Pergamon

0277-5387(94)00487-0

Polyhedron Vol. 14, No. 13–14, pp. 1741–1750, 1995
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0277-5387/95 \$9.50+0.00

RADICAL CATION–RADICAL ANION SALTS: MOLYBDENUM COMPLEXES CONTAINING THE $[TCNQ]^{\bullet -}$ OR $[TCNE]^{\bullet -}$ RADICAL ANIONS. X-RAY CRYSTAL STRUCTURE OF $[Mo(Et_2NCS_2)_4](TCNQ)$

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(*Received* 5 *October* 1994; *accepted* 21 *November* 1994)

Abstract—The reactions between the molybdenum(IV) complexes $[Mo(dtc)_4]$ **1** (dtc = Et_2NCS_2 for **1a** and Me_2NCS_2 for **1b**) and TCNQ produced the 1 : 1 derivatives $[Mo(dtc)_4](TCNQ)$ **2**. Subsequent reaction of **2** with TCNQ gave the 1 : 2 complexes **3** $[Mo(dtc)_4](TCNQ)_2$. Complexes **1** reacted with TCNE under nitrogen to give the 1 : 1 compounds $[Mo(dtc)_4](TCNE)$ **4** while under ambient conditions the pentacyanopropenide derivatives $[Mo(dtc)_4][(NC)_2C—C(CN)—C(CN)_2]$ **5** were obtained. In solution, cyclic voltammetry and ESR studies revealed the presence for all types of complexes of the molybdenum(V) radical cation $[Mo(dtc)_4]^{\bullet +}$ which is associated with the radical anion $TCNX^{\bullet -}$ in **2** (X = Q) and **4** (X = E) and with a 1 : 1 mixture of neutral and anionic TCNQ species in **3**. Complex **2a** has been studied by single crystal X-ray diffraction. The crystal structure consists of monomeric $TCNQ^{\bullet -}$ radical anions and $[Mo(dtc)_4]^{\bullet +}$ cations with a triangular dodecahedral arrangement of S atoms and a point group symmetry which is approximately D_{2d}.

Molecular 'charge-transfer' or donor–acceptor adducts between TCNQ [7,7,8,8-tetracyano-*p*-quinodimethane = 2,2′-(2,5-cyclohexadiene-1,4-diylidene)bispropanedinitrile] or TCNE [tetracyanoethylene = ethenetetranitrile] and various organic electron donors have been known for many years and very widely studied.[1] On the other hand, although also well characterized, there are fewer examples of compounds composed of these unsaturated polynitriles and transition metal complexes. However, such coordination compounds present a very rich chemistry since TCNQ and TCNE are very versatile reagents:[2] (i) as a strong π acceptor,

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TCNX (X = Q, E) gives rise to metal complexes in which it may be coordinated in various oxidation states (TCNX,[3] $TCNX^{\bullet -}$[4] and $TCNX^{2-}$[5]); (ii) with electron-rich and coordinatively saturated metallic donors, TCNX may give charge-transfer salts, more or less strongly bonded 'ion pairs', or salts in which the TCNX unit adopts a fractional oxidation state;[6] and (iii) as unsaturated polynitrile, TCNX can bind metals through one or more of the nitrile lone pairs[7] or through olefinic bonds.[8] It is noteworthy that many of such TCNX derivatives are of considerable interest since they may act as materials exhibiting unusual magnetic,[6,9] and electrical[10] properties. We recently extended the coordination chemistry of these organic molecules to their reactions with dinuclear complexes and, more precisely, with a quadruply bonded molybdenum complex.[11] TCNE reacts with $[Mo_2L_2]$ ($L = C_{22}H_{22}N_4$) to afford, by a monoelectronic transfer process, $[Mo_2L_2]^{\bullet +}(TCNE)^{\bullet -}$ which subsequently reacts with an excess of TCNE in the presence of oxygen to give the oxomolybdenum(V) derivative $[MoOL][C_3(CN)_5]$ as confirmed by an X-ray crystal structure determination.[11] Examples concerning the reactions of TCNQ with molybdenum complexes have also been previously reported. Crystal structure, electrical conductivities and magnetic properties of the charge transfer salts formed of the cubane cluster cation $[Mo_4(\eta^5\text{-}C_5H_4Pr)_4(\mu_3\text{-}Y)_4]^{\bullet +}$ (Y = S, Se) and $(TCNQ)^{\bullet -}$ anion have been reported by Baird *et al.*[12] who also recently studied the reaction of TCNQ with η^7-cycloheptratrienyl derivatives of molybdenum.[13] The trinuclear cationic complexes $[Mo_3Y_7(dtc)_3]$ (dtc) (Y = S, Se; dtc = R_2NCS_2) react with TCNQ affording the $[Mo_3Y_7(dtc)_3]_n(TCNQ)_2$ compounds (n = 1, 2), the structure of which consists of trinuclear cluster cations and $TCNQ^{\bullet -}$ anions.[14]

In this paper, we report the reactions of the eight-coordinated molybdenum(IV) complexes $[Mo(dtc)_4]$ **1** with TCNQ and TCNE. Previous electrochemical studies show that the first oxidation potential of complexes **1**[15] is smaller than the potential required to reduce TCNX (X = Q, E)[3b] and for this reason we expected them to participate in spontaneous electron-transfer reactions with TCNX. Different types of complexes are described: (i) the 1 : 1 Mo/TCNQ complexes $[Mo(dtc)_4](TCNQ)$ **2**, an example of which has been fully characterized in the solid state by an X-ray crystal structure determination; (ii) the 1 : 2 Mo/TCNQ complexes $[Mo(dtc)_4](TCNQ)_2$ **3**; (iii) the TCNE analogues of **2**, $[Mo(dtc)_4](TCNE)$ **4**; and (iv) the pentacyanopropenide derivatives $[Mo(dtc)_4][C_3(CN)_5]$ **5**.

