Bis(η^5-cyclopentadienyl) Complexes of Niobium(IV) and Tantalum(IV); Electron Spin Resonance and Electrochemical Studies and the Molecular Structure of $[Ta(SCOPh)_2(\eta^5-C_5H_5)_2]$†

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Bis(η^5-cyclopentadienyl) dihalides of niobium(IV) and tantalum(IV), $[MX_2(cp)_2]$ (M = Nb or Ta; X = Cl, Br, or I; cp = η^5-C_5H_5) have been prepared by known methods or *via* metathetical displacement of chloride ligands in $[MCl_2(cp)_2]$ by bromide or iodide ions. The new, characterised bis(monothiobenzoate) complexes, $[M(SCOPh)_2(cp)_2]$ (M = Nb or Ta), have been synthesised from $[MCl_2(cp)_2]$ and Tl(SCOPh) in acetone. The molecular structure of $[Ta(SCOPh)_2(cp)_2]$, determined by *X*-ray diffraction of a single crystal [space group $P2_12_12$, a = 7.8458(22), b = 19.903(4), c = 7.028(3) Å, Z = 2, R = 0.031, R' = 0.037] comprises a normal, bent sandwich geometry with monodentate, S-bonded monothiobenzoate ligands. The angle S–Ta–S, 79.4(8)°, is relatively acute for a complex of type $[MX_2(cp)_2]$ with a d^1 electronic configuration. Comparative cyclic voltammetric studies have been performed for $[MX_2(cp)_2]$ (M = Nb or Ta; X = Cl, Br, I, or SCOPh) in dichloromethane solutions. Oxidation to $[MX_2(cp)_2]^+$ is essentially reversible for these systems and ease of oxidation decreases with ligand X in the order SCOPh > Cl > Br > I. Reduction is irreversible in dichloromethane at room temperature for the dihalide complexes, whereas a primary, reversible reduction of $[M(SCOPh)_2(cp)_2]$ may be attributed to the formation of the respective monoanions. All complexes $[MX_2(cp)_2]$ have been investigated by e.s.r. spectroscopy in solutions and in frozen glasses of 2-methyltetrahydrofuran–dichloromethane. Solution spectra yield isotropic parameters g_{iso} and $A_{iso}(M)$ (M = ^{93}Nb or ^{181}Ta) and the variation of these parameters with the nature of X in $[MX_2(cp)_2]$ is discussed: values of g_{iso} or $A_{iso}(M)$ increase or decrease, respectively, with change of X in the sequence Cl, Br, I. Glass spectra of $[MX_2(cp)_2]$ have been analysed in terms of the anisotropic e.s.r. parameters.

Bis(η^5-cyclopentadienyl) derivatives of early transition metals with the d^1 electronic configuration have been the subject of a number of previous investigations. Of the Group 5 transition elements, the derivatives of vanadium(IV) have been well studied.[1,2,3a] Also, a range of niobium(IV) complexes has been reported and some derivatives have been investigated by e.s.r. spectroscopy. Complexes of the type $[NbX_2(cp)_2]$ (cp = η^5-C_5H_5; X = halide, pseudohalide, alkyl, aryl, H, SR, or OCOR)[3b,4] and cationic species $[Nb(L\text{-}L)(cp)_2]^+$ (L–L = dithiocarbamate, dithiophosphate, or xanthate)[5,6] have received varying attention. Fewer bis(η^5-cyclopentadienyl) complexes of tantalum(IV) have been characterised, but species $[TaX_2(cp)_2]$ (X = Cl, Br, σ-C_5H_5, Ph, alkyl, or SR) and $[Ta(Me_2PCH_2CH_2PMe_2)(cp)_2]^{2+}$ are known.[3c,4] We have been interested in paramagnetic derivatives of the type $[MX_2(cp)_2]^{n+}$ over several years,[7,8] and report here some studies on the neutral complexes with M = Nb or Ta and X = Cl, Br, I, or SCOPh.

Results and Discussion

All the halide complexes $[MX_2(cp)_2]$ (M = Nb or Ta; X = Cl, Br, or I), with the apparent exception of the species with M = Ta, X = I, have been previously reported[4,9,10] and the complexes with X = Cl have been subjected to various chemical and physical studies. We prepared $[MCl_2(cp)_2]$ [M = Nb, (**1a**); or Ta, (**1b**)] and $[TaBr_2(cp)_2]$ (**2b**) by literature methods[11,12] but employed metathetical exchange of halide between (**1a**) or (**1b**) to form $[NbBr_2(cp)_2]$ (**2a**) and $[MI_2(cp)_2]$ [M = Nb, (**3a**); or Ta, (**3b**)]. Complexes (**3a**) and (**3b**) are easily obtained from (**1a**) or (**1b**), respectively, by using KI in acetone, whereas exchange between (**1a**) and KBr under the same conditions to form (**2a**) is slow and reaction between (**1a**) and $MgBr_2$ in tetrahydrofuran (thf) was employed. The mixed-halide species $[MCl(X)(cp)_2]$ are intermediates in these metathetical exchanges and their presence can be monitored by e.s.r. spectroscopy: a partial separation of these intermediates from the reaction mixture can be achieved by chromatography on Florisil. The electron-impact (e.i.) mass spectra of complexes (**1**)—(**3**) show molecular ions M^+ and fragment ions with loss of single cp or halide in varying relative intensities; spectra from the iodo-species (**3**) also show significant peaks corresponding to $[M(cp)I]^+$ and $[M(cp)_2]^+$, the latter being predominant for (**3a**).

$$[MCl_2(cp)_2] \xrightarrow{\text{KI or MgBr}_2} [MCl(X)(cp)_2] \longrightarrow [MX_2(cp)_2] \ (X = \text{Br or I}) \qquad (1)$$

Complexes $[M(SCOPh)_2(cp)_2]$ [M = Nb, (**4a**); or Ta, (**4b**)] are produced by reaction between (**1**) and Tl(SCOPh) in acetone. Both show molecular ions in their e.i. mass spectra and fragmentations involve, *inter alia*, formation of cyclopentadienylmetal sulphide ions $[MS(SCOPh)(cp)_2]^+$, $[MS(SCOPh)(cp)]^+$, and $[MS_2(cp)]^+$. The presence of bands due to uncomplexed CO at 1 610 cm^{-1} and of ν(CS) bands at 911 or

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† Bis(η-cyclopentadienyl)bis(thiobenzoato-*S*)tantalum(IV).

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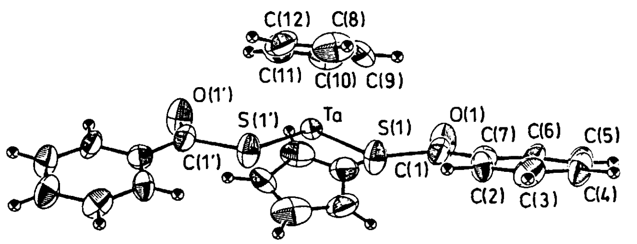

Figure 1. The crystal structure of [Ta(SCOPh)$_2$(cp)$_2$] (**4b**) (ORTEP[45e]). The hydrogen atom labels have been omitted for clarity

Table 1. Fractional co-ordinates of atoms with standard deviations for complex (**4b**)

Atom	*x*	*y*	*z*
Ta	0.000 00(0)	0.000 00(0)	0.563 75(8)
S(1)	0.141 9(4)	0.058 25(17)	0.288 2(5)
O(1)	0.292 3(13)	0.130 1(5)	0.555 3(13)
C(1)	0.289 2(16)	0.117 9(6)	0.387 6(18)
C(2)	0.414 0(15)	0.133 6(6)	0.054 4(20)
C(3)	0.530 3(21)	0.165 6(6)	−0.061 2(23)
C(4)	0.641 4(18)	0.214 0(6)	0.012 1(21)
C(5)	0.628 2(18)	0.231 1(6)	0.203 5(22)
C(6)	0.513(3)	0.199 6(5)	0.318 0(18)
C(7)	0.405 8(14)	0.149 5(6)	0.248 4(17)
C(8)	0.247 4(21)	−0.066 7(8)	0.537 5(23)
C(9)	0.274 1(17)	−0.022 4(7)	0.684(3)
C(10)	0.155 8(18)	−0.039 0(7)	0.829 3(22)
C(11)	0.064 1(17)	−0.092 5(7)	0.765 5(21)
C(12)	0.120 0(20)	−0.112 2(6)	0.592 6(23)

