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FULL PAPER

Synthesis and characterisation of monocyclopentadienyl dithiolato complexes of niobium and tantalum; crystal structures of $[Nb_2(\mu\text{-}O)(\mu\text{-}\eta^2:\eta^2\text{-}S_2C_2H_4)(\eta^5\text{-}C_5H_4Me)_2Cl_4]$ and $[Nb_2(\mu\text{-}\eta^1:\eta^2\text{-}S_2C_2H_4)_2(\eta^5\text{-}C_5H_4Me)_2O(S_2C_2H_4)]$ †

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Reactions of tetrachloro(cyclopentadienyl)niobium with arenedithiolates yielded products $[NbCp(1,2\text{-}S_2C_6H_3R\text{-}4)_2]$ ($Cp = \eta^5\text{-}C_5H_5$; R = H **1** or Me **2**), characterised primarily by analysis, ^1H NMR and mass spectroscopy. Cyclic voltammetric studies on **1** and **2** showed two consecutive, quasi-reversible, reduction processes; ESR spectra of the initial products of chemical reduction were typical of those from niobium(IV) species with an unpaired electron largely centred on the metal and assigned to the anions $[NbCp(1,2\text{-}S_2C_6H_3R\text{-}4)_2]^-$. Similar tantalum derivatives were less tractable, although properties of the more soluble species $[TaCp'(1,2\text{-}S_2C_6H_4)_2]$ ($Cp' = \eta^5\text{-}C_5H_4Me$) are reported. Reactions of tetrachloro(methylcyclopentadienyl)-niobium or -tantalum with salts of ethane-1,2-dithiol (H_2edt) were very susceptible to hydrolysis and the major isolable products of reactions using the sodium reagent (Na_2edt) were $[M_2(\mu\text{-}O)(\mu\text{-}\eta^2:\eta^2\text{-}edt)Cp'_2Cl_4]$ (M = Nb **4** or Ta **5**), containing oxo and symmetrical dithiolate bridges. Reaction of $[NbCp'Cl_4]$ with 2 molar equivalents of Tl_2edt formed the unsymmetrical compound $[Nb_2(\mu\text{-}\eta^1:\eta^2\text{-}edt)_2Cp'_2O(edt)]$ **6**, containing a terminal oxide ligand, one chelating and two unsymmetrically bridging edt groups. Structures of compounds **4** and **6** have been determined in the solid state by X-ray crystallography; 1- and 2-D NMR spectra of the binuclear products support the retention of these structures in solution.

Introduction

The chemistry of monocyclopentadienyl thiolate complexes of the early transition metals has received the attention of several groups of workers in recent years.[1] A number of monocyclopentadienyltitanium complexes with alkane-thiolate and -dithiolate ligands have been investigated[1,2] and some related mononuclear derivatives of the Group 6 metals have also been reported.[3,4] In this area we have studied a number of derivatives of Group 6 metals, including anionic complexes of the type $[MoCp(SR)_4]^-$ ($Cp = \eta^5\text{-}C_5H_5$, R = fluoroaryl group) with four-legged piano stool geometry which act as polydentate ligands to large metal cations,[5] and have also prepared anionic arene-1,2-dithiolate derivatives of titanium which interact with thallium(I) counter ions.[6] These interactions suggest potential applications of polythiolate transition metal complexes as sensors for metal ions.

For Group 5 transition metals simple monocyclopentadienyl polythiolates have only been reported for tantalum, *i.e.* $[TaCp^*(dithiolate)_2]$ ($Cp^* = \eta^5\text{-}C_5Me_5$; dithiolate = ethene-1,2-dithiolate, ethane-1,2-dithiolate and norbornane-*exo*-2,3-dithiolate; norbornane = bicyclo[2.2.1]heptane),[4,7,8] $[TaCp'(SPh)_4]$ ($Cp' = \eta^5\text{-}C_5H_4Me$),[9] and $[TaCp^*(SBu^t)_3(OBu^n)]$,[10] although several pentamethylcyclopentadienyltantalum species with simple sulfide ligands are also known.[6,11] Monocyclopentadienylniobium thiolates have only been described for lower oxidation state derivatives incorporating other ligands, *i.e.* mononuclear $[NbCp(PhC_2Ph)(SPr^i)_2]$, the related heterobimetallics $[(PhC_2Ph)CpNb(\mu\text{-}SPr^i)_2Mo(CO)_4]$ and $[Cl_2CpNb(\mu\text{-}SMe)_2NiCp]$,[12] and the dinuclear compound $[Nb_2(\mu\text{-}SMe)_2Cp_2(CO)_4]$.[13] In this paper we report the results of an investigation of monocyclopentadienyl species of niobium and tantalum, with arene- and ethane-1,2-dithiolate ligands.

Results and discussion

Complexes with arenedithiolates

Reactions of the thallium salts of toluene-3,4-dithiol and benzene-1,2-dithiol with tetrachloro(η^5-cyclopentadienyl)niobium, $[NbCpCl_4]$, in 2 : 1 molar ratios in tetrahydrofuran (thf) afforded the dithiolate derivatives $[NbCp(tdt)_2]$ **1** and $[NbCp(bdt)_2]$ **2** [$H_2tdt = 3,4\text{-}(HS)_2C_6H_3CH_3$; $H_2bdt = 1,2\text{-}(HS)_2C_6H_4$], as dark green crystalline solids in yields of 74 and 28%, respectively, which have been characterised by elemental analysis, ^1H NMR, mass and IR spectroscopy. Both complexes show well defined parent ions in EI mass spectra and fragment ions arising from loss of Cp and dithiolate groups. The ^1H NMR spectra contain typical singlet resonances for the Cp ligands and for the methyl substituent of **1**, and complex resonances for aromatic hydrogens of correct relative intensities; the latter occur as an AA′BB′ multiplet for compound **2**. No evidence can be adduced from these NMR spectra for the presence of isomers involving either *exo*/*endo* placements of the arenedithiolate ligands or *syn* and *anti* orientations of the methyl groups on the tolyl rings of **1**. These findings reflect those for related anionic titanium complexes in solution,[6] but it is notable that variable temperature NMR spectra of $[TaCp^*(SCH{=}CHS)_2]$ support the presence of interchanging *exo* and *endo* ethene-1,2-dithiolate ligands.[7] A basic four-legged piano stool geometry can be assumed for these products but crystals suitable for X-ray diffraction could not be obtained so that the conformations of the thiolate ligands in the solid state conformations were not determined. The IR spectra include bands character-

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† *Supplementary data available*: ^1H–^{13}C-{^1H} correlation NMR spectrum of compound **6**. For direct electronic access see http://www.rsc.org/suppdata/dt/1998/3281/, otherwise available from BLDSC (No. SUP 57423, 2 pp.) or the RSC Library. See Instructions for Authors, 1998, Issue 1 (http://www.rsc.org/dalton).