EXPERIMENTAL

Preparative studies and physical measurements

Unless otherwise stated, all reactions were performed in Schlenk tubes in a dry oxygen-free nitrogen atmosphere. Solvents were distilled by standard techniques and thoroughly deoxygenated before use. Elemental analyses were performed by Service Central d'Analyse du CNRS, Vernaison, France. IR spectra were obtained with a Perkin–Elmer 1430 spectrometer (KBr pellets). ESR spectra were run on a JEOL FE 3X spectrometer (X-band). UV–vis spectra were recorded on a Uvikon 930 (Kontron) spectrometer. The apparatus, the three-compartment microelectrochemical cell, the treatment of the solvent and the supporting electrolyte for the electrochemical studies have all been previously described.[11,16] The reference electrode used is the half-cell: Pt/ferrocenium picrate (10^{-2} M), ferrocene (10^{-2} M), Bu_4NPF_6 (0.2 M), benzonitrile. For comparison of the present results with other works, the Fc^+/Fc formal potential has been measured *vs* SCE in benzonitrile (0.2M Bu_4NPF_6): $E'^{\circ}(Fc^+/Fc) = +0.43$ V *vs* SCE.

The starting molybdenum complex $[Mo(dedtc)_4]$ **1a** (dedtc = Et_2NCS_2) was synthesized by modification of the procedure described by Lozano *et al.*:[17] a mixture of $[Mo(CO)_6]$ (1.0 g, 3.8 mmol) and bis(diethylthiocarbamoyl)disulphide $Et_2NC(S)SSC(S)NEt_2$ (2.25 g, 7.6 mmol) in acetone (40 cm^3) was refluxed for *ca* 2 h. The violet crystals which appeared at room temperature were filtered and washed with pentane (yield *ca* 80%). The methyl analogue **1b** was similarly prepared and purified using toluene instead of acetone.

Complexes **2**. *Complex* **2a**. A dichloromethane solution (30 cm^3) of TCNQ (0.102 g, 0.5 mmol) was slowly added (*ca* 15 min) at room temperature to a dichloromethane solution (30 cm^3) of **1a** (0.344 g, 0.5 mmol). The colour changed from violet to green and stirring was maintained for *ca* 1 h. The solution was then evaporated to dryness under reduced pressure. The residue was extracted with acetonitrile and after filtration the resulting solution was kept at -20°C overnight. Green crystals appeared; they were filtered, washed and dried under reduced pressure (yield *ca* 95%). These crystals have been characterized by X-ray crystal structure determination (see below). ESR: CH_2Cl_2 solution (room temperature, *ca* 10^{-4} M): $TCNQ^{\bullet -}$ multiplet $g = 2.003$; inorganic signal $g = 1.979$, $A_{Mo} = 38.3$ G (throughout this work 1 G = 10^{-4} T). IR (KBr, cm^{-1}): 2180m, 2150m $\nu(CN)$; 1535s, 1520s $\nu(N{-}CS_2)$; 988m $\nu_{as}(CS_2)$; 570w $\nu_s(CS_2)$; 355s $\nu(MoS)$.

Complex **2b**. **2b** was prepared from **1b** by a similar procedure to that described above for **2a** and recrystallized from dichloromethane (yield *ca* 90%). Found: C, 35.2; H, 3.5; N, 13.1. Calc. for [Mo(dmdtc)$_4$](TCNQ)·CH_2Cl_2, [$MoC_{24}H_{28}N_8S_8$·CH_2Cl_2]: C, 34.7; H, 3.5; N, 12.9%. ESR: $(CH_3)_2CO$ solution (room temperature, *ca* 10^{-4} M): TCNQ$^{\bullet-}$ multiplet $g = 2.006$; inorganic signal $g = 1.982$, $A_{Mo} = 37.9$ G. IR (KBr, cm^{-1}): 2180m, 2150m ν(CN); 1550vs ν(N—CS$_2$); 1005m, 985 m ν_{as}(CS$_2$); 570w ν_s(CS$_2$); 355s ν(MoS).

Complexes **3**. *Complex* **3a**. A mixture of TCNQ (0.102 g, 0.5 mmol) and **2a** (0.446 g, 0.5 mmol) was dissolved into CH_3CN (40 cm^3) and stirring was maintained at room temperature for *ca* 12 h. The resulting green solution was kept at −20°C for *ca* 24 h. Dark needles of complex **3a** precipitated; they were filtered, washed with diethyl ether and dried under reduced pressure (yield *ca* 90%). Found: C, 48.4; H, 4.3; N, 15.3. Calc. for [Mo(dedtc)$_4$](TCNQ)$_2$, [$MoC_{44}H_{48}N_{12}S_8$]: C, 48.2; H, 4.4; N, 15.3%. ESR: CH_3CN solution (room temperature, *ca* 10^{-4} M): TCNQ$^{\bullet-}$ multiplet $g = 2.004$; inorganic signal $g = 1.981$, $A_{Mo} = 37.5$ G. IR (KBr, cm^{-1}): 2180 m, 2150 m, ν(CN), 1520s ν(N—CS$_2$), 1080 s br, 355s ν(MoS).

Complex **3b**. **3b** was prepared from **2b** by a similar procedure to that described for **3a** (yield *ca* 90%). Found: C, 44.3; H, 3.4; N, 16.7. Calc. for [Mo(dmdtc)$_4$](TCNQ)$_2$, [$MoC_{36}H_{32}N_{12}S_8$]: C, 43.9; H, 3.3; N, 17.1%. ESR data similar to that given for **3a**.