Table 2. Derived geometrical parameters for complex (**4b**) with estimated standard deviations

Ta–S(1)	2.516(3)	C(2)–C(7)	1.401(17)
Ta–C(8)	2.359(16)	C(3)–C(4)	1.397(20)
Ta–C(9)	2.352(16)	C(4)–C(5)	1.392(19)
Ta–C(10)	2.362(15)	C(5)–C(6)	1.365(20)
Ta–C(11)	2.378(14)	C(6)–C(7)	1.391(19)
Ta–C(12)	2.431(15)	C(8)–C(9)	1.370(23)
S(1)–C(1)	1.798(13)	C(8)–C(12)	1.402(22)
O(1)–C(1)	1.203(15)	C(9)–C(10)	1.421(22)
C(1)–C(7)	1.480(17)	C(10)–C(11)	1.361(20)
C(2)–C(3)	1.378(19)	C(11)–C(12)	1.350(20)
S(1)–Ta–C(8)	80.5(4)	C(3)–C(4)–C(5)	118.6(13)
S(1)–Ta–C(9)	87.6(4)	C(4)–C(5)–C(6)	120.5(13)
S(1)–Ta–C(10)	122.0(4)	C(5)–C(6)–C(7)	121.4(13)
S(1)–Ta–C(11)	136.2(3)	C(1)–C(7)–C(2)	125.2(11)
S(1)–Ta–C(12)	108.4(4)	C(1)–C(7)–C(6)	116.4(11)
C(8)–Ta–C(9)	33.8(6)	C(2)–C(7)–C(6)	118.5(11)
C(8)–Ta–C(10)	56.7(5)	Ta–C(8)–C(9)	72.8(10)
C(8)–Ta–C(11)	55.7(5)	Ta–C(8)–C(12)	75.8(9)
C(8)–Ta–C(12)	34.0(5)	C(9)–C(8)–C(12)	108.5(14)
C(9)–Ta–C(10)	35.1(5)	Ta–C(9)–C(8)	73.4(10)
C(9)–Ta–C(11)	56.4(5)	Ta–C(9)–C(10)	72.8(9)
C(9)–Ta–C(12)	56.1(5)	C(8)–C(9)–C(10)	106.9(14)
C(10)–Ta–C(11)	33.4(5)	Ta–C(10)–C(9)	72.1(9)
C(10)–Ta–C(12)	55.4(5)	Ta–C(10)–C(11)	73.9(9)
C(11)–Ta–C(12)	32.6(5)	C(9)–C(10)–C(11)	106.8(13)
Ta–S(1)–C(1)	106.8(4)	Ta–C(11)–C(10)	72.7(8)
S(1)–C(1)–O(1)	121.8(10)	Ta–C(11)–C(12)	75.9(9)
S(1)–C(1)–C(7)	114.9(8)	C(10)–C(11)–C(12)	110.6(13)
O(1)–C(1)–C(7)	123.3(11)	Ta–C(12)–C(8)	70.2(9)
C(3)–C(2)–C(7)	120.0(12)	Ta–C(12)–C(11)	71.5(9)
C(2)–C(3)–C(4)	120.9(13)	C(8)–C(12)–C(11)	107.0(13)

909 cm^{-1} in the i.r. spectra of (**4a**) or (**4b**), respectively, supports co-ordination of the monothiobenzoate ligands *via* S atoms in monodentate fashion.[13] These complexes slowly decompose on exposure to the atmosphere giving diamagnetic products, including [MS(SCOPh)(cp)$_2$].

Solid-state structure of [Ta(SCOPh)$_2$(cp)$_2$] (**4b**).—A red needle-like crystal of complex (**4b**), obtained from dichloromethane–hexane, was subjected to structural analysis by *X*-ray diffraction. In the crystal, molecules of complex (**4b**) necessarily have a formal C_2 point-group symmetry because they occupy special positions in the space group $P2_12_12$ in which the Ta atom is constrained to lie on a crystallographic two-fold axis. A perspective view of a molecule of complex (**4b**), showing the atomic numbering, is given in Figure 1; Tables 1 and 2, respectively, list fractional atomic co-ordinates and derived geometric parameters. The Ta atom is co-ordinated by the S atoms of the two monodentate monothiobenzoate ligands, which are interrelated by the C_2 symmetry axis [Ta–S 2.516(3) Å], and by two equivalent pentahapto-cyclopentadienyl ligands [Ta–Cp(centroid) 2.066(22), mean Ta–C 2.376 Å]. The pseudo-tetrahedral, bent sandwich structure of (**4b**) is typical of compounds [MX$_2$(cp)$_2$]. The angle between the cyclopentadienyl rings [Cp(centroid)–Ta–Cp(centroid) 132.7(13)°] is within the range 127—145° found for other bis(cyclopentadienyl) complexes of Nb and Ta.[3b,c,4] The two C_5H_5 rings adopt a staggered conformation and the angle Cp(centroid)–Ta–S is 108.3(7)°.

The angle between the two ligands X in complexes [MX$_2$(cp)$_2$] has been related to the electronic configurations of the complexes and for formally d^0, d^1, or d^2 systems the angles X–M–X decrease, having values around *ca.* 95, *ca.* 85, or *ca.* 77°, respectively.[4,14] The frontier molecular orbitals (m.o.s) of such complexes have been discussed in detail elsewhere,[15] and the decrease in X–M–X angle is related to increasing population of the a_1 non-bonding (or weakly antibonding) orbital which is the lowest-unoccupied m.o. (l.u.m.o.) in d^0 species, see Figure 2. This angular variation is illustrated by previously studied complexes of Nb and Ta, although formally d^2 complexes containing the π-accepting CO ligand, [MX(CO)(cp)$_2$], or complexes with an alkylidene ligand [MX(CHR)(cp)$_2$] (M = Nb or Ta), display wider X–M–C angles comparable to those of d^0 systems.

In the formally d^1 complex (**4b**) the angle S–Ta–S [79.4(8)°] is relatively acute. The only related tantalum(IV) complex that has been structurally characterised is [TaCl$_2$(η^5-C$_5$H$_4$Me)$_2$] with Cl–Ta–Cl 84.5°;[16] [TaCl$_2$(cp)$_2$] probably has a closely related geometry, as is the case for the pair of complexes [ZrCl$_2$(cp)$_2$] and [ZrCl$_2$(η^5-C$_5$H$_4$Me)$_2$],[17] and the Cl–M–Cl angle is also close to 85.6° found in [NbCl$_2$(cp)$_2$].[14] The smaller angle X–M–X of (**4b**) may arise partly from the lower electronegativity of S in comparison to Cl, which should increase electron density on the Ta atoms, but also from a π-donor interaction of the S atoms with the singly occupied a_1 m.o. (s.o.m.o.) as shown in Figure 2. It may be noted that the formally d^2 ion [Ta(Me$_2$PCH$_2$CH$_2$PMe$_2$)(cp)$_2$]$^{2+}$ has an angle P–Ta–P of 77.21(4)° which is close to the ligand angle in (**4b**), although this may be influenced by the 'bite' of the diphosphine ligand.[18] Of particular relevance is the recently reported structure of [Nb(SPh)$_2$(cp)$_2$] in which the mean S–Nb–S angle is 75.5(1)° and this angle is increased to 101.4(1)° in the corresponding d^0 cation [Nb(SPh)$_2$(cp)$_2$]$^+$:[19a] it was suggested[19a] that a contributory factor to the abnormally acute angle in the d^1 complex [Nb(SPh)$_2$(cp)$_2$] may be a weak S ··· S bonding interaction. Larger X–M–X angles are found for the niobium(V) thiolate complexes [Ni{Nb(SMe)$_2$(cp)$_2$}$_2$]$^{2+}$ (mean S–Nb–S 97.9°)[19b] and [Nb(SPh)$_2${Mo(CO)$_4$}(cp)$_2$]$^+$ [S–Nb–S 101.8(1)°][19a] or the carbonyl thiolate [Nb(SH)(CO)(cp)$_2$] [S–Nb–C 92.3(5)°].[20]

