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Magnetic properties and fluxional behaviour of heteroleptic cyclopentadienyl–dithiolene d^1 and d^0 niobium complexes†

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Paramagnetic d^1 niobium complexes of general formula [Nb(η-C_5H_4R)$_2$(dithiolene)] [R = $SiMe_3$ or Bu^t; dithiolene = $C_3S_5^{2-}$ (4,5-disulfanyl-1,3-dithiole-2-thionate), $C_3OS_4^{2-}$ (4,5-disulfanyl-1,3-dithiol-2-onate) or dddt^{2-} (5,6-dihydro-1,4-dithiine-2,3-dithiolate)] have been prepared and their redox properties studied. The crystal structure determination of [Nb(η-$C_5H_4SiMe_3$)$_2$(C_3S_5)] showed that the folding angle of the NbS_2C_2 plane along the S–S axis is 34(2)°, an intermediate value compared with those of analogous d^0 (45–50°) and d^2 (0–10°) complexes, as rationalized by extended-Hückel calculations. The Curie-type temperature dependence of the spin susceptibility of [Nb(cp)$_2$(C_3S_5)], [Nb(cp)$_2$(C_3OS_4)] and [Nb(η-C_5H_4R)$_2$(C_3S_5)] (cp = η-C_5H_5) demonstrates that the paramagnetic complexes do not interact with each other in the solid state. Cationic d^0 complexes were obtained either by chemical oxidation (tetracyanoquinodimethane) of the d^1 molecules or from the direct reaction of dddt^{2-} with d^0 [Nb(η-C_5H_4R)$_2Cl_2$][PF_6]. The fluxional behaviour of these d^0 complexes has been investigated by temperature-dependent NMR studies and shown to be comparable with that of isoelectronic d^0 [Ti(cp)$_2$(dithiolene)] complexes.

Compared with the homoleptic metallocenes or metal dithiolene complexes, heteroleptic complexes bearing both cyclopentadienyl and dithiolene ligands exhibit attractive features for the elaboration of novel conducting or magnetic materials. Complexes of general formula M(cp)$_2$(dithiolene) (cp = η-C_5H_5) have been studied in detail mainly with d^0 metals such as Ti^{IV} or Zr^{IV}.[1–3] However, as expected, the formation of radical paramagnetic species from those d^0 complexes is difficult. Reduction to metal(III) species occurs at very low potential and oxidation proved to be irreversible.[2] The dithiolene ligand does not sufficiently stabilize the d^0 M^{IV} atom even when two cp ligands are substituted by the more electron-rich ligands η-C_5Me_5.[4]

On the other hand Mo(cp)$_2$(dithiolene) (M^{IV}, d^2) are well known to exhibit reversible oxidations to the d^1 and the d^0 species.[5,6] Recently we described the solid-state structure and magnetic properties of the 1 : 1 salt resulting from the oxidation of the electron-donor [Mo(cp)$_2$(dddt)] (dddt = 5,6-dihydro-1,4-dithiine-2,3-dithiolate) with the organic acceptor tetracyanoquinodimethane (tcnq).[6] Sulfur-rich dithiolenes such as dddt^{2-} or $C_3S_5^{2-}$ (4,5-disulfanyl-1,3-dithiole-2-thionate) were chosen for their ability to overlap with each other and with cyclopentadienyl ligands of neighbouring molecules in the solid state, thus leading to a network of intermolecular interactions, a prerequisite for collective electronic properties such as conductivity, ferro- or antiferro-magnetism. In [Mo(cp)$_2$(dddt)$^{\bullet +}$][tcnq$^{\bullet -}$] the paramagnetic d^1 cations [Mo(cp)$_2$(dddt)]$^{\bullet +}$ were found to be antiferromagnetically coupled in strongly dimerized chains. Those chains were isolated from each other by diamagnetic (tcnq$^{\bullet -}$)$_2$ dimers which prevented the appearance of a three-dimensional ordered magnetic ground state. In this respect, isoelectronic neutral d^1 complexes of V, Nb or Ta are particularly attractive since they do not necessitate any bulky counter ion. Several such paramagnetic neutral complexes have been reported with Nb[7,8] and V.[3,9] Little is known however about their geometry and their electronic solid-state properties. In the present work we report on the isolation, electrochemical characterization and magnetic susceptibility data of a series of niobium-(IV) or -(V) complexes obtained with substituted cyclopentadienyl anions such as $C_5H_4SiMe_3^-$ and $C_5H_4Bu^{t-}$. By using those solubilizing groups we were able to grow single crystals of [Nb($C_5H_4SiMe_3$)$_2$(C_3S_5)] and solve its structure, the first reported of such [Nb(cp)$_2$(dithiolene)] complexes. These C_3S_5 complexes can be oxidized to the cationic diamagnetic d^0 complexes [Nb(η-C_5H_4R)$_2$(dithiolene)$^+$][A$^-$] (R = Me_3Si or Bu^t, A$^-$ = PF_6^- or tcnq$^{\bullet -}$), the increased solubility of which allows temperature-dependent solution NMR studies. A fluxional behaviour analogous to that reported in the isoelectronic d^0 [Ti(cp)$_2$(dithiolene)] complexes[1,2,10] has been evidenced.

