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Syntheses and electrochemical characterization of heteroleptic cyclopentadienyl–dithiolene d^2 tungsten complexes. Structures and magnetic properties of charge-transfer salts†

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Novel diamagnetic tungsten(IV) complexes of general formula W(η-C_5H_4R)$_2$(dithiolene) [R = H, $SiMe_3$ 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-dithiole-2-onate) or dddt^{2-} (5,6-dihydro-1,4-dithiine-2,3-dithiolate)] have been synthesized and their redox properties investigated by cyclic voltammetry. Two reversible oxidation waves are observed for each complex. The redox half-wave potentials allow [W(cp)$_2$(dddt)] (cp = η-C_5H_5) to react with the organic acceptor tcnq (tetracyanoquinodimethane) while the $C_3S_5^{2-}$ and $C_3OS_4^{2-}$ compounds reduce tcnqf$_4$ (7,7,8,8-tetracyano-1,2,4,5-tetrafluoroquinodimethane). X-Ray crystallographic studies were carried out on [W(cp)$_2$(dddt)]$^{\cdot+}$[tcnq]$^{\cdot-}$ and [W(η-C_5H_4Bu^t)$_2$(C_3S_5)]$^{\cdot+}$[tcnqf$_4$]$^{\cdot-}$. The structural analyses and extended-Hückel calculations showed that the radical anions are strongly dimerised into diamagnetic moieties. The cations form centrosymmetrical dimers and exhibit antiferromagnetic interactions, as deduced from the temperature dependence of the magnetic susceptibility, with $T(\chi_{max})$ = 18 and 22 K for [W(cp)$_2$(dddt)]$^{\cdot+}$[tcnq]$^{\cdot-}$ and [W(η-C_5H_4Bu^t)$_2$(C_3S_5)]$^{\cdot+}$[tcnqf$_4$]$^{\cdot-}$ respectively.

Square-planar M(dithiolene)$_2$ complexes have received much attention as precursors for molecular metals and superconductors over the last 15 years.[1] The importance in this chemistry of sulfur-rich dithiolene ligands such as $C_3S_5^{2-}$ (4,5-disulfanyl-1,3-dithiole-2-thionate) or dddt^{2-} (5,6-dihydro-1,4-dithiine-2,3-dithiolate)[2] is largely due to their ability to overlap with each other and to form extended networks with strong electronic interactions, a prerequisite for collective electronic properties such as conductivity, ferro- or antiferro-magnetism. We have been interested in exploring the co-ordination of these ligands on metallocenes and especially in developing the synthesis of paramagnetic species. Recent reports on d^0 complexes M(cp)$_2$(dithiolene) (cp = η-C_5H_5) with M = Ti[3] or Zr[4] show that radical formation is difficult: the loss of one electron leads to very unstable species and the reduction requires a low potential. Group 5 metals appeared to be more interesting since paramagnetism is found in neutral compounds (d^1). Recently works were published on vanadium and niobium complexes.[4,5] However solution EPR spectra indicated a strong localisation of spin density on the metal centre and SQUID magnetic studies on several Nb(cp)$_2$(dithiolene) complexes showed Curie-type behaviour. This leads to the conclusion that paramagnetic species do not interact in the solid state. Another way to obtain d^1 complexes consists of oxidising diamagnetic Mo(cp)$_2$(dithiolene) compounds where reversible oxidation waves were evidenced.[6] We reported on the presence of strong antiferromagnetic interactions in [Mo(cp)$_2$(dddt)]$^{\cdot+}$[tcnq]$^{\cdot-}$ (tcnq = tetracyanoquinodimethane) which demonstrated the ability of the molecules to interact with each other in the solid state.[7] Thus d^2 complexes M(cp)$_2$(dithiolene) seem to be good precursors of novel materials with interesting electronic properties. In addition, Green *et al.*[8] have shown that changing the metal centre from molybdenum to tungsten in compounds [M(η-C_7H_7)LI$_2$] (L = MeCN or PMe_3) increases the exchange constant in the one-dimensional antiferromagnets. For these reasons we decided to investigate the tungsten chemistry with the aim to establish stronger interactions by changing the nature of the metal. The co-ordination of dithiolene ligands on tungsten is not rare[9,10] but little attention has been devoted to the chemistry of complexes having both cp and sulfur-rich ligands.[11] In this work we report the preparation and characterisation of some W(η-C_5H_4R)$_2$(dithiolene) (R = H, $SiMe_3$ or Bu^t) complexes. Note that substituted cyclopentadienyls were chosen because we expected to take advantage of their higher solubility to grow single crystals. We describe herein the structures and magnetic properties of [W(cp)$_2$(dddt)]$^{\cdot+}$[tcnq]$^{\cdot-}$ and [W(η-C_5H_4Bu^t)$_2$(C_3S_5)]$^{\cdot+}$[tcnqf$_4$]$^{\cdot-}$ (tcnqf$_4$ = 7,7,8,8-tetracyano-1,2,4,5-tetrafluoroquinodimethane). These results are compared to those obtained with [Mo(cp)$_2$(dddt)]$^{\cdot+}$[tcnq]$^{\cdot-}$ and the influence of metal and ligand changes on the structural and magnetic properties of the salts is discussed.

Results and Discussion

Syntheses and electrochemical behaviour

The preparation of [W(η-C_5H_4R)$_2$(C_3S_5)] (R = H **1**, $SiMe_3$ **2** or Bu^t **3**), [W(cp)$_2$(C_3OS_4)] **4** ($C_3OS_4^{2-}$ = 4,5-disulfanyl-1,3-dithiole-2-onate) and [W(cp)$_2$(dddt)] **5** involves the conventional metathesis reaction of the dithiolene dianion with the corresponding metallocene dichloride (Scheme 1). In all cases pink-purple air-stable crystalline solids are isolated. In solution **5** is very sensitive to oxidation and the C_3S_5 and C_3OS_4 compounds slowly decompose in chlorinated solvents such as CH_2Cl_2 and $CHCl_3$. Indeed the UV absorption spectra measured in $CHCl_3$ display a decrease of the absorption at λ = 500 nm for the C_3S_5 compounds while near-infrared transitions appear. The diamagnetic complexes were identified by elemental analysis and ^{1}H NMR spectroscopy (Table 1). As expected, the more electron-rich character of the metal results in a slight shielding of all signals compared to those of analogous molybdenum complexes. Furthermore the characteristic absorption bands for the dithiolene are present in the infrared spectra: that arising from the C=C bond at low frequency

