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Synthesis and X-ray Structure of $(\eta\text{-}C_5H_5)_2Ni_2Fe(CO)_3S$, the First Iron-Nickel Cluster with a Sulphur Atom Nearly Symmetrically Bridging Three Metal Atoms

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The reactions of $[(\eta\text{-}C_5H_5)Ni(CO)]_2$ with carbonyls and alkyne-carbonyls of iron and ruthenium led to the formation of new hetero-metallic iron-nickel and ruthenium-nickel complexes [1–4]. We now report the reaction of the same nickel complex with $Fe_2(CO)_6S_2$ [5] which yields the hetero-metallic $(\eta\text{-}C_5H_5)_2Ni_2Fe(CO)_3S$ (I). This is, to our knowledge, the first iron-nickel-chalcogen complex to be reported.

Complex I is obtained in about 15% yield (on nickel) when refluxing in heptane under nitrogen, for 15 min., $[(\eta\text{-}C_5H_5)Ni(CO)]_2$ and $Fe_2(CO)_6S_2$ in 1.5:1 molar ratio. A 10% yield of $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$ is also obtained, together with about 15% of a yellow, still unidentified, derivative which has no carbonyl absorptions in the IR.

I analyzes as follows. Found: C%, 37.43, Fe%, 13.18, H%, 2.71, Ni%, 27.56; O%, 11.62; S%, 7.50. Calcd. for $C_{13}H_{10}FeNi_2O_3S$: C%, 37.22; Fe%, 13.31, H%, 2.40; Ni%, 27.98; O%, 11.44; S%, 7.64.

The IR spectrum (heptane solution) shows the following absorptions (ν_{CO}): 2020 s, 1956 s(sh), 1947 vs, cm^{-1}. In the mass spectrum, the parent ion (418 m/e, isotopic pattern Ni_2Fe) is observed; release of three CO's and then of two fragments of 65 m/e (probably the cyclopentadienyl ligands) is observed. A signal at 146 m/e can be ascribed to the species $FeNiS^+$.

The crystal structure of I was determined by X-ray diffraction methods. Crystals of I were obtained by cooling at –10 °C heptane–$CHCl_3$ solutions; a dark-brown elongated prism with dimensions of *ca.* 0.11 × 0.13 × 0.30 mm was used for the data collection.

Crystal Data

$C_{13}H_{10}FeNi_2O_3S$; M = 419.55; monoclinic, a = 16.494(9), b = 7.073(7), c = 25.918(12) Å, β = 104.80(8)°, V = 2923(4) Å^3, Z = 8; d_{calc} = 1.907 g/cm^3; $\mu(MoK\alpha)$ = 36.82 cm^{-1}; space group $C2/c$ (from systematic absences and structural determination). Diffraction intensities were measured in the $\theta/2\theta$ scan mode using Nb-filtered MoKα radiation on a Siemens on-line single-crystal diffractometer. A total of 2863 independent reflections was collected in the range $3 < \theta < 26°$; of these 1450 were considered observed (having $I > 2\sigma(I)$) and used in the analysis. The structure was solved by the heavy atom method and refined by full-matrix least-squares with anisotropic thermal parameters for the non-hydrogen atoms. The hydrogen atoms could not be precisely located in a difference Fourier and were placed in their geometrically calculated positions in the final structure factor calculation with uniform isotropic thermal parameters. The final atomic coordinates and thermal parameters for the non-hydrogen atoms are given in Table I. The final R value was 0.065 (observed reflections only). Computer programs used on a CYBER 7600 computer of the 'Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale' (Bologna) were those of SHELX-76 system [6].