Results and Discussion

Synthesis

The complexes with $C_3S_5^{2-}$ and $C_3OS_4^{2-}$ (4,5-disulfanyl-1,3-dithiol-2-onate) dithiolene ligands were prepared by the conventional metathetical reaction with the corresponding metallocene dichloride [Nb(η-C_5H_4R)$_2Cl_2$] (Scheme 1). Also, as a probable consequence of the more electron-rich character of the C_5H_4R *vs.* the unsubstituted cp ligand, the reactivity of [Nb(η-C_5H_4R)$_2Cl_2$] proved to be inferior to that of [Nb(cp)$_2Cl_2$] and the complexes were isolated in fair yields as green crystals. Solutions in halogenated solvents (CH_2Cl_2, $CHCl_3$) are highly sensitive to air oxidation.

We were not able to isolate any clean product from the reaction with dddt^{2-}, probably because of the highly oxidizable character of the expected [Nb(η-C_5H_4R)$_2$(dddt)] (see below). An alternative direct synthesis of the oxidized d^0 cation [Nb(η-C_5H_4R)$_2$(dddt)$^+$][PF_6^-] was then designed. It involved the reaction of dddt^{2-} with the oxidized salt [Nb(η-C_5H_4R)$_2$Cl$_2^+$][PF_6^-] (Scheme 2). Such oxidized metallocene dichloride

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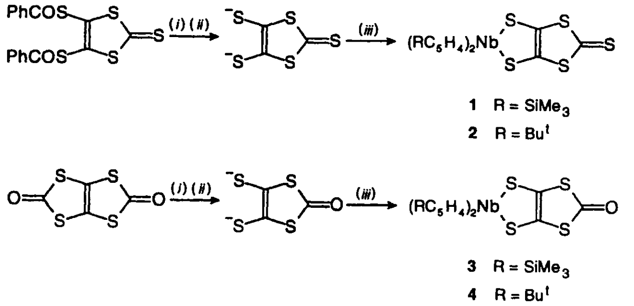
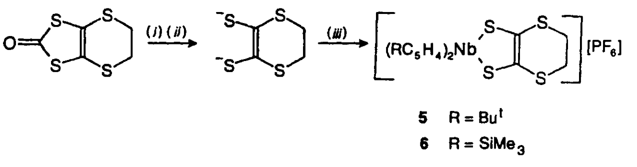
† *Non-SI unit employed:* G = 10^{-4} T.



Scheme 1 (*i*) NaOMe (2 equivalents) in MeOH; (*ii*) Et_2O; (*iii*) [Nb(η-$C_5H_4R)_2Cl_2$], CH_2Cl_2, room temperature (r.t.)



Scheme 2 (*i*) NaOMe (2 equivalents) in MeOH; (*ii*) Et_2O; (*iii*) [Nb(η-$C_5H_4R)_2Cl_2$][PF_6], CH_2Cl_2, r.t

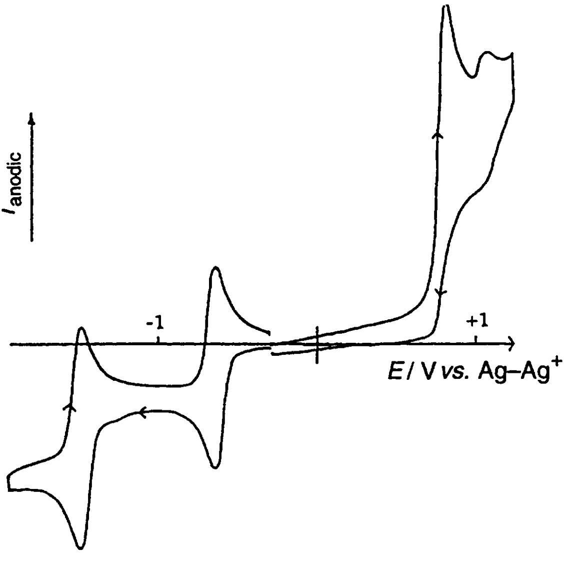


Fig. 1 Cyclic voltammogram of [Nb(η-$C_5H_4Bu^t)_2$(dddt)][PF_6]. Scan rate 100 mV s^{-1}

salts have been shown to exhibit a higher reactivity than that of their neutral counterparts, due to the now more electron-deficient character of the metal centre.[11] The [Nb(η-$C_5H_4R)_2$-$Cl_2{}^+$][$PF_6{}^-$] salts were prepared from [Nb(η-$C_5H_4R)_2Cl_2$] and ferrocenium hexafluorophosphate following a procedure reported recently for the unsubstituted [Nb(cp)$_2Cl_2$].[12]

Cyclic voltammetry experiments performed in MeCN (Table 1) demonstrate that all four d^1 complexes **1**–**4** are reversibly oxidized and reduced to the d^0 and d^2 species respectively. Compared with the unsubstituted cp derivatives, the Me_3Si and Bu^t groups exhibit no significant influence on the $E_{\frac{1}{2}}$ values. This is in accordance with the extended-Hückel calculations performed on those systems which showed that their highest occupied molecular orbital (HOMO) is mainly a combination of a metal orbital with the π orbital of the dithiolene ligand, with little participation, if any, of the cp^- orbitals.[14] Comparison of the oxidation potentials with the $E_{\frac{1}{2}}$ value for the tcnq–tcnq$^{\bullet-}$ couple (−0.31 V *vs.* Ag–$AgClO_4$) shows that this acceptor can indeed be used for the chemical oxidation of **1**–**4** (see below). Note also that the electrochemical reduction of d^0 [Nb(η-$C_5H_4R)_2$(dddt)$^+$][$PF_6{}^-$] occurs in two reversible waves (Fig. 1), the $E_{\frac{1}{2}}$ values of which are comparable with those reported for [Nb(cp)$_2$(dddt)]. An irreversible process is found in the anodic region, as observed in the oxidation of isoelectronic d^0 titanium complexes.[2]

