Synthesis, Cyclic Voltammetric and Electrospray Mass Spectrometric Studies of a Series of Tris-Substituted 1,2-Dithiolene Complexes of Tungsten and Molybdenum

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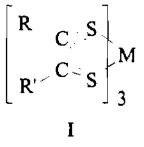
Received January 10, 1995$^{\otimes}$

Ten new nonsymmetric dithiolenes of the general formula $[RR'(C_2S_2)]_3M$ were synthesized, from the corresponding 1,3-dithiol-2-ones, or from the corresponding mixed benzoins and tetraphosphorus decasulfide. The redox properties of these ten complexes together with those of the symmetric ones with R = R′ = Ph and M = Mo or W, were investigated by cyclic voltammetry. Two processes were only observed, assigned to $C \rightarrow C^{1-}$ and $C^{1-} \rightarrow C^{2-}$ (C the complex), for which the quasi-reversible $E_{1/2}$ potentials are highly dependent on the nature of the central metal ion, and for the same metal on the nature of the ligand and on the substituents on the phenyl rings. The ease by which the complexes are reduced is most likely the reason they give ESMS (negative mode) spectra, in spite of the fact they are neutral in solution. The process of this reduction and the parameters affecting it are investigated and discussed.

Introduction

A large number of metal dithiolene complexes have been synthesized and characterized.[3] Because of their very interesting photochemical and electrochemical properties they have been used as antioxidants, OH$^{\bullet}$ scavengers and photostabilizers.[3,4] Recently we showed that the complex tris[1-(4-methoxyphenyl)-2-phenyl-1,2-ethylenedithiolenic-*S*,*S*′]tungsten acts as a photocatalyst−catalyst for the photochemical cleavage of water by visible light.[5] This complex acts first as an antenna, absorbing light in the visible region, and the excited state initiates a photocatalytic cycle resulting in the formation of a mixture of dihydrogen and dioxygen.

For further studies we synthesized a series of prismatic tungsten and molybdenum dithiolenes of the general type shown in formula **I**, where R is the same or different from R′ (Table 1).



I

In order to understand better their role in photochemically induced redox reactions we also investigated their physical and electronic properties by cyclic voltammetric and electrospray mass spectrometric methods.

Cyclic voltammetry is a well-established technique, but electrospray mass spectrometry (ESMS) is a recently developed soft ionization technique, used primarily for the study of large biomolecules.[6] Its main advantage is that it transfers intact ions from the solution directly to the gas phase. These ions, in the case of macromolecules, are normally multiply charged, so that the resulting *m/z* is well within the range of common mass spectrometers. Despite its wide application in biomolecules, however, ESMS has found rather limited application in inorganic compounds[7] and, as far as we know, none with neutral molecules giving negative ions during the measurements.

Experimental Section

Materials. All reactions, unless otherwise stated, were carried out in an argon atmosphere. Ethanol was distilled from sodium metal and kept under dry argon. Dioxane was dried with sodium metal. Hydrochloric acid, benzene, ethanol, hydrazine, and petroleum ether were purchased from Aldrich and used without any further purification. $WBr_4(CH_3CN)_2$,[8] the starting 1,3-dithiol-2-ones,[9] and the mixed benzoins[10] were prepared by literature methods. The purity of the complexes was checked with TLC (silica gel, 20:80 benzene-cyclohexane elution solvent). Elemental analyses were performed with a Perkin Elmer 2400 CHN analyzer, and a LECO HF-10 induction furnace connected to a LECO 532−500 Sulfur Titrator. The numbering of the complexes refers to Table 1.

$^{\otimes}$ Abstract published in *Advance ACS Abstracts,* July 15, 1995.

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Table 1. 1,2-Dithiolene Complexes Studied, Where R, R′, and M Refer to **I**

	R	R′	M
1	*p*-CH_3OPh	H	W
2	*p*-CH_3Ph	H	W
3	Ph	H	W
4	*p*-ClPh	H	W
5	*p*-BrPh	H	W
6	*p*-CH_3OPh	H	Mo
7	*p*-CH_3Ph	H	Mo
8	Ph	H	Mo
9	Ph	Ph	W
10	Ph	Ph	Mo
11	*p*-CH_3OPh	Ph	W
12	*p*-$(CH_3)_2NPh$	Ph	W
13	*p*-CH_3OPh	Ph	Mo

Preparation of 1. Sodium (3.0 g., 0.13 moles) was dissolved in ethanol (40 cm^3), and 4-(4-methoxyphenyl)-1,3-dithiol-2-one (1.02 g, 4.5 mmol) was added. The solution was heated under reflux for 1 h and then cooled to just above its melting point, at about −80 °C, using an acetone−liquid nitrogen bath. Concentrated hydrochloric acid was added (40 cm^3) under stirring and after a few seconds 0.87 g, 1.5 mmol, of $WBr_4(CH_3CN)_2$ were added. The solution was brought up to room temperature and air was bubbled through for half an hour. The complex was extracted with benzene, washed three times with water, and dried with $MgSO_4$, and the solvent was removed in vacuo. The crude complex was recrystallized from benzene by adding light petroleum ether. The complex was finally dried under vacuum. Yield: 0.51 g (45%) of a green-black powder, mp 172 °C, dec. Anal. Calcd for $C_{27}H_{24}O_3S_6W$ C, 42.0; H, 3.1; S, 24.89. Found: C, 41.9; H, 3.1; S, 24.91.