The two monothiobenzoate ligands do not appear to have any steric influence on the size of the S–Ta–S bond angle. The

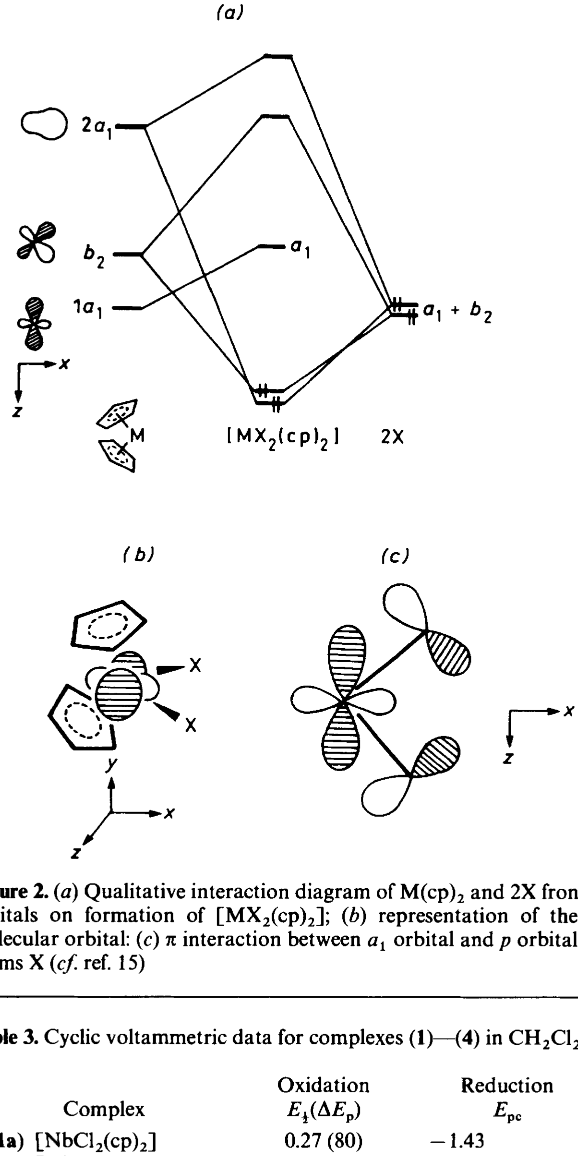

Figure 2. (*a*) Qualitative interaction diagram of M(cp)$_2$ and 2X frontier orbitals on formation of [MX$_2$(cp)$_2$]; (*b*) representation of the a_1 molecular orbital: (*c*) π interaction between a_1 orbital and *p* orbitals of atoms X (*cf.* ref. 15)

Table 3. Cyclic voltammetric data for complexes (**1**)—(**4**) in CH$_2$Cl$_2$[a]

Complex	Oxidation $E_{\frac{1}{2}}(\Delta E_p)$	Reduction E_{pc}
(**1a**) [NbCl$_2$(cp)$_2$]	0.27 (80)	−1.43
(**2a**) [NbBr$_2$(cp)$_2$]	0.34 (85)	−1.19, −1.45
(**3a**) [NbI$_2$(cp)$_2$]	0.35 (70)	−1.15, −1.5
(**4a**) [Nb(SCOPh)$_2$(cp)$_2$]	−0.06[b] (90)	−1.21,[c] −1.6
(**1b**) [TaCl$_2$(cp)$_2$]	−0.11 (80)	−1.59
(**2b**) [TaBr$_2$(cp)$_2$]	−0.03 (145)	−1.44(sh), −1.65
(**3b**) [TaI$_2$(cp)$_2$]	0.045 (85)	−1.28, −1.6
(**4b**) [Ta(SCOPh)$_2$(cp)$_2$]	−0.325 (130)	−1.35[d]

[a] $E_{\frac{1}{2}}$ and E_{pc} (cathodic peak) potentials in volts *vs.* s.c.e., scan rate 50 mV s^{-1}; $\Delta E_p = E_{pa} - E_{pc}$ in mV (measured using platinum-wire pseudo-reference electrode). [b] Also a small irreversible oxidative peak at E_{pa} = 0.6 V. [c] $E_{\frac{1}{2}}$ = 1.15 V (ΔE_p = 95 mV). [d] $E_{\frac{1}{2}}$ = 1.29 V (ΔE_p = 80 mV).

oxygen atoms of the organic carbonyl function in these ligands are projected towards the Ta atoms but the interatomic distance [Ta ··· O 3.460(10) Å] precludes any significant interaction between O and Ta atoms. As found for the benzoate ligands in the 16-electron, d^0 complex [Ti(OCOPh)$_2$(cp)$_2$],[21] the monothiobenzoate ligands in the 17-electron complex (**4b**) are not bidentate.

Electrochemical Studies.—Previous reports of electrochemical studies on bis(η^5-cyclopentadienyl) complexes of niobium(IV) or tantalum(IV) include detailed studies on (**1a**) in thf,[22,23a–c] on [NbCl(SiMe$_3$)(cp)$_2$],[24a] and on related silylated derivatives [NbX$_2$(η^5-C$_5$H$_4$SiMe$_3$)$_2$] (X = Cl[24b] or I[24c]), in the same solvent. The dithiolene complexes [Nb(S$_2$C$_2$R$_2$)(cp)$_2$] (R = Me or Ph)[25] and the ionic complex [Ta(Me$_2$PCH$_2$CH$_2$PMe$_2$)(cp)$_2$]$^{2+}$,[26] both containing bidentate ligands, have also been investigated electrochemically, as have the benzyl complexes [M(CH$_2$Ph)$_2$(cp)$_2$] (M = Nb or Ta) and some related metallacyclic derivatives.[27] Moreover, chemical oxidation or reduction of some of the halogen complexes (**1**)—(**3**) has been utilised in the synthesis of various metal-(V) or -(III) species.[4,9,10,28,29]

Results of cyclic voltammetric studies on complexes (**1**)—(**4**) in dichloromethane solutions are given in Table 3 (*cf.* Figure 3); values for potentials $E_{\frac{1}{2}}$ and E_{pc} are quoted relative to an aqueous saturated calomel electrode (s.c.e.) but peak separations ($\Delta E_p = E_p{}^a - E_p{}^c$) are listed for a cell with a platinum wire as a pseudo-reference electrode to minimise the *IR* drop in the cell (see Experimental section). All complexes exhibit an oxidation wave for which both anodic and cathodic peaks are observed. Since under similar experimental conditions the ferrocenium–ferrocene couple shows ΔE_p = 0.12 V, oxidation processes with ΔE_p < 0.10V may be considered to be essentially reversible. The slightly higher values of ΔE_p of complex (**4b**) and, more notably, (**2b**) may indicate some irreversibility under the conditions used.

Oxidation may be assumed primarily to form cations [MX$_2$(cp)$_2$]$^+$, since cationic halogen species have been isolated for M = Nb, X = Cl, Br, or I[10,28] and M = Ta, X = Cl.[28] Also, the cations [Nb(SR)$_2$(cp)$_2$]$^+$ and [Nb(S$_2$C$_2$R$_2$)(cp)$_2$]$^+$ (R = Ph or Me)[19a,25,30] have been characterised. However, slow reductive elimination of halogen does take place from [NbCl$_2$(cp)$_2$]$^+$ in thf and related one-electron reductive eliminations of RS from electrochemically generated [M(SR)$_2$(cp)$_2$]$^+$ (M = Mo or W) have been reported.[31] Such decomposition pathways may take place in the systems studied here and could account for the larger ΔE_p values for (**2b**) and (**4b**), but an alternative route for decomposition of complexes [M(SCOPh)$_2$(cp)$_2$]$^+$ is the loss of acylium ion with the formation of species [MS(SCOPh)(cp)$_2$], identified among the products of aerial oxidation.