Solution EPR spectra of complexes **1**–**4** exhibit the ten-line signal characteristic of coupling with the nuclear spin of the Nb atom (Fig. 2).[7,8,15] The A_{iso} values of the order of 80 G indicate a strong localization of the spin density on the metal centre with some delocalization on the dithiolene ligand (Table 2). However in this case the partial delocalization of the spin density appears less important than that previously observed with some other sulfur-containing bidentate ligands.[16] Note also that the more easily oxidized complexes are also those exhibiting the smallest A_{iso} values, indicating that the electron-rich dithiolene ligands such as $dddt^{2-}$ or $Me_2C_2S_2{}^{2-}$ are, however, able to accommodate a non-negligible part of the spin density.

The oxidized cationic forms of complexes **1**, **2** and [Nb(cp)$_2$(C_3S_5)] were prepared by oxidation with tcnq, to afford microcrystalline powders of the 1 : 1 salts, as shown from conductimetry measurements[17] and elemental analysis. Furthermore, the IR absorption of the cyano group in the tcnq salts indicates a total charge transfer to the tcnq$^{\bullet-}$ radical anion.[18]

Solid-state properties

Green crystals of the [Nb(η-$C_5H_4R)_2$(C_3S_5)] complexes were obtained by slow diffusion of MeOH into their $CHCl_3$ solutions. Geometrical data (Table 3) obtained from the crystal structure of **1** (R = $SiMe_3$) are compared in Table 4 with the few data reported for analogous d^1 complexes. The molecule is located in a general position and exhibits a characteristic folding of the NbS_2C_2 plane along the S–S axis by a value of 34° (Fig. 3). This value is comparable with the only other reported value for a similar d^1 complex of vanadium.[19] There are numerous examples of analogous d^0 titanocene dithiolene complexes in which folding angles of up to 52° have been reported[1–3,20] as well as several d^2 molecules where little folding, if any, is observed.[6,21] This behaviour has been rationalized on the basis of extended-Hückel calculations[6,14] and involves the overlap between the (cp)$_2$M fragment orbital (with two, one or no electrons) and the dithiolene HOMO of π character. Owing to orbital symmetry, overlap is possible only in the folded conformation which is indeed observed in the formally 16- or 17-electron complexes. With these data in hand, a general scheme can be drawn for all M(cp)$_2$(dithiolene) complexes, with folding angles of 40–50° for the d^0, 30–40° for the d^1 and 0–15° in the d^2 complexes (Scheme 3).

No short intermolecular contacts were identified in the crystal structure; the molecules thus appear to be isolated from each other. Indeed, the temperature dependence of the spin susceptibility obtained by integration of the EPR signal for an oriented single crystal of complex **1** exhibits a Curie law-type behaviour, thus demonstrating that the paramagnetic species do not interact with each other in the solid state. The *g* value is 2.0160 and the linewidth 21 G. On decreasing the temperature to 4 K the *g* value increases monotonically to 2.0272 while Δ*H* increases slightly to 100 G, indicating the absence of correlations in the spin relaxation.

SQUID magnetic susceptibility measurements were also conducted on microcrystalline batches of the unsubstituted [Nb(cp)$_2$(C_3S_5)] and [Nb(cp)$_2$(C_3OS_4)][7] with the expectation that the absence of bulky groups such as Bu^t or Me_3Si would allow for a closer proximity of the molecules in the crystal and eventually stronger intermolecular magnetic interactions. However, Curie-type behaviours were also observed with Curie constants corresponding to 0.92 and 1.0 spin per molecule respectively. This result confirms that the spin density is mainly centred on the metal atom with little, if any, delocalization on the dithiolene ligand, as already postulated from the solution EPR data (see above).

Fluxional behaviour of the d^0 niobium complexes

Given the large folding angle observed in the crystal structure of

Table 1 Electrochemical data for various niobium-(IV) and -(V) complexes, in V *vs.* Ag–AgClO$_4$ (+0.025 V for ferrocenium–ferrocene)

Complex	$E_{\frac{1}{2}}$ Nb^{IV}–Nb^{III}	$E_{\frac{1}{2}}$ Nb^{V}–Nb^{IV}	Ref.
[Nb(cp)$_2$Cl$_2$]	−1.57*	−0.08	7
[Nb(η-C$_5$H$_4$SiMe$_3$)$_2$Cl$_2$]	−1.56*	−0.14	13, This work
[Nb(η-C$_5$H$_4$Bu^t)$_2$Cl$_2$]	−1.60*	−0.17	This work
[Nb(cp)$_2$(C$_3$S$_5$)]	−1.22	−0.33	7
[Nb(η-C$_5$H$_4$SiMe$_3$)$_2$(C$_3$S$_5$)]	−1.21	−0.32	This work
[Nb(η-C$_5$H$_4$Bu^t)$_2$(C$_3$S$_5$)]	−1.27	−0.36	This work
[Nb(cp)$_2$(C$_3$OS$_4$)]	−1.27	−0.39	7
[Nb(η-C$_5$H$_4$SiMe$_3$)$_2$(C$_3$OS$_4$)]	−1.25	−0.36	This work
[Nb(η-C$_5$H$_4$Bu^t)$_2$(C$_3$OS$_4$)]	−1.33	−0.42	This work
[Nb(cp)$_2$(dddt)]	−1.53	−0.64	7
[Nb(η-C$_5$H$_4$SiMe$_3$)$_2$(dddt)][PF$_6$]	−1.52	−0.66	This work
[Nb(η-C$_5$H$_4$Bu^t)$_2$(dddt)][PF$_6$]	−1.45	−0.61	This work

* Irreversible: fast electron transfer–chemical reaction mechanism.

