_2]$,[37] $\mathrm{Na}[\mathrm{Ni}(\mathrm{C_3S_5})_2]$[38] and $[\mathrm{Co}(\eta\text{-}\mathrm{C_5H_5})_2]_n[\mathrm{Ni}(\mathrm{C_3S_5})_2]$ (n = 2 or 1)[21] were prepared according to the literature; $[\mathrm{Co}(\eta\text{-}\mathrm{C_5H_5})_2][\mathrm{Ni}(\mathrm{C_3S_5})_2]$ was also prepared by $\mathrm{I_2}$–NaI oxidation of $[\mathrm{Co}(\eta\text{-}\mathrm{C_5H_5})_2]_2[\mathrm{Ni}(\mathrm{C_3S_5})_2]$ following standard procedures.[37]

$[\mathrm{Co}(\eta\text{-}\mathrm{C_5H_5})_2][\mathrm{Ni}(\mathrm{C_3S_5})_2]_3\cdot 2\mathrm{MeCN}$. This compound is best obtained by electrocrystallization in an H-tube cell following a method similar to that ('largexcess' method) previously described for several closed-shell $[\mathrm{cation}]_x[\mathrm{M}(\mathrm{C_3S_5})_2]$ NIOS complexes.[39] In order to avoid precipitation of $[\mathrm{Co}(\eta\text{-}\mathrm{C_5H_5})_2][\mathrm{Ni}(\mathrm{C_3S_5})_2]$ when mixing solutions of $[\mathrm{NBu_4}][\mathrm{Ni}(\mathrm{C_3S_5})_2]$ and $[\mathrm{Co}(\eta\text{-}\mathrm{C_5H_5})_2]\mathrm{PF_6}$ the cathodic and anodic compartments of the cell were filled separately with acetonitrile solutions of $[\mathrm{NBu_4}][\mathrm{Ni}(\mathrm{C_3S_5})_2]$ (7.8×10^{-4} or 13.4×10^{-4} mol dm^{-3}) and $[\mathrm{Co}(\eta\text{-}\mathrm{C_5H_5})_2]\mathrm{PF_6}$ (2×10^{-2} or 7×10^{-3} mol dm^{-3}), respectively. Galvanostatic (1 or 0.1 μA) electrochemical oxidation for 2–3 weeks at 20 or 50 °C at a platinum anode yielded thin needle-like crystals of $[\mathrm{Co}(\eta\text{-}\mathrm{C_5H_5})_2][\mathrm{Ni}(\mathrm{C_3S_5})_2]_3\cdot 2\mathrm{MeCN}$ the stoichiometry of which was determined by X-ray crystallography. This compound can also be obtained by direct electrochemical oxidation of $[\mathrm{Co}(\eta\text{-}\mathrm{C_5H_5})_2][\mathrm{Ni}(\mathrm{C_3S_5})_2]$, but the crystals obtained were of inferior quality.

$[\mathrm{Ni}(\eta\text{-}\mathrm{C_5H_5})_2]\mathrm{BF_4}$. This salt was prepared following a procedure adapted from that used for the synthesis of $[\mathrm{Fe}(\eta\text{-}\mathrm{C_5Me_5})_2]\mathrm{BF_4}$.[40] 1,4-Benzoquinone (86.0 mg, 0.80 mmol) was dissolved in diethyl ether (50 cm^3) containing $\mathrm{HBF_4}$ (0.45 cm^3, 3.18 mmol). To the resulting yellow solution was added a diethyl ether solution (200 cm^3) of $[\mathrm{Ni}(\eta\text{-}\mathrm{C_5H_5})_2]$ (0.30 g, 1.60 mmol). A brown-green precipitate immediately formed, which was filtered off, washed with diethyl ether and recrystallized from acetone–ether (1 : 2). The yield was ≈80%. The stability of this salt in the solid state seems to be very limited, as indicated by elemental analyses (Found: C, 41.25; H, 4.40. $\mathrm{C_{10}H_{10}BF_4Ni}$ requires C, 43.55; H, 3.65%); even when stored under a nitrogen atmosphere the compound rapidly becomes pale yellow. It can be also generated in acetone or acetonitrile by constant-potential electrolysis (+0.30 V *vs.* saturated calomel electrode, SCE) but these solutions were even more unstable than the solid-state samples and had to be used immediately.

$[\mathrm{Ni}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{C_3S_5})]$. This compound was unexpectedly obtained during the tentative synthesis of $[\mathrm{Ni}(\eta\text{-}\mathrm{C_5H_5})_2][\mathrm{Ni}(\mathrm{C_3S_5})_2]$ (see Results and Discussion section). To a suspension of 4,5-bis(benzoylsulfanyl)-1,3-dithiole-2-thione (1.0 g, 2.48 mmol) was added a methanolic solution (3 cm^3) of sodium (0.17 g, 7.45 mmol). The mixture turned dark red-purple and was stirred until complete disappearance of the thione. The solution was slowly poured into diethyl ether to precipitate the $\mathrm{Na_2(C_3S_5)}$ salt, which was filtered off and washed with diethyl ether (yield: 96%; 0.593 g). This salt was dissolved in acetone yielding a dark purple solution, to which was added dropwise $\mathrm{NiCl_2\cdot 6H_2O}$ (0.31 g, 1.30 mmol) dissolved in methanol (60 cm^3). To the resultant solution of the $\mathrm{Na_2}[\mathrm{Ni}(\mathrm{C_3S_5})_2]$ salt was added a solution of $\mathrm{I_2}$ (0.15 g, 0.59 mmol) and NaI (0.27 g, 1.80 mmol) in acetone (10 cm^3). To this solution of the $\mathrm{Na}[\mathrm{Ni}(\mathrm{C_3S_5})_2]$ salt was added dropwise an equimolar amount of $[\mathrm{Ni}(\eta\text{-}\mathrm{C_5H_5})_2]\mathrm{BF_4}$ dissolved in methanol. Shiny black crystals precipitated, which were filtered off, washed with methanol and dried *in vacuo* (yield ≈ 28%). The elemental analyses were compatible with the formulae $[\mathrm{Ni}(\eta\text{-}\mathrm{C_5H_5})_2][\mathrm{Ni}(\mathrm{C_3S_5})_2]$ and $[\mathrm{Ni}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{C_3S_5})]$ (Found: C, 28.85; H, 1.55. $\mathrm{C_{16}H_{10}Ni_2S_{10}}$ or $\mathrm{C_8H_5NiS_5}$ requires C, 30.00; H, 1.55%). The product was characterized as the latter by mass spectrometry (Found: m/z 321. $\mathrm{C_8H_5NiS_5}$ requires 321), conductimetry measurements in acetone and nitrobenzene {the compound is non-conducting in solution, contrary to what would be expected for $[\mathrm{Ni}(\eta\text{-}\mathrm{C_5H_5})_2][\mathrm{Ni}(\mathrm{C_3S_5})_2]$, and X-ray analysis.

