Fourier-transform infrared study of short-lived highly reduced dithiolene complexes by potential-modulation spectroelectrochemical techniques

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The reduction of $[M(mnt)_3]^{3-}$ (M = V, Mo or Re; mnt = maleonitriledithiolate) has been examined by potential-modulation spectroelectrochemical techniques. Despite the highly reducing potentials required to effect the reductions (−1.57 to −2 V) and the highly unstable character of the reduction products the values of ν(CN) have been obtained for $[M(mnt)_3]^{4-}$ (M = V, Re or Mo) (2164, 2133 and 2134 cm^{-1} respectively). The sensitivity of the ν(CN) values to the identity of the metal for $[M(mnt)_3]^{4-}$ is greater than that found for the corresponding trianions suggesting an increased metal contribution to the frontier orbitals. The application of potential-modulation techniques to the examination of bulk solution species is described and shown to offer significant advantages for highly reactive electrochemically generated species.

The changes in co-ordination number/geometry and/or reactivity with oxidation or reduction of a metal complex are central to co-ordination chemistry and form the basis of the catalytic action of many transition metals. The characterisation of metal complexes in the extremes of oxidation state is of fundamental importance both because it extends the descriptive chemistry known for the metal and because it permits more extensive evaluation of the relationship between electronic and molecular structure. The range of oxidatively unstable species amenable to examination may be extended by application of techniques which permit the *in situ* spectroscopic interrogation of electrochemically generated complexes (*viz.* spectroelectrochemistry).[1,2] A further development of these techniques is now described which permits the examination of the highly reduced end-members of tris complexes of *cis*-1,2-dicyanoethylene-1,2-dithiolate (maleonitriledithiolate, mnt) $[M(mnt)_3]^{4-}$ (M = V, Re or Mo). The tetraanions have proved to be too reactive for study using spectroelectrochemical techniques which involve exhaustive electrolysis of the solution under investigation.[3] Interest in the tris(mnt) complexes stems from the observation that the extent of metal–ligand π bonding, as judged by the metal sensitivity of ν(CN), is highly dependent upon the overall charge on the complex. The mono- and di-anions show negligible metal–ligand π interaction but this increases substantially for the trianions.[3] At present no data are available for the tetraanions.

Spectroelectrochemical techniques designed for the examination of species in bulk solution most commonly involve exhaustive electrolysis of a controlled volume of solution which is examined *in situ* using a range of spectroscopic techniques.[1,2] Control of the volume of solution examined and maximisation of the area of the working electrode reduce the time necessary for electrolysis and thereby permit the study of a wider range of species than is accessible using sampling techniques. While the range of species which can be studied successfully may be extended further by cooling, many species which exhibit well behaved electrochemistry fail to give satisfactory spectroelectrochemical results. Most often these species are of greatest interest owing to pronounced reactivity or bonding changes. An alternative spectroelectrochemical approach involves modulation of the potential applied to the working electrode as employed in EMIRS (electrochemically modulated infrared spectroscopy) and SNIFTIRS (surface normalised interfacial Fourier-transform IR spectroscopy) techniques, these being developed so as to permit examination of the electrode–electrolyte solution interface.[2,4,5] These techniques also offer significant advantages for the study of highly reactive electrogenerated complexes and have permitted examination of the IR spectra of the tetraanions of the tris(mnt) complexes of V, Re and Mo.

Experimental

The compounds $[AsPh_4]_2[V(mnt)_3]$,[6] $[NBu_4]_2[Mo(mnt)_3]$[6] and $[PPh_4]_2[Re(mnt)_3]$[7] were prepared by literature methods and their purity was confirmed by elemental analysis (C, H, N and S).

Electrochemical experiments were carried out by using a PAR 174A polarographic analyser in conjunction with a Metrohm E612 VA scanner. Voltammetry was performed in a conventional one-compartment, three-electrode cell, the electrodes being a platinum-bead working electrode, a platinum-bar counter electrode and a Ag–AgCl reference electrode (against which the ferrocenium–ferrocene couple occurs at 0.55 V). No correction was made for the *iR* drop between the working and reference electrodes. Solutions were 0.5 mol dm^{-3} in supporting electrolyte and were deoxygenated with CH_2Cl_2-saturated nitrogen prior to the addition of the complex. The CH_2Cl_2 was predried over KOH and distilled from CaH_2 immediately prior to use. The supporting electrolyte, tetra-*n*-butylammonium hexafluorophosphate or tetrafluoroborate, was prepared by neutralisation of a 40% aqueous solution of tetra-*n*-butylammonium hydroxide with the appropriate acid. The crude electrolyte was washed extensively with distilled water and recrystallised (twice) from hot absolute ethanol. The purified electrolyte was then dried *in vacuo* at 100 °C for 24 h.