Table 2 Hyperfine coupling constants of various niobium(IV) complexes

Complex	A_{iso}/G	Ref.
[Nb(η-C$_5$H$_5$)$_2$Cl$_2$]	116.1	7
[Nb(η-C$_5$H$_4$SiMe$_3$)$_2$Cl$_2$]	112.9	This work
[Nb(η-C$_5$H$_4$Bu^t)$_2$Cl$_2$]	119.5	This work
[Nb(η-C$_5$H$_5$)$_2$(C$_3$S$_5$)]	83.5	7
[Nb(η-C$_5$H$_5$)$_2$(C$_3$OS$_4$)]	83.2	7
[Nb(η-C$_5$H$_4$SiMe$_3$)$_2$(C$_3$S$_5$)]	82.9	This work
[Nb(η-C$_5$H$_4$SiMe$_3$)$_2$(C$_3$OS$_4$)]	82.1	This work
[Nb(η-C$_5$H$_4$)$_2${S$_2$P(OMe)$_2$}]	81.5	15
[Nb(η-C$_5$H$_4$Bu^t)$_2$(C$_3$S$_5$)]	79.9	This work
[Nb(η-C$_5$H$_4$Bu^t)$_2$(C$_3$OS$_4$)]	79.6	This work
[Nb(η-C$_5$H$_5$)$_2$(dddt)]	79.5	7
[Nb(η-C$_5$H$_5$)$_2$(S$_2$C$_2$Me$_2$)]	76	8
[Nb(η-C$_5$H$_5$)$_2$(S$_2$C$_2$Ph$_2$)]	76	8
[Nb(η-C$_5$H$_5$)$_2$(S$_2$CNMe$_2$)]$^+$	73.3	15

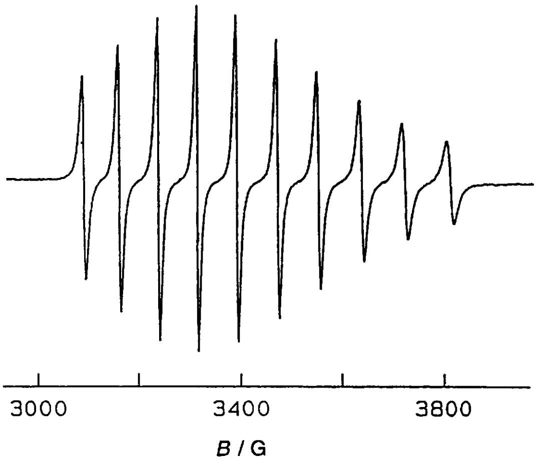


Fig. 2 The EPR spectrum of [Nb(η-C$_5$H$_4$Bu^t)$_2$(C$_3$S$_5$)] in CH$_2$Cl$_2$ at 295 K

[Nb(C$_5$H$_4$SiMe$_3$)$_2$(C$_3$S$_5$)], a fluxional behaviour in solution is expected, as studied extensively for the analogous d^0 titanium complexes by means of temperature-dependent NMR spectroscopy.[2,3] For those (cp)$_2$Ti^{IV} complexes two peaks are observed at low temperature for the protons of the two cyclopentadienyl rings, which eventually coalesce at higher temperatures. The paramagnetic nature of the d^1 niobium species prevents any solution NMR studies but the d^0 oxidized complexes are amenable to such studies.[8] They were performed with the tcnq salts of Nb(cp)$_2$(C$_3$S$_5$), **1** and **2**, as well as with the hexafluophosphates **5** and **6** obtained directly from [Nb(η-C$_5$H$_4$R)$_2$Cl$_2$][PF$_6$]. Note that dissolution of the tcnq salts in

Table 3 Selected bond distances (Å) and angles (°) in [Nb(η-C$_5$H$_4$SiMe$_3$)$_2$(C$_3$S$_5$)]

Nb–S(1)	2.51(1)	Si(1)–C(10)	1.85(2)
Nb–S(2)	2.51(2)	Si(1)–C(15)	1.83(6)
Nb–C(10)	2.44(3)	Si(1)–C(16)	1.80(3)
Nb–C(11)	2.39(5)	Si(1)–C(17)	1.86(4)
Nb–C(12)	2.45(5)	Si(2)–C(20)	1.92(2)
Nb–C(13)	2.41(3)	Si(2)–C(25)	1.83(5)
Nb–C(14)	2.36(2)	Si(2)–C(26)	1.82(3)
Nb–C(20)	2.41(5)	Si(2)–C(27)	1.78(5)
Nb–C(21)	2.43(5)	C(1)–C(2)	1.25(3)
Nb–C(22)	2.45(5)	C(10)–C(11)	1.44(5)
Nb–C(23)	2.36(6)	C(10)–C(14)	1.44(4)
Nb–C(24)	2.37(5)	C(11)–C(12)	1.30(3)
S(1)–C(1)	1.79(5)	C(12)–C(13)	1.35(6)
S(2)–C(2)	1.77(4)	C(13)–C(14)	1.29(3)
S(3)–C(1)	1.75(4)	C(20)–C(21)	1.42(2)
S(3)–C(3)	1.70(4)	C(20)–C(24)	1.33(3)
S(4)–C(2)	1.75(5)	C(21)–C(22)	1.36(3)
S(4)–C(3)	1.70(2)	C(22)–C(23)	1.42(3)
S(5)–C(3)	1.68(5)	C(23)–C(24)	1.37(4)
S(1)–Nb–S(2)	81.3(6)	S(3)–C(1)–C(2)	118(3)
Nb–S(1)–C(1)	97(1)	S(2)–C(2)–S(4)	119(1)
Nb–S(2)–C(2)	97.8(9)	S(2)–C(2)–C(1)	124(3)
C(1)–S(3)–C(3)	95(1)	S(4)–C(2)–C(1)	117(3)
C(2)–S(4)–C(3)	96(2)	S(3)–C(3)–S(4)	114(2)
S(1)–C(1)–S(3)	117(1)	S(3)–C(3)–S(5)	123(1)
S(1)–C(1)–C(2)	125(3)	S(4)–C(3)–S(5)	124(2)