Mixture of $[\mathrm{M}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{C_3S_5})]$ (M = Ni or Co). To a solution of $\mathrm{Na}[\mathrm{Ni}(\mathrm{C_3S_5})_2]$ obtained as described above was added dropwise an equimolar amount of $[\mathrm{Co}(\eta\text{-}\mathrm{C_5H_5})_2]\mathrm{PF_6}$ (0.38 g, 1.14 mmol) dissolved in methanol (50 cm^3). A microcrystalline powder precipitated which was filtered off, washed with methanol and dried *in vacuo* (yield ≈ 48%). The elemental analyses indicated either $[\mathrm{Co}(\eta\text{-}\mathrm{C_5H_5})_2][\mathrm{Ni}(\mathrm{C_3S_5})_2]$ or a mixture of $[\mathrm{M}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{C_3S_5})]$ (M = Ni or Co) [Found: C, 28.30; H, 1.60. $\mathrm{C_{16}H_{10}CoNiS_{10}}$ or $\mathrm{C_8H_5NiS_5}$–$\mathrm{C_8H_5CoS_5}$ (1 : 1) requires C, 30.00; H, 1.60%). Conductimetry measurements in acetone and nitrobenzene confirmed the mixture.

Crystallography

Crystal data. $[\mathrm{Co}(\eta\text{-}\mathrm{C_5H_5})_2][\mathrm{Ni}(\mathrm{C_3S_5})_2]_3\cdot 2\mathrm{MeCN}$, $\mathrm{C_{32}H_{16}CoN_2Ni_3S_{30}}$, M = 1625.3, triclinic, space group $P\bar{1}$, a = 8.913(7), b = 21.370(13), c = 7.413(2) Å, α = 99.19(4), β = 91.06(6), γ = 101.40(6)°, U = 1363(2) Å^3 (by least-squares refinement on diffractometer angles for 19 automatically centred reflections, λ = 0.710 69 Å), Z = 1, D_c = 1.98 g cm^{-3}, $F(000)$ = 813, long flat black needle-like crystal, dimensions 1.25 × 0.10 × 0.03 mm, μ(Mo-Kα) = 24.6 cm^{-1}.

$[\mathrm{Ni}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{C_3S_5})]$, $\mathrm{C_8H_5NiS_5}$, M = 320.13, monoclinic, space group $P2_1$, a = 11.710(2), b = 7.922(2), c = 5.912(2) Å, β = 97.86(2)°, U = 543.3(2) Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, λ = 0.710 69 Å), Z = 2, D_c = 1.96 g cm^{-3}, $F(000)$ = 322, shiny black flat diamond-shaped crystal, dimensions 0.30 × 0.30 × 0.03 mm, μ(Mo-Kα) = 26.7 cm^{-1}.

Data collection and processing. In both cases, the intensity of three reflections was monitored throughout the data collection and no significant decay was observed. For $[\mathrm{Co}(\eta\text{-}\mathrm{C_5H_5})_2][\mathrm{Ni}(\mathrm{C_3S_5})_2]_3\cdot 2\mathrm{MeCN}$, CAD4 diffractometer was used with ω–2θ mode, ω-scan width = 0.80 + 0.35 tan θ, variable ω-scan speed, graphite-monochromated Mo-Kα radiation; 4167 reflections measured ($1.0 \leqslant \theta \leqslant 25°$, $\pm h$, $\pm k$, $+l$), giving 1292 independent with $I \geqslant 3\sigma(I)$. Absorption correction: DIFABS[41] (maximum, minimum correction factors = 1.06, 0.62). For $[\mathrm{Ni}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{C_3S_5})]$ the same procedure gave 1688 reflections ($1 \leqslant \theta \leqslant 30°$, $+h$, $+k$, $\pm l$), of which 993 were independent. An empirical absorption correction based on ψ scans[42] was applied (maximum, minimum correction coefficients = 2.24, 1.00).

Structure analysis and refinement. Direct methods followed by normal heavy-atom procedures. Full-matrix least-squares refinement with the Ni, Co and S atoms anisotropic and C and N atoms isotropic for $[\mathrm{Co}(\eta\text{-}\mathrm{C_5H_5})_2][\mathrm{Ni}(\mathrm{C_3S_5})_2]_3\cdot 2\mathrm{MeCN}$, and all atoms of the $\mathrm{Ni}(\mathrm{C_3S_5})$ unit anisotropic and the C atoms of the $\mathrm{C_5H_5}$ ring isotropic for $[\mathrm{Ni}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{C_3S_5})]$, the $\mathrm{C_5H_5}$ ring of latter was disordered. Attempts to locate hydrogen atoms were unsuccessful in both compounds. No hydrogen atoms were included in the calculations. Final R and R' =