Infrared spectra were recorded using a Bruker 113V Fourier transform interferometer equipped with a liquid-nitrogen cooled MCT detector (Infrared Associates) and a Ge-coated KBr beamsplitter. The IRRAS (infrared reflection absorption spectroscopy) cell used for this study was modified from that described in ref. 8 and is shown in Fig. 1. The modifications reduce contact between the solution under study and air by (*i*)

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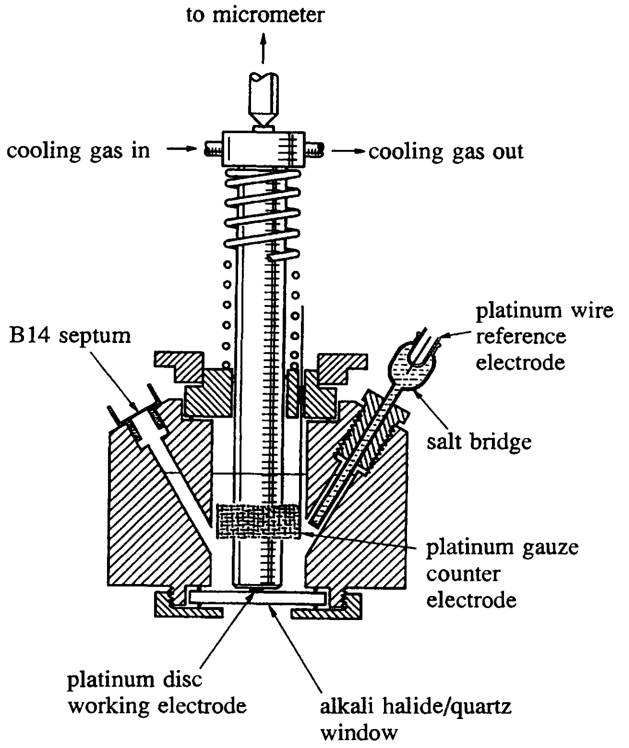


Fig. 1 Schematic diagram of the IRRAS cell

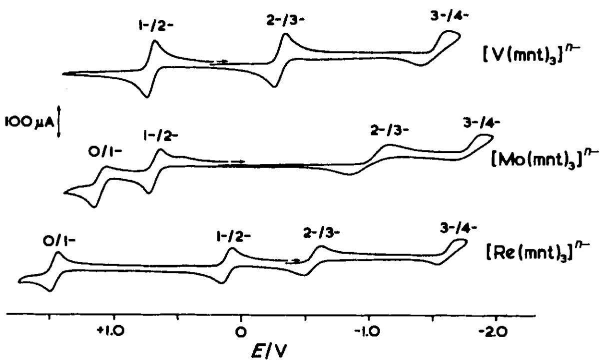


Fig. 2 Cyclic voltammograms of $[AsPh_4]_2[V(mnt)_3]$, $[NBu_4]_2$-$[Mo(mnt)_3]$ and $[PPh_4]_2[Re(mnt)_3]$ in 0.5 mol dm^{-3} $[NBu_4][BF_4]$–CH_2Cl_2 at −60 °C, scan speed 100 mV s^{-1}

Table 1 Redox potentials of the tris(mnt) complexes of vanadium, molybdenum and rhenium

	E^a/V			
Complex	0/1−	1−/2−	2−/3−	3−/4−
$[V(mnt)_3]^{2-}$	—	+0.72	−0.32	−1.57[b]
$[Mo(mnt)_3]^{2-}$	+1.13	+0.69	−1.02	*ca.* −1.8[c]
$[Re(mnt)_3]^{2-}$	+1.48	+0.13	−0.55	−1.64[b]

[a] 0.5 mol dm^{-3} $[NBu_4][PF_6]$–CH_2Cl_2 at −60 °C; *E* with respect to Ag–AgCl. [b] Quasi-reversible. [c] Partially reversible.