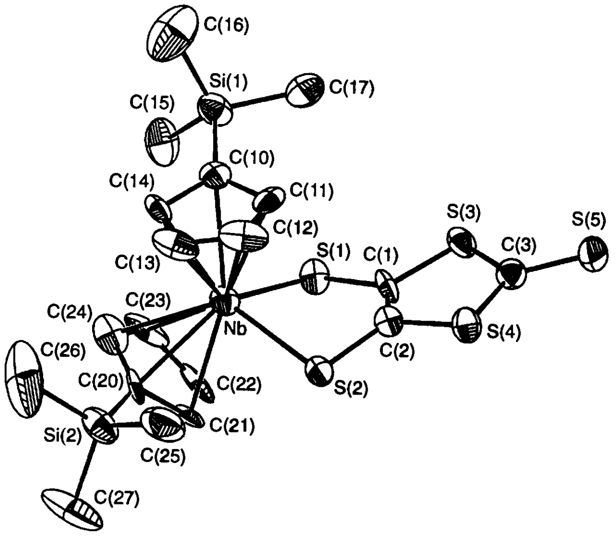
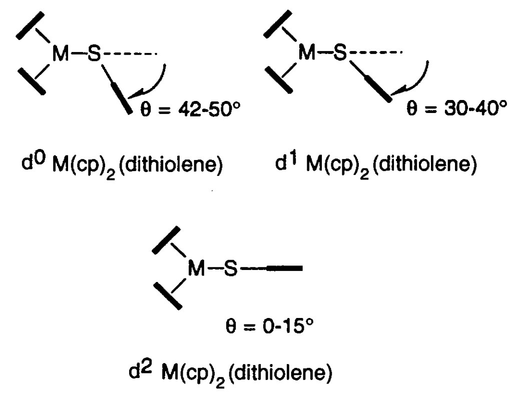


Fig. 3 An ORTEP[19] drawing and numbering scheme for [Nb(η-C$_5$H$_4$SiMe$_3$)$_2$(C$_3$S$_5$)]. Thermal ellipsoids are drawn at the 50% probability level

Table 4 Characteristic bond distances (Å) and angles (°) of d^1 M(η-C_5H_4R)$_2$(dithiolene) complexes

Complex	M–S	C–S	C–C	Cp$_a$–M	Cp$_b$–M	S–M–S	Cp–M–Cp	Fold angle, θ	Ref.
[V(cp)$_2$($S_2C_6H_4$)] (A)	2.431(6)	1.70(2)	—	1.992	1.977	79.7(2)	135.4(6)	38.3(1)	9
(B)	2.426(6)	1.77(2)	—	2.001	1.989	79.9(2)	133.4(6)	38.4(1)	
[Nb(η-$C_5H_4SiMe_3$)$_2$(C_3S_5)]	2.51(1)	1.78(1)	1.25(3)	2.106	2.095	81.3(6)	131(2)	34(2)	This work
[Mo(cp)$_2$(dddt)]$^{\bullet +}$	2.425(7)	1.725(7)	1.373(1)	1.996	1.995	80.43(2)	135.5(3)	32.1(1)	6



Scheme 3

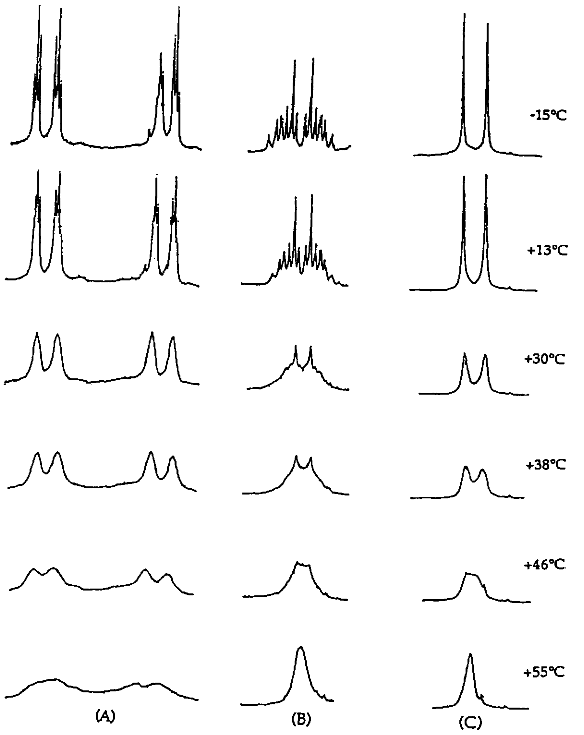


Fig. 4 Variable-temperature ^{1}H NMR study of [Nb(η-C_5H_4-Bu^t)$_2$(dddt)][PF_6]; (A) = (C_5H_4Bu^t)$_2$, (B) = SC_2H_4S, (C) = [$C_5H_4C(CH_3)_3$]$_2$