Preparation of 2. The complex was prepared in the same way as **1** using 4-(4-methylphenyl)-1,3-dithiol-2-one (0.96 g, 4.6 mmol) and $WBr_4(CH_3CN)_2$ (0.89 g, 1.53 mmol). Yield: 0.440 g (40%) of a green-black powder, mp 175 °C dec. Anal. Calcd for $C_{27}H_{24}S_6W$: C, 44.7; H, 3.3; S, 26.56. Found: C, 44.7; H, 3.4; S, 26.55.

Preparation of 3. The complex was prepared in the same way as **1** using 4-phenyl-1,3-dithiol-2-one (0.88 g., 4.55 mmol) and $WBr_4(CH_3CN)_2$ (0.88 g, 1.51 mmol). Yield: 0.61 g (59%) of a green-black powder, mp 177 °C dec. Anal. Calcd for $C_{24}H_{18}S_6W$: C, 42.2; H, 2.6; S, 28.18. Found: C, 42.1; H, 2.7; S, 28.15.

Preparation of 4. The complex was prepared in the same way as **1** using 4-(4-chlorophenyl)-1,3-dithiol-2-one (0.97 g, 4.28 mmol) and $WBr_4(CH_3CN)_2$ (0.84 g, 1.42 mmol). Yield: 0.91 g (81%) of a green-black powder, mp 215 °C dec. Anal. Calcd for $C_{24}H_{15}Cl_3S_6W$: C, 36.7; H, 1.9; S, 24.47. Found: C, 36.8; H, 1.9; S, 24.44.

Preparation of 5. The complex was prepared in the same way as **1** using 4-(4-bromophenyl)-1,3-dithiol-2-one (1.26 g, 4.63 mmol) and $WBr_4(CH_3CN)_2$ (0.90 g, 1.54 mmol). Yield: 0.96 g (68%) of a green-black powder, mp 167 °C dec. Anal. Calcd for $C_{24}H_{15}Br_3S_6W$: C, 31.4; H, 1.6; S, 20.92. Found: C, 31.4; H, 1.5; S, 20.94.

Preparation of 6. The complex was prepared in the same way as **1** using $Na_2MoO_4{\cdot}2H_2O$ (0.79 g, 1.5 mmol). Yield: 1.15 g (51%) of a green-black powder, mp 160 °C, dec. Anal. Calcd for $C_{27}H_{24}MoO_3S_6$: C, 47.35; H, 3.54; S, 28.09. Found: C, 47.5; H; 3.61; S, 28.12.

Preparation of 7. The complex was prepared in the same way as **2** using $Na_2MoO_4{\cdot}2H_2O$ (0.81 g, 1.53 mmol). Yield: 1.82 g (59%) of a green-black powder, mp 160 °C dec. Anal. Calcd for $C_{27}H_{24}MoS_6$: C, 50.92; H, 3.81; S, 30.21. Found: C, 50.41; H, 3.75; S, 30.05.

Preparation of 8. The complex was prepared in the same way as **3** using $Na_2MoO_4{\cdot}2H_2O$ (0.80 g, 1.51 mmol). Yield: 1.66 g (84%) of a green-black powder, mp 138 °C dec. Anal. Calcd for $C_{24}H_{18}MoS_6$: C, 48.46; H, 3.06; S, 32.35. Found: C, 48.40; H, 3.02; S, 32.27.

Preparation of 9−11. The preparation of these complexes has been described in the literature.[11]

