Synthesis and characterisation of $[(C_5Me_4R)_2NbS_2]_2M$ complexes (M = Fe, Co; R = Me, Et): organometallic tetrathiometalates with niobocene ligands

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Abstract

Irradiation of $Cp_2^*Nb(\eta^2-S_2)H$ ($Cp^* = C_5Me_5$) 1a in the presence of $Fe(CO)_5$ gives the CO-free complex $[Cp_2^*NbS_2]_2Fe$ 2a. The core of 2a contains an FeS_4 tetrahedron which is ligated by two niobocene ligands as shown by X-ray diffraction analysis. In the reaction of 1a or $Cp_2^xNb(\eta^2-S_2)H$ ($Cp^x = C_5Me_4Et$) 1b with $Co_2(CO)_8$, compounds 3a and 3b of the same type are formed. Electrochemical studies of 2a and 3a,b show that they undergo three reversible $1e^-$ steps. The oxidation of 3b exerts a considerable influence on its absorption spectrum. A qualitative EHMO analysis is in agreement with a strong delocalisation of electron density over the whole NbS_2MS_2Nb system.

Keywords: Iron; Cobalt; Niobocene; Tetrathiometalates

1. Introduction

Organometallic tetrathiometalates represent an interesting subgroup of polynuclear tetrathiometalate complexes [1]. Of particular interest are their electronic structures, electrochemical behaviour [2], and potential for new materials [3]. Up to now they have been prepared in metathesis reactions between MS_4^{n-} salts ($n = 1$, M = Re; $n = 2$, M = Mo, W) and organometallic halide derivatives bearing diene, arene, cyclopentadienyl and/or carbonyl ligands [1–4]. The neutral products may be of di- or trinuclear character. The MS_4 unit provides two and six electrons respectively, and the organometallic fragments in relatively low oxidation states serve as "terminal" ligands. Alternatively, the reaction of $(C_5H_5)_2NbH_3$ and $Mo(S^tBu)_4$ gives $[(C_5H_5)_2NbS_2]_2Mo$, for which no properties have been described except its structure [5]. We now wish to report on a new synthetic approach for trinuclear complexes starting from organometallic sulphido complexes, e.g. niobocene sulphides 1a, 1b and binary metal carbonyls, and on first investigations of their structural and electronic properties.

2. Results and discussion

Irradiation of a THF solution of $Cp_2^*Nb(\eta^2-S_2)H$ [6] ($Cp^* = C_5Me_5$) 1a and 0.5 equiv. $Fe(CO)_5$ gives a dark solution from which the green–brown CO-free complex 2a is obtained in 65% yield after column chromatography. CO-containing intermediates have been observed but could not be isolated. Analytical and mass spectroscopic data are consistent with the composition $Cp_4^*Nb_2S_4Fe$. The ^1H NMR spectrum of 2a exhibits a singlet at 1.83 ppm. Reaction of 1a with $Fe_2(CO)_9$ also gives 2a, but it does not require irradiation.

The crystal structure of 2a (Fig. 1, Table 1) shows a linear Nb–Fe–Nb arrangement comprising a central FeS_4 tetrahedron and the niobocene units in an orthogonal orientation to each other. The Nb–Fe distances of

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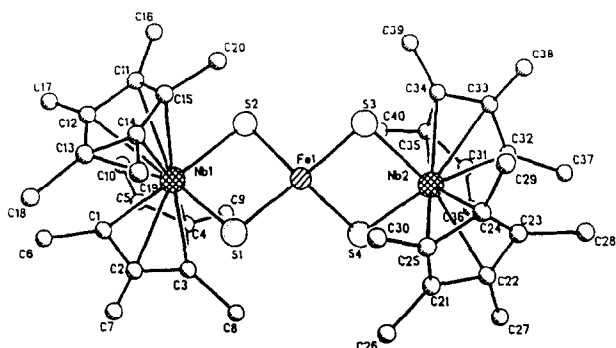
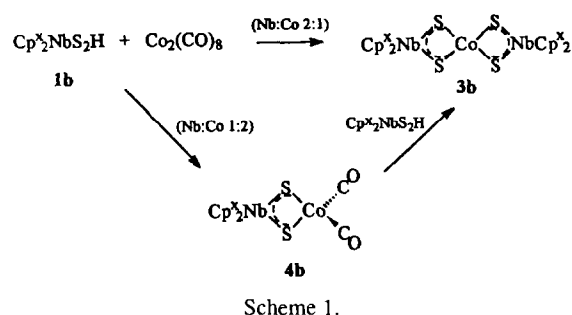Fig. 1. Crystal structure of [(C$_5$Me$_5$)$_2$NbS$_2$]$_2$Fe **2a**.