CF_3CO_2D led to acid-decomposition reactions of the tcnq$^{\bullet -}$ radical anion as observed by Melby *et al.*[22]

Owing to the Bu^t and Me_3Si substituents, the NMR spectra of the C_5H_4R protons are complex (Fig. 4, peaks A and C). Thus, the coalescence temperature and activation energy values given in Table 5 were determined from the temperature dependance of the methyl signals (peaks C in Fig. 4). These values compare favourably with reported data on the isoelectronic [Ti(cp)$_2$(dithiolene)] complexes[2] having the same electron-rich dithiolenes $C_3S_5^{2-}$ and dddt^{2-}, indicating that the d^0 niobium species should exhibit comparable folding angles. In the niobium series the smaller T_c values observed for the Bu^t$C_5H_4^-$ and $Me_3SiC_5H_4^-$ derivatives, when compared with that of the unsubstituted [Nb(cp)$_2$(C_3S_5)]$^+$, may indicate a smaller folding angle. Indeed, in the titanium series,[2] smallest folding angles were associated with the lowest T_c and $\Delta G^\ddagger$ values, corresponding to a decreased overlap between the empty (cp)$_2$Ti^{2+} fragment orbital and the HOMO of the dithiolene ligand. From the electrochemical data we know that the Bu^t and Me_3Si substituents do not modify substantially the redox character of the complexes, when compared with that of the unsubstituted [Nb(cp)$_2$(dithiolene)] species. Thus, the differences between Bu^t-, Me_3Si-substituted complexes and [Nb(cp)$_2$(C_3S_5)]$^+$ are in our opinion merely attributable to a steric effect of these large substituents which appears to limit the dithiolene folding, as already postulated for [Ti(η-C_5Me_5)$_2$(C_3S_5)].[4]

Experimental

Solvents were dried and distilled just prior to use and the air-sensitive dithiolenes manipulated under argon using standard vacuum-line techniques. Elemental analysis was performed at the Institut de Chimie des Substances Naturelles, CNRS, Gif/Yvette.

Preparations

[Nb(η-$C_5H_4SiMe_3$)$_2$$Cl_2$] and [Nb($\eta$-$C_5H_4$Bu^t)$_2$$Cl_2$]. The two compounds were prepared as previously described from the reaction of $NbCl_4$·2thf with 2 equivalents of the corresponding lithium salt Li(C_5H_4R) in refluxing tetrahydrofuran (thf).[23] The crude products were washed with water and ethanol and their purity checked by comparison of their IR spectra with those of reference compounds.

[Nb(η-$C_5H_4SiMe_3$)$_2$$Cl_2$][$PF_6$] and [Nb($\eta$-$C_5H_4$Bu^t)$_2$$Cl_2$]-[$PF_6$]. The two salts were obtained by chemical oxidation of a CH_2Cl_2 solution of the above neutral complexes with an equivalent amount of ferrocenium hexafluorophosphate.[12] After stirring overnight, the solvent was evaporated and the solid residue triturated with pentane in order to remove the ferrocene formed (Found: C, 39.0; H, 4.5; Cl, 11.3; P, 5.2. $C_{18}H_{26}Cl_2F_6NbP$ requires C, 39.2; H, 4.75; Cl, 12.9; P, 5.6. Found: C, 33.95; H, 4.5; Cl, 11.3; P, 4.6. $C_{16}H_{26}Cl_2F_6NbPSi_2$ requires C, 32.9; H, 4.5; Cl, 12.2; P, 5.5%).

(4,5-Disulfanyl-1,3-dithiole-2-thionato)bis(η-trimethylsilyl-cyclopentadienyl)niobium(IV) 1. Equimolar quantities (1 mmol) of [Nb(η-$C_5H_4SiMe_3$)$_2$$Cl_2$] and $Na_2[C_3S_5]$[24] were stirred in dichloromethane (50 cm^3) overnight. The precipitated sodium choride was filtered off and the solution concentrated under vacuum. Slow addition of methanol afforded green needles (0.280 g, 50%) of [Nb($C_5H_4SiMe_3$)$_2$(C_3S_5)] 1 (Found: C, 41.2; H, 4.8. $C_{19}H_{26}NbS_5Si_2$ requires C, 40.5; H, 4.6%); $\tilde{\nu}$(KBr)/cm^{-1} 3038w (C–H), 3062w and 2942w, 1058s (C=S), 823s ($C_5H_4SiMe_3$).