Preparation of 12. 4-(Dimethylamino)benzoin (8.55 g, 33.5 mmol) was dissolved in 100 mL of dioxane, and tetraphosphorus decasulfide (P_4S_{10}, 11 g, 24.7 mmol) was added. The mixture was heated under reflux with constant stirring under an argon atmosphere for 2 h. Large amounts of H_2S are evolved during this step, and the use of a good hood is necessary or the apparatus should be connected to a lead acetate trap. The brown thiophosphoric ester formed was deposited on the wall of the flask in the form of a resin. The mixture was allowed to cool to room temperature, and the solvent was removed under vacuum. $Na_2WO_4{\cdot}2H_2O$ (2.49 g, 7.54 mmol) dissolved in 30 cm^3 of 6 mol·dm^{-3} HCl was added and the resulting mixture was heated under reflux until all the resinous substance was dissolved. The dark green solution produced was cooled to room temperature, and the dithiolene was deposited as a dark green solid. The precipitate was filtered, refluxed with ethanol, and filtered again. Benzene and a 5 mol·dm^{-3} NaOH (30 cm^3 each) solution were added and the complex was dissolved in the benzene layer. The benzene solution was washed repeatedly with water, and then 30 cm^3 of conc. hydrazine solution was added and the mixture shaken until all the complex has passed into the hydrazine layer. The violet hydrazine layer was washed repeatedly with benzene, and 60 cm^3 benzene was added. HCl, 6 mol·dm^{-3} was added dropwise and the mixture was kept under stirring at approximately 5°C in an ice bath. The addition was stopped when all the complex had passed into the benzene layer. The benzene layer was then washed several times with water and dried with $MgSO_4$, and the solvent was removed under vacuum. The solid complex was refluxed three times with ethanol. It was then redissolved in benzene and precipitated with the addition of petroleum ether. The precipitate was dried under vacuum. Yield: 1.70 g (14%) of a brown-black powder, mp 190 °C dec. Anal. Calcd for $C_{48}H_{45}N_3S_6W$: C, 55.4; H, 4.37; S, 18.45; N, 4.04. Found: C, 55.5; H, 4.32; S, 18.43; N, 4.03.

Preparation of 13. The complex was prepared in the same way as **9** using $Na_2MoO_4{\cdot}2H_2O$ instead of $Na_2WO_4{\cdot}2H_2O$. Yield: 4.9 g (13%) of a green-black powder, mp 210 °C dec. Anal. Calcd for $C_{45}H_{36}O_3MoS_6$: C, 59.2; H, 3.98; S, 21.04. Found: C, 59.2; H, 3.93; S, 21.04.

Cyclic Voltammetry. The electrochemical instrumentation consisted of a PAR Model 174A polarographic analyzer operating in conjunction with a PAR 175 universal programmer and with a LINSEIS LY 18100 X-Y recorder used to record the resultant wave form. All experiments were carried out in a conventional three electrode glass cell, using a platinum working electrode as well as a platinum auxiliary electrode. The reference electrode was Ag−AgCl in acetone containing 0.1 mol·dm^{-3} LiCl, separated from the voltammetric cell by 0.1 mol·dm^{-3} $[(n\text{-}C_4H_9)_4N]ClO_4$ in acetone salt bridge.[12] Measurements were performed in dichloromethane with 0.1 mol·dm^{-3} $[(n\text{-}C_4H_9)_4N]ClO_4$ as supporting electrolyte or in acetonitrile with 0.1 mol·dm^{-3} $[(C_2H_5)_4N]ClO_4$ as supporting electrolyte. The dithiolene solutions were approximately 1 mmol·dm^{-3}. Special argon (purity 99.999%) was passed through the solution for 15 min prior to taking the measurements, and an argon blanket was maintained above the solution during the experiments. Dichloromethane was dried with $CaCl_2$ and distilled from phosphorus pentoxide. Acetonitrile was distilled over molecular sieves, type 5Å.

ESMS Measurements. The ESMS spectra were recorded on a Fisons VG Quattro instrument with a VG Biotech Electrospray source, having a hexapole lens. Nitrogen 99.99% pure, was used as the nebulizing and bath gas at flows of 20 and 150 $dm^3{\cdot}min^{-1}$ respectively. The samples were injected in the flow of solvent of a Varian 9012 solvent delivery system, *via* a Fisons interface with a Rheodyne 7125 injector. The capillary voltage was optimum at about 3 kV, but it was varied to lower values in order to determine the appearance potentials. The value of the appearance potential was taken to be the value at which a peak with signal to noise ratio of at least 2 appears. The high voltage lens potential was kept at 0.56 kV. The focus and skimmer lenses voltages were 40 and 45 V, respectively, in the majority of the measurements, as these values produced the highest peak intensities and minimum fragmentation. These voltages were varied to higher values to study the collissionaly activated dissociation phenomena. HPLC grade acetonitrile or acetone were used as solvents. Ap-