3.006 Å seem to be a border line case for a metal–metal bond. EHMO calculations [7] suggest strong bonding through the sulphur bridges and a weak Nb···Fe interaction [8]. The Fe–S and Nb–S distances fall in the expected range (2.257(4) Å (d_{Fe-S}) to 2.373(4) Å (d_{Nb-S})).

The reaction of **1a** or Cp$_2^x$Nb(η^2-S$_2$)H [6] (Cp^x = C$_5$Me$_4$Et) **1b** with Co$_2$(CO)$_8$ (Nb:Co = 2:1; toluene, 20 °C, 15 h) gives dark red Cp$_4^{(x)}$Nb$_2$S$_4$Co **3a,b** in 50–54% yield respectively. Upon variation of stoichiometry (Nb:Co = 1:2) and reaction conditions (toluene, 20 °C, 30 min) **1b** and Co$_2$(CO)$_8$ give, after chromatographic workup, Cp$_2^x$NbS$_2$Co(CO)$_2$ **4b** as the only product (47% yield). As **4b** reacts with **1b** to give **3b** in 30% yield, it may be considered as an intermediate product in the reaction of **1b** with Co$_2$(CO)$_8$ (Scheme 1). **4b** is a diamagnetic 16e compound with respect to Co in which the Cp$_2^x$NbS$_2$ unit formally serves as a chelate ligand. In this regard it resembles a dithiocarboxylato ligand [9] in which the central carbon is substituted by the Cp$_2^x$Nb moiety. The ν(CO) absorptions in the infrared are consistent with a bent M(CO)$_2$ fragment.
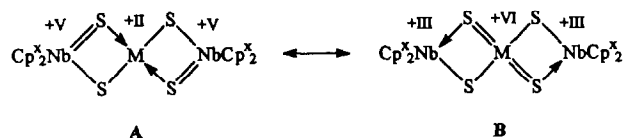
The electronic structures of the sulphido-bridged trinuclear complexes **2** and **3** may be formally described

Scheme 1.

by the resonance forms **A** and **B**. Thus, type **A** would be a bischelate of the metalladithiocarboxylato anion [Cp$_2^{(x)}$Nb^{V}S$_2$]$^-$ arising from S–S bond breaking and hydride abstraction in **1a,b**, whereas type **B** represents a derivative of a "conventional" tetrathiometalate (MS$_4^{2-}$) with two niobocene(III) ligands (Cp$_2^{(x)}$Nb$^+$). Delocalised bond systems have already been established for other tetrathiometalates with organometallic components [1a].

A qualitative EHMO analysis carried out on unsubstituted [Cp$_2$NbS$_2$]$_2$Co is also in agreement with a strong delocalisation of electron density over the whole NbS$_2$CoS$_2$Nb system. The analysis shows that the valence molecular orbitals 18e, 7b$_1$, and 12a$_1$ (Fig. 2) are

Table 1
Selected bond lengths (Å) and angles (°) for Cp$_4^*$Nb$_2$S$_4$Fe **2a**