0.047 and 0.047 for $[Co(\eta\text{-}C_5H_5)_2][Ni(C_3S_5)_2]_3\cdot 2MeCN$ (unit weight), and 0.042 and 0.047 for $[Ni(\eta\text{-}C_5H_5)(C_3S_5)]$ [$w = w'\{1 - [\Delta F/6\sigma(F)]^2\}^2$; $w' = 1/[3.74T_0(x) + 1.49T_1(x) + 2.40T_2(x) + 0.755T_3(x)$ where $T_i(x)$ are Chebyshev polynomials and $x = F_c/F_c(\text{max.})$[43]]. The maximum shift/e.s.d. in the final refinements were 0.17 and 0.48 respectively, the maximum and minimum residual densities in the final Fourier-difference maps 0.76, −0.66 and 0.93, −0.35 e Å^{-3}. All calculations were performed on a personal computer. Programs used and sources of scattering factor data are given in ref. 43.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/22.

Conductivity

Temperature-dependent (300–4 K) single-crystal conductivity measurements were carried out following the standard four-probe technique. Electrical contacts were obtained by glueing four gold wires to the crystal with Emetron M8001 gold paint. The sample mounted on a MOTOROLA printed circuit was placed in an Oxford Instruments, model CF 200, continuous-flow cryostat. Temperature control and temperature-resistance data acquisition were achieved using an Oxford Instruments, model DTC2, PID temperature controller, and a Hewlett-Packard, Model 4263A, LCR Meter, respectively, both driven by a personal computer running in-house software.

Conductimetry

Conductimetry measurements were performed in acetone and nitrobenzene solutions (10^{-4} mol dm^{-3}).

ESR spectroscopy

The ESR measurements were performed on a Brucker ESP300 spectrometer at room temperature and at 100 K on microcrystalline powders.

Results and Discussion

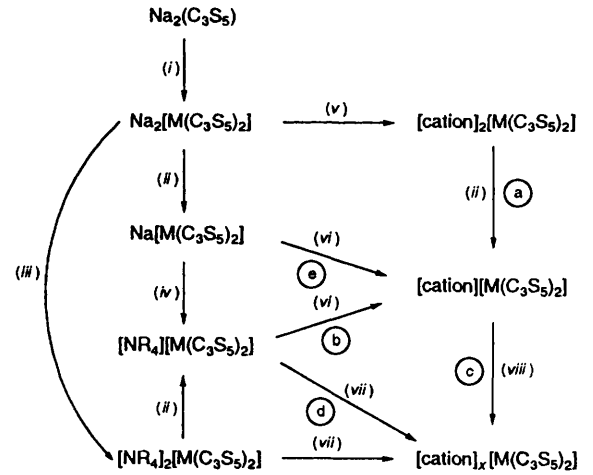
$[Co(\eta\text{-}C_5H_5)_2][Ni(C_3S_5)_2]_3\cdot 2MeCN$

There are several routes available for preparing $[\text{cation}]_x[M(C_3S_5)_2]$ NIOS compounds (Scheme 1) and the choice of the most convenient depends on the nature of the metal M and the cation. With closed-shell cations and M = Ni the most used route is a + c in which the $[\text{cation}]_2[Ni(C_3S_5)_2]$ and $[\text{cation}][Ni(C_3S_5)_2]$ salts are prepared successively, followed by electrolysis of a solution of the 1 : 1 salt.[1-4] The synthesis of the salt $[Co(\eta\text{-}C_5H_5)_2][Ni(C_3S_5)_2]$ may be achieved either (*i*) by chemical oxidation of the 2 : 1 salt (Scheme 1, route a or (*ii*) by cation exchange (route b).[21] The synthesis of the NIOS complex $[Co(\eta\text{-}C_5H_5)_2][Ni(C_3S_5)_2]_3\cdot 2MeCN$ may be achieved by electrochemical oxidation of $[Co(\eta\text{-}C_5H_5)_2][Ni(C_3S_5)_2]$ (route c), although crystals of better quality have been obtained by electrochemical oxidation of $[NBu_4][Ni(C_3S_5)_2]$ in the presence of $[Co(\eta\text{-}C_5H_5)_2]PF_6$ (route d) (see Experimental section).

The asymmetric unit of $[Co(\eta\text{-}C_5H_5)_2][Ni(C_3S_5)_2]_3\cdot 2MeCN$ contains one $Ni(C_3S_5)_2$ unit, one $Ni(C_3S_5)$ entity, one $Co(\eta\text{-}C_3S_5)$ unit and one molecule of acetonitrile (Fig. 1, Table 1). The two nickel atoms are crystallographically independent. The Ni(1) and the Co atoms are located on inversion centres. Consequently, the cyclopentadienyl rings are staggered. The observed 1 : 3 stoichiometry is rather unusual for a $[Ni(C_3S_5)_2]$-based NIOS compound; only two complexes with such a stoichiometry have been reported, namely $[PPh_4][Ni(C_3S_5)_2]_3$[44] and $[\text{tsf}][Ni(C_3S_5)_2]_3$ (tsf = tetraselenafulvalene).[45] The average Co–C distance is 2.01(1) Å, comparable to those (2.03–2.08 Å) found in several cobaltocenium salts,[31,46] and to 2.037(16) Å in $[Co(\eta\text{-}C_5H_5)_2][Ni(C_3S_5)_2]$[21b] but much shorter than 2.096(8) Å in neutral cobaltocene.[47] No significant differences are observed in the distances and angles within the two symmetry-unrelated $Ni(C_3S_5)_2$ units, indicating that the charges of both units are identical or very similar. Both these $Ni(C_3S_5)_2$ units are planar [largest deviation 0.041 Å for the Ni(1) unit and 0.055 Å for the Ni(2) unit]. Within the estimated standard deviations (e.s.d.s) the distances and angles in the $Ni(C_3S_5)_2$ units are comparable to those found in $[PPh_4][Ni(C_3S_5)_2]_3$[44] and $[\text{tsf}][Ni(C_3S_5)_2]_3$.[45]