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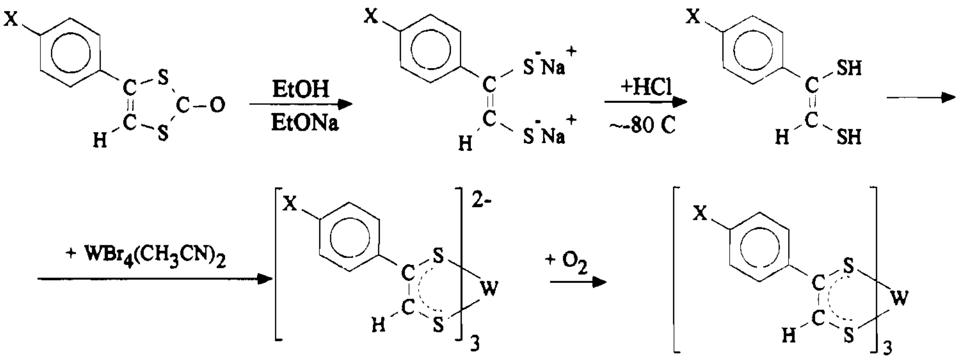
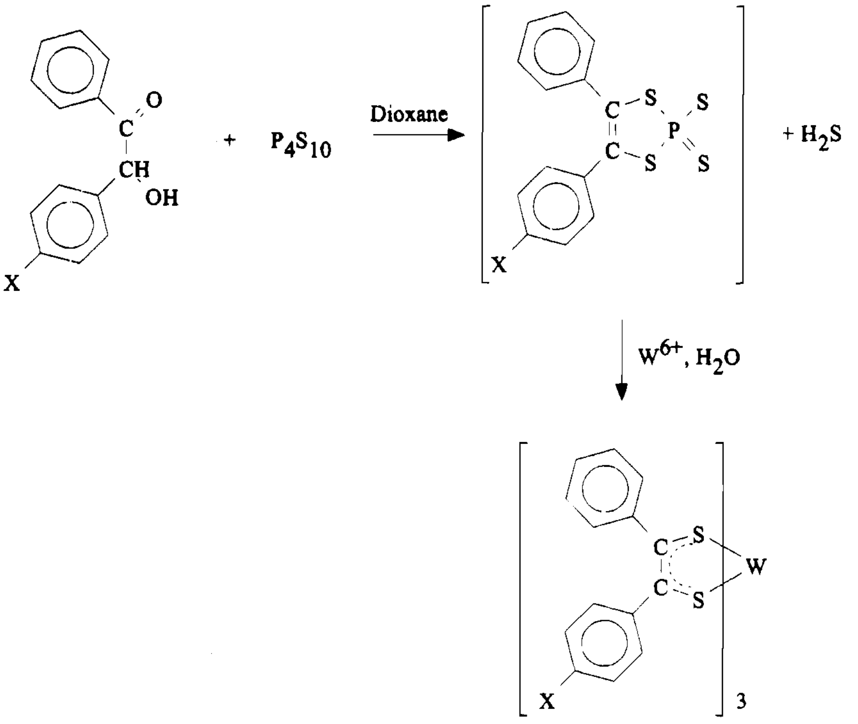
Scheme 1



Scheme 2



proximately 10 μl of 50 μmol·dm^{-3} solutions in acetonitrile or acetone were injected in each experiment.

Results and Discussion

Complexes **1**−**8** (Table 1) were prepared from the corresponding 1,3-dithiol-2-ones by properly adjusting and refining a method described in the literature,[13] as illustrated in Scheme 1.

After the formation of the disodium salt of the dithiole ligand from the basic cleavage of the dithiol-2-one ring, the reaction mixture is cooled to approximately −80 °C, and then the acid is added. This low-temperature technique was found to give the purest complexes, probably because the side reactions that would have otherwise produced the impurities are either slowed down or completely stopped. The starting material for tungsten was $WBr_4(CH_3CN)_2$, as this is much easier to handle than WCl_6 or some other tungsten halide. Use of Na_2WO_4 gave poor yields and impure products. Any other attempt, such as the use of tungsten(III) or lower oxidation states (for example $W(CO)_6$), was not successful. It seems that the starting material has to be some form of tungsten(IV) or higher oxidation state. The purple dianion formed after the addition of the metal is readily oxidized by air to the neutral complex.

An alternative route was also tried. Instead of treating with base, the 1,3-dithiol-2-one was illuminated in the UV in the presence of the corresponding metal carbonyl, as described in ref 14. In this case the metal must be in a low oxidation state. The yields, however, were poor, mainly because the metal carbonyl was decomposed by light to elemental tungsten that could not react further, and thus this route was abandoned.

Complexes **9**−**13** were prepared by a method based on the reaction of the corresponding mixed benzoin with tetraphosphorus decasulfide, as suggested by Schrauzer et al.[15] (Scheme 2).

These complexes were purified by conversion to the dianion with hydrazine followed by repeated washing of the hydrazine

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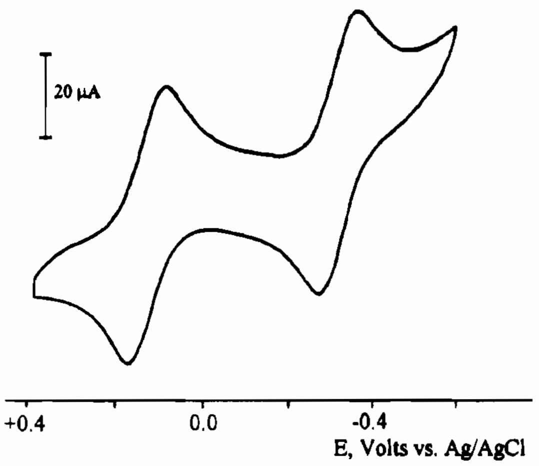

Figure 1. Cyclic voltammogram of a 1 mmol·dm^{-3} solution of complex 13 in CH_2Cl_2 containing 0.1 mol·dm^{-3} $[(n\text{-}C_4H_9)_4N]ClO_4$. Scan rate: 100 mV·s^{-1}

layer with benzene. Complex **12** presented some difficulty in the preparation. The thiophosphoric ester was deposited on the walls of the flask as a resin, probably because of the formation of phosphite salts with the dimethylamino group. The excess P_4S_{10} was not filtered out as happened with the other complexes because it was trapped in the resin. It was removed later during the purification procedures. The dimethylamino group existed in the neutral or protonated form depending on the medium used. In acid media it was protonated and the complex was green while in neutral or basic media it was neutral and the complex was brown. The dominating form in solution can be controlled by addition of NaOH or HCl.