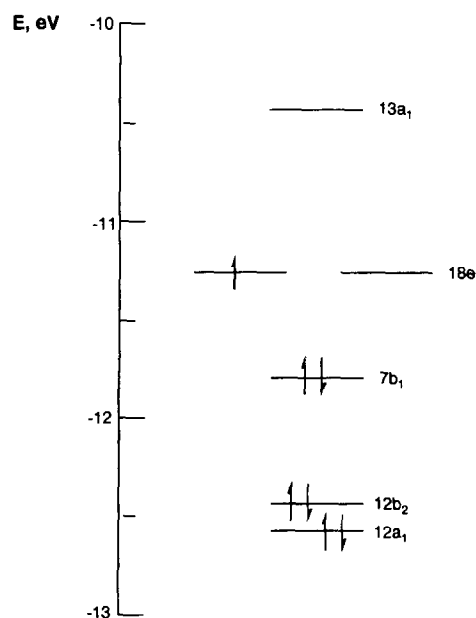|			
Fe(1)–Nb(1)	3.008(2)	S(1)–Fe(1)–S(3)	113.4(1)
Fe(1)–Nb(2)	3.015(2)	S(2)–Fe(1)–S(3)	112.1(1)
Fe(1)–S(1)	2.262(4)	Nb(2)–Fe(1)–S(3)	51.0(1)
Fe(1)–S(2)	2.257(4)	Nb(1)–Fe(1)–S(4)	126.0(1)
Fe(1)–S(3)	2.262(4)	S(1)–Fe(1)–S(4)	112.7(1)
Fe(1)–S(4)	2.282(4)	S(2)–Fe(1)–S(4)	115.3(1)
Nb(1)–S(1)	2.368(4)	Nb(2)–Fe(1)–S(4)	50.8(1)
Nb(1)–S(2)	2.371(3)	S(3)–Fe(1)–S(4)	101.9(1)
Nb(1)–S(3)	2.373(4)	Fe(1)–Nb(1)–S(1)	48.0(1)
Nb(2)–S(4)	2.368(3)	Fe(1)–Nb(1)–S(2)	47.8(1)
		S(1)–Nb(1)–S(2)	95.6(1)
Nb(1)–Fe(1)–S(1)	51.1(1)	Fe(1)–S(1)–Nb(1)	81.0(1)
Nb(1)–Fe(1)–S(2)	51.2(1)	Fe(1)–S(2)–Nb(1)	81.0(1)
S(1)–Fe(1)–S(2)	101.9(1)	Fe(1)–Nb(2)–S(3)	47.9(1)
Nb(1)–Fe(1)–Nb(2)	176.6(1)	Fe(1)–Nb(2)–S(4)	48.4(1)
S(1)–Fe(1)–Nb(2)	127.7(1)	S(3)–Nb(2)–S(4)	96.2(1)
S(2)–Fe(1)–Nb(2)	130.3(1)	Fe(1)–S(3)–Nb(2)	81.1(1)
Nb(1)–Fe(1)–S(3)	132.2(1)	Fe(1)–S(4)–Nb(2)	80.8(1)

Fig. 2. Qualitative diagram of valence orbitals for the model complex [(C$_5$H$_5$)$_2$NbS$_2$]$_2$Co in D_{2d} symmetry.

essentially formed by the CoS_4 fragment (87, 72, and 92%), whereas the $13a_1$ and especially $12b_2$ orbitals are delocalised over the seven heavy atoms. While the $12b_2$ orbital is slightly polarised towards Co (56% vs 25% of the two Nb atoms), $13a_1$ exhibits a 70% participation of the niobium atoms. Thus, the charge transfer transitions in the UV-visible spectra of 3a,b should involve the $13a_1$ orbital in excited states. In a simple ligand field model, the allowed transitions are $7b_1 \rightarrow 18e$ and $18e \rightarrow 13a_1$. However, the excited state $(7b_1)^1(18e)^1(13a_1)^1$ in the strong field approach is not forbidden. An absorption at 565 nm in the spectrum of 3b (Fig. 3) may be assigned to the ligand-to-metal charge transfer $18e \rightarrow 13a_1$ of the type $CoS_4 \rightarrow Nb$, owing to a 46% participation of the sulphur ligands in the 18e orbital. Compared with $[Co(WS_4)_2]^{2-}$ the band is more than 200 nm shifted to high energy [10]. The ESR signal could not be detected. The EHMO calculations suggest that the unpaired electron of the molecule occupies a doubly degenerated level which gives rise to a strong spin–orbit coupling and thus to a broadening of the ESR signal.

The electrochemical behaviour of the new complexes 2a and 3b has been studied. Both compounds exhibit three reversible $1e^-$ steps at -1.06, -0.03, and $+1.30$ V for 2a, and at -1.50, -0.02, and $+1.27$ V for 3b (Fig. 4). Irreversible waves are observed at -2.87 V (2a) and -2.66 V (3b). The only difference between the compounds concerns the first reduction potential. It is interesting to note that 2a and 3b are more redox-active than other organometallic tetrathiometalates [1a,2]. Concomittant with the electron transfer, a change in the absorption spectra is observed as shown for the first oxidation step of 3b in Fig. 3.