Complexes **4**. *Complex* **4a**. TCNE (0.060 g, 0.5 mmol) and **1a** (0.344 g, 0.5 mmol) were separately dissolved into CH_2Cl_2 (30 cm^3). The TCNE solution was slowly added to the violet molybdenum solution and stirring was maintained at room temperature for *ca* 15 min. The resulting brown solution was then evaporated to dryness under reduced pressure. The residue was extracted with acetonitrile or acetone (20 cm^3) and diethyl ether added to produce immediate precipitation of **4a** as a brown microcrystalline powder (yield *ca* 70%). Found: C, 38.2; H, 5.3; N, 13.5 Calc. for [Mo(dedtc)$_4$](TCNE), [$MoC_{26}H_{40}N_8S_8$]: C, 38.2; H, 4.9; N, 13.7%. ESR: CH_3CN solution (room temperature, *ca* 10^{-4} M): TCNE$^{\bullet-}$ multiplet $g = 2.006$; inorganic signal $g = 1.982$, $A_{Mo} = 38$ G.

Complex **4b**. **4b** was prepared from **1b** by a similar procedure to that described for **4a** (yield *ca* 70%). Found: C, 30.6; H, 3.5; N, 15.9. Calc. for [Mo(dmdtc)$_4$](TCNE), [$MoC_{18}H_{24}N_8S_8$]: C, 30.7; H, 3.4; N, 15.9%. ESR data similar to that given for **4a**.

Complexes **5**. *Complex* **5a**. An acetonitrile solution (30 cm^3) of **4a** (0.40 g, 0.5 mmol) was kept at ambient atmosphere for *ca* 1 week. The brown precipitate was filtered and washed with diethyl ether (yield *ca* 20%). Found: C, 37.8; H, 4.4; N, 14.0. Calc. for [Mo(dedtc)$_4$][$C_3(CN)_5$]·$2H_2O$, [$MoC_{28}H_{40}N_9S_8$·$2H_2O$]: C, 37.7; H, 5.0; N, 14.2%. ESR: CH_3CN solution (room temperature, *ca* 10^{-4} M): inorganic signal $g = 1.981$, $A_{Mo} = 37.5$ G. IR (KBr, cm^{-1}): 2200 F ν(CN).

Complex **5b**. **5b** was prepared from **4b** by a similar procedure to that described for **4a** (yield *ca* 20%). Found: C, 31.3; H, 3.2; N, 15.8. Calc. for [Mo(dmdtc)$_4$][$C_3(CN)_5$]·$2H_2O$, [$MoC_{20}H_{24}N_9S_8$·$2H_2O$]: C, 30.8; H, 3.6; N, 16.2%. IR (KBr, cm^{-1}): 2200 F ν(CN).

Crystal structure determination of **2a** [Mo (Et$_2$NCS$_2$)$_4$](TCNQ)

Crystals of **2a** were grown from MeCN–Et$_2$O as dark prisms and that used had dimensions *ca* 0.45 × 0.40 × 0.25 mm. Diffracted intensities were collected using a Siemens *R3m/v* four-circle diffractometer at 293 K. Of the 4063 data collected (Wyckoff ω-scan, $2\theta < 50°$), 2966 unique data had $F > 5\sigma(F)$, and only these were used for structure solution and refinement. The data were corrected for Lorentz, polarization and X-ray absorption effects. An empirical absorption correction was applied for the latter using a method based upon azimuthal scan data.[18]

Crystal data. $C_{32}H_{44}MoN_8S_8$, $M = 893.2$, monoclinic, space group $C2/c$, $a = 15.470(6)$, $b = 13.709(5)$, $c = 21.033(8)$ Å, $\beta = 104.86(3)°$, $U = 4312(3)$ Å^3, $Z = 4$, $D_c = 1.38$ g cm^{-3}, $F(000) = 1848$, μ(Mo-$K\alpha$) = 7.24 cm^{-1}, Mo-$K\alpha$ X-radiation (graphite monochromator) $\lambda = 0.71073$ Å, $T = 293$ K.

Several crystals were evaluated prior to data collection but all showed similar rather broad peak profiles. A reasonable data collection was achieved using Wyckoff ω-scans but it is possible that a small degree of peak overlap may have occurred for intense low angle data. The structure was solved by conventional heavy atom methods and successive difference Fourier syntheses were used to locate all non-hydrogen atoms which were refined with anisotropic thermal parameters. The unit cell contains four [Mo(Et$_2$NCS$_2$)$_4$]$^{\bullet+}$ cations and four TCNQ$^{\bullet-}$ anions. The Mo cations have crystallographically imposed two-fold symmetry, whilst the TCNQ anions lie across inversion centres and have crystallographically imposed $\bar{1}$ symmetry. With the exception of H(23a) whose position was refined, hydrogen atoms were included in calculated positions with fixed isotropic thermal parameters (Uiso = 0.08). Final $R = 0.049$ ($R_w = 0.062$) with a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.0006F^2]$. The final electron density difference synthesis showed no peaks > 1.39 or < -0.92 e Å^{-3}. All calculations were performed on a DEC microVax II computer with the SHELXTL PLUS system of programs.[18] Scattering factors with corrections for anomalous dispersion were taken from International Tables.[19]

Additional material available from the Cambridge Crystallographic Data Centre, Cambridge, comprises non-hydrogen and hydrogen atomic coordinates, thermal parameters and remaining bond lengths and angles. List of observed and calculated structure factors are available upon request from the corresponding author.

RESULTS AND DISCUSSION

Syntheses

Reaction of TCNQ with 1 equivalent of **1** [Mo(dtc)$_4$] (**1a**, dedtc = Et_2NCS_2; **1b**, dmdtc = Me_2NCS_2) in dichloromethane at room temperature quickly resulted in a colour change of the solution from violet to green. Recrystallization of the resulting solid in acetonitrile or in dichloromethane afforded green crystals of complex **2** in almost quantitative yield. Elemental analyses for complex **2b** indicated the formation of the 1 : 1 complex [Mo(dmdtc)$_4$](TCNQ) in agreement with the results of the single-crystal structure determination for complex **2a** (see below).