The cyclic voltammetric studies were performed on a platinum electrode, in dichloromethane or acetonitrile. In both solvents and for each complex, two well-defined, quasi-reversible reduction waves were observed. Thorough removal of any trace of oxygen before recording the voltammogram is necessary. The cathodic–anodic peak separations (ΔE_p) were 90 and 100 mV for the two processes respectively, which is the proof of quasi-reversible redox processes. For a completely reversible process a 60 mV peak to peak separation is generally observed, while higher ΔE_p values usually indicate slower heterogeneous electron transfer.

Furthermore we examined the effect of the scan rate on the cyclic voltammogram. Thus, freshly deaerated solutions showed that the ratio of the cathodic–anodic peak currents (i_{pc}/i_{pa}) for both processes was very near to 1, even for scan rates of 10 mV·s^{-1}.

Figure 1 shows a typical voltammogram for complex **13** in dichloromethane. The ΔE_p value is slightly smaller than 90 mV for both steps. Smaller ΔE_p values usually indicate faster heterogeneous electron transfer. The current i_p is linearly correlated to $v^{1/2}$, indicating diffusion-controlled processes.[16] The observed linear dependence of i_p on $v^{1/2}$ for both processes and both cathodic and anodic currents between 5 and 100 mV·s^{-1}, as well as the fact that in any case the ratio i_{pc}/i_{pa} is equal to 1, shows that there is no deposition of the complex on the electrode and that the metal center can approach the electrode surface close enough for electron transfer, which is the only reaction that takes place.

Table 2 summarizes cyclic voltammetry parameters obtained in deaerated dichloromethane solutions for eight tungsten and five molybdenum complexes. Both tungsten and molybdenum complexes undergo two redox processes, assigned to the one electron reactions between neutral and monoanionic (process 1) and between monoanionic and dianionic (process 2) species:

Table 2. Half-Wave Potentials ($E_{1/2}$) from Cyclic Voltammograms of the Complexes of Table 1[a]

	$E_{1/2}$, V	
complex	process: $C + e \rightarrow C^{1-}$	process: $C^{1-} + e \rightarrow C^{2-}$
1	−0.068	−0.483
2	+0.060	−0.410
3	+0.130	−0.320
4	+0.195	−0.180
5	+0.160	−0.260
6	+0.070	−0.290
7	+0.122	−0.247
8	+0.144	−0.239
9	+0.145	−0.320
10	−0.005	−0.485
11	+0.097	−0.367
12	−0.008	−0.455
13	+0.135	−0.315

[a] Solvent: CH_2Cl_2. Reference cell: Ag/AgCl.[13] Scan rate: 100 mV·s^{-1}.

$$C + e^- \rightarrow C^- \qquad (1)$$

$$C^- + e^- \rightarrow C^{2-} \qquad (2)$$

It is important to note that in all cases there was no evidence of trianionic species formation. On the other hand, no oxidation wave was detected either. The cathodic–anodic peak current ratio (i_{pc}/i_{pa}) was always equal to 1 and was independent of the scan rate, indicating stability of the reduced species. The reduced compounds are, however, very sensitive to oxygen; they are spontaneously oxidized to the neutral form.

A careful examination of the voltammetric data reveals some interesting trends. The half-wave potentials ($E_{1/2}$) are highly dependent on the nature of the central metal ion, and for the same metal, on the nature of the ligand. In the case of ligands bearing the groups $-C_6H_4X$, $E_{1/2}$ depends on the nature of the ring substituent X.

In fact, as can be seen in Table 2, in the case of nonsymmetric ligands (R′ = Ph or H, R = Ph, *p*-MePh, or *p*-MeOPh), for both processes 1 and 2 the $E_{1/2}$ values for molybdenum complexes are more positive than those of equivalent tungsten complexes. This means that the former complexes are more easily reduced than the latter, in good agreement with the results quoted by McCleverty[3] for symmetric species. Furthermore, for asymmetrically substituted tungsten complexes of the type $WS_6C_6H_3$(p-XPh)$_3$ differing only on the ring substituent X, the nature of X has a profound effect on the half-wave potentials (Table 2). Comparison of these potentials for both processes 1 and 2 indicates that the series for the ease of reduction is the following:

$$Cl > Br > H > CH_3 > OCH_3$$

Analogous behavior is observed with the corresponding asymmetrically substituted molybdenum complexes $MoS_6C_6H_3$(*p*-XPh)$_3$. In fact, comparison of the $E_{1/2}$ potentials for complexes **6–8**, for both processes 1 and 2 shows that the ease for reduction follows the same order: H > CH_3 > OCH_3.