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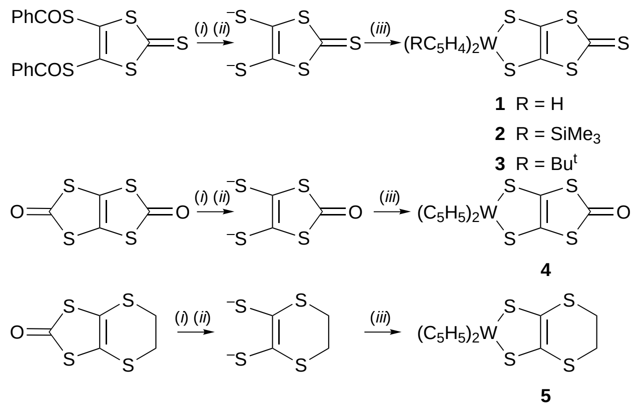
† *Non-SI units employed*: emu = SI × 10^6/4π; eV ≈ 1.60 × 10^{-19} J.

Table 1 Proton NMR data

Complex	M = Mo[7,12]	M = W
[M(cp)$_2$(C$_3$S$_5$)]	5.40 (s, C$_5$H$_5$)	5.36 (s, C$_5$H$_5$)
[M(η-C$_5$H$_4$Bu^t)$_2$(C$_3$S$_5$)]	5.44 (m, 4 H, C$_5$H$_4$), 5.19 (m, 4 H, C$_5$H$_4$), 1.22 (s, 18 H, Bu^t)	5.46 (m, 4 H, C$_5$H$_4$), 5.00 (m, 4 H, C$_5$H$_4$), 1.26 (s, 18 H, Bu^t)
[M(η-C$_5$H$_4$SiMe$_3$)$_2$(C$_3$S$_5$)]	5.58 (m, 4 H, C$_5$H$_4$), 5.07 (m, 4 H, C$_5$H$_4$), 0.25 (s, 18 H, SiMe$_3$)	5.61 (m, 4 H, C$_5$H$_4$), 4.86 (m, 4 H, C$_5$H$_4$), 0.29 (s, 18 H, SiMe$_3$)
[M(cp)$_2$(C$_3$OS$_4$)]	5.37 (s, C$_5$H$_5$)	5.35 (s, C$_5$H$_5$)
[M(cp)$_2$(dddt)]	5.37 (s, C$_5$H$_5$), 3.13 (s, 4 H, dddt)	5.26 (s, C$_5$H$_5$), 3.03 (s, 4 H, dddt)



Scheme 1 (*i*) NaOMe (2 equivalents) in MeOH; (*ii*) Et$_2$O; (*iii*) [W(η-C$_5$H$_4$R)$_2$Cl$_2$], tetrahydrofuran (thf), reflux

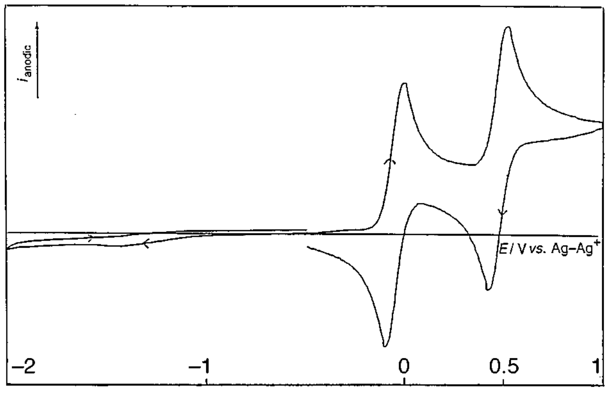


Fig. 1 Cyclic voltammogram of [W(η-C$_5$H$_4$Bu^t)$_2$(C$_3$S$_5$)]. Scan rate 100 mV s^{-1}

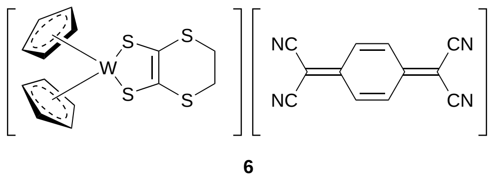
(≈1430–1450 cm^{-1}) and an absorption at 1050 cm^{-1} due to the C=S bond of the C$_3$S$_5$$^{2-}$ ligand.

Cyclic voltammetry experiments performed in MeCN at scan rate 100 mV s^{-1} (Fig. 1) evidence the same behaviour as with molybdenum dithiolene compounds which consists of two reversible oxidation waves. The obtention of d^1 and d^0 species demonstrates the electron-rich character of dithiolene ligands since the second wave of thiolate complexes [M(cp)$_2$(SR)$_2$] (M = Mo or W, R = Me or Ph) was described by Kotz *et al.*[13] as an irreversible oxidation. No significant differences were observed for the redox potentials of the first oxidation between molybdenum and tungsten compounds (Table 2). This is in contrast with the results reported by Kotz for thiolate and dihalide complexes for which the potentials for tungsten were shifted toward cathodic potentials by respectively ≈ 0.1 and 0.2 V. Thus, dithiolene ligands appear to be involved in the first oxidation and they level out the influence of the electron-density difference between Mo and W.