Formation of the primary cation on oxidation involves the loss of an electron from the metal-based, weakly π-antibonding s.o.m.o. of a_1 symmetry (see Figure 2) and will lead to an increase in the X–M–X bond angle.[15,32] The oxidation of complexes (**1**)—(**4**) occurs at potentials 0.25—0.38V more positive for the niobium than for the related tantalum derivative, and this reflects the generally observed redox differences between Nb and Ta. The ease of oxidation of complexes of either metal, as indicated by the more negative values of $E_{\frac{1}{2}}$ for this process, varies with ligand X in the order X = SCOPh > Cl > Br > I, although the variation among halogen complexes is small. The order of the halogen ligands can be related to electronegativity effects, with higher electronegativities favouring the higher oxidation state, and also to the decrease in π-donor ability of the halogen in the sequence Cl > Br > I, since π donation into the s.o.m.o. will destabilise the metal(IV) complex relative to the d^0 metal(V) species {*cf.* similar effects in [WX$_2$(cp)$_2$] species[33]}. The more facile oxidation of the monothiobenzoato complexes cannot be accounted for by the electronegativity of sulphur but may arise largely from the π-donor character of the S atoms. It is also possible that an unco-ordinated organic carbonyl group of the monothiobenzoate ligands could chelate to the 16-electron metal(V) cation and hence give additional stability to the oxidised species, however it should be noted that in the 16-electron complex [Ti(OCOPh)$_2$(cp)$_2$] only monodentate carboxylate ligands are present.[21]

Complexes (**1**)—(**4**) show one or two reduction waves (see Table 3) but in most cases only the cathodic peak is observed so

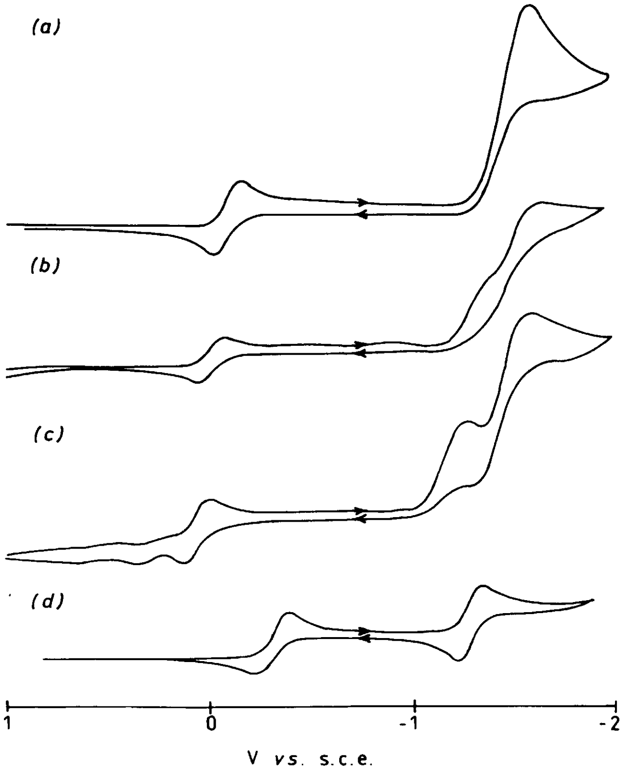

Figure 3. Cyclic voltammograms in CH_2Cl_2 at 50 mV s^{-1}: (*a*) $[TaCl_2(cp)_2]$, (*b*) $[TaBr_2(cp)_2]$, (*c*) $[TaI_2(cp)_2]$, and (*d*) $[Ta(SCOPh)_2(cp)_2]$

that irreversible processes are evidently taking place. On electrochemical reduction of (**1a**) in thf it has been reported that the primary anion $[NbCl_2(cp)_2]^-$, formed reversibly at −30 °C, is unstable to loss of Cl^- and species such as the dimer $[Nb_2Cl_3(cp)_4]^-$ are produced, depending on the experimental conditions;[23a—c] at −30 °C in dimethylformamide (dmf) a neutral solvated dimer $[Nb_2Cl_2(dmf)(cp)_2]$ is formed.[23d] Related halide-ion loss by complexes (**1**)—(**3**) in dichloromethane probably accounts for the electrochemical irreversibility of the first reduction process. The monothiobenzoato complexes (**4**) both undergo initial reduction processes which appear to be essentially reversible and these probably involve the formation of respective monoanions. It has been reported that the dithiolene anions $[Nb(S_2C_2R_2)(cp)_2]^-$ (R = Me or Ph) are formed by reversible reduction of the neutral niobium(IV) species[25] and complexes of the type $[MR_2(cp)_2]$ (M = Nb or Ta, R = benzyl or related ligand) are also reversibly, electrochemically reduced to monoanions.[27] Recent studies have shown $[Nb(SPh)_2(cp)_2]$ also to be reversibly reduced.[19a] For complexes (**1**)—(**4**) the niobium species are reduced at more positive potentials than tantalum analogues and E_{pc} values of halide complexes decrease in the same order (X = I > Br > Cl) that is found for $E_{\frac{1}{2}}$ values for the reversible oxidation process.

E.S.R. Studies.—Solution spectra. Complexes (**1**)—(**4**) show e.s.r. spectra in solution with hyperfine coupling to the metal atom (^{93}Nb, $I = 4.5$, a decet; ^{181}Ta, $I = 3.5$, an octet) but without the resolvable superhyperfine coupling to the ligand atoms found in some isoelectronic cations $[MX_2(cp)_2]^+$ (M = Mo or W).[7] Values of g_{iso} and A_{iso} (^{93}Nb or ^{181}Ta) are listed in Table 4. The solution spectra (*cf.* Figure 4) all show asymmetry due to variations in the linewidths of the hyperfine components.[34] E.s.r. spectra of complex (**1a**) in solution have been reported in several papers and approximate data have also been given for (**2a**),[35] see Table 4. A detailed e.s.r. study of (**1b**) has also appeared[36] but, as with related frozen-solution spectra (see below), the parameters obtained in the previous work show very poor agreement with our results. We find no significant changes in e.s.r. parameters of any complexes (**1**)—(**4**) on using 2-methyltetrahydrofuran (mthf), dichloromethane, or a mixed solvent of these components to record spectra and the discrepancy between our values for (**1b**) and those of the earlier work is not easy to explain. However, we did note that preparation of (**1b**) by using $MgPr^iBr$ as a reductant did result in some exchange of chloride by bromide in the product [*cf.* the preparation of (**2a**) from $MgBr_2$] whereas the reaction of $SnBu^n_3(cp)$ and $TaCl_5$, by which (**1b**) was prepared for this study, cannot cause halide exchange: the essential purity of our product was confirmed by elemental analysis (Found: C, 31.30; H, 2.75; Cl, 18.50. Calc. for $C_{10}H_{10}Cl_2Ta$: C, 31.45; H, 2.65, Cl, 18.55%) and by its mass spectrum (peaks of highest *m*/*z*: M^+, $[M - Cl]^+$, $[M - cp]^+$, with appropriate $^{35/37}Cl$ ratios). Another value of $g_{iso} = 1.94$ has been reported for complex (**1b**) in dichloromethane solution[12] and although this is higher than our value of 1.91 it is not inconsistent with the lower value if a second-order correction to the experimentally determined result was not carried out.