Such a behavior is not surprising. It has been shown that trends of this kind, in general, follow the electron-withdrawing ability of the dithiolene ligand, i.e. the greater the electron-attracting ability of the ligand the more easily the complex can accommodate the incoming electron.[17] Complexes with ligands

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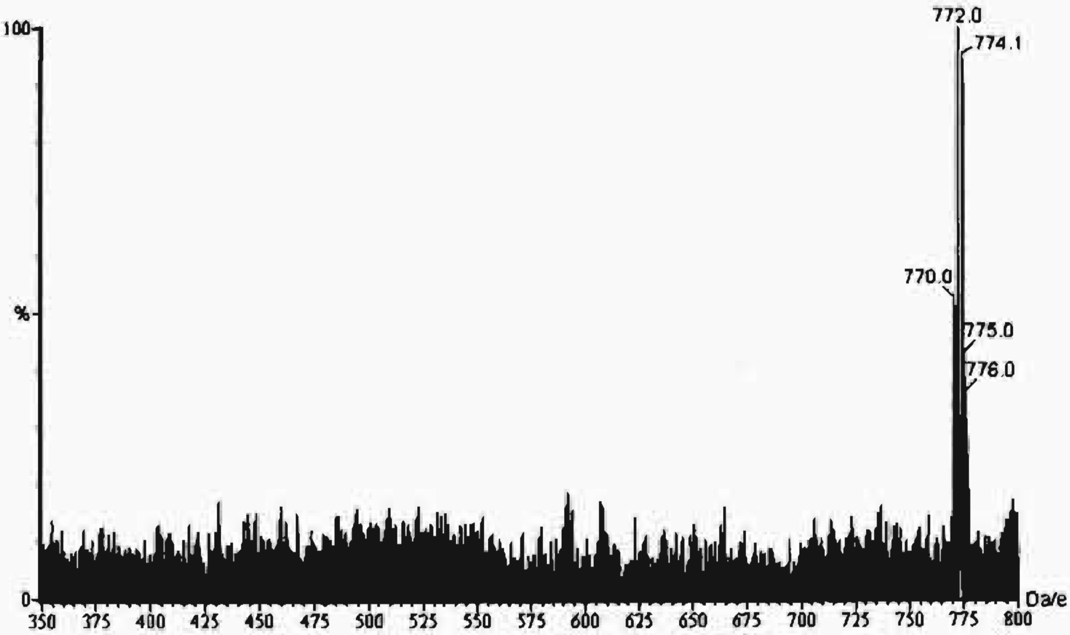

Figure 2. ESMS spectrum of an acetonitrile solution of complex 1. Concentration: 50 μmol·dm^{-3}. Capillary voltage: 3 kV. Focus: 40 V. Skimmer: 45 V.

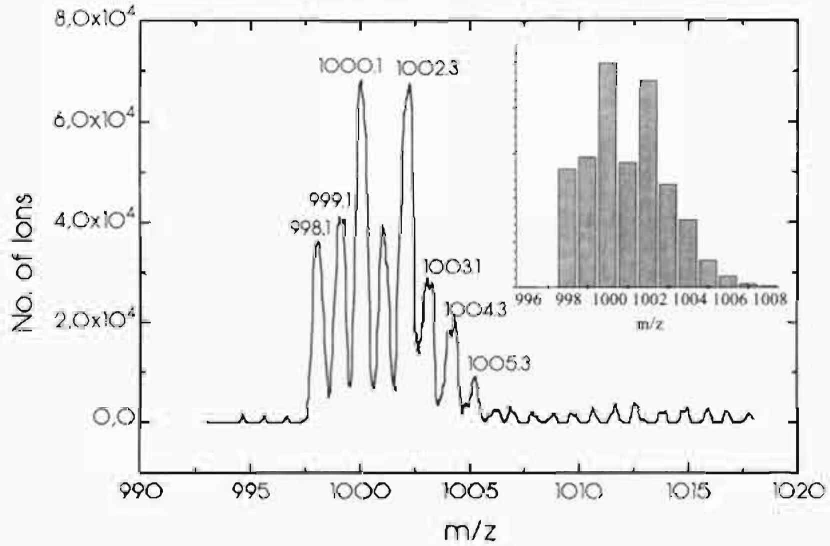

Figure 3. ESMS spectrum of complex 11 at the molecular ion region and calculated isotopic distribution pattern (inset). 50 μmol·dm^{-3} solution in CH_3CN. Conditions as in Figure 2.

containing the phenyl group instead of hydrogen have more a positive $E_{1/2}$ due to the electron-attracting character of the phenyl group.