providing a suba seal port for filling the cell, (*ii*) establishing an o-ring seal between the cell and the reference electrode, and (*iii*) using a socket assembly to establish electrical contact with the counter electrode. These modifications ensured that the cell could both be loaded and operated with an airtight seal. Careful optimisation of the optical alignment of the cell has permitted the effective use of small working electrode areas (0.03 cm^2), which greatly improves the response time of the cell to a change of potential. The platinum-disc electrode was polished first using 1–2 μm cerium oxide followed by 0.075 and finally 0.03 μm alumina and cleaned by sonication in CH_2Cl_2. Cooling of the solution in contact with the working electrode was achieved in the manner outlined in ref. 8.

The FTIR and electrochemical experiments were synchronised using a digital pulse derived from the white-light interferometer of the FTIR spectrometer. A personal computer was used to generate time delays and to control the output potential of the potentiostat. The potential was only switched at the end of a data-collection scan of the moving mirror of the interferometer. The dwell time following the potential step can be adjusted in units of the cycle time of the moving mirror. This is dependent upon the resolution of the measurement and the scan speed of the mirror, *e.g.* the cycle time is 0.73 s for a 2 cm^{-1} resolution scan with a mirror velocity of 1.33 cm s^{-1}.

Results

Electrochemistry

The voltammetry of the organo-soluble $[M(mnt)_3]^{z-}$ complexes (M = V, Mo or Re) has been re-examined in carefully dried dichloromethane–electrolyte solutions, both at room temperature and −60 °C. Several of the complexes were also examined in acetonitrile. The vanadium complex displays three couples spanning $[M(mnt)_3]^-$ to $[M(mnt)_3]^{4-}$ while the molybdenum and rhenium complexes undergo an additional oxidation. The reduction potentials for the 0/1−, 1−/2− and 2−/3− couples were in good agreement with the literature values.[9] The 3−/4− couple occurs at quite extreme potentials, in the range −1.5 to −2.0 V, depending on the identity of the metal. Cooling the solutions to −60 °C generally resulted in considerable stabilisation of the tetraanion, and an improvement in reversibility of the 3−/4− couple. In the case of M = Mo the 3−/4− couple is best described as partially reversible, in that some portion of the return wave is observed. For M = V and Re the couples become quasi-reversible on cooling. The low-temperature voltammograms are given in Fig. 2 and the voltammetric results are summarised in Table 1.

Spectroelectrochemistry

Previous efforts to obtain reliable infrared spectra of the tetraanions were unsuccessful owing to rapid decomposition of the complexes.[3] Further attempts to obtain satisfactory results for the vanadium and molybdenum complexes were conducted using smaller working electrode surface areas (0.03 cm^2) and low temperature (−20 °C). In both cases the spectroscopic results were inconclusive since it was not possible to generate significant concentrations of the trianion by oxidation of the corresponding tetraanion. In cases where the 3−/4− couple gives a quasi-reversible cyclic voltammetric response the $[M(mnt)_3]^{4-}$ species must be comparatively well defined and long-lived in the electrochemical experiment. Failure to generate a satisfactory spectroelectrochemical response therefore relates to the different characteristics of the two experiments. In this regard the greater extent of electrolysis and the longer time-scale of the spectroelectrochemical experiments outlined above are likely to be critical. The application of potential-modulation techniques greatly increases control over both the extent and duration of electrosynthesis.

Modulation techniques

In most conventional spectroelectrochemical experiments the potential applied to the working electrode is changed from an initial, or rest, potential, V_i, to a final potential, V_f, at the start of the experiment, t_0, and the solution is exhaustively electrolysed [Fig. 3(*a*) and 3(*b*)]. Spectra are collected during the electrosynthesis, which in the case of the Bruker 113V FTIR spectrometer is during the forward scans of the moving mirror