Complexes **2** further reacted with 1 equivalent of TCNQ in acetonitrile at room temperature giving, in very good yield, the 1 : 2 complexes [Mo(dtc)$_4$] (TCNQ)$_2$ **3** as dark microcrystalline needles. Unfortunately, despite many attempts using a variety of solvent systems and crystallization techniques, it was not possible to grow suitable crystals of **3** for an X-ray study. Only very thin needles were obtained and, as a result, in order to obtain insights into the structure, particularly the molybdenum oxidation state and the charge state of the TCNQ moieties, we have had to rely on various techniques [cyclic voltammetry (CV), IR, UV–vis, ESR].

In a dry oxygen-free nitrogen atmosphere, reaction of **1** with TCNE in dichloromethane at ambient temperature produced a quasi immediate colour change from violet to brown. After further work up (evaporation to dryness and extraction with acetonitrile or acetone), diethyl ether was added in order to obtain immediate precipitation of complexes **4** [Mo(dtc)$_4$](TCNE) as brown microcrystals. All attempts to precipitate these complexes slowly in order to obtain suitable monocrystals for an X-ray study failed and resulted in decomposition of the TCNE$^{\bullet -}$ anion and formation of decomposition products as shown by the IR absorptions in the νCN range. These decomposition products **5** can be obtained in a pure state by allowing evolution of the above solutions at ambient atmosphere. Analytical data, as well as CV and IR data (see below), were in agreement with the [Mo(dtc)$_4$][C$_3$(CN)$_5$] formulation of **5**. It is noteworthy that formation of the pentacyanopropenide anion [(NC)$_2$C—C(CN)—C(CN)$_2$]$^-$ from TCNE$^{\bullet -}$ has previously been reported by our group.[11] This anion has also been shown to arise from hydrolysis of TCNE in the presence of a base B according to eq. (1).[20]

$$2C_2(CN)_4 + 4B + 2H_2O \rightarrow 4BH^+ + [C_3(CN)_5]^- + 3CN^- + CO_2 \qquad (1)$$

Solution studies

Electrochemical studies. CV of complex **2a** in benzonitrile (PhCN) is shown in Fig. 1(a), and reveals five redox processes. Except for the more cathodic one, the other processes display the usual criteria of electrochemical reversibility ($i_{pa}/i_{pc} \approx 1$ and $\Delta E_p \approx 60$ mV independent of the scan rate, $i_p/v^{1/2} \approx$ constant). In reference to previous work, the two processes labelled as 3 and 4 in Fig. 1 are associated with the TCNQ moiety[3b] ($E_3'^{\circ}$ (TCNQ$^{\bullet -/2-}$) = −0.81 V, $E_4'^{\circ}$ (TCNQ$^{0/\bullet -}$) = −0.21 V) [eq. (2)], and the others are attributed to the inorganic cation [Mo(dedtc)$_4$]$^{\bullet +}$ [15] ($E_{p(irr)1} = -1.68$ V, $E_2'^{\circ} = -0.91$ V, $E_5'^{\circ} = 0.70$ V) [eq. (3)]. The potentials are quoted *vs* the Fc$^+$/Fc system. These potential values are the same as those obtained for pure solutions of TCNQ and [Mo(dtc)$_4$], previously reported[3b,15] or recorded separately in the present experimental conditions. The electrochemical behaviour of complex **2a** can thus be reported as the sum of the following two independent sets of redox reactions:

$$[\mathrm{TCNQ}]^{2-} \underset{e^-}{\overset{E_3}{\rightleftharpoons}} [\mathrm{TCNQ}]^{\bullet -} \underset{e^-}{\overset{E_4}{\rightleftharpoons}} [\mathrm{TCNQ}] \qquad (2)$$

$$\mathrm{X} \xleftarrow[E_{1(irr)}]{e^-} [\mathrm{Mo^{IV}(dtc)_4}] \underset{e^-}{\overset{E_2}{\rightleftharpoons}} [\mathrm{Mo^{V}(dtc)_4}]^{\bullet +} \underset{e^-}{\overset{E_5}{\rightleftharpoons}} [\mathrm{Mo^{VI}(dtc)_4}]^{2+} \qquad (3)$$

The zero current-potential located at *ca* −0.5 V reflects the TCNQ$^{\bullet -}$ radical formulation for the anion, and an oxidation state of V for the molybdenum atom. Taking into account a slightly (*ca* 30%) slower diffusion for the cation, the small difference of peak heights between these two sets