As in $[\text{tsf}][Ni(C_3S_5)_2]_3$, the $Ni(C_3S_5)_2$ units in $[Co(\eta\text{-}C_5H_5)_2][Ni(C_3S_5)_2]_3\cdot 2MeCN$ are associated in triads stacked along the [101] direction (Fig. 2). The interplanar distances within a triad and between triads are almost identical, 3.56 {compared to 3.54 Å in $[\text{tsf}][Ni(C_3S_5)_2]_3$[45]} and 3.55 Å {compared to 3.63 Å in $[\text{tsf}][Ni(C_3S_5)_2]_3$[45]}, respectively. Within a triad the $Ni(C_3S_5)_2$ units are not face-to-face but transversely shifted (Fig. 3). Between two triads the units are also shifted, transversely and longitudinally. Intra- and inter-stack S ··· S contacts shorter than the van der Waals separation of 3.70 Å[48] are observed between the units (Fig. 4 and Table 2), such that a two-dimensional array of closely spaced units is formed. These $Ni(C_3S_5)_2$-containing layers are separated by sheets of cations and solvent molecules lying on both sides of the longitudinal axis of the $Ni(C_3S_5)_2$ units.

The crystal used for the X-ray analysis was used for the conductivity measurements. Results were verified by use of other crystals. The room-temperature conductivity of $[Co(\eta\text{-}C_5H_5)_2][Ni(C_3S_5)_2]_3\cdot 2MeCN$ is 0.06 S cm^{-1} and this compound behaves like a semiconductor (E_a = 0.18 eV) between 300 and 250 K. The ESR spectra obtained on



Scheme 1 (*i*) M^{2+}; (*ii*) chemical oxidation; (*iii*) 2 NR_4^+; (*iv*) NR_4^+ (*v*) 2[cation]$^+$; (*vi*) [cation]$^+$; (*vii*) [cation]$^+$ (excess), electrochemical oxidation; (*viii*) chemical or electrochemical oxidation

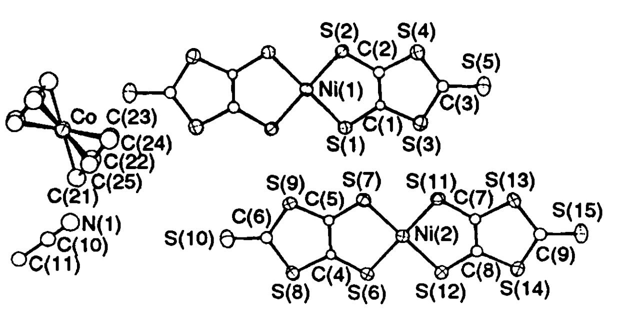


Fig. 1 Atomic numbering scheme for $[Co(\eta\text{-}C_5H_5)_2][Ni(C_3S_5)_2]_3\cdot 2MeCN$

Table 1 Selected bond lengths (Å) and angles (°) for $[Co(\eta\text{-}C_5H_5)_2][Ni(C_3S_5)_2]_3\cdot 2MeCN$

Ni(1)–S(1)	2.174(6)	Ni(1)–S(2)	2.168(6)	Ni(2)–S(6)	2.150(6)
Ni(2)–S(7)	2.160(6)	Ni(2)–S(11)	2.153(7)	Ni(2)–S(12)	2.169(6)
Co–C(21)	2.00(3)	Co–C(22)	2.02(3)	Co–C(23)	1.99(3)
Co–C(24)	2.02(3)	Co–C(25)	2.03(3)	S(1)–C(1)	1.70(2)
S(2)–C(2)	1.74(2)	S(3)–C(1)	1.74(2)	S(3)–C(3)	1.76(2)
S(4)–C(2)	1.74(2)	S(4)–C(3)	1.73(2)	S(5)–C(3)	1.62(2)
S(6)–C(4)	1.64(2)	S(7)–C(5)	1.66(2)	S(8)–C(4)	1.73(2)
S(8)–C(6)	1.81(2)	S(9)–C(5)	1.72(2)	S(9)–C(6)	1.73(2)
S(10)–C(6)	1.58(2)	S(11)–C(7)	1.69(2)	S(12)–C(8)	1.69(2)
S(13)–C(7)	1.75(2)	S(13)–C(9)	1.76(2)	S(14)–C(8)	1.77(2)
S(14)–C(9)	1.75(2)	S(15)–C(9)	1.62(2)	C(1)–C(2)	1.35(2)
C(4)–C(5)	1.45(2)	C(7)–C(8)	1.37(2)		

S(1)–Ni(1)–S(2)	93.6(2)	S(6)–Ni(2)–S(7)	92.7(3)
S(11)–Ni(2)–S(12)	93.3(2)	Ni(1)–S(1)–C(1)	102.0(7)
Ni(1)–S(2)–C(2)	100.8(8)	C(1)–S(3)–C(3)	96.8(10)
C(2)–S(4)–C(3)	96.8(11)	Ni(2)–S(6)–C(4)	103.6(7)
Ni(2)–S(7)–C(5)	103.1(7)	C(4)–S(8)–C(6)	98.2(9)
C(5)–S(9)–C(6)	99.0(10)	Ni(2)–S(11)–C(7)	101.7(7)
Ni(2)–S(12)–C(8)	101.7(7)	C(7)–S(13)–C(9)	97.4(10)
C(8)–S(14)–C(9)	96.7(10)	S(1)–C(1)–C(2)	121.8(16)
S(3)–C(1)–C(2)	115.8(17)	S(2)–C(2)–C(1)	121.7(17)
S(4)–C(2)–C(1)	117.5(17)	S(3)–C(3)–S(4)	113.1(14)
S(3)–C(3)–S(5)	121.5(13)	S(4)–C(3)–S(5)	125.4(15)
S(6)–C(4)–C(5)	120.8(15)	S(8)–C(4)–C(5)	114.1(14)
S(7)–C(5)–C(4)	119.8(15)	S(9)–C(5)–C(4)	116.7(15)
S(8)–C(6)–S(9)	111.9(11)	S(8)–C(6)–S(10)	122.5(13)
S(9)–C(6)–S(10)	125.5(13)	S(11)–C(7)–C(8)	121.8(17)
S(13)–C(7)–C(8)	116.2(16)	S(12)–C(8)–C(7)	121.5(17)
S(14)–C(8)–C(7)	116.5(17)	S(13)–C(9)–S(14)	113.2(13)
S(13)–C(9)–S(15)	123.8(14)	S(14)–C(9)–S(15)	122.9(13)