In conclusion, a new synthetic access to organometallic tetrathiometalates is described. Now, the central "inorganic" part arises from a binary transition metal carbonyl, and electronic and spectroscopic characteristics should provide new information on the bonding
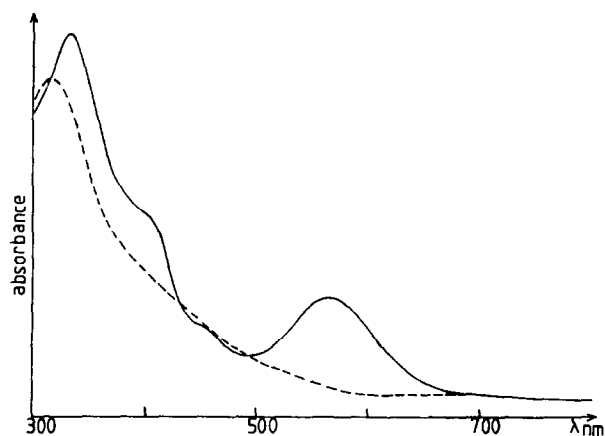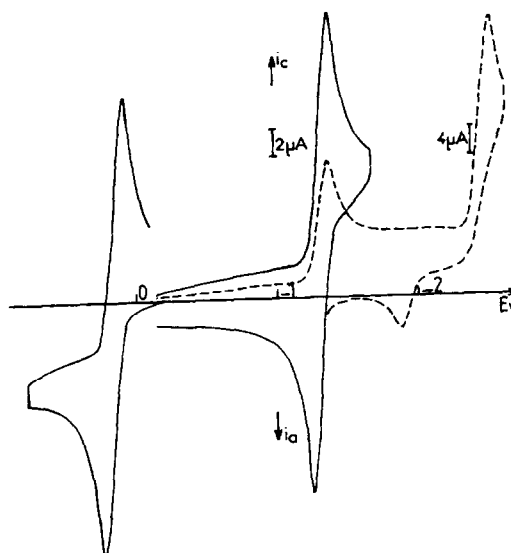

Fig. 4. Cyclic voltammogram of 3b in a 0.2 M solution of NBu_4PF_6 in THF. Starting potential: -0.15 V, sweep rate: 0.1 V s^{-1} (the dashed line corresponds to a different current scale ($\times 2$)).

system in these compounds. An extension to other metals is under way along with studies of redox chemistry and spectroscopic behaviour.

3. Experimental section

Voltammetric analyses were carried out in a standard three-electrode cell with a Tacussel UAP4 unit. The reference electrode was a saturated calomel electrode separated from the solution by a sintered glass disk. The auxiliary electrode was a Pt wire. For all voltammetric measurements the working electrode was a vitreous carbon disk electrode. For the polarograms, a three-electrode Tacussel Tipol polarograph was used. The dropping Hg electrode characteristics were $m = 3$ mg s^{-1} and $E = 0.5$ s. The controlled potential electrolyses were performed with an Amel 552 potentiostat coupled to an Amel 721 electronic integrator. In all cases the electrolyte was a 0.2 M solution of $^nBu_4NPF_6$ in THF.

3.1. Synthesis of $[Cp_2^* NbS_2]_2 Fe$ 2a

A solution of 220 mg (0.52 mmol) of 1a and 50 mg (0.255 mmol) of $Fe(CO)_5$ in 200 ml of THF was irradiated for 2 h (Hg immersion lamp, 150 W, water-cooled jacket), while the solution quickly turned dark. After evaporation of the solvent the dark residue was dissolved in 10 ml of toluene. Chromatography on SiO_2 (column 17 × 3 cm^2) first gave thin coloured bands which were discarded. With toluene/ether 40:1 a dark

Fig. 3. Absorption spectra of 3b before (———) and after (- - - - - -) $1e^-$ oxidation at $+0.15$ V/ECS.

green–brown band was eluted, containing **2a** in 65% yield.