Normally the complexes should not give an ESMS spectrum as they are known to be neutral in solution. However it was shown by Cole et al.[18] that neutral metallocenes can undergo oxidation on the capillary tip, which is kept at a positive voltage of a few kilovolts, thus yielding positive ions. In our case the ions are formed from a negatively charged tip (of a few kilovolts) and are negative.

Figure 2 shows the ESMS spectrum of a freshly prepared acetonitrile solution of complex **1**. The peaks at approximately 772 correspond to the monoanion of the complex. Similar peaks were observed for all the complexes. The isotopic distribution pattern of the observed peaks agreed perfectly with the theoretically predicted pattern, as is illustrated in Figure 3 for complex **11**. The spectra shown in these two figures are representative of the spectra recorded for the whole series of complexes.

The signal to noise ratios (complex **2**) was found to be as high as 28 for acetonitrile and 30 for acetone. These ratios are considered low. Yet, attempts were made to improve them further by injecting separately prepared (electrolytically) monoanions into the system, using helium sparged solvent. These efforts, however, failed. The monoanions did not survive the injection process. There are many "oxygen leaks" in the system and the monoanion is readily oxidized. We were also unable to find a reducing agent capable of reducing the neutral complex to the monoanion, not destroying the complex, being compatible with the instrument materials, and surviving the process.

The fact that similar spectra are observed in acetone solutions leads us to the conclusion that the anions did not preexist in solution.

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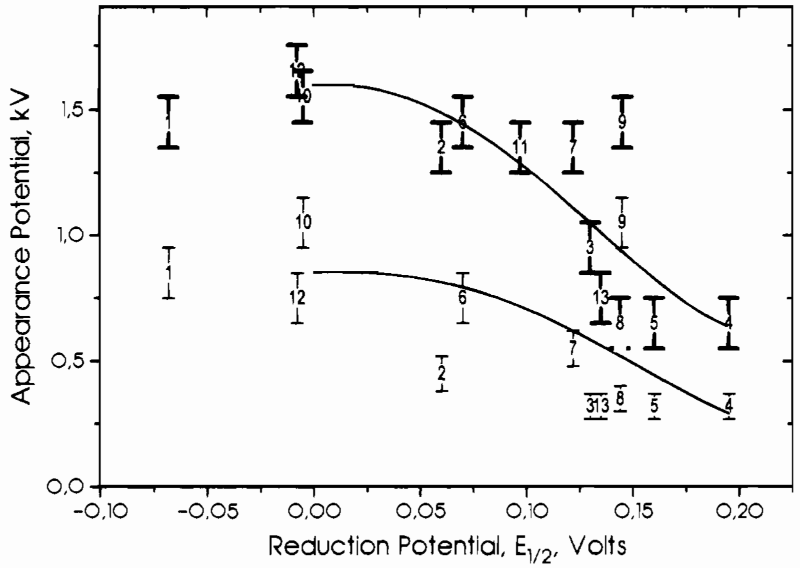

Figure 4. Graph of the appearance potential vs $E_{1/2}$ reduction potential of the complexes in acetonitrile (thick lines) and acetone (thin lines). The fitted curves shown were produced from nonlinear least-squares fits with 4th order polynomial reggression. These curves illustrate the general trends.

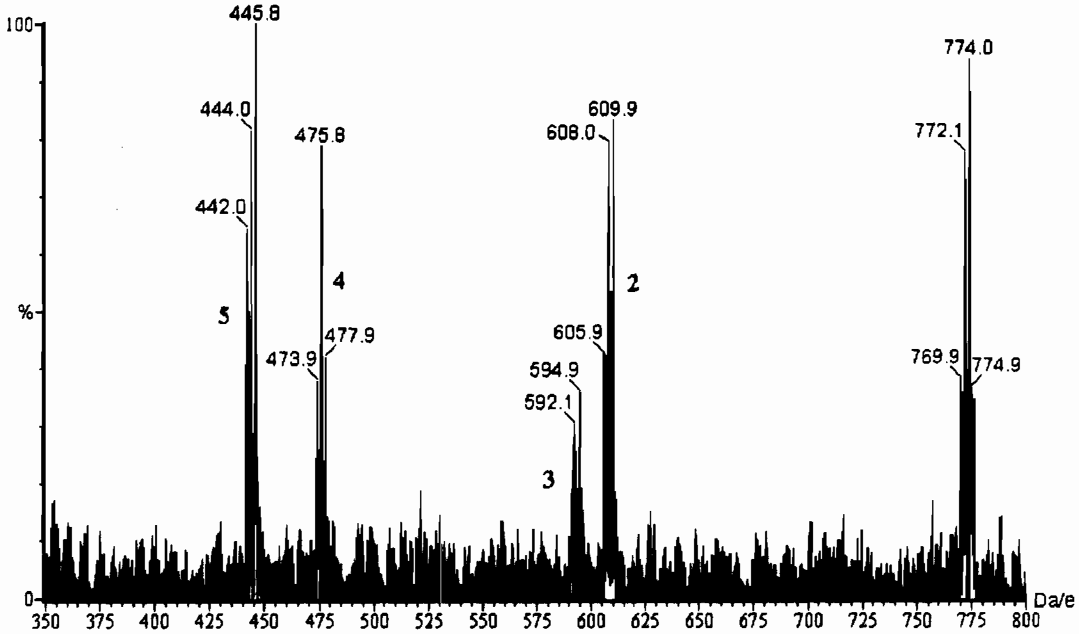

Figure 5. Fragmentation in the ESMS spectrum of an acetonitrile solution of complex 1. Concentration: 50 μmol·dm^{-3}. Capillary voltage: 3 kV. Focus: 100 V. Skimmer: 105 V. The numbers next to the peaks correspond to the formula number suggested for each one.