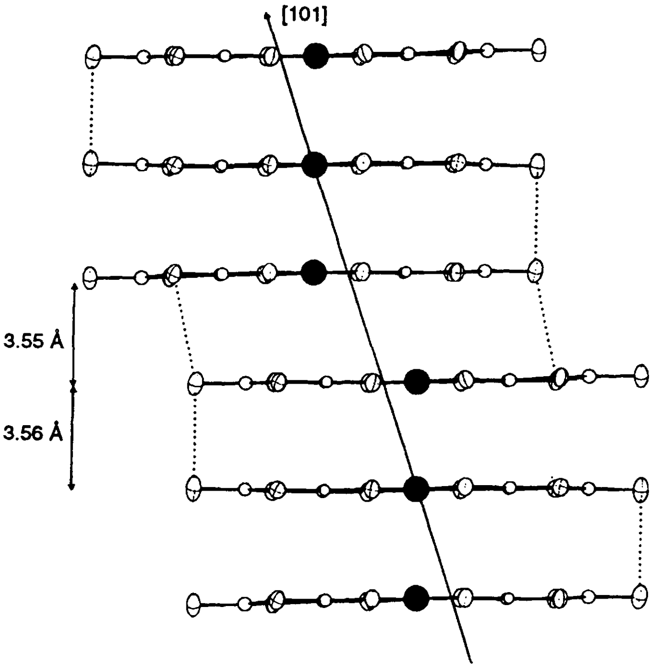


Fig. 2 Stacks of $Ni(C_3S_5)_2$ triads along the [101] direction in $[Co(\eta\text{-}C_5H_5)_2][Ni(C_3S_5)_2]_3\cdot 2MeCN$

microcrystalline powder samples exhibit a weak and broad signal at $g = 2.048$.[49]

It is interesting that, unlike the closed-shell 'spectator' cations such as $[NMe_4]^+$, the metallocenes can undergo various oxidation (as in the case of ttf) or reduction processes, and can exist as neutral, positively and negatively charged units.[50] In several cases a simple cation-exchange reaction between a $[M(\eta\text{-}C_5Me_5)_2]^+$ salt and a $[M(C_3S_5)_2]^-$ salt (route b or e in Scheme 1) leads to the expected $[M(\eta\text{-}C_5Me_5)_2][M(C_3S_5)_2]$ compound, for example M = Ni,[17] Au[18] or Fe.[19] However, the NIOS compound $[Fe(\eta\text{-}C_5Me_5)_2]_{0.7}[Fe(C_3Se_5)_2]$[19] was obtained by a similar reaction between $[Fe(\eta\text{-}C_5Me_5)_2]BF_4$ and $[NBu_4][Fe(C_3Se_5)_2]$. This would be reminiscent of the methathesis reaction between $[ttf]_3[BF_4]_2$ and $[NBu_4][Ni(C_3S_5)_2]$ in the preparation of $[ttf][Ni(C_3S_5)_2]_2$,[51] in which the ttf molecule bears a partial charge of 0.75.[10] In the present case such a partial oxidation reaction does not seem to take place when treating a $[Co(\eta\text{-}C_5H_5)_2]^+$ salt with a

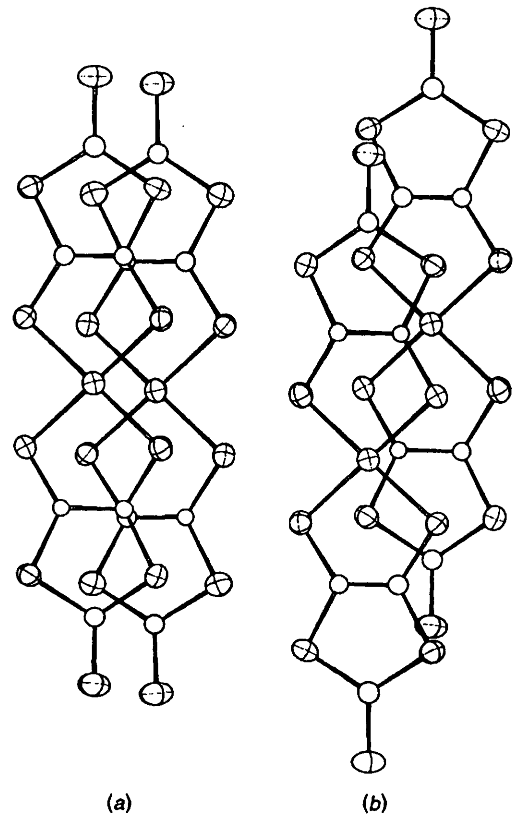

(*a*) (*b*)

Fig. 3 Molecular overlap of the $Ni(C_3S_5)_2$ units in $[Co(\eta\text{-}C_5H_5)_2][Ni(C_3S_5)_2]_3\cdot 2MeCN$: (*a*) intra-triad; (*b*) inter-triad