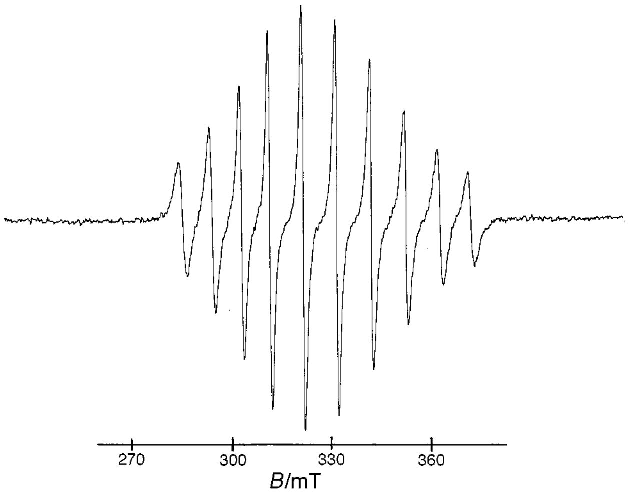
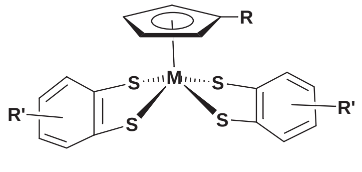


Fig. 1 The ESR spectrum of compound **1** in thf after reduction by sodium metal.

istic of the cyclopentadienyl and aromatic ligands, and the electronic spectra contain strong bands in the visible region, *e.g.* $\lambda_{max} = 409$, 451 and 660 nm for **1** in toluene.



1 M = Nb, R = H, R' = Me
2 M = Nb, R = R' = H
3 M = Ta, R = R' = Me

Cyclic voltammetric studies of complexes **1** and **2** in thf show the presence of two reduction processes having well defined cathodic and anodic peaks with $E_{\frac{1}{2}} = -0.69$, -2.00 V and -0.84, -2.14 V, for **1** and **2**, respectively (values quoted relative to $[FeCp_2]^{+/0}$). The anodic–cathodic peak separations, ΔE_{pp} 150–180 mV, are slightly greater than for the reversible ferrocene couple under the same experimental conditions but the ratios of cathodic to anodic peak currents are close to unity. These results support the occurrence of two quasi-reversible redox reactions forming mono- and di-anionic species of Nb^{IV} and Nb^{III}, as in eqn. (1). Similar two step redox processes have

$$[NbCp(S_2C_6H_3R)_2] \overset{+e}{\underset{-e}{\rightleftharpoons}} [NbCp(S_2C_6H_3R)_2]^- \overset{+e}{\underset{-e}{\rightleftharpoons}} [NbCp(S_2C_6H_3R)_2]^{2-} \quad (1)$$

been reported for bis(cyclopentadienyl) derivatives of niobium: complexes with unsaturated dithiolate ligands, $[NbCp_2(dithiolate)]$, show two reversible 1-electron processes linking niobium(V) and -(III) states,[14] and other niobium(IV) species, $[NbCp_2X_2]$, undergo 1-electron oxidations and reductions although chemical irreversibility has been noted in some systems.[15]

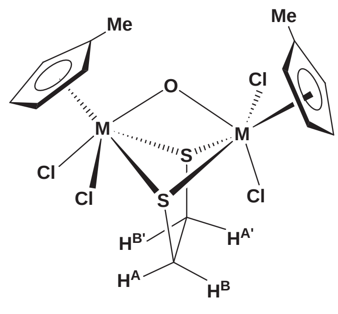
Brief reactions of complexes **1** or **2** in thf with a sodium mirror in an evacuated ESR cell caused the deep green solutions to become deep red-orange, and the resulting solutions from either precursor gave similar ten-line ESR spectra typical of d^1 niobium(IV) species with $g_{iso} = 1.991$ and $A_{iso}(^{93}Nb) = 0.0090$ cm^{-1} (see Fig. 1). The paramagnetic species are likely to be the anions $[NbCp(S_2C_6H_3R)_2]^-$ and the g and A values are consistent with an unpaired electron primarily located on Nb^{IV} with a little delocalisation onto the ligands.[15] Similar ESR spectra have been reported for bis(cyclopentadienyl)niobium(IV) complexes with sulfur ligands.[14b–17] Reaction of **1** with an equimolar amount of cobaltocene in thf also forms an orange-brown soluble product which gives an ESR spectrum with parameters identical to the product of sodium reduction and can be assigned to $[CoCp_2][NbCp(tdt)_2]$, but this reaction also produces some insoluble material. Attempts to isolate the niobium(IV) complex anion in a pure solid, either as the cobaltocenium or the $[N(PPh_3)_2]^+$ salt, were unsuccessful.

Although reactions of $[TaCpCl_4]$ with thallium salts of toluene-3,4-dithiolate or benzene-1,2-dithiolate gave insoluble products which were not characterised, the methylcyclopentadienyl derivative, $[TaCp'Cl_4]$, gave products which were more soluble. The ^1H NMR spectrum of the dark blue, hydrocarbon-soluble solid formed from toluene-3,4-dithiolate supported its formulation as $[TaCp'(tdt)_2]$ **3**; the EI mass spectrum included the ion $[M - Cp']^+$. However, attempts to purify this product, or the related benzenedithiolate, led to some decomposition with the liberation of free dithiol so that analytically pure samples could not be obtained.