The halide complexes (**1**)—(**3**) show an increase in g_{iso} value in the sequence X = Cl < Br < I and this arises partly from the increasing spin–orbit coupling constant of the halogen ligand in the same order, as previously discussed for related molybdenum and tungsten complexes.[7] Other factors, including the reduction in the metal spin–orbit coupling constant as the effective charge on the metal decreases and any changes in the energies of filled or unfilled orbitals relative to the s.o.m.o., will also contribute to variations in g_{iso} (*cf.* ref. 2). Values of $|A_{iso}|$ decrease on changing the halide ligand in the order Cl > Br > I; in accordance with previous studies on related systems, A_{iso} will have a negative sign,[6,17,37] and the increasing positive trend reflects greater covalency with decreasing electronegativity of X. Any change in X–M–X bond angle will alter the relative contributions of $d_{x^2-y^2}$ and d_{z^2} orbitals to the s.o.m.o. and also the extent of π interaction with ligands X, both causing variations in $A_{iso}(M)$. However, only the chloro-complexes (**1a**) and $[TaCl_2(\eta^5\text{-}C_5H_4Me)_2]$ have been structurally characterised by *X*-ray analysis[14,16] so that bond-angle variations for these halides are unknown. The mixed halides $[NbCl(X)(cp)_2]$ (X = Br, I) have g_{iso} and A_{iso} values close to the arithmetic means for the parent homodihalides, as found for the mixed-halide cations of molybdenum and tungsten, $[MCl(Br)(cp)_2]^+$ (M = Mo or W).[7] In spectra of the latter cations, resolvable coupling to $^{79/81}Br$ appears as a quartet ($A_{iso} = 15 \times 10^4$ or 23×10^4 cm^{-1} for M = Mo or W, respectively). These four-line signals do *not* arise from electrochemically generated ClO_2, as suggested in a later paper by Symons and Maguire,[38] since they are only formed from *chemical* exchange reactions in the absence of $NBu^n_4ClO_4$, and when M = Mo well defined satellites arising from coupling with $^{95/97}Mo$ nuclei are also observed.[7]

Literature values of solution e.s.r. parameters for other complexes $[MX_2(cp)_2]$ (M = Nb or Ta) with monodentate ligands, X, are presented in Table 5. Of the few reported examples containing S-co-ordinated ligands, the data for the complex with X = $SPS(OR)_2$ and M = Nb[39] closely reflect those of (**4a**), whereas data for analogous species with X = SMe or SPh show greater divergences from those of the respective complexes (**4a**) or (**4b**).[30,40,41] Two inconsistent sets of e.s.r. parameters have been quoted for complexes $[Nb(SR)_2(cp)_2]$ (R = Me or Ph).[30,40] Although it seems unlikely that the low $A_{iso}(^{93}Nb)$ parameters of ref. 30 are correct [a low value of $A_{iso}(Nb) = 3.59$ mT is also given for (**1a**) in this paper], it may be noted that a sample of $[Nb(SPh)_2(cp)_2]$ prepared by us gave $g_{iso} = 1.9895$, consistent with ref. 30, but with $A_{iso} = 97$ mT

Table 4. E.s.r. parameters for complexes (**1**)—(**4**) in dichloromethane–2-methyltetrahydrofuran[a]

	Complex	g_{iso}	$-A_{iso}$/ 10^{-4} cm^{-1}	g_x	$-A_x$/ 10^{-4} cm^{-1}	g_y	$-A_y$/ 10^{-4} cm^{-1}	g_y	$-A_z$/ 10^{-4} cm^{-1}
(**1a**)	$[NbCl_2(cp)_2]$[b]	1.978	106	1.980	106	1.945	159	2.006	55
	$[NbCl(Br)(cp)_2]$[c]	1.996	102	—	—	—	—	—	—
	$[NbCl(I)(cp)_2]$[c]	2.017	98	—	—	—	—	—	—
(**2a**)	$[NbBr_2(cp)_2]$[d]	2.010	99	2.015	80[e]	2.017	146	1.998	71
(**3a**)	$[NbI_2(cp)_2]$	2.069	86	2.070	70	2.144	123	1.997	66
(**4a**)	$[Nb(SCOPh)_2(cp)_2]$	1.989	86.5	1.989	85	1.973	136	2.005	40
(**1b**)	$[TaCl_2(cp)_2]$[f]	1.909	117	1.88_5	122	1.76	150	2.08	83
(**2b**)	$[TaBr_2(cp)_2]$	1.937	108	1.88	124	1.82	127	2.11	73
(**3b**)	$[TaI_2(cp)_2]$	2.008	93	*ca.* 1.94_5	*ca.* 93	*ca.* 2.03_5	*ca.* 136	*ca.* 2.04	*ca.* 50
(**4b**)	$[Ta(SCOPh)_2(cp)_2]$	1.957	88	2.00	104	1.89	118	1.98	42

[a] Values of g_{iso} and A_{iso}(^{93}Nb or ^{181}Ta) from fluid solutions at *ca.* 10 °C (estimated errors: $g_{iso} < \pm 0.002$, $A_{iso} < \pm 1$); g_x,g_y,g_z and A_x,A_y,A_z (^{93}Nb or ^{181}Ta) values from frozen glassy solutions at *ca.* −140 °C [niobium complexes, estimated errors $g < \pm 0.005$, $A < \pm 3$; tantalum complexes, errors and co-ordinate assignments of *g* and *A* less certain (see text)]. [b] Literature values in various solvents are g_{iso} 1.974—1.983, A_{iso} 106 × 10^{-4} – 110 × 10^{-4} cm^{-1} (refs. 6, 37, and 40; I. H. Elson, J. K. Kochi, U. Klabunde, L. E. Manzer, G. W. Parshall, and F. N. Tebbe, *J. Am. Chem. Soc.*, 1974, **96**, 7374; I. H. Elson and J. K. Kochi, *ibid.*, 1975, **97**, 1262; R. Broussier, H. Normand, and B. Gautheron, *J. Organomet. Chem.*, 1978, **155**, 337; A. H. Al-Mowali, *J. Chem. Soc., Dalton Trans.*, 1980, 426). Comparable frozen solution e.s.r. parameters are given in refs. 6 and 37. [c] In dichloromethane solution. [d] Literature values: g_{iso} *ca.* 2.0, A_{iso} 10.4 mT.[35] [e] $A(^{79/81}Br) = (30 \pm 2) \times 10^{-4}$ cm^{-1}. [f] Contrast literature values: g_{iso} 1.970, g_x,g_y,g_z 1.983, 1.939, 1.985, A_{iso} 0.0106, A_x,A_y,A_z 0.0071, 0.0182, 0.006 95 cm^{-1}.[36]

Table 5. Reported isotropic e.s.r. parameters for complexes $[MX_2(cp)_2]$ (M = Nb or Ta, X = unidentate ligand)

	M = Nb			M = Ta		
X	g_{iso}	$-A_{iso}(^{93}Nb)/10^{-4}$ cm^{-1}	Ref.	g_{iso}	$-A_{iso}(^{181}Ta)/10^{-4}$ cm^{-1}	Ref.
F	2.01	108	*a*	—	—	—
H	2.0097	43	*b*	2.006	62	*b*
Me	1.9984	83	*b,c*	1.993	87	*d*
CH_2Ph	1.9956	82	*e*	2.0001	82	27
CH_2SiMe_3	1.9961	89	*e*	(2.021	92)[f]	*g*
σ-C_5H_5	1.9880	92	37	1.9765	98	*h*
Ph	1.9982	83	*b*	1.988	87	*b*
CN	1.995	84	37	—	—	—
$SPS(OR)_2$ (R = Et or Pr^i)	1.986	89	39	—	—	—
SMe	1.9772	89	40	1.972[i]	105[i]	41
	1.991	23	30			
SPh	1.9750	91	40	1.972[i]	102.5[i]	41
	1.989	28	30			
NCS	1.975	103	37	—	—	—
OCOBu^t	1.971	115	*j*	—	—	—
OBu^t	1.95	116	*b*	—	—	—