Bis(η-*tert*-butylcyclopentadienyl)(4,5-disulfanyl-1,3-dithiole-2-thionato)niobium(IV) 2. This was prepared as described above from equimolar quantities (1 mmol) of [Nb(η-C_5H_4Bu^t)$_2$$Cl_2$]

Table 5 Variable-temperature ^{1}H NMR data

Complex	Solvent	T_c/°C	$\Delta G^‡$/kJ mol^{-1}	Ref.
$[Nb(cp)_2(S_2C_2Ph_2][PF_6]$	$(CD_3)_2CO$	−6	54	8, 15
$[Nb(cp)_2(S_2C_2Me_2)][PF_6]$	$(CD_3)_2CO$	+37	63	8, 15
$[Nb(cp)_2(C_3S_5)][tcnq]$	CF_3CO_2D	+56	65.5	This work
$[Nb(\eta\text{-}C_5H_4SiMe_3)_2(C_3S_5)][tcnq]$	CF_3CO_2D	+27	64	This work
$[Nb(\eta\text{-}C_5H_4SiMe_3)_2(dddt)][PF_6]$	$(CD_3)_2CO$	+26	65	This work
$[Nb(\eta\text{-}C_5H_4Bu^t)_2(C_3S_5)][tcnq]$	CF_3CO_2D	+46	67	This work
$[Nb(\eta\text{-}C_5H_4Bu^t)_2(dddt)][PF_6]$	$(CD_3)_2CO$	+47	67.5	This work
$[Ti(cp)_2(C_3S_5)]$	$CDCl_3$	+35	60	1, 2
$[Ti(cp)_2(dddt)]$	$CDCl_3$	+53	67	2

and $Na_2[C_3S_5]$. Yield 0.265 g (50%) (Found: C, 47.2; H, 4.9; S, 29.9. $C_{21}H_{26}NbS_5$ requires C, 47.5; H, 4.9; S, 30.1%); $\tilde{\nu}$(KBr)/cm^{-1} 3100w (C–H), 3078w, 2958w and 2900w, 1056s (C=S), 819s ($C_5H_4Bu^t$).

(4,5-Disulfanyl-1,3-dithiol-2-onato)bis(η-trimethylsilylcyclopentadienyl)niobium(IV) 3. This was prepared as described for complex **1** from equimolar quantities (1 mmol) of $[Nb(\eta\text{-}C_5H_4SiMe_3)_2Cl_2]$ and $Na_2[C_3OS_4]$.[25] Yield 0.275 g (50%) (Found: C, 41.3; H, 4.85; S, 22.1. $C_{19}H_{26}NbOS_4Si_2$ requires C, 41.65; H, 4.80; S, 23.45%); $\tilde{\nu}$(KBr)/cm^{-1} 3102w (C–H) and 2950w, 1656s (C=O) and 1058s, 828s ($C_5H_4SiMe_3$).

Bis(η-*tert*-butylcyclopentadienyl)(4,5-disulfanyl-1,3-dithiol-2-onato)niobium(IV) 4. When the reaction of $[Nb(\eta\text{-}C_5H_4Bu^t)_2Cl_2]$ and $Na_2[C_3OS_4]$ was conducted as described above the at first green solution slowly turned brown indicating partial decomposition of the product **4**. A shorter reaction time (2 h) allowed the isolation of impure **4** in low yield (10%).

Bis(η-*tert*-butylcyclopentadienyl)(5,6-dihydro-1,4-dithiine-2,3-dithiolato)niobium(V) hexafluorophosphate 5. Equimolar quantities (1 mmol) of $[Nb(\eta\text{-}C_5H_4Bu^t)_2Cl_2]PF_6$ and $Na_2(dddt)$[26] were dissolved at room temperature in dichloromethane (80 cm^3). After stirring overnight the dark blue solution was filtered and the filtrate concentrated under vacuum. Chromatography [SiO_2, CH_2Cl_2 then CH_2Cl_2–acetone (9 : 1)] afforded a yellow solid which was recrystallized from acetone–heptane as golden needles (0.200 g, 30%) (Found: C, 42.7; H, 5.05; S, 19.35; P, 3.75. $C_{22}H_{30}F_6NbPS_4{\cdot}Me_2CO$ requires C, 41.8; H, 5.05; S, 17.85; P, 4.30%); $\tilde{\nu}$(KBr)/cm^{-1} 3100w (C–H), 2960w, 2923w and 2850w, 833s ($C_5H_4Bu^t$), 560s (P–F). δ_H[200 MHz, $(CD_3)_2CO$, $SiMe_4$, 258 K] 6.75 (2 H, dd, 2 CH), 6.65 (2 H, dd, 2 CH), 6.18 (2 H, dd, 2 CH), 6.10 (2 H, dd, 2 CH), 3.70 (4 H, m, CH_2CH_2), 1.28 (9 H, s, 3 Me) and 1.17 (9 H, s, 3 Me).

(5,6-Dihydro-1,4-dithiine-2,3-dithiolato)bis(η-trimethylsilylcyclopentadienyl)niobium(V) hexafluorophosphate 6. This was prepared as described for complex **5**. Yield 20% (Found: C, 37.45; H, 4.80; S, 16.25; P, 3.85. $C_{20}H_{30}F_6NbPS_4Si_2{\cdot}Me_2CO$ requires C, 36.8; H, 4.85; S, 17.1; P, 4.15%); $\tilde{\nu}$(KBr)/cm^{-1} 550s (P–F). δ_H[200 MHz, $(CD_3)_2CO$, $SiMe_4$, 278 K] 6.82 (4 H, s, 4CH), 6.30 (2 H, dd, 2CH), 6.23 (2 H, dd, 2CH), 3.72 (4 H, m, CH_2CH_2), 0.30 (9 H, s, 3 Me) and 0.25 (9 H, s, 3 Me).