Complexes with ethane-1,2-dithiolate

Reactions were conducted between tetrachloro(cyclopentadienyl)-niobium or -tantalum reagents and ethane-1,2-dithiolates with the intention of producing bis(dithiolate) complexes analogous to those described above but containing a saturated dithiolate ligand. However, these systems were highly susceptible to hydrolysis and all reactions led only to the isolation of characterised products in which an oxygen ligand derived from the presence of adventitious moisture was also introduced. The metal tetrachloride starting materials were unhydrolysed and it is believed that the small amounts of water were introduced by the use of incompletely dried ethane-1,2-dithiolate salts. The addition of oxygen ligands to early transition metals during the preparation of thiolate derivatives has also been reported by other workers.[3,4] It should be noted that although $[TaCp^*(edt)_2]$ (H_2edt = ethane-1,2-dithiol) has been prepared and its stability may be enhanced by the presence of the bulky pentamethylcyclopentadienyl ring, this compound is reported to be moisture sensitive and liable to C–S bond cleavage.[4]

$[M_2(\mu\text{-}O)(\mu\text{-}\eta^2\!:\!\eta^2\text{-}S_2C_2H_4)Cp'_2Cl_4]$ (M = Nb or Ta). The reaction of an excess of Na_2edt with $[NbCp'Cl_4]$ in toluene gave a high yield of a deep red crystalline product characterised as $[Nb_2(\mu\text{-}O)(\mu\text{-}edt)Cp'_2Cl_4]$ **4**. A similar reaction with $[TaCp'Cl_4]$ in dichloromethane gave yellow $[Ta_2(\mu\text{-}O)(\mu\text{-}edt)Cp'_2Cl_4]$ **5** as the only isolable product but in lower yield. The formulation of these unexpected products was based primarily on elemental analyses, ^1H NMR spectra and EI mass spectroscopy, and confirmed for **4** by a crystal structure determination.



4 M = Nb
5 M = Ta

The ^1H NMR spectrum of complex **4** indicated the presence of one edt and two Cp′ ligands; one singlet resonance is observed from the methyl groups on two equivalent Cp′ groups and three multiplet resonances of relative intensities 2 : 1 : 1 are assigned to four inequivalent ^1H nuclei on each ring, with two signals overlapping. The inequivalence of all ring hydrogens arises from the asymmetry of a molecule which also generates an AA′BB′ system from the hydrogen nuclei of edt, as illustrated in the structural diagram. The shifts and coupling constants of the AA′BB′ multiplet were assigned by simulation (see

Table 1 Selected bond lengths (Å) and angles (°) for compound **4**

Nb(1)–O(1)	1.928(2)	Nb(1)–S(1)	2.5795(10)
Nb(1)–Cl(1)	2.4523(10)	Nb(1)–S(1A)	2.6443(9)
Nb(1)–Cl(2)	2.4123(10)	S(1)–C(1)	1.811(4)
Nb(1)–Cp′(1)	2.128(2)	C(1)–C(1A)	1.540(7)
O(1)–Nb(1)–Cl(1)	152.84(9)	Nb(1)–O(1)–Nb(1A)	116.2(2)
O(1)–Nb(1)–Cl(2)	91.24(5)	Nb(1)–S(1)–Nb(1A)	77.58(3)
Cl(1)–Nb(1)–Cl(2)	90.68(3)	C(1)–S(1)–Nb(1)	103.90(13)
O(1)–Nb(1)–S(1)	76.20(8)	C(1)–S(1)–Nb(1A)	105.36(13)
Cl(1)–Nb(1)–S(1)	88.36(3)	C(1A)–C(1)–S(1)	113.42(12)
Cl(2)–Nb(1)–S(1)	148.68(3)	Cp′(1)–Nb(1)–O(1)	101.38(7)
O(1)–Nb(1)–S(1A)	74.58(8)	Cp′(1)–Nb(1)–Cl(1)	104.14(3)
Cl(1)–Nb(1)–S(1A)	79.19(3)	Cp′(1)–Nb(1)–Cl(2)	105.74(3)
Cl(2)–Nb(1)–S(1A)	79.18(3)	Cp′(1)–Nb(1)–S(1)	104.83(2)
S(1)–Nb(1)–S(1A)	69.89(4)	Cp′(1)–Nb(1)–S(1A)	173.86(2)

Symmetry transformations used to generate equivalent atoms: A $-x + 1$, y, $-z + \frac{1}{2}$. Cp′(1) = Centroid of η^5-methylcyclopentadienyl ring bonded to Nb(1).

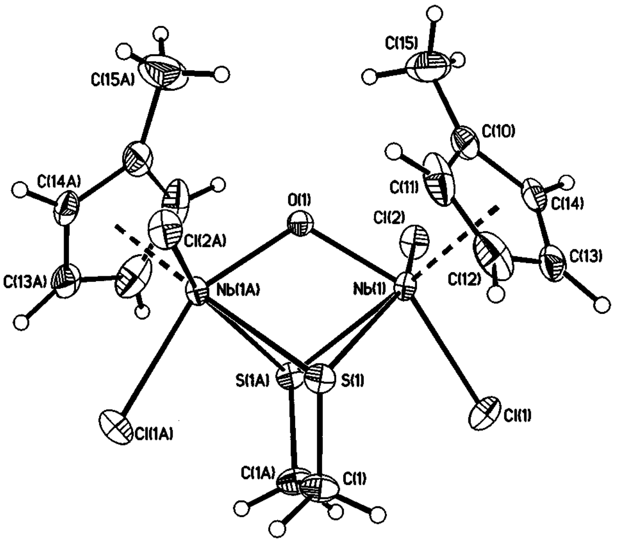


Fig. 2 Perspective view of compound **4** (50% probability displacement ellipsoids).

Experimental section). The tantalum analogue, **5**, has a related ^{1}H NMR spectrum and is assigned the same structure.

A red crystal of complex **4** obtained from dichloromethane–light petroleum was structurally analysed by X-ray diffraction at 160 K. Fig. 2 shows a perspective view of the binuclear structure which contains a single oxygen bridge and an edt ligand bridging in a η^2:η^2 manner. Each molecule is chiral but has a C_2 symmetry axis which generates equivalent pairs of atoms; overall, the crystal consists of a racemic mixture. Table 1 lists selected geometrical parameters. The structure is similar to that found for [{Nb(η^5-$C_5H_4SiMe_3$)Cl_2}$_2$(μ-O)(μ-Cl)$_2$][18] in which two bridging chlorines replace the dithiolate ligand. If the Cp′ ring is considered to occupy one site each Nb atom is formally six-co-ordinate with a distorted octahedral arrangement of ligands. The Cp′ ligand is *trans* to a bridging S atom with an angle Cp′ (centroid)–Nb–S of 173.86(2)°, and the other ligands are *cis* to Cp′ with angles in the range 101.4–105.7°. The terminal Nb–Cl bond lengths and the bent Nb–O–Nb bridge [angle 116.2(2)°] are comparable to those found in [{Nb(η^5-$C_5H_4SiMe_3$)Cl_2}$_2$(μ-O)(μ-Cl)$_2$].[18] The Nb-Cl(1) bond *trans* to O(1) [2.4523(10)Å] is somewhat longer than Nb-Cl(2) *trans* to S(1) [2.4123(10)Å].