Comparison of the oxidation potentials with the reduction potential of the couple tcnq–tcnq$^{\bullet-}$ ($E_{\frac{1}{2}} = -0.31$ V *vs.* Ag–0.1 M AgClO$_4$) shows that only [W(cp)$_2$(dddt)] can reduce this electron acceptor. Despite the substitution of tungsten for molybdenum and the presence of alkyl-substituted cyclopentadienyl rings, neither compounds derived from C$_3$S$_5$$^{2-}$ nor C$_3$OS$_4$$^{2-}$ undergo a reaction with tcnq. However, oxidation of these novel electron donors can be investigated with the stronger oxidiser tcnqf$_4$ ($E_{\frac{1}{2}} = +0.07$ V *vs.* Ag–0.1 M AgClO$_4$). Another interesting organic acceptor is tcne (tetracyanoethylene) which can be a smaller anionic counterpart and is presumed to favour interactions in the solid state compared to the cyclic tcnq and tcnqf$_4$. Tetracyanoethylene ($E_{\frac{1}{2}} = -0.14$ V *vs.* Ag–0.1 M AgClO$_4$) oxidises only [W(cp)$_2$(dddt)] to form a salt of 1 : 1 stoichiometry, as determined by elemental analysis. Reaction with tcnq occurs in the same way as for [Mo(cp)$_2$(dddt)]:[7] at first a green solid, of 2 : 3 stoichiometry, precipitates and after cooling we obtained black crystals of 1 : 1 stoichiometry (**6**) the structure of which was solved. With the C$_3$S$_5$ and C$_3$OS$_4$ compounds only tcnqf$_4$ salts of 1 : 1 stoichiometry appear as product {[W(η-C$_5$H$_4$R)$_2$(C$_3$S$_5$)]$^{\bullet+}$[tcnqf$_4$]$^{\bullet-}$ (R = Bu^t **7** or H **8**) and [W(cp)$_2$(C$_3$OS$_4$)]$^{\bullet+}$[tcnqf$_4$]$^{\bullet-}$ **9**}. As expected, the use of substituted cyclopentadienyl favours the development of single crystals and allows the crystal structure determination of **7**.

Table 2 Electrochemical data (in V *vs.* Ag–0.1 M AgClO$_4$)

Complex	$E_{\frac{1}{2}}$(M^{V}–M^{IV})	$E_{\frac{1}{2}}$(M^{VI}–M^{V})	Ref.
[W(cp)$_2$(C$_3$S$_5$)]	−0.06	0.42	This work
[Mo(cp)$_2$(C$_3$S$_5$)]	−0.01	0.57	7
[W(η-C$_5$H$_4$Bu^t)$_2$(C$_3$S$_5$)]	−0.05	0.46	This work
[Mo(η-C$_5$H$_4$Bu^t)$_2$(C$_3$S$_5$)]	−0.04	0.53	12
[W(η-C$_5$H$_4$SiMe$_3$)$_2$-(C$_3$S$_5$)]	−0.03	0.50	This work
[Mo(η-C$_5$H$_4$SiMe$_3$)$_2$-(C$_3$S$_5$)]	−0.04	0.56	12
[W(cp)$_2$(C$_3$OS$_4$)]	−0.11	0.43	This work
[Mo(cp)$_2$(C$_3$OS$_4$)]	−0.08	0.55	7
[W(cp)$_2$(dddt)]	−0.36	0.15	This work
[Mo(cp)$_2$(dddt)]	−0.34	0.26	7



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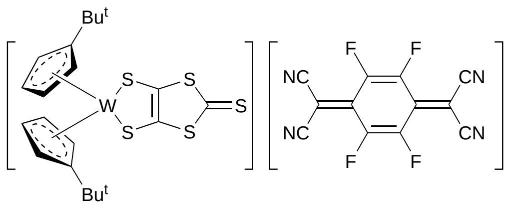

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Solid-state structure

The complex [W(cp)$_2$(dddt)]$^{\bullet+}$[tcnq]$^{\bullet-}$ crystallises in the triclinic system, space group $P\bar{1}$; the structure is similar to that of the analogous [Mo(cp)$_2$(dddt)]$^{\bullet+}$[tcnq]$^{\bullet-}$. Molecules are located in general positions in the unit cell (Fig. 2). Note that data were collected at 200 K due to the high thermal parameters which occur at ambient temperature. The 1 : 1 salt [W(η-

Table 3 Selected bonds (Å) and angles (°) of $M(cp)_2$(dithiolene) complexes

Complex	M–S	C–S	C–C	$Cp_{(1)}$–M	$Cp_{(2)}$–M	S–M–S	Cp–M–Cp	θ*	Ref.
$[W(cp)_2(S_2C_6H_4)]$	2.421(2)	1.753(8)	—	2.004	2.004	82.3(3)	137	8.1	15
$[V(cp)_2(S_2C_6H_4)]$ (A)	2.431(6)	1.70(2)	—	1.992	1.977	79.7(2)	135.4(6)	38.3	16
(B)	2.426(6)	1.77(2)	—	2.001	1.989	79.9(2)	133.4(6)	38.4	
$[Nb(C_5H_4SiMe_3)_2(C_3S_5)]$	2.51(1)	1.78(1)	1.25(3)	2.106	2.095	81.3(6)	131(2)	34	5
$[Mo(cp)_2(dddt)][tcnq]$	2.425(7)	1.725(7)	1.373(1)	1.996	1.995	80.38(2)	135.5(3)	32.1	7
$[W(cp)_2(dddt)][tcnq]$	2.413(2)	1.74(2)	1.373(11)	2.011	2.007	80.66(6)	135.3	33.22	This work
$[W(C_5H_4Bu^t)_2(C_3S_5)][tcnqf_4]$	2.4335(2)	1.7275(8)	1.372(10)	2.012	2.017	82.61(7)	133.5	29.28	This work

* Folding angle between S–M–S and dithiolene planes.

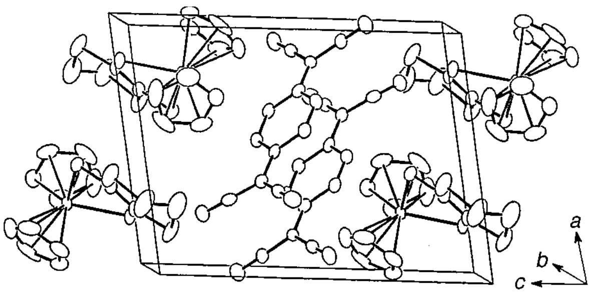


Fig. 2 An ORTEP[14] view of the unit cell of $[W(cp)_2(dddt)]^{\bullet +}[tcnq]^{\bullet -}$ **6**; H atoms are omitted for clarity