The structure of I is represented in Fig. 1 and selected bond distances and angles are given in Table II. The complex, having an approximate m symmetry, is formed by an equilateral triangle of metal atoms; one cyclopentadienyl ligand is η bonded to each nickel atom and three terminal carbonyls are disposed on the iron atom. The metal–metal bond distances are: Ni(1)–Ni(2) = 2.404(5), Ni(1)–Fe = 2.427(4), Ni(2)–Fe = 2.419(4) Å. These metal bonds can be compared with those found in the complex $(\eta\text{-}C_5H_5)_2Ni_2Fe(CO)_3(C_2Ph_2)$ [7] [Ni–Ni = 2.405(2), Ni–Fe = 2.381(3) and 2.387(3) Å].

The sulphur atom is capping the three metals in a nearly symmetrical way, the metal–sulphur bonds being: Ni(1)–S = 2.109(5), Ni(2)–S = 2.114(5) and Fe–S = 2.158(6) Å. The sulphur as threefold bridge and four electron donor has been discussed by Vahrenkamp [8]; this behaviour is rather common and complex I is a further example. The angles at the

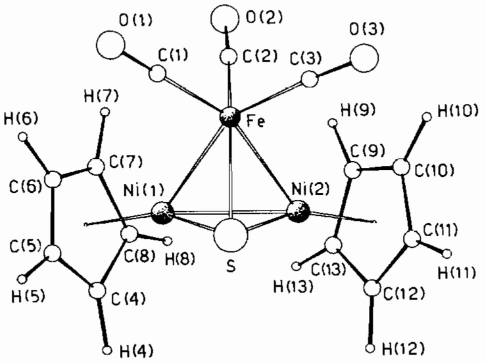

Fig. 1. Structure of the cluster.

TABLE I. Fractional Atomic Coordinates ($\times 10^4$) and Thermal Parameters ($\times 10^4$) for the Non-hydrogen Atoms (e.s.d.'s in parentheses). Anisotropic thermal parameters are in the form: $\exp[2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})]$.

	x/a	*y/b*	*z/c*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
NI(1)	3613(1)	3322(3)	3477(1)	321(10)	352(11)	448(12)	43(11)	147(9)	13(10)
NI(2)	2142(1)	3311(3)	3440(1)	295(10)	343(11)	413(12)	6(11)	80(8)	−3(10)
FE	3102(1)	5076(4)	4135(1)	427(12)	402(13)	368(12)	−33(12)	95(10)	−15(11)
S	2820(2)	5700(5)	3293(2)	462(22)	262(19)	443(23)	102(17)	137(19)	32(18)
O(1)	4570(9)	7243(23)	4694(6)	888(110)	944(129)	919(113)	−163(93)	−242(89)	−408(102)
O(2)	3388(9)	1818(24)	4839(6)	866(101)	928(117)	795(102)	343(102)	301(81)	185(102)
O(3)	1780(9)	6925(22)	4510(6)	704(89)	804(109)	765(99)	−119(85)	191(77)	221(86)
C(1)	3993(11)	6404(31)	4475(7)	525(108)	649(138)	665(120)	150(107)	156(93)	−41(104)
C(2)	3260(11)	3157(34)	4570(7)	552(104)	749(150)	558(115)	−4(120)	221(90)	76(116)
C(3)	2326(12)	6223(29)	4379(7)	575(112)	666(147)	378(101)	−16(94)	−1(86)	30(103)
C(4)	4142(12)	1863(33)	2948(8)	569(119)	798(148)	798(131)	−305(125)	66(102)	357(118)
C(5)	4716(12)	3163(33)	3231(11)	455(100)	708(148)	1506(194)	−95(163)	598(121)	21(117)
C(6)	4883(13)	2781(38)	3754(11)	581(138)	937(196)	920(197)	228(157)	85(134)	215(130)
C(7)	4444(15)	1286(34)	3828(9)	1021(161)	625(156)	1149(163)	686(134)	672(136)	687(138)
C(8)	3926(11)	565(20)	3340(12)	504(97)	176(68)	2652(277)	−455(112)	786(139)	−140(67)
C(9)	1644(15)	953(32)	3710(11)	838(153)	673(120)	1016(190)	403(134)	−203(140)	−547(120)
C(10)	1122(13)	2454(39)	3715(10)	630(123)	1177(184)	965(174)	−546(154)	571(130)	−602(132)
C(11)	838(10)	3126(27)	3200(8)	403(89)	473(108)	813(138)	−77(108)	231(90)	35(86)
C(12)	1156(11)	2053(30)	2864(8)	432(100)	715(143)	751(134)	−55(113)	152(94)	−216(101)
C(13)	1681(12)	639(31)	3186(13)	395(105)	495(139)	2009(256)	−336(165)	339(137)	−49(101)