Bridging η^2:η^2-edt ligands have been reported in complexes of other early transition metals, including vanadium and molybdenum derivatives, [V_2(edt)$_4$]$^{2-}$,[19] [V_2Cp_2(edt)$_2$][20] and [$Mo_2Cp_2(S_2C_2H_3R)_2$]$^{n+}$ (n = 0, 1 or 2; R = H or Me),[21] but these species have short metal–metal distances. The absence of a Nb–Nb bond in **4** is evident from the intermetallic separation of 3.2728(7)Å. Moreover, the Nb(1)-S-Nb(1A) angles in **4** of 77.58(3)° are greater than in the structurally characterised vanadium and molybdenum complexes and are probably largely determined by the geometry of the oxygen bridge. The two Nb–S bonds differ, with the longer bond being *trans* to the Cp′ ligand.

The presence of four chloride ligands in these binuclear products suggested the possibility of further substitution by thiolate ligands. Therefore, compound **4** in thf was treated for 16 h at room temperature with Tl_2bdt in a 1:2 molar ratio. After filtration, a green solid was obtained from the filtrate which, on the basis of its ^{1}H NMR spectrum and similar physical properties, was identified as [NbCp′(bdt)$_2$], analogous to **2**. It appears that the unsaturated benzene-1,2-dithiolate is a significantly better ligand to the Cp′Nb entity and completely displaces chloride, oxide and ethanedithiolate ligands from one of the niobium centres. This comparative stability of the arenedithiolate complex and the displacement of an oxygen ligand may also explain why no obvious interference from trace amounts of water was encountered in the preparations of compounds **1** and **2**.

[Nb_2(μ-η^1:η^2-1,2-$S_2C_2H_4$)$_2$Cp′$_2$O($S_2C_2H_4$)]. The reaction of [NbCp′Cl_4] with 2 molar equivalents of Tl_2edt in thf afforded a red crystalline solid as the only isolable product in approximately 50% yield. This solid product was characterised as the monodichloromethane solvate [Nb_2(μ-η^1:η^2-edt)$_2$Cp′$_2$O(edt)]·CH_2Cl_2 **6**, on the basis of elemental analysis, NMR studies and determination of its molecular structure by X-ray diffraction. The ^{1}H and ^{13}C-{^{1}H} NMR spectra confirmed the stoichiometry of Cp′ and ethanedithiolate ligands in the complex but showed a range of reproducible inequivalent resonances consistent with a rigid but highly unsymmetrical species so that assignment of the spectra was not possible until the solid state molecular structure had been established.

A dark purple crystal of complex **6**, as the monodichloromethane adduct, was subjected to X-ray diffraction at ambient temperature. The crystal contains two independent, but structurally similar, asymmetric binuclear molecules. The two structures are depicted in Fig. 3 with important atom labelling; geometric parameters differ only slightly between the two forms and the major difference lies in the orientations of the methyl groups of the Cp′ rings. Selected bond distances and angles are given in Table 2. Each Nb atom is η^5 bonded to a methylcyclopentadienyl ligand and one Nb atom in a molecule also has a terminal oxygen ligand. The ethanedithiolate ligands show two bonding modes: one edt ligand chelates the Nb atom without a terminal oxygen, and two edt ligands bridge the two metals in an unsymmetrical η^1:η^2 manner. The closest contacts between the metal complexes and the dichloromethane molecules of solvation are weak being on the boundaries of the sum of the van der Waals radii of the involved atoms [O(2)···H(60B) 2.399(9), O(1)···H(60A) 2.499(10) and H(26B)···Cl(4) 2.610(16)Å].

In each molecule one Nb atom is six-co-ordinate with a distorted octahedron of three terminal sulfurs, two bridging sulfurs and Cp′ as ligands. The other Nb atom is five-co-ordinate with an oxygen, one terminal sulfur, two bridging sulfurs and Cp′ as ligands and the Cp′ is approximately *trans* to a bridging sulfur [e.g. Cp′ (centroid)–Nb(2)–S(6) 163.6(1)°] but has angles of *ca.* 100° to other ligands; the overall geometry can be viewed either as a distorted square pyramid with Nb=O occupying the axial site or as a distorted trigonal bipyramid with axial Cp′ and equatorial Nb=O. The bonding of the Cp′ ligands is normal, although all mean Nb–Cp′ bond distances are slightly longer than in compound **4**, despite data on **6** being collected at room temperature, and the longest bonds are to the Nb atoms carrying a terminal oxygen ligand. The bond length of the terminal oxygen (mean 1.735 Å) is shorter than the bridging Nb–O length in **4**, as expected for double-bond character.