$[Nb(\eta\text{-}C_5H_4R)_2(C_3S_5)][tcnq]$ salts. The following procedure is representative. Warm dichloromethane solutions of equimolar quantities (0.5 mmol) of tcnq and $[Nb(\eta\text{-}C_5H_4R)_2(C_3S_5)]$ were mixed. Concentration afforded a blue precipitate which was filtered off and washed with dichloromethane. Yield: *ca.* 60%. $[Nb(cp)_2(C_3S_5)][tcnq]$ **7** (Found: C, 47.7; H, 2.25; N, 8.7; S, 25.7. $C_{25}H_{14}N_4NbS_5$ requires C, 48.15; H, 2.25; N, 9.0; S, 25.7%); $\tilde{\nu}$(KBr)/cm^{-1} 2180s (CN); δ_H(CF_3CO_2D, $SiMe_4$, 295 K) 6.56 (5 H, s, cp) and 6.02 (5 H, s, cp). $[Nb(\eta\text{-}C_5H_4SiMe_3)_2(C_3S_5)][tcnq]$ **8** (Found: C, 48.85; H, 3.50. $C_{31}H_{30}N_4NbSi_2S_5$ requires C, 48.5; H, 3.95%): $\tilde{\nu}$(KBr)/cm^{-1} 3096w (C–H), 3075w and 2954w, 2178s (CN), 1074s (C=S), 838s ($C_5H_4SiMe_3$); δ_H(CF_3CO_2D, $SiMe_4$, 295 K) 6.64 (4 H, s, 4 CH), 6.07 (4 H, br s, 4 CH) and 0.33 (18 H, br s, 6 Me). $[Nb(\eta\text{-}C_5H_4Bu^t)_2(C_3S_5)][tcnq]$ **9** (Found: C, 53.95; H, 4.05. $C_{33}H_{30}N_4NbS_5$ requires C, 53.85; H, 4.10%): $\tilde{\nu}$(KBr)/cm^{-1} 3098w (C–H), 3080w and 2957w; 2179s (CN), 1078s (C=S), 838s ($C_5H_4Bu^t$); δ_H(CF_3CO_2D, $SiMe_4$, 295 K) 6.59 (2 H, s, 2 CH), 6.50 (2 H, s, 2 CH), 5.98 (2 H, s, 2 CH), 5.93 (2 H, s, 2 CH), 1.37 (9 H, s, 3 Me) and 1.27 (9 H, s, 3 Me); Λ = 100 Ω^{-1} cm^2 mol^{-1} at 293 K for a 10^{-3} mol dm^{-3} solution in $MeNO_2$.

Electrochemical measurements

Cyclic voltammetry experiments were performed with a SOTELEM P/T potentiostat coupled with a PAR 175 universal programmer and a TGM 164 SEFRAM recorder. Acetonitrile dried on molecular sieves with 0.1 mol dm^{-3} $NBu^n_4PF_6$ was used as an electrolyte. A three-compartment cell was fitted with a platinum working electrode (diameter 2 mm), a platinum counter electrode and a Ag–0.1 mol dm^{-3} $AgClO_4$ reference electrode. Solutions were degassed by argon bubbling prior to each experiment and an argon flow was maintained throughout. The reference electrode was checked against the ferrocene–ferrocenium couple (+0.025 V) after each set of experiments. Electrochemical criteria for reversibility[27] were satisfied at low sweep rates (below 250 mV s^{-1}).

Crystallography

Crystal data and data collection parameters for $[Nb(\eta\text{-}C_5H_4SiMe_3)_2(C_3S_5)]$. $C_{19}H_{26}NbS_5Si_2$, M = 563.81, orthorhombic, space group $Pca2_1$ (no. 29), a = 19.423(1), b = 7.914(1), c = 16.066(1) Å, U = 2469.6(4) Å^3 (by least-squares refinement on diffractometer angles of 25 centred reflections, $12.5 < 2\theta < 22.5°$), T = 293 K, graphite-monochromated Mo-Kα radiation, λ = 0.710 73 Å, Z = 4, D_c = 1.516 Mg m^{-3}, green plate with dimensions 0.36 × 0.12 × 0.03 mm, μ(Mo-Kα) = 14.4 cm^{-1}, semiempirical absorption correction based on ψ scans, transmission factors 1.005, 1.1314; Enraf-Nonius CAD4F diffractometer, ω–2θ scans, data collection range $5 < 2\theta < 52°$, $+h$, $+k$, $+l$, three standard reflections showed no significant loss of intensity; 3151 reflections measured, 2867 unique (R_{int} = 0.004), 1259 observed reflections with $I > 3\sigma(I)$.

Structure solution and refinement. The structure was solved by direct methods and subsequent Fourier-difference techniques, and refined anisotropically, by full-matrix least squares on F (program XTAL 3.0).[28] Hydrogen atoms were introduced at calculated positions (C–H 0.95), included in structure-factor calculations but not refined. A weighting scheme of the form $w = 1/[\sigma^2(F_o) + 0.0025F_o^2]$ was applied; $R(F)$ = 0.058, R'(F) = 0.075 for 244 variables and 1463 reflections used, goodness of fit = 1.06, maximum Δ/σ = 0.01, maximum $\Delta\rho$ = 1.84 e Å^{-3}.

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 186/206.

Magnetic studies

X-Band EPR spectra were recorded on a Brüker ESP 300 spectrometer in dichloromethane and solid-state EPR spectra on a Varian X-band spectrometer (9.3 GHz) equipped with an Oxford ESR helium cryostat.

Variable-temperature ^{1}H NMR studies

Experiments were conducted on a 200 MHz Brücker spectrometer, the temperature being stabilized for 30 min before each measurement. Data were exploited using the Eyring equation[29] $\tau^{-1} = 2^{-\frac{1}{2}}\pi\Delta\nu$ where $\Delta G^{\ddagger} = RT_c \ln(k_B T_c \tau/h)$ and T_c = coalescence temperature.

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