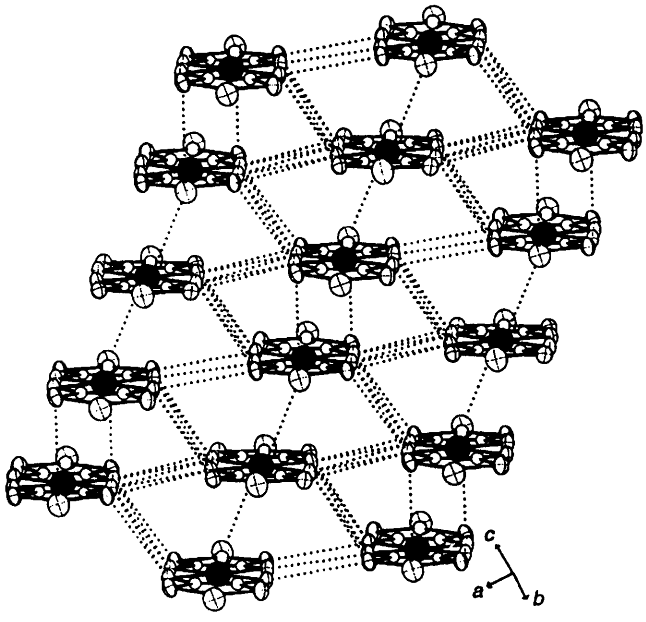


Fig. 4 Layers of $Ni(C_3S_5)_2$ units in $[Co(\eta\text{-}C_5H_5)_2][Ni(C_3S_5)_2]_3\cdot 2MeCN$. Dotted lines indicate S · · · S contacts shorter than 3.70 Å

Table 2 Intermolecular S · · · S distances (Å) for $[Co(\eta\text{-}C_5H_5)_2][Ni(C_3S_5)_2]_3\cdot 2MeCN$

S(1) · · · S(6)	3.641(8)	S(1) · · · S(7)	3.647(7)
S(1) · · · S(8^{I})	3.647(8)	S(1) · · · S(11^{IV})	3.665(9)
S(2) · · · S(6^{II})	3.571(6)	S(2) · · · S(7^{III})	3.680(8)
S(2) · · · S(9^{III})	3.641(9)	S(2) · · · S(12^{II})	3.632(8)
S(3) · · · S(11^{IV})	3.664(9)	S(4) · · · S(12^{II})	3.685(8)
S(5) · · · S(10^{V})	3.68(1)	S(6) · · · S(6^{I})	3.54(1)
S(6) · · · S(12^{I})	3.699(9)	S(7) · · · S(7^{III})	3.52(1)
S(8) · · · S(12^{I})	3.602(8)	S(9) · · · S(11^{III})	3.622(7)
S(10) · · · S(14^{VI})	3.60(1)		

Symmetry operations: I $-x, -y, -z$; II $1 + x, 1 + y, 1 + z$; III $1 - x, -y, 1 - z$; IV $x, y, 1 - z$; V $1 - x, 1 + y, 1 + z$; VI $-x, -y, 1 - z$.

$[Ni(C_3S_5)_2]^-$ salt.[21] Likewise, electrochemical oxidation of solutions of neutral $[Fe(\eta\text{-}C_5H_5)_2]$ and $[NBu_4][Au(C_3S_5)_2]$ was reported to lead to the NIOS compound $[Fe(\eta\text{-}C_5H_5)_2]_{0.33}[Au(C_3S_5)_2]$.[18] This again would be reminiscent of the preparation of $[ttf][Ni(C_3S_5)_2]_2$ by electrochemical oxidation of solutions of neutral ttf and $[NBu_4][Ni(C_3S_5)_2]$.[51] From the crystal-structure determination of $[Co(\eta\text{-}C_5H_5)_2][Ni(C_3S_5)_2]_3\cdot 2MeCN$ the observed Co–C distances clearly indicate that the $Co(\eta\text{-}C_5H_5)_2$ entity in this compound is present as the cobaltocenium cation $[Co(\eta\text{-}C_5H_5)_2]^+$.

$[Ni(\eta\text{-}C_5H_5)(C_3S_5)]$

All attempts to prepare the analogous NIOS compounds $[Ni(\eta\text{-}C_5H_5)_2]_x[Ni(C_3S_5)_2]$ by using the same method (route d) as that previously described for the cobalt complex failed; no material grew on the anode during the electrochemical oxidations. Several salts of the type $[M(\eta\text{-}C_5H_5)_2][M'L_2]$ were prepared by route b,[16] [19,21,52] including $[Co(\eta\text{-}C_5H_5)_2][Ni(C_3S_5)_2]$ (see above), but all attempts to prepare the $[Ni(\eta\text{-}C_5H_5)_2][Ni(C_3S_5)_2]$ compound by treating $[NBu_4][Ni(C_3S_5)_2]$ with a chemically or electrochemically generated $[Ni(\eta\text{-}C_5H_5)_2]^+$ salt also failed. Finally, attempts to prepare the $[Ni(\eta\text{-}C_5H_5)_2][Ni(C_3S_5)_2]$ salt through route e, by treating $Na[Ni(C_3S_5)_2]$ with $[Ni(\eta\text{-}C_5H_5)_2]BF_4$ led to a compound which was characterized by mass spectrometry, conductimetry and X-ray analysis as the unexpected $[Ni(\eta\text{-}C_5H_5)(C_3S_5)]$.