The bonding of the terminal bidentate edt to the six-co-

Table 2 Selected bond lengths (Å) and angles (°) for compound **6**

Nb(1)–S(1)	2.445(2)	Nb(4)–S(7)	2.460(2)	Nb(2)–Cp′(2)	2.197(1)	Nb(3)–Cp′(3)	2.190(1)
Nb(1)–S(2)	2.577(2)	Nb(4)–S(8)	2.584(2)	S(1)–C(1)	1.807(7)	S(7)–C(55)	1.819(7)
Nb(1)–S(3)	2.435(2)	Nb(4)–S(9)	2.412(2)	S(2)–C(2)	1.834(7)	S(8)–C(56)	1.828(7)
Nb(1)–S(4)	2.576(2)	Nb(4)–S(10)	2.583(2)	C(1)–C(2)	1.515(11)	C(55)–C(56)	1.501(10)
Nb(1)–S(6)	2.565(2)	Nb(4)–S(12)	2.558(2)	S(3)–C(3)	1.818(7)	S(9)–C(51)	1.813(8)
Nb(2)–S(4)	2.590(2)	Nb(3)–S(10)	2.582(2)	S(4)–C(4)	1.821(7)	S(10)–C(52)	1.816(7)
Nb(2)–S(5)	2.484(2)	Nb(3)–S(11)	2.466(2)	C(3)–C(4)	1.496(10)	C(51)–C(52)	1.506(10)
Nb(2)–S(6)	2.615(2)	Nb(3)–S(12)	2.622(2)	S(5)–C(5)	1.818(7)	S(11)–C(53)	1.818(7)
Nb(2)–O(1)	1.729(5)	Nb(3)–O(2)	1.741(5)	S(6)–C(6)	1.824(7)	S(12)–C(54)	1.822(6)
Nb(1)–Cp′(1)	2.144(1)	Nb(4)–Cp′(4)	2.138(1)	C(5)–C(6)	1.513(10)	C(53)–C(54)	1.503(9)
S(1)–Nb(1)–S(2)	79.07(7)	S(7)–Nb(4)–S(8)	79.03(6)	S(4)–Nb(2)–S(6)	70.52(5)	S(10)–Nb(3)–S(12)	70.56(5)
S(1)–Nb(1)–S(3)	98.72(7)	S(7)–Nb(4)–S(9)	98.81(6)	S(5)–Nb(2)–S(6)	78.27(6)	S(11)–Nb(3)–S(12)	79.13(6)
S(1)–Nb(1)–S(4)	84.30(6)	S(7)–Nb(4)–S(10)	82.95(6)	Nb(1)–S(4)–Nb(2)	102.11(6)	Nb(3)–S(10)–Nb(4)	100.68(6)
S(1)–Nb(1)–S(6)	146.86(6)	S(7)–Nb(4)–S(12)	145.96(6)	Nb(1)–S(6)–Nb(2)	101.69(6)	Nb(4)–S(12)–Nb(3)	100.28(6)
S(2)–Nb(1)–S(3)	149.25(6)	S(8)–Nb(4)–S(9)	149.62(7)	Cp′(1)–Nb(1)–S(1)	101.1(1)	Cp′(4)–Nb(4)–S(7)	101.8(1)
S(2)–Nb(1)–S(4)	71.28(6)	S(8)–Nb(4)–S(10)	71.93(5)	Cp′(1)–Nb(1)–S(2)	111.0(1)	Cp′(4)–Nb(4)–S(8)	110.7(1)
S(2)–Nb(1)–S(6)	71.99(6)	S(8)–Nb(4)–S(12)	71.95(5)	Cp′(1)–Nb(1)–S(3)	99.6(1)	Cp′(4)–Nb(4)–S(9)	99.4(1)
S(3)–Nb(1)–S(4)	77.97(6)	S(9)–Nb(4)–S(10)	77.72(6)	Cp′(1)–Nb(1)–S(4)	174.4(1)	Cp′(4)–Nb(4)–S(10)	174.9(1)
S(3)–Nb(1)–S(6)	98.01(6)	S(9)–Nb(4)–S(12)	97.40(6)	Cp′(1)–Nb(1)–S(6)	104.0(1)	Cp′(4)–Nb(4)–S(12)	104.8(1)
S(4)–Nb(1)–S(6)	71.52(5)	S(10)–Nb(4)–S(12)	71.56(5)	Cp′(2)–Nb(2)–O(1)	108.8(2)	Cp′(3)–Nb(3)–O(2)	107.1(2)
O(1)–Nb(2)–S(4)	90.8(2)	O(2)–Nb(3)–S(10)	92.4(2)	Cp′(2)–Nb(2)–S(4)	105.3(1)	Cp′(3)–Nb(3)–S(10)	105.8(1)
O(1)–Nb(2)–S(5)	102.6(2)	O(2)–Nb(3)–S(11)	102.9(2)	Cp′(2)–Nb(2)–S(5)	100.3(1)	Cp′(3)–Nb(3)–S(11)	99.6(1)
O(1)–Nb(2)–S(6)	87.3(2)	O(2)–Nb(3)–S(12)	86.2(2)	Cp′(2)–Nb(2)–S(6)	163.6(1)	Cp′(3)–Nb(3)–S(12)	166.5(1)
S(4)–Nb(2)–S(5)	145.37(7)	S(10)–Nb(3)–S(11)	144.98(6)				

Cp′(x) = Centroid of η^5-methylcyclopentadienyl ring.

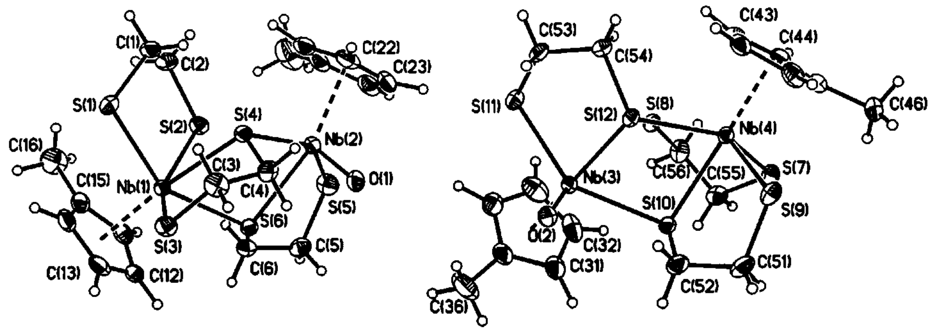
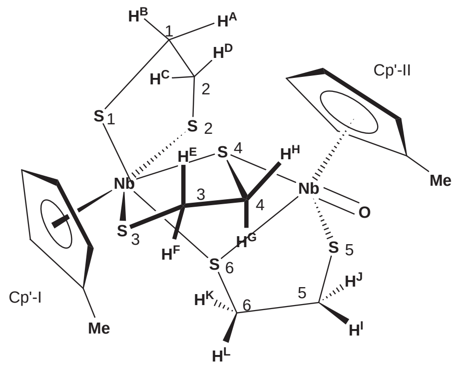


Fig. 3 Perspective view of the two structurally different units of compound **6** (30% probability displacement ellipsoids).

ordinate niobium centres is distinctly asymmetric and the two Nb–S distances differ by 0.12–0.13 Å, with the shorter bond being *trans* to a bridging sulfur and the longer *trans* to a terminal sulfur of a μ-η^2:η^1-edt ligand. The shorter bonds are closer to Nb–S lengths in $[Nb(edt)_3]^-$ [2.425(1)–2.4422(9)Å][22] but the bite angle of the chelating ligand [79.07(7)°] in **6** is smaller than 81.58(4)–82.14(4)° observed in the less hindered homoleptic complex anion. The bridging edt ligands in **6** clearly show shorter Nb–S bonds for terminal than for bridging S donors, and both types of bond are all slightly longer at the Nb with a Nb=O bond. A pair of edt bridges of similar orientation has been structurally confirmed in the titanium complexes $[Ti_2(\mu\text{-}\eta^1{:}\eta^2\text{-edt})_2X_2Cp_2]$ (X = Cl or SPh).[23] In the structurally characterised diniobium(IV) anion $[Nb_2(\mu\text{-OMe})(\mu\text{-}\eta^1{:}\eta^2\text{-pdt})_2(OMe)_2(pdt)]^-$,[24] there are two similar unsymmetrical propane-1,3-dithiolate (pdt) bridges but both terminal S donors are attached to the same Nb, and a terminal chelating pdt is bonded to the other Nb.