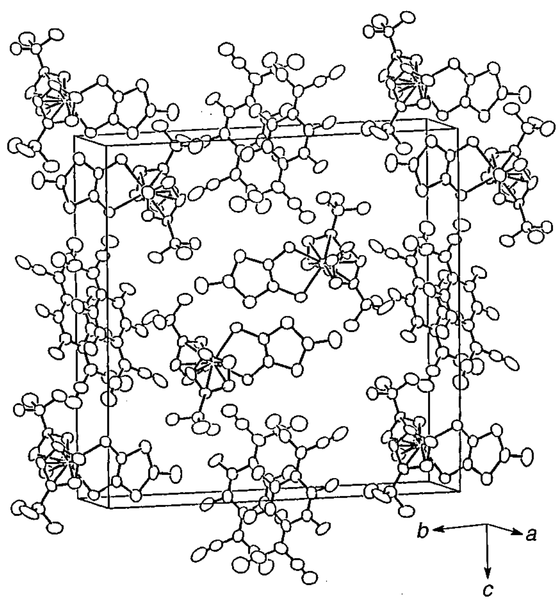


Fig. 3 An ORTEP[14] view of the unit cell of $[W(\eta\text{-}C_5H_4Bu^t)_2(C_3S_5)]^{\bullet +}[tcnqf_4]^{\bullet -}$ **7**; H atoms and MeCN molecules are omitted for clarity

$C_5H_4Bu^t)_2(C_3S_5)]^{\bullet +}[tcnqf_4]^{\bullet -}$ **7** crystallises with a solvent molecule (MeCN), in the monoclinic space group $P2_1/n$. Both the cation and the anion are located in general position in the unit cell (Fig. 3).

The important geometrical features of the cation are compared on the one hand with values reported for d^1 complexes and on the other hand with the characteristics of neutral tungstenocene compounds in Table 3. Both cations of **6** and **7** present a folding angle (θ) between the ligand plane and the S–M–S plane in the range of those observed for d^1 compounds (30–40°) (Fig. 4). This behaviour is now well known and experimental results have been rationalised on the basis of extended-Hückel calculations.[7,17] The lower value observed in the case of **7** is attributable to the steric crowding induced by the substituted cyclopentadienyl as already demonstrated for $[Ti(\eta\text{-}C_5Me_5)_2(C_3S_5)]$.[18] Note also that d^1 neutral compounds present a more important folding than do the d^1 cations as a consequence, may be, of the dithiolene contribution upon oxidation. Indeed, the higher the electron density on the metal, the less is the folding of the ligand. Furthermore, we have previously noticed the participation of $dddt^{2-}$ ligand in oxidation, the formation of $[Mo(cp)_2(dddt)]^{\bullet +}$ leading to a more diketonic structure for the dithiolene.[7]

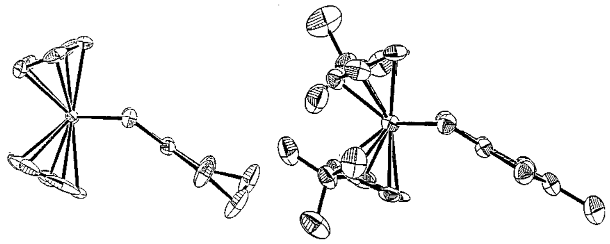
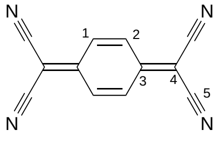


Fig. 4 The ORTEP[14] diagrams showing eclipse views of $[W(cp)_2(dddt)]^{\bullet +}$ (left) and $[W(\eta\text{-}C_5H_4Bu^t)_2(C_3S_5)]^{\bullet +}$ (right); H atoms are omitted for clarity

The reduction of the organic acceptor induces a slight shift from a quinonoid to a benzenoid form in both **6** and **7**. The extracyclic C=C bond lengthens especially while the C–C bond lengths shorten. In addition, a comparison of the geometrical features (Table 4) confirms the association into dimers observed in Fig. 2 for salt **6**. Note also that Fig. 3 reveals the same behaviour for the anionic species $tcnqf_4^{\bullet -}$. The intradimer plane-to-plane distances are similar to those reported for fully reduced dianionic $(tcnq)_2^{2-}$ moieties (Table 4). Extended-Hückel calculations were performed in order to calculate the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the dimeric dianionic moieties. The values are 0.896 (tcnq) and 0.888 eV ($tcnqf_4$), thus confirming a strong overlap which allows one to consider these diradical moieties as being in a singlet state at room temperature and below; for comparison we calculate a value of 0.837 eV for $[Mo(cp)_2(dddt)]^{\bullet +}[tcnq]^{\bullet -}$.

As for the anionic species, the organometallic dimers are organised centrosymmetrically with parallel dithiolene ligand planes. The plane-to-plane distances are 2.19 (**6**) and 2.27 Å (**7**) and the intermolecular M · · · M distance increases from 7.07 to 9.54 Å when the substituted cyclopentadienyl is present. Contrary to the anionic components which tend to a face-to-face arrangement, the dithiolenes lie side by side. In the case of $[W(cp)_2(dddt)]^{\bullet +}[tcnq]^{\bullet -}$ the cationic species are stacked along the *a* axis within a layer structure parallel to the *ab* plane, the layers being separated from each other by the tcnq dimers (Fig. 5). The situation is somewhat different with the salt **7** since only columns of dimers are identified along the *a* axis (Fig. 6). As expected from the intermolecular M · · · M and plane-to-plane distances (molecules 1 and 2 in Figs. 5 and 6), the intradimer interaction calculated by extended-Hückel calculations is found to be stronger in $[\{W(cp)_2(dddt)\}_2]^{2+}$ than in $[\{W(\eta\text{-}C_5H_4Bu^t)_2(C_3S_5)\}_2]^{2+}$, 0.16 and 0.08 eV respectively. These interactions rely mainly on S · · · S overlap due to the following short contacts: $S(2)_1 \cdots S(2)_2$ (3.730 Å) in $[W(cp)_2(dddt)][tcnq]$,

Table 4 Experimental geometric parameters (Å) for tcnq^n and tcnqf$_4$^{n} (n = 0 or −1)



Distance	tcnq[19]	tcnq in **6**	[Mo(cp)$_2$(dddt)][tcnq][7]	[Fe(C$_5$Me$_5$)$_2$][tcnq][20]	tcnqf$_4$[21]	tcnqf$_4$ in **7**
C(1)–C(2)	1.345	1.353	1.352	1.365	1.335	1.340
C(2)–C(3)	1.445	1.428	1.425	1.420	1.439	1.421
C(3)–C(4)	1.373	1.412	1.420	1.410	1.373	1.393
C(4)–C(5)	1.438	1.424	1.418	1.421	1.440	1.423
C(5)–N	1.139	1.152	1.143	1.146	1.142	1.145
*	—	3.16	3.20	3.15	—	3.25

* Plane to plane distance.