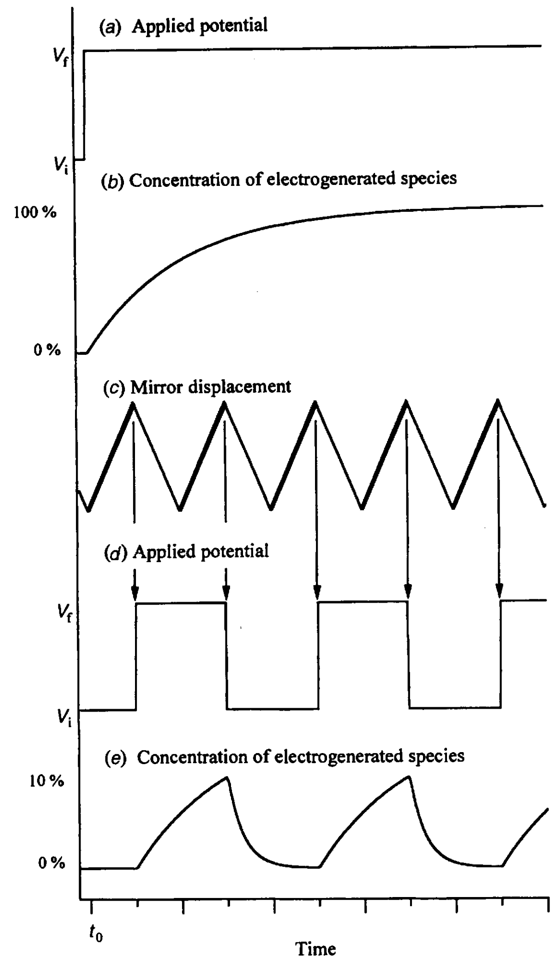


Fig. 3 Timing diagram for bulk synthetic, (*a*) and (*b*), and modulation, (*d*) and (*e*), spectroelectrochemical experiments. The mirror displacement indicated in (*c*) relates to the moving mirror of the FTIR spectrometer, with data collection occurring during the forward mirror displacements (indicated by the darker line)

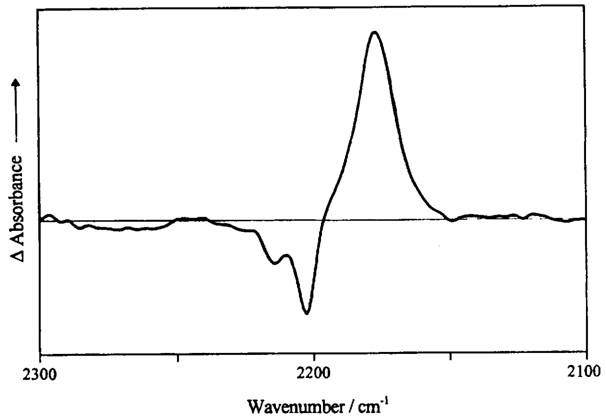


Fig. 4 Differential absorption spectra of $[Mo(mnt)_3]^{2-}$–$[Mo(mnt)_3]^{3-}$ obtained by modulating the potential between −0.5 (V_i) and −1.4 V (V_f) with a 3 s interval between each change of potential. The reference and sample spectra were obtained by coadding 100 alternate interferograms with an applied potential of −0.5 and −1.4 V respectively

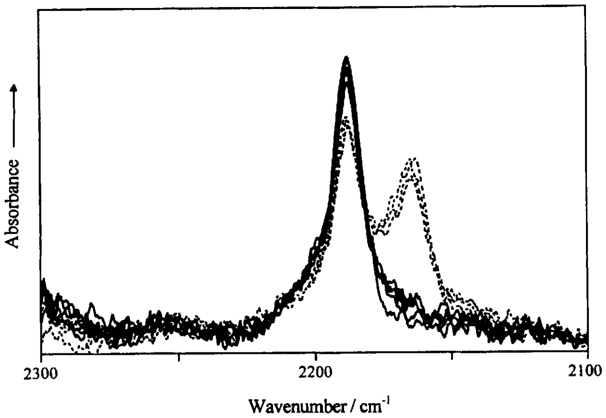


Fig. 5 A set of 10 absorption spectra of $[V(mnt)_3]^{3-}$–$[V(mnt)_3]^{4-}$ collected with the applied potential modulated between −0.6 (V_i) and −1.8 V (V_f) with a 3 s interval between each change of potential. The spectra collected with a potential of −1.8 V are indicated by the dashed line