It is clear from the solid state structure that all H and C atoms of the edt and Cp′ ligands in a molecule of complex **6** are in different chemical environments. If this structure is retained in solution these nuclei, other than the two sets of three H atoms of freely rotating methyl groups, should give rise to inequivalent NMR resonances. However, the two structural forms observed in the solid state should become equivalent *via* rotation of Cp′ ligands at normal temperatures.



6

The ^1H and ^{13}C-{^1H} NMR spectra of complex **6** in $CDCl_3$ have been assigned with the aid of ^1H–^1H COSY and NOESY and ^1H–^{13}C-{^1H} correlation spectra (*e.g.* see SUP 57423) and are consistent with a rigid asymmetric binuclear structure related to that in the crystals. The ^1H nuclei of methyl groups of the inequivalent Cp′ ligands, labelled I and II in the structural diagram, resonate as two singlets and the four C–H units on each ring give rise to separate multiplets in the range δ 5.78–6.76; similarly all corresponding ^{13}C resonances occur as separate resonances. Assignment of resonances to specific rings have been made from the 2-D spectra (see Experimental section) and differentiation between rings I and II has been tentatively made on the basis of chemical shifts and the observation of positive NOE interactions between ring hydrogens and hydrogens of neighbouring edt ligands. All hydrogen (H^A–H^L) and carbon (C^1–C^6) atoms of the ethanedithiolate ligands give separate resonances, although three of the ^{1}H signals occur as overlapping multiplets (*i.e.* H^{B}/H^{J}, H^{D}/H^{I} and H^{F}/H^{K}); most probable assignments of these resonances derived from the 2-D correlation spectra, from magnitudes of *vic*-^{1}H–^{1}H coupling constants which show typical axial/equatorial behaviour, and from differences in chemical shifts are given in the Experimental section with values for resolvable coupling constants.

These results show that the novel asymmetric structure of compound **6** is found both in solution and solid states; the differing co-ordination modes of ethane-1,2-dithiolate ligands in the two binuclear compounds **6** and **4** are of interest. It is not clear at which stage of the reaction hydrolysis forms the oxide ligands in compounds **4** and **6** but this only occurs in the presence of ethanedithiolate which is the likely source of water and may also promote the hydrolysis. It is possible that compound **4** is a precursor in the formation of **6**. The preparations of complexes **1** and **2** with unsaturated arenedithiolates are notably less susceptible to hydrolysis.

Experimental

Reactions and operations were conducted under an atmosphere of dry, oxygen-free nitrogen gas, using Schlenk techniques. Solvents were thoroughly dried, using sodium (toluene), sodium–benzophenone (diethyl ether, tetrahydrofuran, light petroleum) or calcium hydride (dichloromethane), and freshly distilled before use. Light petroleum had a boiling range of 60–80°C. Starting materials [MCpCl$_4$] and [MCp′Cl$_4$] (M = Nb or Ta) were prepared by a literature method.[25] Benzene-1,2-dithiol, toluene-3,4-dithiol, ethane-1,2-dithiol, and thallium(I) acetate were obtained commercially (Lancaster, Fluka or Aldrich Chemical Companies) and used as supplied. Thallium dithiolates were made by reaction of thallium(I) acetate and dithiol in methanol and disodium ethane-1,2-dithiolate was produced from finely divided sodium and ethane-1,2-dithiolate in diethyl ether; these dithiolate salts were washed with diethyl ether and light petroleum, and dried *in vacuo* at ambient temperature before use, but still retained traces of water which influenced the course of some reactions. The IR spectra were measured on a Nicolet Impact 400 FT spectrometer, EI mass spectra on an upgraded VG MS9 instrument and ^{1}H and ^{13}C-{^{1}H} NMR spectra using Bruker AC 200 and DPX 400 spectrometers with SiMe$_4$ as internal reference. Cyclic voltammograms were measured at ambient temperature with a scan rate of 0.1 V s^{-1} on thf solutions containing 0.1 M NBu$^{n}_{4}$PF$_6$ as supporting electrolyte, using platinum electrodes and an aqueous SCE reference electrode; no compensation was made for solution *IR* drop and under these conditions $E_{\frac{1}{2}} = 0.51$ V and $\Delta E_{pp} = 120$ mV for [FeCp$_2$]$^{+/0}$. The ESR spectra were measured at ambient temperature on a JEOL PE1 X band spectrometer, using diphenylpicrylhydrazyl as reference and a Bruker NMR field marker. Elemental analyses were carried out at UMIST, Manchester, UK, and at Heriot-Watt University.

Preparations

[Nb(η^{5}-C$_5$H$_5$)(3,4-S$_2$C$_6$H$_3$CH$_3$-1)$_2$] 1. The compound [NbCpCl$_4$] (0.20 g, 6.7 × 10^{-4} mol) was suspended in thf (20 cm^3). To the stirred suspension was added 3,4-(TlS)$_2$C$_6$H$_3$CH$_3$ (0.74 g, 1.3 × 10^{-3} mol). The red-orange suspension quickly changed to deep green and was left to stir at room temperature for 16 h. Filtration and evaporation of solvent from the filtrate *in vacuo* yielded a dark green solid. Recrystallisation from toluene–light petroleum gave pure [NbCp(S$_2$C$_6$H$_3$CH$_3$)$_2$] (0.23 g, 74%) (Found: C, 48.6; H, 3.5; S, 27.7. C$_{19}$H$_{17}$NbS$_4$ requires C, 48.9; H, 3.7; S, 27.5%). ^{1}H NMR (CDCl$_3$, 20 °C): δ 2.3 (s, 6 H, CH$_3$), 6.1 (s, 5 H, C$_5$H$_5$), 7.0 (m, 2 H, H^{6} of C$_6$H$_3$) and 7.5 (complex, 4 H, H^{2} and H^{5} of C$_6$H$_3$). IR (KBr) significant bands, cm^{-1}: 3108, 1580, 1440, 1082, 1017, 824 and 806. EI MS, *m*/*z* significant ions: 466 (100, [M]$^+$), 401 (73 [M − Cp]$^+$), 308 {4, [(S$_2$C$_7$H$_6$)$_2$]$^+$} and 154 (3, [S$_2$C$_7$H$_6$]$^+$).