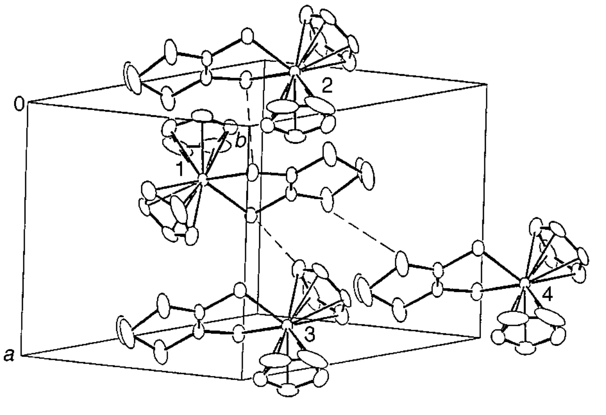


Fig. 5 Intermolecular contacts between [W(cp)$_2$(dddt)]$^{\bullet +}$ moieties in complex **6**

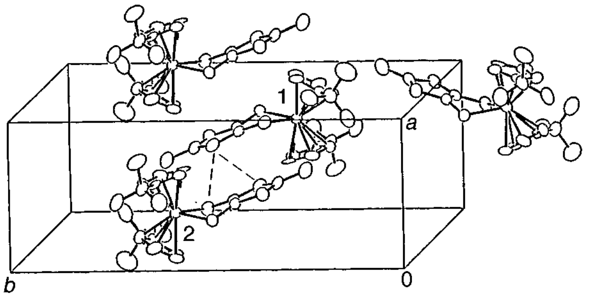


Fig. 6 Intermolecular contacts between [W(η-C$_5$H$_4$Bu^t)$_2$(C$_3$S$_5$)]$^{\bullet +}$ moieties in complex **7**

S(4)$_1$···S(4)$_2$ (3.793) and S(4)$_1$···S(2)$_2$ (3.811 Å) in [W(η-C$_5$H$_4$Bu^t)$_2$(C$_3$S$_5$)][tcnqf$_4$]. In the case of [W(η-C$_5$H$_4$Bu^t)$_2$(C$_3$S$_5$)]$^{\bullet +}$ cations, there is no evidence of interdimer interactions while short contacts S···S or S···C between molecules are present in the layer of the cationic entities of **6**. However extended-Hückel calculations indicate that the interdimer interactions remain weak (<0.06 eV) compared to the intradimer interaction.

Finally, comparison of the analysis above with the results obtained in the case of [Mo(cp)$_2$(dddt)]$^{\bullet +}$[tcnq]$^{\bullet -}$ leads to the following preliminary conclusions: (*i*) acceptors are organised as dimers with strong interactions, contrary to the situation observed in most organic tcnq salts where the anions exhibit a strong tendency to stack in the solid state; (*ii*) changing the metal centre from molybdenum to tungsten in [M(cp)$_2$(dddt)]$^{\bullet +}$-[tcnq]$^{\bullet -}$ gives an isostructural salt in which intermolecular contacts are a little shorter (Table 5); (*iii*) isolated centrosymmetrical dimers are present with [W(η-C$_5$H$_4$Bu^t)$_2$(C$_3$S$_5$)]$^{\bullet +}$ but the introduction of the large Bu^t substituent weakens the interactions.

Table 5 Selected intermolecular distances (Å) in [M(cp)$_2$(dddt)][tcnq]

Distance	M = Mo	M = W
Intradimer M···M	7.15	7.07
Intradimer plane to plane dithiolene	2.25	2.19
Interdimer plane to plane dithiolene	4.50	4.37
S(2)$_1$···S(2)$_2$ (Fig. 5)	3.739	3.730
S(3)$_1$···S(3)$_3$ (Fig. 5)	3.598	3.569
S(1)$_1$···C(7)$_4$ (Fig. 5)	3.684	3.616

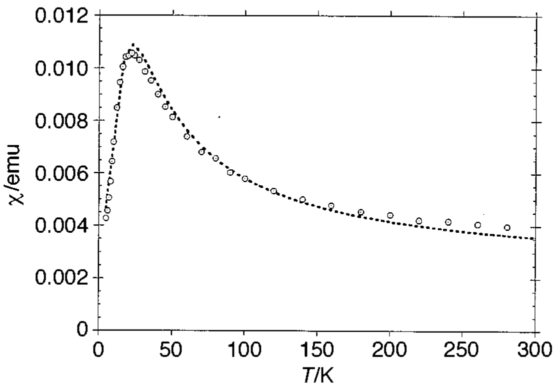


Fig. 7 Temperature dependence of magnetic susceptibility for complex **6**

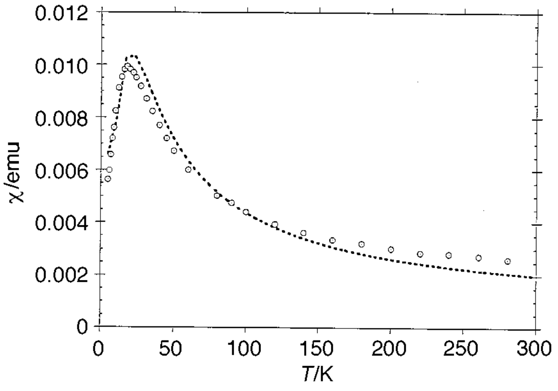


Fig. 8 Temperature dependence of magnetic susceptibility for complex **7**

Antiferromagnetic interactions

The magnetic susceptibilities of [W(η-C$_5$H$_4$Bu^t)$_2$(C$_3$S$_5$)]$^{\bullet +}$-[tcnqf$_4$]$^{\bullet -}$ and [W(cp)$_2$(dddt)]$^{\bullet +}$[tcnq]$^{\bullet -}$ have been measured in the temperature range 5–300 K. The data are collected in Figs. 7 and 8. The shape of the curves is characteristic of antiferromagnetic exchange interactions with $T(\chi_{max})$ = 22 for **7** and 18 K for **6**. Since the structural analysis and extended-Hückel calculations predicted isolated dimers for $[W(\eta\text{-}C_5H_4Bu^t)_2(C_3S_5)]^{\bullet+}$, we attempted to fit the data as a sum of a Bleaney–Bower law which assumes exchange (*J*) to be significant only within a dimer[22] and a Curie tail which takes traces of paramagnetic impurities into account, expression (1).