of the interferometer [Fig. 3(*c*)]. The SNIFTIRS approach involves modulation of the potential applied to the working electrode between V_i and V_f with the changes in potential being synchronised with data collection by the FTIR spectrometer.[4] If the potential is switched at the end of each scan of the moving mirror then a square wave is applied to the working electrode [Fig. 3(*d*)]. In practice the electrolysis time for oxidation and reduction may be adjusted in units of the scan time of the FTIR spectrometer, but in all cases spectra were collected only on the final scan of the moving mirror prior to switching the potential. The extent of electrolysis depends on its duration, the overpotential for the redox reaction and the rates of diffusion and heterogeneous electron transfer. In the modulation experiments this is controlled by the final potential and the duration of the potential step, *e.g.* as in Fig. 3(*e*). In systems where the chemistry is fully reversible interferograms collected in the modulation experiments may be analysed by coadding spectra collected at the same potential and computing the differential absorbance or transmittance spectra (Fig. 4). This maximises the signal-to-noise ratio. Alternatively, in cases where the chemistry is less well defined, each interferogram may be computed separately and the repeatability of the spectral changes with each potential step may be monitored (Fig. 5). For the study of the tetraanions of the tris(mnt) complexes the latter approach was found to be the most informative. In parallel with the spectroscopic results, the repeatability of the chemistry and the state of the working electrode was monitored using the current response of the cell to a change in potential.

The time response of the electrochemical cell is of key importance to the effectiveness of the modulation experiments. For a given electrode configuration and solvent system the time response is optimised by minimising the area of the working electrode. In our experiments satisfactory spectroscopic results could be obtained using a flat, highly polished 2 mm diameter platinum-disc working electrode.

The operation of the modulation technique is demonstrated by the one-electron reduction of $[Mo(mnt)_3]^{2-}$. In this case both the di- and tri-anions are stable and give well defined spectra. The modulation experiment utilised a square-wave potential with a 3 s interval between each change of potential (between −0.5 and −1.4 V). Under these conditions the current response of the cell was highly repeatable as were the individual spectra collected at the two potentials. The extent of electrolysis was estimated to be *ca.* 5% based on the intensity of the bands due to ν(CN). The spectra were collected alternately at −0.5 and −1.4 V and the differential absorbance spectra, obtained by coadding 100 interferograms collected at each of the two potentials, are shown in Fig. 4. The negative bands at 2203 and 2213 cm^{-1} are due to the depletion of the starting material $[Mo(mnt)_3]^{2-}$, and the positive band at 2178 cm^{-1} is due to the product $[Mo(mnt)_3]^{3-}$. The wavenumbers and intensities of the bands due to ν(CN) of $[Mo(mnt)_3]^{2-/3-}$ are in excellent agreement with those published.[3]

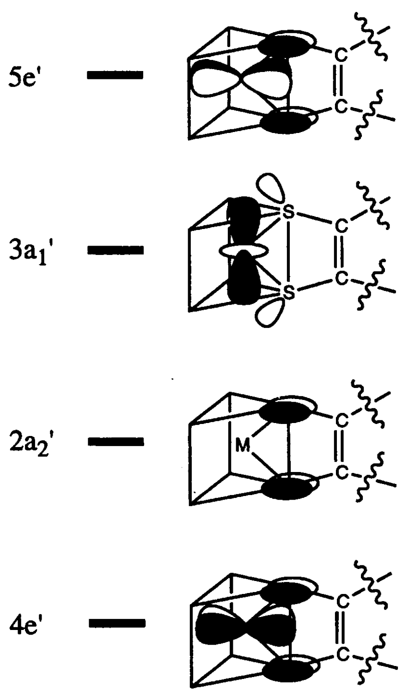
$[V(mnt)_3]^{4-}$. Despite the relatively positive value of $E[V(mnt)_3{}^{3-/4-}]$, low-temperature spectroelectrochemical experiments failed to give reversible generation of the tetraanion. In these experiments reduction leads to loss of the ν(CN) band of $[V(mnt)_3]^{3-}$ (2188 cm^{-1}) with the appearance of a strong band at 2164 cm^{-1} which decays before electrosynthesis is complete. During the course of the reaction there is a marked decrease in the rate of reduction, consistent with the build-up of species which passify the surface of the electrode. Returning the potential applied to the working electrode to the initial value (−0.6 V) results in only a small increase in intensity of the band due to the trianion. Whereas the spectral changes attendant on reduction suggest assignment of the band at 2164 cm^{-1} to $[V(mnt)_3]^{4-}$, this interpretation is undermined by the failure to regenerate a significant proportion of the starting material. The interconvertibility of the species giving rise to the bands at 2188 and 2164 cm^{-1} can, however, be established conclusively using modulation techniques as shown in Fig. 5. In this experiment the potential applied to the working electrode was cycled between −0.6 and −1.8 V with a period of 3.0 s between each change in potential. Over a period of 15–20 cycles the current and spectroscopic response of the cell was repeatable (Fig. 5), however over a more extended period the response of the cell declined. A similar decline in the current response is apparent in cyclic voltammetric experiments.