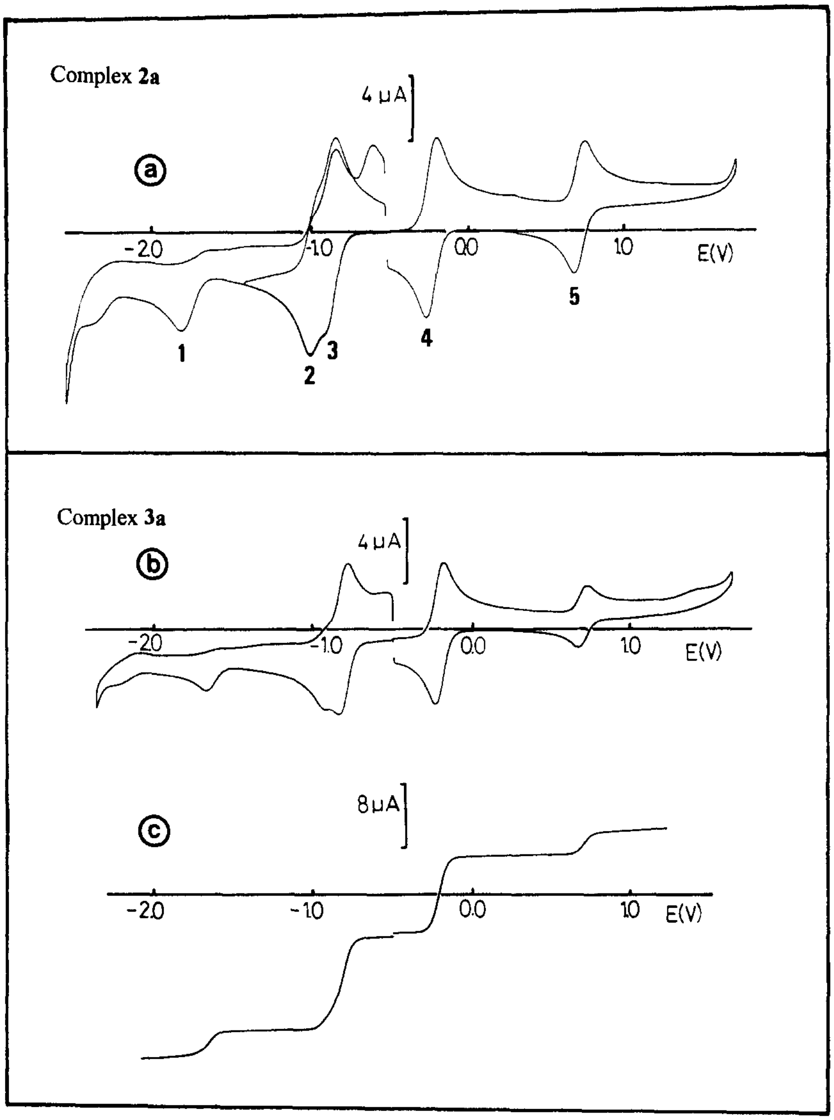

Fig. 1. (a) Complex **2a**, cyclic voltammetry; (b) complex **3a**, cyclic voltammetry; and (c) complex **3a**, rotating disc electrode voltammetry, in PhCN, 0.1 M Bu_4NPF_6; Pt electrode; scan rate 0.1 V s^{-1}; V *vs* Fc^+/Fc.

of systems is in accordance with a stoichiometric mixture of the $TCNQ^{\bullet-}$ anion and the inorganic cation $[Mo^V(dtc)_4]^{\bullet+}$.

The CV of complex **2b** presents similar features with $E_{p(irr)1} = -1.62$ V, $E_2'^{\circ} = -0.89$ V, $E_5'^{\circ} = 0.71$ V.

The CV of complex **3a**, shown in Fig. 1(b), exhibits exactly the same redox processes as those observed for compound **2a** [eqs (2) and (3)]. However, (i) the peak heights of the TCNQ unit are twice as high as those of the cation (still plus *ca* 30%), (ii) as clearly emphasized on the voltammogram at a rotating ring disc electrode [Fig. 1(c)], the zero current for a solution of **3a** corresponds to the half wave potential of the $TCNQ^0/TCNQ^{\bullet-}$ redox process. This result establishes without any ambiguity that in solution complex **3a** consists of $[Mo^V(dtc)_4]^{\bullet+}$ cations and a 1 : 1 mixture of $TCNQ^0$ and $TCNQ^{\bullet-}$.

Complexes **4** and **5** arising from reactions of **1** with TCNE can be easily distinguished by their cyclic voltammograms. That of complexes **4** reveal five redox processes, three of them being associated with the $[Mo(dtc)_4]^{\bullet+}$ cation [E_1, E_2, E_5, eq. (3)]. Comparison with previous work indicates that the other two are associated with the $TCNE^{\bullet-}$ radical anion (reversible reduction at $E_6'^{\circ} = -1.27$ V; reversible oxidation at $E_7'^{\circ} = -0.21$ V). Of these five redox processes, only the three associated with the inorganic cation are observed for complexes

5, that corresponding to the TCNE species being obviously absent. However, two supplementary redox processes corresponding, respectively, to a reversible reduction ($E_8'^{\circ} = -1.90$ V) and an irreversible oxidation ($E_{(irr)9} = 1.10$ V) are also observed. Comparison with the CV of the tetraethylammonium pentacyanopropenide Et_4N $[C_3(CN)_5]$ clearly indicates that these processes are assignable to the $[(CN)_2C—C(CN)—C(CN)_2]$ anion.[11]

ESR. Dilute (*ca* 10^{-4} M) acetonitrile or dichloromethane solutions of complexes **2** and **3** present isotropic room temperature ESR spectra similar to the 'organic' signal associated with the $TCNQ^{\bullet -}$ radical anion[21] at $g = 2.003$–2.006 and an 'inorganic' signal which consists of an intense central line ($g =$ *ca* 1.980) arising from the $I_{Mo} = 0$ isotopes ($^{94,96,98,100}Mo$, natural abundance *ca* 75%) and a satellite sextet ($A_{Mo} =$ *ca* 38 G) arising from hyperfine coupling with the $I_{Mo} = 5/2$ isotopes ($^{95,97}Mo$, natural abundance *ca* 25%).[22] The small difference (<2%) in magnetic moments of the last two isotopes does not give rise to observable splittings.[22] ESR spectra of complexes **4** and **5** also show such a molybdenum signal, the usual multiplet corresponding to $TCNE^{\bullet -}$ ($g = 2.003$; $A_N =$ *ca* 1.6 G) being also observed for **4**. In agreement with the electrochemical results, observation of such spectra clearly corroborates the presence in solution for all of these complexes of the paramagnetic molybdenum(V) cationic species $[Mo(dtc)_4]^{\bullet +}$ associated with the paramagnetic anion $TCNX^{\bullet -}$ for **2**, **3** and **4** and with a diamagnetic anion for **5**.

As in many free radical systems, line widths and spectral appearances are drastically influenced by concentration. As example, for a *ca* 10^{-2} M CH_2Cl_2 solution of **2a**, only a single symmetric signal is observed at $g = 1.992$ ($\Delta H_{pp} =$ *ca* 28 G). These observations clearly indicate electron exchanges between the radical species.

UV–vis. It has been previously shown that such spectra allow the determination of the charges on the TCNQ units by comparison of the absorption intensities I_{395} and I_{842} at 395 and 842 nm, respectively.[23] Calculations with eq. (4) derived from Murakami *et al.*[12,23]

$$([TCNQ^0]/[TCNQ^{\bullet -}]) = 0.759[(I_{395}/I_{852}) - 0.422] \quad (4)$$

give a $[TCNQ^0]/[TCNQ^{\bullet -}]$ ratio of 0.15 for **2** and 1.1 for **3**. These values again indicate that in solution there are essentially monoanionic $TCNQ^{\bullet -}$ species for **2** and a 1 : 1 neutral TCNQ and anionic radical $TCNQ^{\bullet -}$ mixture for **3**.