$$\chi_{\mathrm{mol}} = C_0 + \frac{C_1}{T} + \frac{Ng^2\beta^2}{kT}\,\frac{1}{3 + \exp(-2J/kT)} \qquad (1)$$

Fig. 7 shows that in this way the calculated curve corresponds satisfactorily to the experimental data with the following parameters: $C_0 = 2.31 \times 10^{-3}$ emu, $C_1 = 1.07 \times 10^{-2}$ K^{-1} and $J/k = -18.6$ K. In contrast the model of isolated dimers did not give a completely satisfactory fit in the case of $[W(cp)_2(dddt)]^{\bullet+}[tcnq]^{\bullet-}$ (Fig. 8). This result suggests that the interdimer interactions are not insignificant in this complex. Also, it was tempting to simulate the data by an equation including those interactions. The numerical values of magnetic susceptibility for an alternating chain with two interaction parameters *J* and αJ ($0 < \alpha < 1$) have been fitted by Hatfield[23,24] using the analytical expression (2) where *A*, *B*, *C*, *D*, *E* and *F* are polynomial

$$\chi_{\mathrm{mol}} = C_0 + \frac{C_1}{T} + \frac{Ng^2\beta^2}{kT}\,\frac{A + Bx + Cx^2}{1 + Dx + Ex^2 + Fx^3} \qquad (2)$$

functions of α and $x = |J|/kT$. This model allows a better simulation of the experimental data especially with $\alpha = 0.5\text{–}0.6$ ($R = 0.998$) and the different fits carried out indicate for J/k a value of the order of -16 K. Note, however, that the fits proposed by Hatfield correspond to a one-dimensional model and therefore these results should be analysed cautiously since layers of cations were identified in the solid-state arrangement. Nevertheless the value of α confirms that the magnetic exchange is not only present within a dimer.

This complex exhibits $T(\chi_{\max})$ and J/k values suggesting that the antiferromagnetic interaction is of the same order of magnitude as that in complex **7** and half that in $[Mo(cp)_2(dddt)]^{\bullet+}[tcnq]^{\bullet-}$ [$T(\chi_{\max}) = 32$ K, $J/k = -26$ K]. Surprisingly the experimental data [$T(\chi_{\max})$] do not confirm the extended-Hückel calculations which predict comparable interdimer interactions in the two isostructural salts **6** and $[Mo(cp)_2(dddt)][tcnq]$.‡ In conclusion we have prepared a series of $W(\eta\text{-}C_5H_4R)_2$(dithiolene) complexes which could be precursors of materials with interesting properties. Further investigations are in progress with the aim to rationalise the dimensionality of the interaction according to the nature of the metal and dithiolene ligand.

Experimental

All reactions were carried out under argon using standard Schlenk techniques. Solvents were dried over molecular sieves and distilled just prior to use. The compound $[W(cp)_2Cl_2]$ was prepared according to the literature method;[25] $[W(\eta\text{-}C_5H_4R)_2Cl_2]$ ($R = SiMe_3$ or Bu^t) were synthesised with a similar procedure from the reaction of $[WCl_4(dme)]$[26] (dme = 1,2-dimethoxyethane) with the corresponding salt $Li(C_5H_4R)$ in diethyl ether. Both tcnq and tcne are commercially available and were used without purification. The method described by Wheland and Martin[27] was employed for the synthesis of $tcnqf_4$. The NMR spectra were recorded on a 200 MHz Bruker spectrometer in $CDCl_3$ with $SiMe_4$ as the internal reference. Elemental analyses were performed at the Service Central d'Analyse, CNRS, Vernaison, France.

Preparations

Bis(η^5-cyclopentadienyl)(4,5-disulfanyl-1,3-dithiole-2-thionato)tungsten(IV), $[W(cp)_2(C_3S_5)]$ 1. Equimolar quantities (1 mmol) of $[W(cp)_2Cl_2]$ and $Na_2C_3S_5$[28] were refluxed in thf (50 cm^3) overnight. After filtration, the solvent was removed under reduced pressure and the residue extracted with CH_2Cl_2. The complex $[W(cp)_2(C_3S_5)]$ was isolated as a violet powder after concentration. Yield 0.214 g (42%) (Found: C, 31.0; H, 2.2; S, 29.3. $C_{13}H_{10}S_5W$ requires C, 30.6; H, 1.95; S, 31.35%); $\tilde{\nu}$(KBr)/cm^{-1} 3100w (C–H), 1450s (C=C), 1050s (C=S) and 835s (cp).

(4,5-Disulfanyl-1,3-dithiole-2-thionato)bis(η^5-trimethylsilylcyclopentadienyl)tungsten(IV), $[W(\eta\text{-}C_5H_4SiMe_3)_2(C_3S_5)]$ 2. As above from equimolar quantities (1 mmol) of $[W(\eta\text{-}C_5H_4SiMe_3)_2Cl_2]$ and $Na_2C_3S_5$. Yield 0.196 g (30%) (Found: C, 35.15; H, 4.05; S, 23.75. $C_{19}H_{26}S_5Si_2W$ requires C, 34.85; H, 4.0; S, 24.45%); $\tilde{\nu}$(KBr)/cm^{-1} 3100w (C–H), 2950w (C–H), 1465s (C=C), 1055s (C=S) and 835s ($C_5H_4SiMe_3$).

Bis(η^5-*tert*-butylcyclopentadienyl)(4,5-disulfanyl-1,3-dithiole-2-thionato)tungsten(IV) $[W(\eta\text{-}C_5H_4Bu^t)_2(C_3S_5)]$ 3. This was prepared as above from equimolar quantities (1 mmol) of $[W(\eta\text{-}C_5H_4Bu^t)_2Cl_2]$ and $Na_2C_3S_5$. Yield 0.205 g (33%) (Found: C, 39.2; H, 4.25; S, 25.85. $C_{21}H_{26}S_5W$ requires C, 40.5; H, 4.2; S, 25.7%); $\tilde{\nu}$(KBr)/cm^{-1} 3100w (C–H), 2950w (C–H), 1450s (C=C), 1050s (C=S) and 840s ($C_5H_4Bu^t$).