$[Re(mnt)_3]^{4-}$. The reduction of $[Re(mnt)_3]^{3-}$ gives a similar electrochemical response to that of the vanadium complex. Modulation experiments were conducted on a solution held at a temperature of −20 °C and the potential was switched between −1.0 and −2.0 V. Reoxidation of the tetraanion occurs on a time-scale slower than reduction of the trianion and repeatable spectroscopic and current response was obtained with a 3 s reduction–10 s reoxidation cycle. The band due to ν(CN) of $[Re(mnt)_3]^{4-}$ (2133 cm^{-1}) is significantly broader than that of the trianion (2179 cm^{-1}). A similarly large increase in the widths of the ν(CN) bands is apparent on reduction of $[W(mnt)_3]^{2-}$.[3]

$[Mo(mnt)_3]^{4-}$. The lower stability of $[Mo(mnt)_3]^{4-}$ which is evident in the cyclic voltammetry is also evident in the spectroelectrochemical experiments. Modulation experiments were conducted at −20 °C in CH_2Cl_2 with the potential switched between −1.3 and −1.9 V with a 3.0 s interval between each change of potential. Under these conditions only 2–3% of the complex was reduced in each cycle. A broad, asymmetric band centred on 2134 cm^{-1} was generated reproducibly in the spectra collected at −1.9 V and is assigned to ν(CN) of $[Mo(mnt)_3]^{4-}$.

Discussion

The co-ordination geometries of tris(dithiolene) complexes range from trigonal prismatic to octahedral, with the observed structure depending on the charge on the complex, the ligand and possibly the d-electron count of the metal. As negative charge is added to a neutral dithiolene complex there is an increasing tendency to distort from trigonal-prismatic towards octahedral geometry.[10,11] This change in geometry runs in the opposite direction to that expected on the basis of the size of the metal since the neutral complex has the metal in its highest formal oxidation state and smallest size. The cavity formed by three bidentate ligands will be largest when the arrangement of co-ordinating atoms is trigonal prismatic and smallest when octahedral, provided that the bite of the ligand is approximately constant. Interligand interactions are thought to be important in stabilising the trigonal-prismatic geometry.[12] The crystal structures of tris(mnt) complexes (mono- and di-anions) are best described as distorted octahedral,[13–16] however qualitative discussions of the bonding have generally been based on trigonal-prismatic (D_{3h}) geometry.[12,17] For the purpose of this discussion the molecular orbital scheme first proposed by Steifel *et al.*[12] is used. The frontier orbitals are, in order of increasing energy, 4e′, 2a$_2$′, 3a$_1$′ and 5e′ (Scheme 1), where 4e′ and 2a$_2$′ are fully occupied for all of the stable tris(mnt) complexes and 3a$_1$′ and 5e′ are occupied to the extent of the formal d-electron occupancy of the metal (treating mnt as a dianion). In D_{3h} symmetry 2a$_2$′ is derived from the highest occupied ligand-based π orbital normal to, and extending over, the plane of the ligand (π_v), 4e′ and 5e′ are molecular orbitals with significant metal d and ligand π_v character and 3a$_1$′ is a combination of metal d and in-plane sulfur p_π orbitals (π_h). Lowering the symmetry to D_3 (to a distorted-octahedral geometry) permits mixing between the d_{xz} and d_{yz} (4e″, D_{3h}) and the 4e′ and 5e′ orbitals.