Solid state chemistry

Crystal and molecular structure of complex **2a** $[Mo(dedtc)_4](TCNQ)$. Figure 2 gives the overall geometries of the inorganic cation and the organic anion and the atom numbering system while selected internuclear distances and angles are given in Table 1.

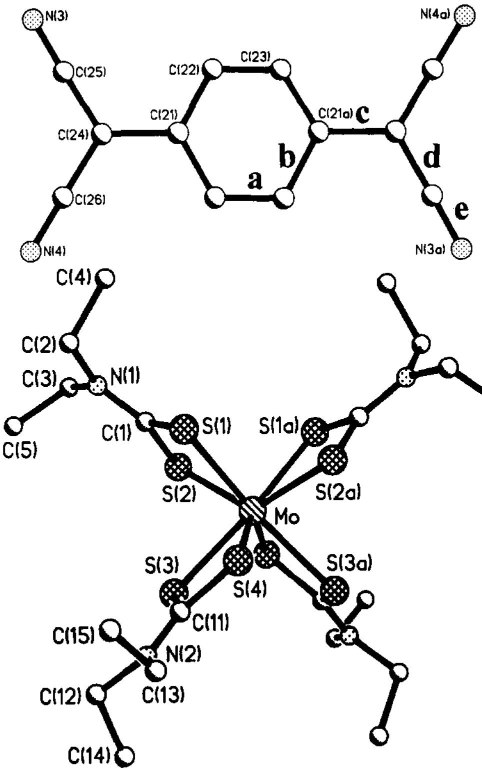

Fig. 2. Molecular structure of complex **2a**: $[TCNQ]^{\bullet -}$ anion and $[Mo(dedtc)_4]^{\bullet +}$ cation with the labelling scheme and the bond nomenclature for the anion.

The unit cell contains four $[Mo(Et_2NCS_2)_4]$ units and four polynitrile entities.

The organic fragments lie across inversion centres and have crystallographically imposed $\bar{1}$ symmetry. The bond lengths of the TCNQ units have been shown to be a useful guide towards an estimate of their charges. In fact, and using the nomenclature of Flandrois and Chasseau[24] (Fig. 2 and Table 2), three empirical schemes have been used for estimating the degree of charge-transfer based on the TCNQ geometry.[24–26] All take into consideration the shortening of the formal single bonds b and d and the lengthening of the formal double bonds a and c as the structure becomes more benzenoid in character with increasing negative charge, the difference lying in the fact that each estimate the degree of charge-transfer on the basis of slightly different approaches for comparison of the bond lengths, namely by comparison of the values of $(b-c)$ and $(c-d)$,[24] $(a+c)/(b+d)$,[25] or $c/(b+d)$,[26] respectively. For **2a**, the bonds a are equal by symmetry as are also the bonds c while for

Table 1. Selected internuclear distances (Å) and angles (°) for **2a**

Mo—S(1)	2.499(2)	Mo—S(2)	2.548(1)	Mo—S(3)	2.493(2)	Mo—S(4)	2.534(2)
S(1)—C(1)	1.696(4)	S(2)—C(1)	1.718(5)	S(3)—C(11)	1.704(5)	S(4)—C(11)	1.713(4)
N(1)—C(1)	1.323(6)	N(1)—C(2)	1.471(8)	N(1)—C(3)	1.469(6)	N(2)—C(11)	1.315(7)
N(2)—C(12)	1.470(6)	N(2)—C(13)	1.469(7)	C(2)—C(4)	1.531(9)	C(3)—C(5)	1.496(9)
C(12)—C(14)	1.489(9)	C(13)—C(15)	1.514(10)	N(3)—C(25)	1.150(10)	N(4)—C(26)	1.146(9)
C(21)—C(22)	1.417(8)	C(21)—C(24)	1.415(8)	C(21)—C(23A)	1.415(7)	C(22)—C(23)	1.356(8)
C(23)—C(21A)	1.415(7)	C(24)—C(25)	1.406(9)	C(24)—C(26)	1.401(9)		

S(1)—Mo—S(2)	67.6(1)	S(1)—Mo—S(3)	93.9(1)	S(2)—Mo—S(3)	78.6(1)
S(1)—Mo—S(4)	78.4(1)	S(2)—Mo—S(4)	130.1(1)	S(3)—Mo—S(4)	68.0(1)
S(1)—Mo—S(1A)	93.2(1)	S(2)—Mo—S(1A)	80.8(1)	S(3)—Mo—S(1A)	153.7(1)
S(4)—Mo—S(1A)	138.2(1)	S(1)—Mo—S(2A)	80.8(1)	S(2)—Mo—S(2A)	133.7(1)
S(3)—Mo—S(2A)	138.5(1)	S(4)—Mo—S(2A)	70.6(1)	S(1)—Mo—S(3A)	153.7(1)
S(2)—Mo—S(3A)	138.5(1)	S(3)—Mo—S(3A)	90.8(1)	S(4)—Mo—S(3A)	79.5(1)
S(1)—Mo—S(4A)	138.2(1)	S(2)—Mo—S(4A)	70.6(1)	S(3)—Mo—S(4A)	79.5(1)
S(4)—Mo—S(4A)	133.4(1)	Mo—S(1)—C(1)	91.8(2)	Mo—S(2)—C(1)	89.7(1)
Mo—S(3)—C(11)	91.4(2)	Mo—S(4)—C(11)	89.8(2)	C(1)—N(1)—C(2)	120.2(4)
C(1)—N(1)—C(3)	121.6(4)	C(2)—N(1)—C(3)	118.1(4)	C(11)—N(2)—C(12)	121.3(4)
C(11)—N(2)—C(13)	121.3(4)	C(12)—N(2)—C(13)	117.4(5)	S(1)—C(1)—S(2)	110.8(3)
S(1)—C(1)—N(1)	124.9(4)	S(2)—C(1)—N(1)	124.3(3)	N(1)—C(2)—C(4)	111.0(6)
N(1)—C(3)—C(5)	112.2(5)	S(3)—C(11)—S(4)	110.8(3)	S(3)—C(11)—N(2)	124.9(3)
S(4)—C(11)—N(2)	124.3(3)	N(2)—C(12)—C(14)	112.9(5)	N(2)—C(13)—C(15)	112.7(5)
C(22)—C(21)—C(24)	121.6(5)	C(22)—C(21)—C(23A)	116.4(5)	C(24)—C(21)—C(23A)	122.0(5)
C(21)—C(22)—C(23)	122.1(5)	C(22)—C(23)—C(21A)	121.5(6)	C(21)—C(24)—C(25)	121.4(6)
C(21)—C(24)—C(26)	121.9(5)	C(25)—C(24)—C(26)	116.6(5)	N(3)—C(25)—C(24)	178.0(9)
N(4)—C(26)—C(24)	179.2(8)				