The complexes pick up an electron from the negatively charged stainless steel capillary. To investigate this further we measured the appearance potential, that is the capillary potential at which the peaks appear. The results are plotted in Figure 4 against the $E_{1/2}$ values of the first reduction. There is considerable scattering in this figure, yet with our instrument, the results are quite reproducible.

An inspection of the data in Figure 4 shows that the trend is similar in the two solvents and that the complexes that are more easily reduced appear at lower potentials, whereas there is a leveling effect at negative $E_{1/2}$'s. Comparing the two solvents, we see that the appearance potentials are solvent dependent and that they are generally lower in acetone.

The best results for most of the complexes were obtained with a capillary voltage of 3 to 3.3 kV. Higher potentials (up to 5 kV) were also tried, but no difference was observed. In fact at potentials near 5 kV the peaks are reduced.

We also checked for the possible appearance of a dianion or even a trianion at these potentials. No such species were observed. The potential for the formation of the dianions (or even of possible trianions) is much higher than that for the monoanions and under the conditions of our experiments the charged capillary cannot cause such reductions.

It has been shown that collissionaly induced dissociation can be effected if the focus and skimmer potentials are increased.[19] Figure 5 shows the spectrum obtained for the same solution of complex **1** as that of Figure 2 but with a focus potential of 100 V and a skimmer potential of 106 V. The fragmentation is significant. The peaks observed can be tentatively assigned to

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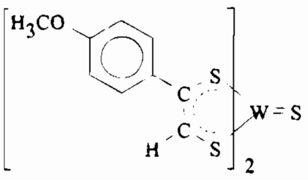
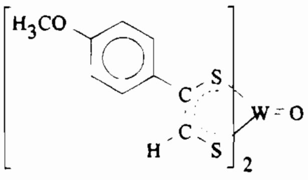
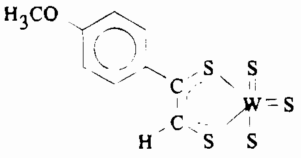


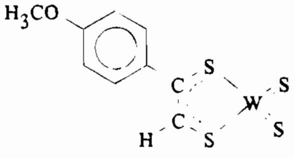
II



III



IV



V

the fragments shown in formulas **II**–**V**. The peaks have the correct mass distribution for the molecular formula suggested, but we do not have any other information about them. The presence of oxygen in the system is also evident in this fragmentation pattern.

Minimum fragmentation, is obtained with a focus voltage of 40 V and a skimmer voltage of 45 V. Lower voltages did not give peaks at all. It should also be mentioned that there has to be a difference of 5–6 V between the two electrodes as this is the optimum condition for the instrument.

The system was also run in the positive ion mode. The conditions in this case are the reverse, and an oxidation was expected, but no peaks were observed. This is in agreement with the cyclic voltammetric results that did not indicate formation of positive ions. Even if a positive ion is formed its lifetime is perhaps shorter than 10 μs, which is the characteristic time range for ESMS.

The formation of positive ions in electrospray has been described as an electrochemical process of a special kind.[18,20] Alternatively it can be regarded as an electric discharge, depending on the dielectric constants of the solvents. In our case the discharge takes place at lower voltage in acetone (ϵ = 21.2) than in acetonitrile (ϵ = 36); i.e., it is easier in the solvent which favors charge separation. Compared to ordinary electrochemistry the voltages in ESMS are much higher, and ions are transported in solution but also in the gas phase. Moreover, the process takes place in a microscopically rough tip of a capillary and not on the surface of an electrode and the measurements show considerable scattering. These features are characteristic of an electric breakdown.

In the oxidation of neutral solute species or of the metallic tip material[20] charge conservation is believed to require a flow of electrons from the tip to the counter electrode through the wire connecting the two electrodes. In our case the balance requires a reverse movement.

In conclusion ESMS is a very useful technique for inorganic chemistry, as it provides a means by which solution species can be transferred directly to the gas phase and analyzed by a mass spectrometer. It should not though be considered as soft as with biomolecules, as many changes can happen during the transition from the liquid to the gas state. One must carefully control the experimental parameters to minimize these side effects in order to obtain reliable results.

Acknowledgment. This work was partly supported by the Greek General Secreteriat for Research and Development; the authors wish to express their thanks.

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