[a] J. Sala-Pala, J. Amaudrut, J. E. Guerchais, and R. Mercier, *J. Organomet. Chem.*, 1981, **204**, 347. [b] I. H. Elson, J. K. Kochi, U. Klabunde, L. E. Manzer, G. W. Parshall, and F. N. Tebbe, *J. Am. Chem. Soc.*, 1974, **96**, 7374; I. H. Elson and J. K. Kochi, *ibid.*, 1975, **97**, 1262. [c] L. E. Manzer, *Inorg. Chem.*, 1977, **16**, 525; R. Broussier, H. Normand, and B. Gautheron, *J. Organomet. Chem.*, 1978, **155**, 337. [d] D. F. Foust and M. D. Rausch, *J. Organomet. Chem.*, 1982, **226**, 47. [e] P. B. Hitchcock, M. F. Lappert, and C. R. C. Milne, *J. Chem. Soc., Dalton Trans.*, 1981, 180. [f] Incorrect, high values of g_{iso} = 2.037, A_{iso} = 9.7 mT (0.0092 cm^{-1}) are reported in this preliminary communication for the related niobium complex, so that these parameters are also probably too high. [g] M. F. Lappert and C. R. C. Milne, *J. Chem. Soc., Chem. Commun.*, 1978, 925. [h] A. H. Al-Mowati, *J. Chem. Soc., Dalton Trans.*, 1980, 426. [i] Average values of the anisotropic data derived from glass spectra. [j] A. A. Pasynskii, Yu. V. Skripkin, and V. T. Kalinnikov, *J. Organomet. Chem.*, 1978, **150**, 51.

(0.0090 cm^{-1}). The relatively low $|A_{iso}|$ values for (**4a**) and (**4b**) compared with those for complexes (**1**)—(**3**) may be attributed to significant ligand donor p_π contribution to the s.o.m.o. causing delocalisation of unpaired electron density and this is consistent with the smaller S–Ta–S angle of (**4b**).

Considering the data from Tables 4 and 5, it is apparent that g_{iso} values of niobium complexes $[NbX_2(cp)_2]$ decrease with the following sequence of co-ordinated atoms in ligand X: $I > Br \approx F \approx H > C > S > Cl > O$ and A_{iso} values increase with the sequence $H < C \approx I \approx S < Br < Cl < F < O$. For tantalum complexes the sequences are similar with slight variations, *i.e.* g_{iso}, $I \approx H > C > S > Br > C$ and A_{iso}, $H < C < S \approx I < Br < Cl$. These ligand effects results from combinations of the factors mentioned in the discussion above and may have useful applications for identification of products from reactions in solution.

Glass spectra. E.s.r. spectra of complex (**1a**) in frozen solutions have been analysed previously and the parameters are consistent with a metal-based s.o.m.o., equation (2), in which $a^2 \gg b^2$.[6,32,37] However, it has also been noted that, although

$$|\psi_{s.o.m.o.}\rangle = a|d_{x^2}\rangle + b|d_{x^2-y^2}\rangle \qquad (2)$$

no superhyperfine coupling to $^{35/37}$Cl nuclei is resolved, the data do support significant delocalisation (≈40%) of spin density onto the ligands.[6] In frozen mthf–CH_2Cl_2 solution complex (**1a**) yields e.s.r. parameters close to those previously reported (see

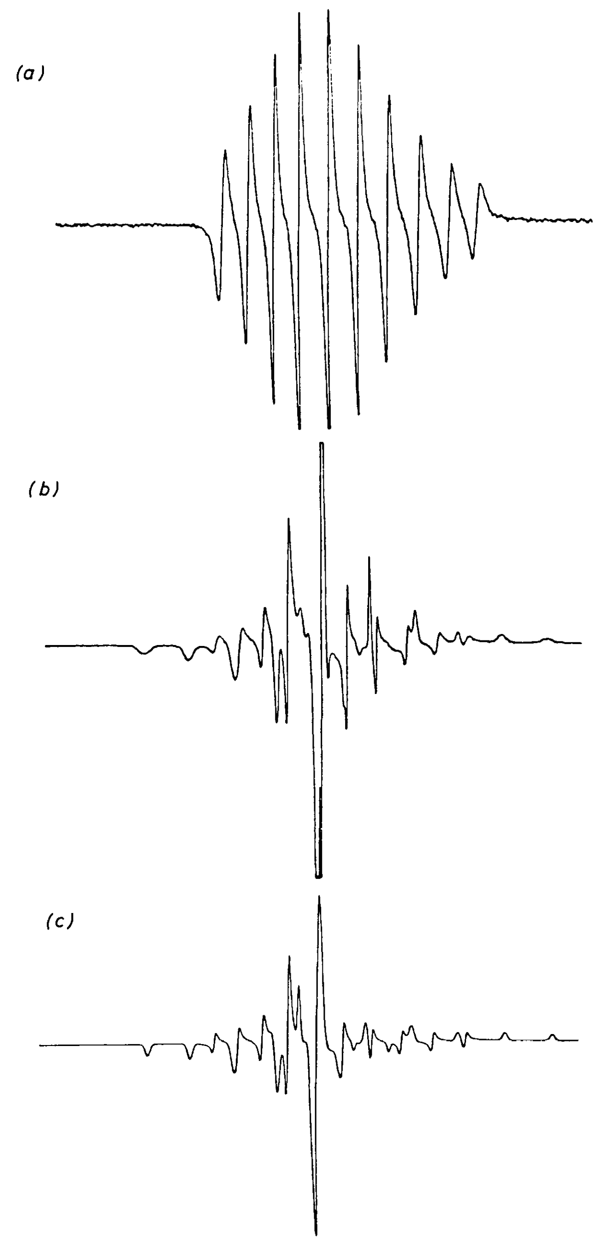

Figure 4. E.s.r. spectra of $[Nb(SCOPh)_2(cp)_2]$ at 9.211 GHz in mthf–CH_2Cl_2: (*a*) solution at *ca.* 10 °C; (*b*) glass at *ca.* −140 °C; and (*c*) simulated glass spectrum with g_x,g_y,g_z and A_x,A_y,A_z of Table 4 (linewidths σ_x, σ_y, and σ_z of 0.5, 0.8, and 0.5 mT, respectively)

Table 4): values of $a^2 = 0.93$ and $b^2 = 0.07$ can be derived by using the analysis outlined in ref. 6.

The bis(monothiobenzoato) complex (**4a**) in a frozen glass exhibits an e.s.r. spectrum resembling that of (**1a**) and analysis, supported by spectral simulation (see Figure 4), gives the parameters in Table 4: assuming a s.o.m.o. defined by equation (2), values of $a^2 = 0.92$ and $b^2 = 0.08$ can be derived. Thus, the s.o.m.o. of (**4a**) does not differ markedly from that of (**1a**), although the hyperfine parameter,[6] $P = g_e g_n \gamma_e \gamma_n \langle r^{-3} \rangle$, of 0.0093 cm^{-1} for (**4a**) is a little lower than for (**1a**) (0.0099 cm^{-1}) and this could indicate more electron delocalisation involving the sulphur ligands. Such delocalisation has been reported for species containing bidentate sulphur ligands, $[NbL_2(cp)_2]^+$ [$L_2 = S_2CNR$, S_2COR, or $S_2P(OR)_2$][5,6] and for monodentate complexes $[Nb\{SPS(OR)\}_2(cp)_2]$[39] and $[Nb(SR)_2(cp)_2]$.[40]