2a: Anal. Found: C, 55.81; H, 6.55. $C_{40}H_{60}FeNb_2S_4$ (910.8). Calc.: C, 55.29; H, 6.78% (calculated with 0.7 toluene). FD mass spectroscopy (MS) (from toluene): 910.0. ^1H NMR (60 MHz, $CDCl_3$): 1.83 ppm. UV (CH_2Cl_2): ϵ(440 nm) = 9590, ϵ(584 nm) = 4818 M^{-1} cm^{-1}.

3.2. The reaction of 1b with $Co_2(CO)_8$

Synthesis of $[Cp_2'^* \, {}^)NbS_2]_2Co$ 3a,b.

To the solution of 0.48 mmol of **1a,b** in 50 ml of toluene, 41 mg (0.12 mmol) of $Co_2(CO)_8$ were added while the orange colour immediately turned dark brown. After stirring for 15 h at room temperature the solvent was evaporated, the residue dissolved in 10 ml of toluene and chromatographed on silica gel (column 20 × 3 cm^2). Elution with toluene gave a dark red band containing **3a,b** in 50–54% yield.

3a: Anal. Found: C, 52.29; H, 6.76. $C_{40}H_{60}CoNb_2S_4$ (913.9). Calc.: C, 52.57; H, 6.57%. FD-MS (from toluene): 913.2. ^1H NMR (250 MHz, $CDCl_3$): 5.87 ppm ($h_{1/2}$ = 178 Hz). UV (CH_2Cl_2): ϵ(332 nm) = 20350, ϵ(399 nm) = 10350(sh), ϵ(563 nm) = 6224 M^{-1} cm^{-1}.

3b: Anal. Found: C, 53.96; H, 7.06. $C_{44}H_{68}CoNb_2S_4$ (970.0). Calc.: C, 54.48; H, 7.07%. FD-MS (from toluene): 969.7. ^1H NMR (250 MHz, $CDCl_3$): 6.01 ppm ($h_{1/2}$ = 75.9 Hz). UV (CH_2Cl_2): ϵ(356 nm) = 20373, ϵ(385 nm) = 10812(sh), ϵ(565 nm) = 6716 M^{-1} cm^{-1}.

Synthesis of $Cp_2^xNbS_2Co(CO)_2$ 4b.

To the solution of 150 mg (0.44 mmol) of $Co_2(CO)_8$ in 50 ml of toluene a solution of 200 mg (0.44 mmol) of **1b** in 20 ml of toluene was added dropwise at room temperature under vigorous stirring. After 30 min the solvent was evaporated and the residue extracted with 15 ml of toluene/pentane 1:1. The soluble fraction was chromatographed on SiO_2 (column 20 × 3 cm^2). With toluene/pentane 1:1 a brown band was eluted, containing **4b** in 47% yield.

4b: Anal. Found: C, 50.11; H, 5.85. $C_{24}H_{34}CoNbO_2S_2$ (570.3). Calc.: C, 50.57; H, 6.01%. FD-MS (from toluene): 570.6. ^1H NMR (250 MHz, $CDCl_3$): 0.82 (t, 6H, CH_3), 1.64 (s, 12H, CH_3), 1.65 (s, 12H, CH_3), 1.91 (q, 4H, CH_2) ppm. IR (toluene): ν_{CO} 2002 vs, 1950 s cm^{-1}.

3.3. Crystallographic data for 2a

$C_{40}H_{60}Nb_2FeS_4 \cdot 0.7C_7H_8$, orthorhombic D_2^4, $P2_12_12_1$ (No. 19); cell: a = 10.738(5), b = 13.248(4), c = 33.18(1) Å, V = 4720.1 $Å^3$, Z = 4; empirical absorption correction: 8 reflections 6.0 < 2θ55.0°. Trans-

mission factor (min/max) 0.74/1.00, d(calc) = 1.33 g cm^{-3}, μ 0.96 mm^{-1}. Intensity data were measured on a Syntex R3 diffractometer. Mo $K\alpha$ radiation, graphite monochromator, 6560 unique observed reflections, 4770