Bis(η^5-cyclopentadienyl)(4,5-disulfanyl-1,3-dithiole-2-onato)tungsten(IV), $[W(cp)_2(C_3OS_4)]$ 4. Equimolar quantities (1 mmol) of $[W(cp)_2Cl_2]$ and $Na_2C_3OS_4$ were employed.[29] Yield 0.173 g (35%) (Found: C, 31.0; H, 2.2; S, 27.3. $C_{13}H_{10}OS_4W$ requires C, 31.6; H, 2.0; S, 25.9%); $\tilde{\nu}$(KBr)/cm^{-1} 3100w (C–H), 1655 and 1600s (C=O), 1420s (C=C) and 835s (cp).

Bis(η^5-cyclopentadienyl)(5,6-dihydro-1,4-dithiine-2,3-dithiolato)tungsten(IV), $[W(cp)_2(dddt)]$ 5. As for complex **1** from equimolar quantities (1 mmol) of $[W(cp)_2Cl_2]$ and Na_2dddt.[30] Yield 0.247 g (50%) (Found: C, 34.1; H, 2.95; S, 25.85. $C_{14}H_{14}S_4W$ requires C, 34.0; H, 2.85; S, 25.9%); $\tilde{\nu}$(KBr)/cm^{-1} 2900w (C–H), 1450s (C=C) and 810s (cp).

$[W(cp)_2(dddt)][tcnq]$ 6. Warm solutions of $[W(cp)_2(dddt)]$ (50 mg, 0.1 mmol) in MeCN (30 cm^3) and tcnq (21 mg, 0.1 mmol) in MeCN (15 cm^3) were mixed and cooled. After filtration of a green precipitate (2:3 stoichiometry) and concentration, dark crystals of product **6** were isolated: $[W(cp)_2(dddt)][tcnq]$, yield *ca.* 0.045 g (65%) (Found: C, 43.3; H, 2.9; N, 7.35. $C_{26}H_{18}N_4S_4W$ requires C, 44.7; H, 2.6; N, 8.0%); $[W(cp)_2(dddt)_2][tcnq]_3$ (Found: C, 47.65; H, 2.3; N, 10.5. $C_{32}H_{20}N_6S_4W$ requires C, 48.0; H, 2.5; N, 10.5%).

$[W(\eta\text{-}C_5H_4R)_2(C_3S_5)][tcnqf_4]$ ($R = Bu^t$ 7 or H 8). A warm solution of $[W(\eta\text{-}C_5H_4R)_2(C_3S_5)]$ (0.05 mmol) in CH_2Cl_2 (10 cm^3) was added to an equimolar proportion of $tcnqf_4$ (14 mg, 0.05 mmol) in MeCN (10 cm^3). Concentration and cooling afforded black crystals in quantitative yield: $[W(\eta\text{-}C_5H_4Bu^t)_2(C_3S_5)][tcnqf_4]$ (Found: C, 44.3; H, 3.3; N, 7.2. $C_{33}H_{26}F_4N_4S_5W\cdot CH_3CN$ requires C, 44.7; H, 3.1; N, 7.45%); $[W(\eta\text{-}C_5H_5)_2(C_3S_5)][tcnqf_4]$ (Found: C, 37.85; H, 1.65; N, 6.85. $C_{25}H_{10}F_4N_4S_5W$ requires C, 38.15; H, 1.25; N, 7.1%).

$[W(cp)_2(C_3OS_4)][tcnqf_4]$ 9. As above from equimolar quantities of $[W(cp)_2(C_3OS_4)]$ and $tcnqf_4$. Yield *ca.* 0.030 g (80%) (Found: C, 38.4; H, 1.3; N, 6.95. $C_{25}H_{10}F_4N_4S_5W$ requires C, 38.95; H, 1.3; N, 7.25%).

Electrochemical measurements

Cyclic voltammetry experiments were performed with a Radiometer PGP 201 potentiostat. The electrolyte consisted of a

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‡ The intradimer interaction calculated by extended-Hückel calculations is 0.15 eV in $[\{Mo(cp)_2(dddt)\}_2]^{2+}$.

Table 6 Crystallographic data for complexes **6** and **7**[a]

	6	**7**
Formula	$C_{26}H_{18}N_4S_4W$	$C_{35}H_{29}F_4N_5S_5W$
M	698.53	939.78
Crystal size/mm	0.18 × 0.16 × 0.024	0.21 × 0.12 × 0.09
T/K	200	293
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a/Å	9.5090(14)	7.9560(13)
b/Å	10.5400(14)	21.020(3)
c/Å	12.385(2)	21.722(4)
α/°	84.310(14)	
β/°	81.45(2)	96.390(14)
γ/°	89.32(2)	
U/Å^3	1221.4(3)	3610.1(10)
Z	2	4
D_c/g cm^{-3}	1.899	1.729
μ/mm^{-1}	5.095	3.544
T_{max}, T_{min}	0.86, 0.44	0.277, 0.203
Minimum, maximum, h, k, l	−10, 10; −12, 12; −14, 14	−9, 9; −23, 23; −24, 24
F(000)	680	1856
Collected reflections	10 218	22 608
Independent reflections	3624	5715
Goodness of fit	1.019	0.848
R, R'	0.0366, 0.0865	0.0358, 0.0667
Minimum, maximum residual peak/e Å^{-3}	−3.075, 1.627[b]	−1.522, 0.560[b]

[a] Details in common: black parallelepiped crystal; θ_{max} 24.2°; $R = \Sigma||F_o| - |F_c||/\Sigma F_o$; $R' = \{\Sigma w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)]^2\}^{\frac{1}{2}}$. [b] Found near the W atom at a distance less than 1 Å.

0.1 M $NBu^n_4PF_6$ solution in acetonitrile dried on molecular sieves. A three-compartment cell was used with a platinum working electrode (diameter 2 mm), a platinum counter electrode, and an Ag–0.1 M $AgClO_4$ reference electrode. Experiments were performed under an argon flow. After each measurement the reference electrode was checked against the ferrocene–ferrocenium couple (+0.025 V).