[Nb(η^{5}-C$_5$H$_5$)(1,2-S$_2$C$_6$H$_4$)$_2$] 2. The compound [NbCpCl$_4$] (0.27 g, 9.0 × 10^{-4} mol) was dissolved in thf (50 cm^3) and 1,2-(TlS)$_2$C$_6$H$_4$ (1.0 g, 1.8 × 10^{-3} mol) added. The mixture quickly changed from orange to dark green, with formation of insoluble TlCl. It was stirred for 5 h and then filtered. Solvent was removed from the filtrate and the product dried *in vacuo* overnight. Recrystallisation from CH$_2$Cl$_2$–light petroleum yielded dark green microcrystals of [NbCp(S$_2$C$_6$H$_4$)$_2$] (0.11 g, 28%) (Found: C, 45.9; H, 3.1. C$_{17}$H$_{13}$NbS$_4$ requires C, 46.6; H, 3.0%). ^{1}H NMR (CDCl$_3$, 20 °C): δ 6.18 (s, 5 H, C$_5$H$_5$), 7.20 (BB′ part of AA′BB′, m, 4 H, H^{4,5} of C$_6$H$_4$) and 7.75 (AA′ part of AA′BB′, m, 4 H, H^{3,6} of C$_6$H$_4$). IR (KBr) significant bands, cm^{-1}: 3090, 1636, 1437, 1236, 1112, 1018, 824 and 748. EI MS, *m*/*z* significant ions: 438 (100, [M]$^+$), 373 (100 [M − Cp]$^+$) and 297 (34, [M − S$_2$C$_6$H$_4$]$^+$).

[Ta(η^{5}-C$_5$H$_4$Me)(3,4-S$_2$C$_6$H$_3$CH$_3$-1)$_2$] 3. Reaction of [TaCp′Cl$_4$] and 3,4-(TlS)$_2$C$_6$H$_3$CH$_3$ in 1 : 2 molar ratio under conditions described above yielded a dark blue solid as the primary product, but purification by recrystallisation from various solvents was unsuccessful. ^{1}H NMR (CDCl$_3$, 20 °C): δ 2.3 (s, 6 H, C$_6$H$_3$C*H*$_3$), 2.4 (s, 3 H, C$_5$H$_4$*Me*), 5.8 and 6.02 (AA′ and BB′ components, 4 H, C$_5$*H*$_4$Me), 6.95 (m, 2 H, H^{6} of C$_6$H$_3$), 7.41 (m, 2 H, H^{2} of C$_6$H$_3$) and 7.47 (d, 2 H, H^{5} of C$_6$H$_3$). EI MS, *m*/*z* significant ions: 489 ([M − Cp′]$^+$) and 308 ([S$_2$C$_6$H$_3$CH$_3$]$_2$$^+$].

[Nb$_2$(μ-O)(μ-η^{2} : η^{2}-1,2-S$_2$C$_2$H$_4$)(η^{5}-C$_5$H$_4$Me)$_2$Cl$_4$] 4. The compound [NbCp′Cl$_4$] (0.18 g, 5.7 × 10^{-4} mol) was dissolved in toluene (10 cm^3) and 1,2-(NaS)$_2$C$_2$H$_4$ (0.16 g, >2 equivalents) added. Soon after mixing the mixture acquired a red coloration and was stirred for 3 h at room temperature. Filtration through Celite, followed by removal of solvent *in vacuo*, yielded a dark red solid. Purification from CH$_2$Cl$_2$-light petroleum afforded red, crystalline [Nb$_2$(μ-O)(μ-S$_2$C$_2$H$_4$)Cp′$_2$Cl$_4$] (0.16 g, 93%) (Found: C, 28.3; H, 3.0. C$_{14}$H$_{18}$Cl$_4$Nb$_2$OS$_2$ requires C, 28.3; H, 3.0%). ^{1}H NMR (CDCl$_3$, 20 °C) δ 2.32 (s, 6 H, C$_5$H$_4$*Me*), 3.48 and 4.01 {AA′BB′ system, 4 H, $^{2}J_{AB(gem)} = -7.5$, $^{3}J_{AB'(cis)} = 11.0$, $^{3}J_{AA'(trans)} \approx {}^{3}J_{BB'(trans)} = 2.5$ Hz (±0.5), S$_2$C$_2$H$_4$}, 6.33 (m, 2 H, C$_5$*H*$_4$Me), 6.63 (m, 2 H, C$_5$*H*$_4$Me) and 6.85 (m, 4 H, C$_5$*H*$_4$ Me). EI MS *m*/*z* (^{35}Cl): 564 (1%, [M − C$_2$H$_4$]$^+$); 306 (1%, [Cp′NbCl$_2$S$_2$]$^+$; 274 (31%, [Cp′NbCl$_2$S]$^+$); 258 (53%, [Cp′NbCl$_2$O]$^+$).

[Ta$_2$(μ-O)(μ-η^{2} : η^{2}-1,2-S$_2$C$_2$H$_4$)(η^{5}-C$_5$H$_4$Me)$_2$Cl$_4$] 5. The compound [TaCp′Cl$_4$] (0.20 g, 5.0 × 10^{-4} mol) was dissolved in CH$_2$Cl$_2$ (10 cm^3) and 1,2-(NaS)$_2$C$_2$H$_4$ (0.14 g, 1 × 10^{-3} mol) added. The mixture was stirred at room temperature for 16 h. Filtration through Celite and removal of solvent from the filtrate yielded a yellow-orange solid. Recrystallisation from CH$_2$Cl$_2$–light petroleum afforded yellow [Ta$_2$(μ-O)(μ-S$_2$C$_2$H$_4$)-Cp′$_2$Cl$_4$] (0.050 g, 26%) (Found: C, 21.9; H, 2.3; Cl, 18.1; S, 8.1. C$_{14}$H$_{18}$Cl$_4$OS$_2$Ta$_2$ requires C, 21,8; H, 2.3; Cl, 18.4; S, 8.3%). ^{1}H NMR (CDCl$_3$, 20 °C): δ 2.46 (s, 6 H, C$_5$H$_4$*Me*), 3.51 and 4.29 (AA′BB′ system, 4 H, S$_2$C$_2$H$_4$), 6.15 (m, 2 H, C$_5$*H*$_4$Me), 6.41 (m, 2 H, C$_5$*H*$_4$Me) and 6.60 (m, 4 H, C$_5$*H*$_4$Me).