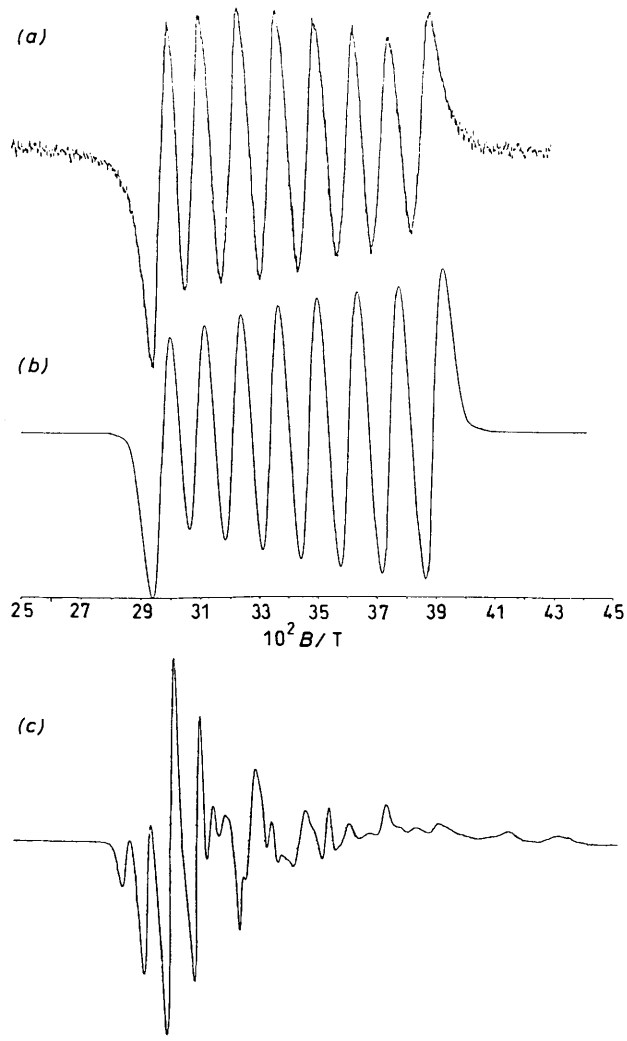

Figure 5. E.s.r. spectra of $[TaCl_2(cp)_2]$ at 9.209 GHz in mthf–CH_2Cl_2: (*a*) solution at *ca.* 10 °C; (*b*) simulated isotropic spectrum, $g_{iso} = 1.909$, $A_{iso} = 0.0117$ cm^{-1}, and linewidth 4 mT; and (*c*) glass at *ca.* −140 °C

Analyses of glass spectra for dibromo- and di-iodo-complexes (**2a**) and (**3a**) have not been easy to perform but reasonable-fit, simulated spectra are obtained by using the e.s.r. parameters given in Table 4. The spectrum of (**2a**) is complicated by the presence of coupling to $^{79/81}$Br ligands and there is considerable overlapping of resonance bands in the spectrum of (**3a**) with, also, the possible inclusion of coupling to ^{127}I.

In line with earlier studies, the largest component of the ^{93}Nb coupling tensor may be assigned as $A_y(^{93}Nb)$; for the dihalide complexes this value decreases in the order Cl > Br > I, whilst the corresponding value of g_y increases. No resolvable coupling to halogen ligands is observed in the y orientation. The x and z components may be tentatively assigned as in Table 4. For (**2a**) the hyperfine components, $A_x(^{93}Nb)$, are further split by coupling to two approximately equivalent $^{79/81}$Br atoms with $A(^{79/81}Br)$ *ca.* 30 × 10^{-4} cm^{-1}. In a single-crystal e.s.r. study of $[NbCl_2(\eta^5-C_5H_4Me)_2]$, coupling to $^{35/37}$Cl was reported for certain orientations with the magnetic field parallel to the ClNbCl plane.[17] The observation of coupling to halogen in complex (**2a**) and not in (**1a**) is consistent with the larger well resolved isotropic halogen coupling for $[MX_2(cp)_2]^+$ (M = Mo or W) when X = Br, relative to X = Cl.[7] The broadness of

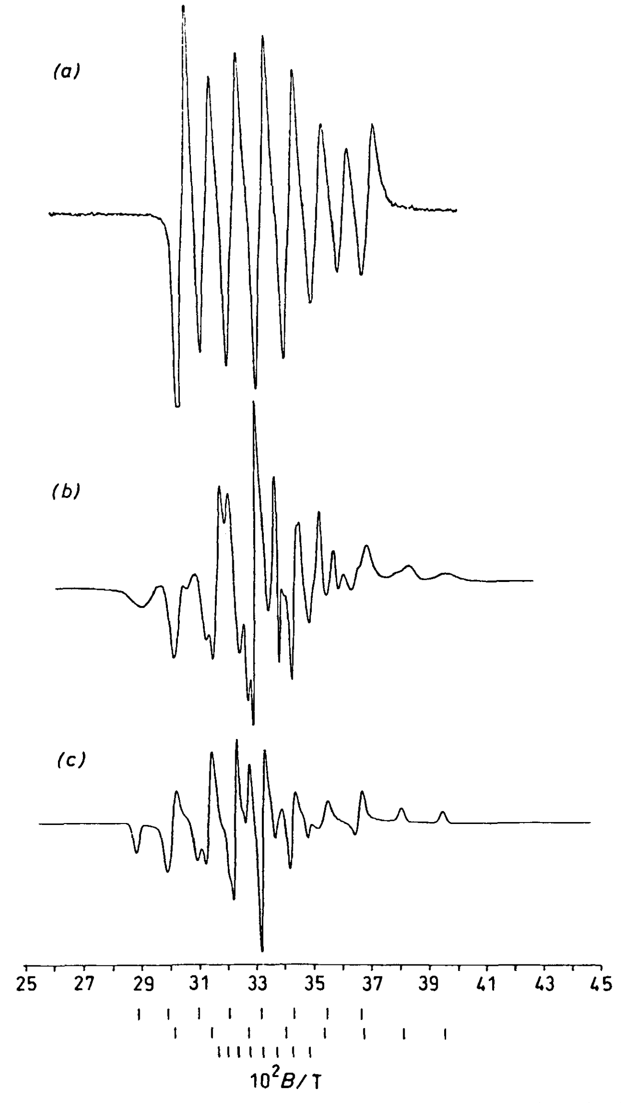

Figure 6. E.s.r. spectra of $[Ta(SCOPh)_2(cp)_2]$ at 9.21 GHz in mthf: (*a*) solution at *ca.* 10 °C; (*b*) glass at *ca.* −140 °C; and (*c*) simulated glass spectrum with g_x,g_y,g_z and A_x,A_y,A_z of Table 4 (linewidths σ_x, σ_y, and σ_z of 1.0, 1.0, and 0.6 mT, respectively)

resonances in the glass spectra of (**3a**) prevents clear observation of any coupling to ^{127}I.

Glass spectra of tantalum complexes (**1b**)—(**4b**) have been difficult to analyse. The best-fit simulations were not ideal, although reproduction of most components of the observed first-derivative spectra are achieved with the parameters listed in Table 4 (*cf.* Figure 6). The simulations were generated by using a simple spin Hamiltonian, $\mathscr{H} = \beta\, \mathbf{S}\cdot\mathbf{g}\cdot\mathbf{B} + \mathbf{S}\cdot\mathbf{A}\cdot\mathbf{I}$, where the principal axes of the symmetric **g** and **A** tensors are coincident and the lineshapes are Gaussian with fixed linewidth parameters for *x*, *y*, and *z* components (σ_x, σ_y, and σ_z); it is possible that quadrupolar effects of ^{181}Ta are important but various simulations[42] involving an additional term $Q'[I_z^2 - \frac{1}{3}I(I - 1)]$ or simulations in which the principal axes *x* and *y* of **g** were rotated about the *z* axis relative to the co-ordinate system of **A** did not significantly improve the analyses. Other complicating factors, involving the 5*d* transition metal, delocalisation on to ligand, and resulting ligand-hyperfine couplings with consequent linewidth variations, may account for the observed glass spectra. Thus, anisotropic e.s.r. parameters for complexes $[TaX_2(cp)_2]$, although apparently the best sets of self-consistent data, must be considered to be approximate. Therefore no detailed discussion of the data will be presented although some trends similar to those of related niobium complexes occur.

It must be noted that the e.s.r. spectrum of $[TaCl_2(cp)_2]$ in the glass is distinctly different to that shown in ref. 36, and simulation using the previously assigned values for components of the *g* and *A* tensors produce a completely different spectrum to that illustrated in Figure 5.