TABLE II. Selected Bond Distances (Å) and Angles (°).

Ni(1)–Ni(2)	2.404(9)	Ni(2)–B[a]	1.71(1)
Ni(1)–Fe	2.427(4)	Fe–C(1)	1.78(2)
Ni(1)–S	2.109(5)	Fe–C(2)	1.74(2)
Ni(2)–Fe	2.419(4)	Fe–C(3)	1.76(2)
Ni(2)–S	2.114(5)	C(1)–O(1)	1.14(3)
Fe–S	2.158(5)	C(2)–O(2)	1.16(3)
Ni(1)–A[a]	1.69(1)	C(3)–O(3)	1.15(3)
Ni(2)–Ni(1)–Fe	60.1(1)	S–Fe–C(1)	109.3(6)
Fe–Ni(2)–Ni(1)	60.4(1)	S–Fe–C(2)	140.6(7)
Ni(1)–Fe–Ni(2)	59.5(1)	S–Fe–C(3)	106.3(6)
Ni(2)–Ni(1)–S	55.4(1)	C(1)–Fe–C(2)	97.1(9)
Fe–Ni(1)–S	56.3(2)	C(1)–Fe–C(3)	99.4(9)
Fe–Ni(2)–S	56.4(2)	C(2)–Fe–C(3)	97.4(9)
S–Ni(2)–Ni(1)	55.2(1)	C(2)–Fe–Ni(1)	92.0(7)
S–Fe–Ni(1)	54.4(1)	C(2)–Fe–Ni(2)	92.4(7)
S–Fe–Ni(2)	54.7(1)	C(3)–Fe–Ni(1)	154.3(6)
Ni(1)–S–Ni(2)	69.4(1)	C(3)–Fe–Ni(2)	96.2(6)
Ni(1)–S–Fe	69.3(2)	Fe–C(1)–O(1)	179(2)
Ni(2)–S–Fe	69.0(2)	Fe–C(2)–O(2)	176(2)
C(1)–Fe–Ni(1)	103.1(6)	Fe–C(3)–O(3)	176(2)
C(1)–Fe–Ni(2)	160.6(6)		

[a] A and B are the centroids of the two cyclopentadienyl rings.

sulphur are: Ni(1)–S–Fe = 69.3(2), Ni(2)–S–Fe = 69.0(2) and Ni(1)–S–Ni(2) = 69.4(1)°; they are narrower than in $FeCo_2(CO)_9S$, the only reported chalcogen mixed cluster [9], and in $Co_3(CO)_9S$ [10], in which average values of 72.6 and 76.1° were found respectively, but the metal–metal bonds were longer (average values: 2.554 and 2.637 Å, respectively).

Alkyne substituted complexes having found or proposed structures similar to those of complexes substituted with chalcogen atoms are well known; $H_2Ru_3(CO)_9X$ (X = S, Se, Te) [11] and $H_2Ru_3(CO)_9(C_2Ph_2)$ [12] are examples of the above analogy, complex I and $(\eta\text{-}C_5H_5)_2Ni_2Fe(CO)_3(C_2Ph_2)$ [7] are two other terms of this series.

Further studies are in progress on the reactivity of several metal derivatives towards $Fe_2(CO)_6S_2$, $Fe_2(CO)_6(SR)_2$ and $Fe_3(CO)_9S_2$.

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