Table 2. Comparison of some bond lengths (Å) of the TCNQ moiety (for bond nomenclature see Fig. 2)

Compound	Ref.	a	b	c	d	e	$b-c$	$c-d$	$(a+c)/(b+d)$	$c/(b+d)$
2a[a]	This work	1.356(8)	1.416(8)	1.415(8)	1.404(9)	1.148(9)	0.001	0.011	0.983	0.502
$TCNQ^{\bullet -}$	28	1.373(1)	1.423(3)	1.420(1)	1.416(8)	1.153(7)	0.003	0.004	0.984	0.500
$TCNQ^{0}$	27	1.346(3)	1.448(4)	1.374(3)	1.441(4)	1.140(1)	0.074	−0.067	0.942	0.476

[a] Estimation of the charge ρ of the TCNQ unit using Kistenmacher relation[26] $\rho = A[c/(b+d)]+B$ with $A = -41.667$ and $B = 19.833$ gives $\rho = -1.07$.

bonds b, d and e there is no significant difference between chemically but not crystallographically equivalent bonds. Table 2 lists the mean bond lengths of the TCNQ entities in compound **2a** together with reported data for neutral $TCNQ^{0}$[27] and $Rb^{+}(TCNQ)^{\bullet -}$[28] along with the values of $(b-c)$, $(c-d)$, $(a+c)/(b+d)$ and $c/(b+d)$. It can be concluded that the degree of electron transfer in compound **2a** is nearly the same as that in $Rb^{+}(TCNQ)^{\bullet -}$, i.e. that as expected the degree of charge transfer is very close to one (Table 2). Therefore, **2a** is composed of molybdenum monocations and TCNQ monoanions.

In the $[Mo(Et_2NCS_2)_4]^{\bullet +}$ cation, the molybdenum atom is surrounded by eight approximately equidistant sulphur atoms from bidentate S_2CNEt_2 ligands. The angle between the S(1)S(2)S(3a)S(4a) and S(1a)S(2a)S(3)S(4) trapezoids ($\theta = 90.3°$) indicates that the idealized coordination polyhedron is a dodecahedron (theoretical value $\theta = 90°$) and not a square antiprism (theoretical value $\theta = 77.4°$).[29] The cation has crystallographically imposed two-fold symmetry but in addition to the crystallographic two-fold axis there are two non-crystallographic pseudo two-fold axes and two pseudo mirror planes. The point group is therefore approximately D_{2d} with a triangular dodecahedral arrangement of S atoms in which, although quite similar, the Mo—S bond lengths [mean 2.518(2)Å] display a slight non-equivalence according to whether or not the sulphur atoms occupy dodecahedral A or B sites[29] [means are Mo—S(A) 2.541(1) and Mo—S(B) 2.496(2)Å]. These bond lengths are very close to those previously reported for [Mo(dedtc)$_4$][Mo$_6$O$_{19}$] **4**,[30] [Mo(dedtc)$_4$]Cl **5**[30] and [Mo(dedtc)$_4$]I$_3$ **6**[31] [means are Mo—S(A) 2.536(15) in **4**, 2.531(9) in **5**, 2.545(2) Å in **6**; Mo—S(B) 2.491(8) in **4**, 2.505(12) in **5**, 2.500(2) Å in **6**]. It is noteworthy that the coordination sphere is quite different from that observed in the starting molybdenum(IV) complex [Mo(dedtc)$_4$].[32] The M—S bond length inequalities observed in the [Mo(dedtc)$_4$] cation are common in D_{2d} octahedral complexes containing bidentate sulphur ligands.[30] It seems likely that they arise from differences in ligand–ligand repulsions[29,33] rather than from differences in ligand-to-metal $p\pi - d\pi$ bonding as also reported[34] since no significant differences are observed in the C—S(A) and C—S(B) bond lengths. As in most dedtc complexes, the S$_2$CNEt$_2$ ligands present a conformation in which the two terminal methyl groups are oriented *trans* with respect to the S$_2$CNEt$_2$ plane.[30] Bond lengths in the ligands are in good agreement with those from other studies: means S—C 1.708(5), C—N 1.319(7), N—C 1.470(7) and C—C 1.508(9) Å.

There are no close interplanar contacts between the TCNQ radical anions, i.e. there is always a molybdenum cation lying between anions. The anions alone adopt a 'herring bone' pattern but anions and cations alternate in the solid state avoiding stacking of the TCNQ anions. Since TCNQ$^{\bullet-}$ usually stacks or dimerises, this is one of the rare examples of structural characterization of an isolated TCNQ$^{\bullet-}$ in the solid state. Although no short contacts between the cation and the anion were found, the distance of 3.35 Å between the cation [N(2) atom] and the anion [N(3) atom], corresponding to a N(3)—Mo distance of 5.48 Å, do not allow consideration of cations and anions as perfectly isolated. If we take into account these slight interactions, TCNQ$^{\bullet-}$ anion (A) acts as a bridging ligand for two [Mo(dedtc)$_4$]$^{\bullet+}$ cations (C) and vice versa, thus to lead to 1D -A-C-A-C- isolated chains in the [101] direction (Fig. 3).