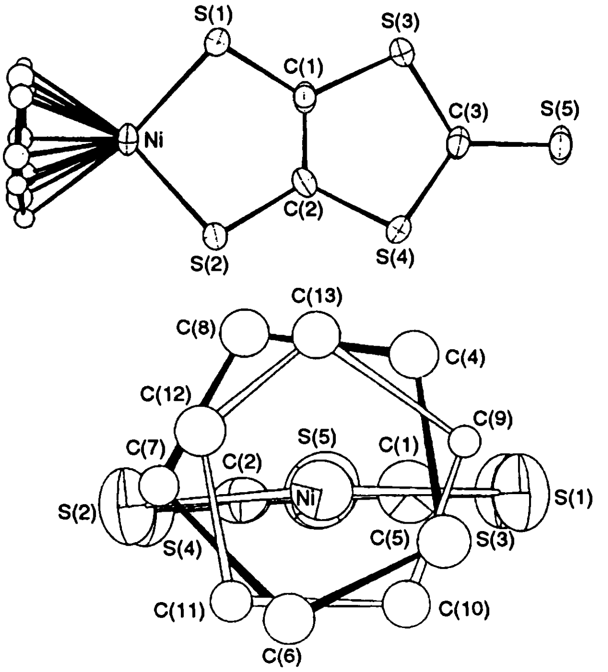


Fig. 5 Atomic numbering scheme for $[Ni(\eta\text{-}C_5H_5)(C_3S_5)]$

The asymmetric unit consists of one $[Ni(\eta\text{-}C_5H_5)(C_3S_5)]$ entity (see Fig. 5, Table 3). The C_5H_5 ring is disordered over two positions, one position [cp_1; atoms C(4)–C(8)] being occupied at 65% and the other [cp_2; atoms C(9)–C(13)] at 35%. The two rings are not exactly coplanar, with a shift of ≈3.6° between each plane. The $Ni(C_3S_5)$ unit is planar (largest deviation 0.054 Å) and is almost perpendicular to the C_5H_5 rings (94.1 or 92.5° depending on the ring involved). The distances between the Ni atom (formally Ni^{III}) and the carbon atoms of the C_5H_5 rings range from 2.07 to 2.17 Å (average 2.12 Å) (for cp_1), and from 2.05 to 2.15 Å (average 2.11 Å) (for cp_2). These values are similar to those found in the triple-decker sandwich-type compound $[Ni_2(\eta\text{-}C_5H_5)_3]BF_4$[53] (2.074–2.107 and 2.082–2.129; average 2.090 and 2.109 Å) and to those found in $[Ni_2(\eta\text{-}C_5Me_5)_2(C_2S_4)]$[54] (2.073–2.124; average 2.102 Å) but shorter than 2.196(4) Å observed in nickelocene which involves Ni^{II}.[55] This is not in agreement with the increase in the Ni–C bond length when going from $[Ni^0(\eta\text{-}C_5H_5)(C_3Ph_3)]$ (2.100 Å)[56] to $[Ni^{II}(\eta\text{-}C_5H_5)_2]$ (2.196 Å).[55] An increase in the metal–carbon bond length is also observed when going from ferrocene (Fe^{II}) to ferrocenium (Fe^{III}).[57] The Ni–C distances in $[Ni(\eta\text{-}C_5H_5)(C_3S_5)]$, which were smaller than expected, may be explained by the electron-donating and/or π-acceptor ability of the 1,2-dithiolate ligand. The C–C bond distances range from 1.38 to 1.53 Å in the cp_1 ring and from 1.22 to 1.48 Å in cp_2, and are similar to those found for $[Ni^0(\eta\text{-}C_5H_5)(C_3Ph_3)]$[56] (1.24–1.51 Å). The distances within the $Ni(C_3S_5)$ unit (Ni–S 2.136, S–C 1.711 and C=C 1.36 Å) are similar to those found in $[Ni(C_3S_5)_2]$ (Ni–S 2.147, S–C 1.699 and C=C 1.391 Å).[37b] This is consistent with the fact that both $[Ni(\eta\text{-}C_5H_5)(C_3S_5)]$ and $[Ni(C_3S_5)_2]$ are neutral complexes. The $[Ni(\eta\text{-}C_5H_5)(C_3S_5)]$ units are not stacked but are arranged in layers in the *ac* plane with two short S · · · S distances (3.62 and 3.57 Å) (Fig. 6).

The formation of $[Ni(\eta\text{-}C_5H_5)(C_3S_5)]$ from the reaction of $[Ni(\eta\text{-}C_5H_5)_2]BF_4$ with $Na[Ni(C_3S_5)_2]$ is somewhat puzzling. The ligand-exchange reaction (1) is the most straightforward explanation. The elemental analysis (Ni : Co = 1 : 1) and conductimetry measurements (non-conducting in solution) of a compound obtained by the reaction analogous to (1) between

$$Na[Ni(C_3S_5)_2] + [Ni(\eta\text{-}C_5H_5)_2]BF_4 \longrightarrow 2[Ni(\eta\text{-}C_5H_5)(C_3S_5)] + NaBF_4 \quad (1)$$

$Na[Ni(C_3S_5)_2]$ and $[Co(\eta\text{-}C_5H_5)_2]PF_6$ indicate that this compound actually is a mixture of $[M(\eta\text{-}C_5H_5)(C_3S_5)]$ (M =

Table 3 Selected bond lengths (Å) and angles (°) for $[Ni(\eta-C_5H_5)(C_3S_5)]$

Ni–S(1)	2.138(2)	Ni–S(2)	2.133(2)	S(1)–C(1)	1.706(8)
S(2)–C(2)	1.716(7)	S(3)–C(1)	1.750(8)	S(3)–C(3)	1.726(9)
S(4)–C(2)	1.733(8)	S(4)–C(3)	1.711(9)	S(5)–C(3)	1.660(7)
C(1)–C(2)	1.36(1)	Ni–C(4)	2.15(2)	Ni–C(5)	2.07(2)
Ni–C(6)	2.12(2)	Ni–C(7)	2.11(1)	Ni–C(8)	2.17(2)
Ni–C(9)	2.09(2)	Ni–C(10)	2.11(3)	Ni–C(11)	2.15(3)
Ni–C(12)	2.05(3)	Ni–C(13)	2.13(3)	C(4)–C(5)	1.53(3)
C(4)–C(8)	1.38(2)	C(5)–C(6)	1.40(3)	C(6)–C(7)	1.51(3)
C(7)–C(8)	1.42(2)	C(9)–C(10)	1.39(4)	C(9)–C(13)	1.48(4)
C(10)–C(11)	1.41(4)	C(11)–C(12)	1.39(5)	C(12)–C(13)	1.22(5)