Experimental

All preparations were carried out under a dry nitrogen atmosphere or *in vacuo* using predried solvents in Schlenk-type apparatus. The complexes $[MX_2(cp)_2]$ with M = Nb, X = Cl[11] or M = Ta, X = Cl and Br[12] were prepared by reported methods and purified, as necessary, by column chromatography using CH_2Cl_2–Me_2CO (10:1 v/v) on Florisil. The reagent Tl(SCOPh) was precipitated from the reaction between thallium acetate and monothiobenzoic acid in methanol. Elemental analyses were performed by Butterworth Laboratories, Teddington, or by Analytische Laboratorien, Engelskirken, West Germany.

The following metathetical exchange reactions were employed to synthesise other derivatives.

$[NbBr_2(cp)_2]$.—The complex $[NbCl_2(cp)_2]$ (300 mg, 1.0 mmol) and excess of freshly prepared $MgBr_2$ (from Mg metal and 1,2-dibromoethane) were allowed to react in tetrahydrofuran (thf) at 60 °C for 5 d. After cooling and addition of toluene, partial separation of the soluble product from $MgCl_2/MgBr_2$ was achieved. Further recrystallisation from CH_2Cl_2–Et_2O and final chromatography on Florisil with CH_2Cl_2–Me_2CO gave pure $[NbBr_2(cp)_2]$, *ca.* 90% (Found: C, 31.2; H, 2.7. Calc. for $C_{10}H_{10}Br_2Nb$: C, 31.4; H, 2.6%).

$[NbI_2(cp)_2]$.—The complex $[NbCl_2(cp)_2]$ (300 mg, 1.0 mmol) and excess of KI (350 mg) were stirred in Me_2CO (20 cm^3) at ambient temperature for 4 d. After evaporation of the solvent the product was extracted from the solid residue with CH_2Cl_2 and chromatographed on Florisil. Dichloromethane eluted pure $[NbI_2(cp)_2]$ which was obtained as dark brown crystals, *ca.* 80% (Found: C, 25.1; H, 2.2 Calc. for $C_{10}H_{10}I_2Nb$: C, 25.2; H 2.1%). A little unreacted $[NbCl_2(cp)_2]$ and some $[NbCl(I)(cp)_2]$ could also be eluted from the column by using mixtures of CH_2Cl_2 and Me_2CO.

$[TaI_2(cp)_2]$.—A similar procedure to the above reaction using $[TaCl_2(cp)_2]$ and KI gave dark green–brown $[TaI_2(cp)_2]$ (*ca.* 80%) (Found: C, 22.9; H, 2.1. Calc. for $C_{10}H_{10}I_2Ta$: C, 21.3; H, 1.8%). E.i. mass spectrum: *m/e* (relative intensity) 565 (M^+, 67), 499 ($M^+ - C_5H_5$, 14), 438 (M^+ − I, 100), 374 ($M^+ - C_5H_5I$, 14), 311 (M^+ − 2I, 17), and 127 (I^+, 56).

$[Nb(SCOPh)_2(cp)_2]$.—The complex $[NbCl_2(cp)_2]$ (441 mg, 1.5 mmol) and Tl(SCOPh) (1.02 g, 3.0 mmol) were stirred in Me_2CO (30 cm^3) at ambient temperature for 2 d. The resulting solution was filtered free of suspended thallium salts and evaporated to dryness. Crystallisation of the resulting solid product from CH_2Cl_2–Et_2O gave purple-red needles of $[Nb(SCOPh)_2(cp)_2]$ (502 mg, 58%) (Found: C, 57.8; H, 4.1; S, 13.0. Calc. for $C_{24}H_{20}NbO_2S_2$: C, 58.0; H, 4.0; S, 12.9%). I.r. (Nujol), major bands: 1 610vs, 1 577s, 1 201vs, 1 165s, 911vs, 820s, and 691vs cm^{-1}. E.i. mass spectrum: 497 (M^+, 3), 432 (6.5), 392 (3), 360 (44), 327 (4), 287 (7), and 105 ($PhCO^+$, 100).

$[Ta(SCOPh)_2(cp)_2]$.—By a similar procedure to that employed for the niobium analogue, $[TaCl_2(cp)_2]$ (233 mg, 0.61 mmol) and Tl(SCOPh) (416 mg, 1.22 mmol) in Me_2CO (30

cm^3) gave red needles of $[Ta(SCOPh)_2(cp)_2]$ (85 mg, 24%) (Found: C, 48.7; H, 3.3; S, 11.6. Calc. for $C_{24}H_{20}O_2S_2Ta$: C, 49.2; H, 3.4; S, 10.9%). I.r. (Nujol), major bands; 1 610vs, 1 577s, 1 200s, 1 165s, 909vs, 830vs, and 690s cm^{-1}. E.i. mass spectrum: 585 (M^+, 0.4), 520 (0.3), 480 (12), 415 (14), 375 (6.5), and 105 ($PhCO^+$, 100).

Physical Measurements.—Cyclic voltammetric studies were carried out at scan rates 0.02—0.1 V s^{-1} under argon on *ca*. 10^{-3} mol dm^{-3} solutions of complex in CH_2Cl_2 containing 0.1 mol dm^{-3} $NBu^n{}_4PF_6$ as supporting electrolyte using a PAR 174A analyser with a micro-platinum working electrode and a platinum-wire counter electrode. No compensation was made for *IR* drop and voltammograms were recorded both with a platinum wire in the solution as a pseudo-reference electrode to minimise the cell resistance, and with an aqueous s.c.e. connected *via* a bridge of 0.1 mol dm^{-3} NBu^nPF_6 in CH_2Cl_2 as reference: potentials are quoted relative to the latter although ΔE_p values were significantly greater under these conditions [$E_{\frac{1}{2}}$ (ferrocenium–ferrocene) = +0.385V].

E.s.r. spectra were recorded on a JEOL PE1 *X*-band spectrometer as previously described;[43] all data were corrected for second-order effects by using a modified form of the Breit–Rabi equation[44] and analyses were verified when possible by spectral simulation (see Discussion). I.r. spectra were obtained with a Perkin-Elmer 580 instrument and mass spectra with a Vacuum Generators updated AEI MS9.

X-Ray Crystal Structure Determination of $[Ta(SCOPh)_2(cp)_2]$ (**4b**).—*Crystal data*. $C_{24}H_{20}O_2S_2Ta$, $M = 585.5$, orthorhombic, space group $P2_12_12$ (No. 18), $a = 7.8458(22)$, $b = 19.903(4)$, $c = 7.028(3)$ Å, $U = 1\,097.5$ Å^3, $Z = 2$, $D_c = 1.772$ g cm^{-3}, $F(000) = 570$, μ(Mo-K_α) = 51.49 cm^{-1}, crystal dimensions 0.5 × 0.125 × 0.1 mm.

Data collection. The intensity data were collected on an Enraf-Nonius CAD-4 diffractometer over the quadrant (*h* 0—9, *k* 0—23, *l* 0—8) in the range $1.5 < \theta < 25.0°$ using ω—2θ scanning and Mo-K_α *X*-radiation ($\lambda = 0.710\,693$ Å). Of 1 157 unique data, 911 were found to have $I > 3\sigma(I)$ and were used in subsequent structure solution and refinement. The data were corrected for Lorentz and polarisation effects and absorption (DIFABS[45a]).

Structure solution and refinement. The position of the Ta atom was readily deduced from the Patterson map (SHELXS 86[45b]). The remaining non-hydrogen atoms of the unique portion of the complex were located from a series of successive Fourier difference syntheses. The structure was refined (SHELX 76[45c]) using full-matrix least-squares methods with anisotropic thermal parameters for the non-hydrogen atoms. The hydrogen atoms were placed at idealised positions [d(C–H) 0.95 Å, U_{iso} 0.10 Å^2]. At convergence, the discrepancy factors R and R' were 0.031 and 0.037 respectively, where the weighting scheme $w^{-1} = [\sigma^2(F) + 0.000\,612F^2]$ gave satisfactory analyses of variance. The final difference Fourier map was essentially featureless (general noise level *ca*. ±0.35 e Å^{-3}) apart from a cluster of peaks <0.72 e Å^{-3} in the vicinity of the tantalum atom. Incidental crystallographic calculations were carried out using CALC.[45d]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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