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Cp_4^x Nb_2S_4Fe$ **2a**

Atom	x	y	z	U_{eq} [a]
Fe(1)	2927(2)	11265(1)	8625(1)	58(1)
Nb(1)	2027(1)	9433(1)	8176(1)	51(1)
Nb(2)	3975(1)	13090(1)	9049(1)	47(1)
S(1)	3504(3)	9634(3)	8700(1)	74(1)
S(2)	1367(3)	11141(2)	8171(1)	66(1)
S(3)	2293(3)	11997(3)	9206(1)	74(1)
S(4)	4542(3)	12283(3)	8439(1)	60(1)
C(1)	2582(19)	8455(16)	7547(5)	114(9)
C(2)	3677(19)	8598(15)	7793(6)	115(9)
C(3)	4041(14)	9607(12)	7776(4)	82(6)
C(4)	3082(16)	10080(12)	7572(4)	83(6)
C(5)	2225(14)	9415(14)	7428(4)	78(6)
C(6)	2279(19)	7487(14)	7374(5)	162(10)
C(7)	4388(21)	7859(20)	7921(7)	245(21)
C(8)	5250(12)	10004(13)	7921(4)	117(8)
C(9)	3197(16)	11139(13)	7422(5)	122(8)
C(10)	1206(17)	9605(18)	7137(4)	182(13)
C(11)	-217(13)	9243(11)	8315(6)	90(7)
C(12)	109(16)	8404(14)	8135(5)	92(7)
C(13)	1008(22)	7852(12)	8391(7)	123(9)
C(14)	1072(20)	8420(19)	8726(5)	122(9)
C(15)	325(16)	9268(14)	8685(6)	97(7)
C(16)	-1243(15)	9948(14)	8161(7)	232(17)
C(17)	-574(18)	8104(19)	7739(6)	242(18)
C(18)	1505(24)	6820(13)	8354(8)	374(26)
C(19)	1807(20)	8141(21)	9090(6)	372(26)
C(20)	175(19)	9991(15)	9022(5)	219(14)
C(21)	5902(17)	12119(18)	9236(5)	103(8)
C(22)	6152(15)	13206(16)	9285(5)	102(8)
C(23)	5477(15)	13513(11)	9605(4)	72(5)
C(24)	4739(16)	12796(13)	9734(4)	89(6)
C(25)	5050(22)	11892(13)	9517(6)	118(9)
C(26)	6531(20)	11325(18)	8982(6)	353(22)
C(27)	7175(14)	13738(19)	9061(5)	211(16)
C(28)	5712(19)	14463(12)	9848(5)	179(12)
C(29)	3843(19)	12919(19)	10123(4)	232(17)
C(30)	4541(20)	10846(11)	9661(7)	199(14)
C(31)	3933(15)	14642(10)	8622(5)	83(6)
C(32)	3905(15)	14976(9)	9001(5)	83(6)
C(33)	2750(18)	14644(13)	9173(4)	93(7)
C(34)	2115(14)	14169(11)	8874(6)	90(7)
C(35)	2859(16)	14186(10)	8531(5)	81(6)
C(36)	4882(18)	14874(13)	8298(5)	174(11)
C(37)	4682(18)	15800(11)	9157(6)	217(15)
C(38)	2357(22)	14949(17)	9574(5)	243(17)
C(39)	755(15)	13884(17)	8854(8)	316(23)
C(40)	2481(17)	13900(11)	8099(4)	133(9)
C(41)	2996(22)	8035(17)	331(5)	148(10)
C(42)	2095	7283	369	158(11)
C(43)	1751	6939	751	150(11)
C(44)	2309	7346	1094	142(10)
C(45)	3211	8098	1055	210(16)
C(46)	3555	8442	674	177(13)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

independent reflections $(I \geq 2.5\sigma(I))$. Structure solution by Patterson and difference Fourier methods. **2a** crystallises with 0.7 toluene (disordered) per formula unit. All H atoms were included in calculated positions. $R = 0.061$, $R_w = 0.057$; residual electron density (max/min) $0.72/ -0.65$ $e\text{Å}^{-3}$, shift/esd(max) 0.9, GOF = 3.86. Atomic coordinates are given in Table 2 [11].

Acknowledgement

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[11] Details of the structure solution and full structural parameters can be requested from the authors.