IR. Complexes **2** present very well resolved spectra showing two sharp bands at 2180 and 2150 cm^{-1} assignable to ν(CN) vibrations. The ν(CN) stretch has been shown to be sensitive to the extent of reduction of TCNQ species (2220 cm^{-1} for TCNQ; 2179 and 2153 cm^{-1} for TCNQ$^{\bullet-}$; 2150 and 2105 cm^{-1} for TCNQ^{2-})[35] due to population of the out-of-plane antibonding π b_{3g} orbital which results in a decrease in bond order between carbon and nitrogen.[36,37] The ν(CN) values observed for complexes **2** are therefore consistent with the presence of a singly reduced TCNQ species. Although very well crystallized, complexes **3** present relatively broad absorptions not only in the ν(CN) range but also

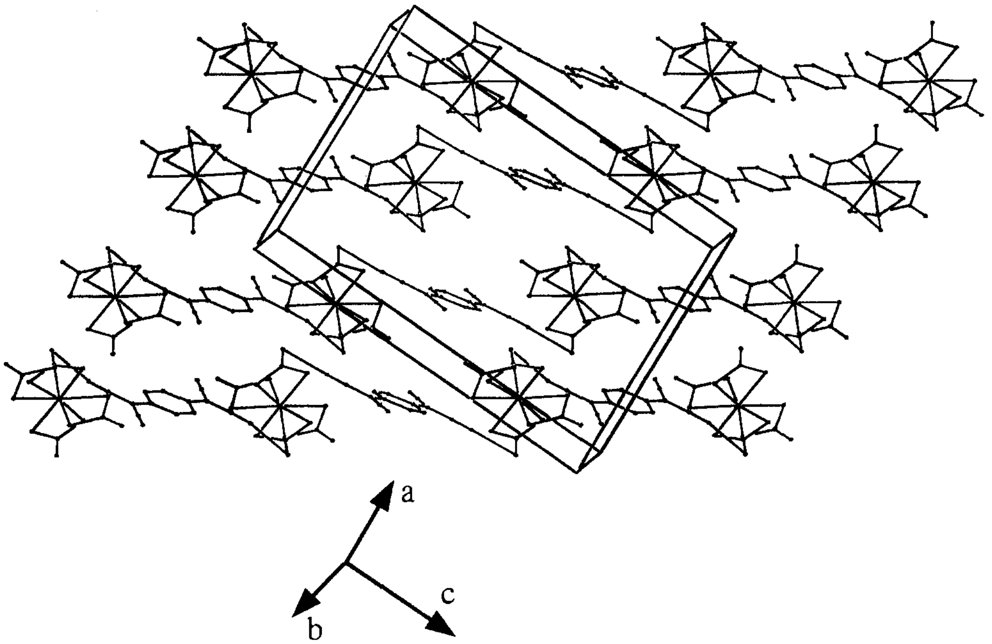

Fig. 3. Projection of the structure of **2a** showing slight interactions between the cation [N(2) atom] and the anion [N(3) atom]: d[N(2)—N(3)] = 3.35 Å. Mo—TCNQ barycentre intrachain distance: 6.23 Å; Mo—Mo interchain distance: 10.33 Å. Ethyl groups of Et$_2$NCS$_2$ groups are omitted for clarity.

at *ca* 1080 and 1300 cm^{-1} as usually observed for complexes showing electronic interactions between TCNQ units in different oxidation states.[36]

Complexes **4** and **5** present rather different spectra in the ν(CN) range. In agreement with previously reported studies, complexes **4** exhibit the usual two bands (2185 and 2145 cm^{-1}) characteristic of TCNE$^{\bullet-}$ while complexes **5** only show one ν(CN) band (*ca* 2200 cm^{-1}) assignable to $[C_3(CN)_5]^-$.

The selected dithiocarbamato ligand frequencies given in the Experimental section and their assignment are in accordance with previously reported results. It is noteworthy that as previously observed by Nieuwpoort *et al.*[38] the ν(N—CS$_2$) stretching frequency increases on oxidation, e.g. from 1520 to 1550 cm^{-1} on passing from **1b** to **2b**.

CONCLUSIONS

For the 1 : 1 Mo/TCNX complexes, $[Mo(dtc)_4]$(TCNX) (**2** : X = Q ; **4** : X = E), all physical measurements and the X-ray crystal structure determination clearly agree with the $[Mo(dtc)_4]^{\bullet+}$ TCNX$^{\bullet-}$ formulation which includes, both in the solid state and in solution, a molybdenum(V) radical cation and a radical monoanionic organic species. The instability of TCNE$^{\bullet-}$ corresponds to the formation of the diamagnetic pentacyanopropenide anion without any change of the cation affording complexes **5**. The 1 : 2 Mo/TCNQ complexes **3**, $[Mo(dtc)_4](TCNQ)_2$, also contain the molybdenum(V) radical cation $[Mo(dedtc)_4]^{\bullet+}$. In solution, this moiety is present with TCNQ and TCNQ$^{\bullet-}$ species but in absence of a crystal structure determination the interactions in the solid state between neutral and anionic organic species cannot be defined. Further work is in progress to obtain more information on these and other molybdenum complexes with TCNQ and TCNE, particularly about their magnetic properties which will be reported subsequently.

Acknowledgements—CNRS, Région Bretagne and Université de Bretagne Occidentale are acknowledged for financial support. We thank J. M. Kerbaol (Brest) for help in preparation of the compounds and Dr S. Triki (Brest) for stimulating and encouraging discussions.

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