S(1)–Ni–S(2)	94.97(8)	S(1)–Ni–C(4)	105.8(5)
Ni–S(1)–C(1)	100.8(3)	Ni–S(2)–C(2)	100.9(3)
C(1)–S(3)–C(3)	97.2(4)	C(2)–S(4)–C(3)	97.3(4)
S(1)–C(1)–C(2)	121.9(6)	S(3)–C(1)–C(2)	115.1(6)
S(2)–C(2)–C(1)	121.2(6)	S(4)–C(2)–C(1)	116.7(5)
S(3)–C(3)–S(4)	113.7(4)	S(3)–C(3)–S(5)	123.4(6)
S(4)–C(3)–S(5)	122.9(5)	C(5)–C(4)–C(8)	106.6(14)
C(4)–C(5)–C(6)	108.1(17)	C(5)–C(6)–C(7)	106.7(16)
C(6)–C(7)–C(8)	107.2(13)	C(4)–C(8)–C(7)	111.2(14)
C(10)–C(9)–C(13)	106.8(20)	C(9)–C(10)–C(11)	108.6(24)
C(10)–C(11)–C(12)	101.1(25)	C(11)–C(12)–C(13)	120.1(32)
C(9)–C(13)–C(12)	103.3(27)		

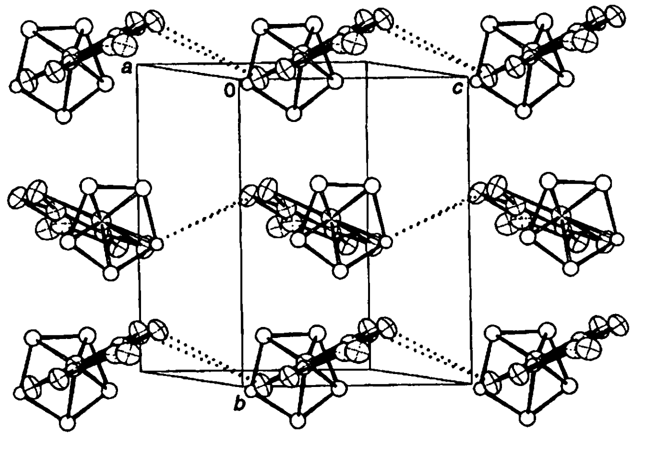


Fig. 6 Layers of $[Ni(\eta-C_5H_5)(C_3S_5)]$ units in the *ac* plane

Ni or Co). Such reactions are already known for various metallocenes and 1,2-dithiolato compounds, but often require more forcing conditions. For example, reaction of $[NEt_4]_2[Zn(C_3S_5)_2]$ with $[Ti(\eta-C_5H_5)_2Cl_2]$ in refluxing tetrahydrofuran (thf) results in $[Ti(\eta-C_5H_5)_2(C_3S_5)]$.[32] The complex $[Co(\eta-C_5H_5)(C_3S_5)]$ has been obtained from the reaction of $[NEt_4]_2[Zn(C_3S_5)_2]$ with $[Co(\eta-C_5H_5)I_2(CO)]$.[33] These reactions involve the generation of free $C_3S_5^{2-}$ obtained after cleavage of the Zn–S bond in $[NEt_4]_2[Zn(C_3S_5)_2]$. This is consistent with previous studies by McCleverty and co-workers[30] which show that the metal–cyclopentadienyl bond can be cleaved by 1,2-dithiolate ligands. For example, formation of various metal complexes (Cr, Mo, W and Ti) containing a cyclopentadienyl ring and a 1,2-dithiolate ligand such as $[S_2C_2(CN)_2]^{2-}$ has been achieved by reaction of the appropriate metal cyclopentadienyl carbonyl complex with an excess of the sodium salt of the appropriate ligand.[30]

Mixed metallocenium–1,2-dithiolato compounds may be also obtained directly by reaction of a metallocenium salt and a 1,2-dithiolato salt. For example, $[Co(\eta-C_5H_5)(C_3OS_4)]$ ($C_3OS_4^{2-}$ = 4,5-disulfanyl-1,3-dithiol-2-onate) has been prepared by treatment of $[Co(\eta-C_5H_5)I_2(CO)]$ by $Na_2(C_3OS_4)$.[35] Likewise, $[Ti(\eta-C_5H_5)_2(C_3S_5)]$ has been obtained from $Na_2(C_3S_5)$ and $[Ti(\eta-C_5H_5)_2Cl_2]$.[34] Thus, another explanation for the unexpected formation of $[Ni(\eta-C_5H_5)(C_3S_5)]$ could be related to the presence of residual unreacted $Na_2(C_3S_5)$ species in the solutions of $Na[Ni(C_3S_5)_2]$ {see Scheme 1; $Na[Ni(C_3S_5)_2]$ cannot be isolated because of its very high solubility and instability}. Consequently, the formation of $[Ni(\eta-C_5H_5)(C_3S_5)]$ could also result *via* reaction (2).

$$Na_2(C_3S_5) + [Ni(\eta-C_5H_5)_2]BF_4 \longrightarrow [Ni(\eta-C_5H_5)(C_3S_5)] + Na(C_5H_5) + NaBF_4 \quad (2)$$

However, the high yields observed would be more consistent with reaction (1). Moreover, a similar reaction (2) between $[Co(\eta-C_5H_5)_2]PF_6$ and the residual $Na_2(C_3S_5)$ present in the solution of $Na[Ni(C_3S_5)_2]$ should have led to $[Co(\eta-C_5H_5)(C_3S_5)]$ alone, and not a mixture of $[M(\eta-C_5H_5)(C_3S_5)]$ (M = Co or Ni).

Acknowledgements

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