Crystallography

Crystals were mounted in glass capilleries using araldite glue. Data were collected on a Stoe-IPDS diffractometer, with graphite-monochromated Mo-Kα radiation (λ 0.710 73 Å). Details are given in Table 6. Empirical absorption corrections were made for complex **7** (multi-scan, X-PREP, SHELXTL 5.04[31]) and a numerical one for **6** (FACEIT, Stoe). Structures were solved by direct methods and refined anisotropically by full-matrix least squares on F^2 (program SHELXTL 5.04). Hydrogen atoms were placed in calculated positions (C–H 0.93 Å), included in structure-factor calculations but not refined.

CCDC reference number 186/807.

See http://www.rsc.org/suppdata/dt/1998/483/ for crystallographic files in .cif format.

Extended-Hückel calculations

Extended-Hückel calculations were performed with double-ζ quality orbitals for C, W, S, F, N and with single-ζ orbitals for H taken from ref. 32.

Magnetic susceptibility measurements

Magnetic susceptibility data were collected on a commercial Quantum Design MPMS5 SQUID susceptometer. Data were corrected for molecular diamagnetism and holder contribution.

References

1 P. Cassoux, L. Valade, H. Kobayashi, R. A. Clar and A. E. Underhill, *Coord. Chem. Rev.*, 1991, **110**, 115; S. Q. Sun, B. Zhang, P. J. Wu and D. B. Zhu, *J. Chem. Soc., Dalton Trans.*, 1997, 277.
2 R. M. Olk, B. Olk, W. Dietzsch, R. Kirmse and E. Hoyer, *Coord. Chem. Rev.*, 1992, **177**, 99.
3 H. Ushijima, S. Sudoh, M. Kajitani, K. Shimizu, T. Akiyama and A. Sugimori, *Appl. Organomet. Chem.*, 1991, **5**, 221; F. Guyon, C. Lenoir, M. Fourmigué, J. Larsen and J. Amaudrut, *Bull. Soc. Chim. Fr.*, 1994, **131**, 217.
4 S. Zeltner, W. Dietzsch, R. M. Olk, R. Kirmse, R. Richter, U. Schröder, B. Olk and E. Hoyer, *Z. Anorg. Allg. Chem.*, 1994, **620**, 1768.
5 F. Guyon, M. Fourmigué, R. Clérac and J. Amaudrut, *J. Chem. Soc., Dalton Trans.*, 1996, 4093.
6 M. L. H. Green, W. B. Heuer and G. C. Saunders, *J. Chem. Soc., Dalton Trans.*, 1990, 3789.
7 M. Fourmigué, C.Lenoir, C. Coulon, F. Guyon and J. Amaudrut, *Inorg. Chem.*, 1995, **34**, 4979.
8 M. L. H. Green, A. Harrison, P. Mountford and D. K. P. Ng, *J. Chem. Soc., Dalton Trans.*, 1993, 2215.
9 P. K. Baker, M. G. B. Drew, E. E. Parker, N. Robertson and A. E. Underhill, *J. Chem. Soc., Dalton Trans.*, 1997, 1429.
10 G. Matsubayashi, K. Douki, H. Tamura, M. Nakano and W. Mori, *Inorg. Chem.*, 1993, **32**, 5990.
11 M. L. H. Green and W. E. Lindsell, *J. Chem. Soc. A*, 1967, 1455.
12 F. Guyon, Ph.D. Thesis, Université de Besançon, 1994.
13 J. C. Kotz, W. Vining, W. Coco, R. Rosen, A. R. Dias and M. H. Garcia, *Organometallics*, 1983, **2**, 68.
14 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
15 T. Debaerdemacker and A. Kutoglu, *Acta Crystallogr., Sect. B*, 1973, **29**, 2664.
16 D. W. Stephan, *Inorg. Chem.*, 1992, **31**, 4218.
17 J. W. Lauher and R. Hoffmann, *J. Am. Chem. Soc.*, 1976, **98**, 1729.
18 F. Guyon, M. Fourmigué, P. Audebert and J. Amaudrut, *Inorg. Chim. Acta*, 1995, **239**, 117.
19 R. E. Long, R. A. Sparks and K. N. Trueblood, *Acta Crystallogr.*, 1965, **18**, 932.
20 J. S. Miller, J. H. Zhang, W. M. Reiff, D. A. Dixon, L. D. Preston, A. H. Reis, E. Gebert, M. Extine, J. Troup, A. J. Epstein and M. D. Ward, *J. Phys. Chem.*, 1987, **91**, 4344.
21 T. J. Emge, M. Maxfield, D. O. Cowan and T. J. Kistenmach, *Mol. Cryst. Liq. Cryst.*, 1981, **65**, 161.
22 J. C. Bonner, H. W. J. Blöte, J. W. Bray and I. S. Jacobs, *J. Appl. Phys.*, 1979, **50**, 1810.
23 W. E. Hatfield, *J. Appl. Phys.*, 1981, **52**, 1985.
24 O. Kahn, *Molecular Magnetism*, VCH, Weinheim, 1993, ch. 11.
25 C. Persson and C. Andersson, *Organometallics*, 1993, **12**, 2370.
26 C. Persson and C. Andersson, *Inorg. Chim. Acta*, 1993, **203**, 235.
27 R. C. Wheland and E. L. Martin, *J. Org. Chem.*, 1975, **40**, 3101.
28 K. S. Varma, A. Bury, N. J. Harris and A. Underhill, *Synthesis*, 1987, 837.
29 R. R. Shumaker and E. M. Engler, *J. Am. Chem. Soc.*, 1977, **99**, 5521.
30 J. Larsen and C. Lenoir, *Synthesis*, 1989, 134.
31 G. M. Sheldrick, SHELXTL, version 5, Siemens Analytical X-Ray Division, Madison, WI, 1994.
32 M.-H. Whangbo, J. M. Williams, P. C. W. Leung, M. A. Beno, T. J. Emge, H. H. Wang, K. D. Carlson and G. W. Crabtree, *J. Am. Chem. Soc.*, 1985, **105**, 5815; E. Clementi and C. Roetti, *At. Data Nucl. Data Tables*, 1974, **14**, 177.

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