[Nb$_2$(μ-η^{1} : η^{2}-1,2-S$_2$C$_2$H$_4$)$_2$(η^{5}-C$_5$H$_4$Me)$_2$O(1,2-S$_2$C$_2$H$_4$)]·CH$_2$Cl$_2$ 6. The compound [NbCp′Cl$_4$] (0.19 g, 6.0 × 10^{-4} mol) was suspended in thf (10 cm^3) and 1,2-(TlS)$_2$C$_2$H$_4$ (0.60 g, 1.2 × 10^{-3} mol) was suspended in thf. The two suspensions were mixed and the reaction stirred overnight at room temperature. The red mixture was filtered through Celite and the solvent removed *in vacuo*, yielding a red solid. Purification by recrystallisation from CH$_2$Cl$_2$–light petroleum afforded red crystals of [NbCp′$_2$O(S$_2$C$_2$H$_4$)$_3$]·CH$_2$Cl$_2$ (0.10 g, 46%) (Found: C, 31.4; H, 3.7. C$_{19}$H$_{28}$Cl$_2$Nb$_2$OS$_6$ requires C, 31.6; H, 3.9%). ^{1}H NMR (CDCl$_3$, 20 °C): δ 2.23 (s and m, 4 H, C$_5$H$_4$*Me*-I and H^{A} of S$_2$C$_2$H$_4$), 2.45 (s, 3 H, C$_5$H$_4$*Me*-II), 2.67 (m, $^{2}J_{gem} = 13$,

Table 3 Crystallographic data for complexes **4** and **6**

	4	**6**
Formula	$C_{14}H_{18}Cl_4Nb_2OS_2$	$C_{18}H_{26}Nb_2OS_6\cdot CH_2Cl_2$
M	594.02	721.49
T/K	160(2)	293(2)
System	Monoclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$
a/Å	11.744(2)	10.2778(7)
b/Å	9.4404(13)	11.3022(8)
c/Å	18.031(2)	23.120(2)
α/°		98.609(7)
β/°	106.489(9)	96.039(9)
γ/°		90.532(5)
U/Å^3, Z	1916.8(4), 4	2639.8(4), 4
μ(Mo-Kα)/mm^{-1}	1.970	1.557
Data measured	2195	10987
Unique data	1668 (R_{int} = 0.0292)	9279 (R_{int} = 0.0354)
R, $wR2$ [$I > 2\sigma(I)$ data]	0.0293, 0.0785	0.0459, 0.0953
(all data)	0.0345, 0.0841	0.0809, 0.1198

$^3J_{trans}$ = 13.3, $^3J_{cis}$ = 4.2, 1 H, H^E of $S_2C_2H_4$), 3.02 (m, $^2J_{gem}$ = 13.6, $^3J_{trans}$ = 13.6, $^3J_{cis}$ = 3.3, 1 H, H^C of $S_2C_2H_4$), 3.25 (m, 2 H, overlapping H^F and H^K of μ-$S_2C_2H_4$), 3.51 (m, 2 H, overlapping H^D of $S_2C_2H_4$ and H^I of μ-$S_2C_2H_4$), 3.72 (m, 2 H, overlapping H^B and H^J of μ-$S_2C_2H_4$), 3.99 (m, $^2J_{gem}$ = 12, $^3J_{cis}$ = 4, 1 H, H^H of μ-$S_2C_2H_4$), 4.14 (m, $^2J_{gem}$ = 12.6, $^3J_{trans}$ = 13.6, $^3J_{cis}$ = 4.1, 1 H, H^G of μ-$S_2C_2H_4$), 4.23 (m, $^2J_{gem}$ = 12.2, $^3J_{trans}$ = 4.0, $^3J_{cis}$ = 1.2 Hz, 1 H, H^L of μ-$S_2C_2H_4$), 5.78 (m, 1 H, H^2 of Cp′-II), 6.13 (m, 1 H, H^3 or H^4 of Cp′-I), 6.17 (m, 2 H, H^4 or H^3 of Cp′-I and H^3 of Cp′-II), 6.21 (m, 1 H, H^5 of Cp′-I), 6.25 (m, 1 H, H^2 of Cp′-I), 6.28 (m, 1 H, H^5 of Cp′-II) and 6.76 (m, 1 H, H^4 of Cp′-II). ^{13}C-{^{1}H} NMR ($CDCl_3$, 20 °C): δ 14.4 (C_5H_4*Me*-I), 16.2 (C_5H_4*Me*-II), 36.5 (CH_2, C^2 of $S_2C_2H_4$), 41.4 (CH_2, C^1 of $S_2C_2H_4$), 43.6 (CH_2, C^3 of μ-$S_2C_2H_4$), 43.8 (CH_2, C^5 of μ-$S_2C_2H_4$), 46.5 (CH_2, C^6 of μ-$S_2C_2H_4$), 46.7 (CH_2, C^4 of μ-$S_2C_2H_4$), 110.4 (CH, C^4 or C^3 of Cp′-I), 111.1 (CH, C^3 or C^4 of Cp′-I), 112.3 (CH, C^5 of Cp′-I and C^3 of Cp′-II), 114.6 (CH, C^4 of Cp′-II), 116.2 (CH, C^2 of Cp′-I), 116.4 (CH, C^2 of Cp′-II), 118.0 (CH, C^5 of Cp′-II), 127.95 (quaternary C, C^1 of Cp′-I) and 128.2 (quaternary C, C^1 of Cp′-II).

X-Ray data and crystal structure determinations

Single crystals of complexes **4** and **6**, as a dichloromethane solvate, were grown by slow diffusion of dichloromethane solutions with light petroleum at −15 °C. Single crystals of **4** were coated in Nujol and vacuum grease, mounted on a glass fibre, data collected with a Siemens P4 diffractometer[26] at 160 K, cooled by an Oxford Cryosystems Cryostream, whilst crystals of **6** were mounted in epoxy resin glue in a sealed, thin-walled glass capillary under dry nitrogen and data were collected at room temperature. Details of the crystal structure determinations of **4** and **6** are given in Table 3.

CCDC reference number 186/1112.

See http://www.rsc.org/suppdata/dt/1998/3281 for crystallographic files in .cif format.

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