Scheme 1 Representation of the metal–sulfur interactions of the frontier orbitals of trigonal-prismatic (D_{3h}) $[M(mnt)_3]$

It has previously been shown that the wavenumber of the band due to ν(CN) may be used to examine the metal–ligand π interaction of mnt complexes.[3] This follows from the involvement of π orbitals of the CN group in the π_v orbitals of the mnt ligand, these orbitals being involved in the metal–ligand π bonding. Since the lowest unoccupied π_v orbital of the ligand is antibonding with respect to the CN group an increase in π donation by the metal will result in a decrease in the value of ν(CN). The intensities of the bands due to ν(CN) increase with an increase in the electron occupancy of the π orbitals. The general trend of a shift to lower wavenumber and an increase in intensity of ν(CN) on reduction is apparent in the spectra of bis- and tris-(mnt) complexes[3,18] including the reductions to the tetraanions discussed herein. The ν(CN) values of $[M(mnt)_3]^{1-}$ (M = V, Cr, Mo, W or Re) exhibit little sensitivity to the identity of the metal and fall within the range 2213.7–2216.9 cm^{-1}. A similar situation pertains to the corresponding dianions having M = V, Cr, Mn, Fe, Mo, W or Re where the range of ν(CN) is 2200.0–2203.1 cm^{-1}. The occupancy of the 3a$_1$′ and 5e′ orbitals depends on the identity and formal oxidation number of the metal and the spin state, where unlike their second- or third-row counterparts the first-row transition metals give high-spin electron configurations.[19] The insensitivity of the ν(CN) values of the mono- and di-anions of the tris(mnt) complexes to the identity of the metal has been interpreted in terms of there being a small ligand contribution to the 3a$_1$′ and 5e′ orbitals when the metal is in a high formal oxidation state. While the ESR spectra of the 'd^1' complexes of V and the Group 6 elements indicate some ligand-orbital contribution to the molecular orbitals[6,20] this, apparently, is insufficient to perturb significantly the CN force constant.

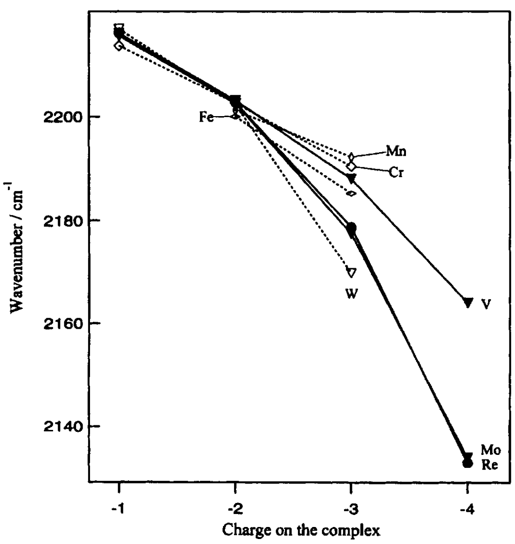


Fig. 6 The wavenumber of the principal component of the band due to ν(CN) plotted against the charge on the $[M(mnt)_3]$ complex. Data for the the mono-, di- and tri-anions taken from ref. 3

For the trianions an increased metal–ligand orbital interaction is reflected by a greater sensitivity of ν(CN) to the identity of the metal (Fig. 6).[3] For the first-row transition metals there are small increases in ν(CN) on moving from V, Cr to Mn followed by an 8 cm^{-1} decrease on moving from Mn to Fe. An increase in the occupancy of the $3a_1'$ and $5e'$ orbitals is expected to have markedly different effects on ν(CN) since only the $5e'$ orbital has a significant contribution from the ligand π_v orbital, having CN antibonding character. Thus, for the complexes of V, Cr and Mn the number of electrons occupying the $5e'$ orbital is expected to be constant, suggesting the electron configurations $(5e')^2(3a_1')^0$, $(3a_1')^1(5e')^2$ and $(3a_1')^2(5e')^2$. For the iron complex there is an increase in the occupancy of the $5e'$ orbital, giving $(3a_1')^2(5e')^3$. While this interpretation involves a changeover in the energies of the $3a_1'$ and $5e'$ orbitals we note that the tetraphenyl-phosphonium and -arsonium salts of $[Cr(mnt)_3]^{3-}$ have magnetic moments which suggest the presence of three unpaired electrons and consequently that the energies of the $3a_1'$ and $5e'$ orbitals are similar for the first-row transition metals. The second- and third-row transition metals give low-spin electron configurations and comparison between the complexes of Mo (and W) and Re must be on the basis of $(3a_1')^2(5e')^1$ and $(3a_1')^2(5e')^2$ electron configurations respectively. The markedly lower values of ν(CN) for the complexes of Mo, W and Re relative to the corresponding first-row transition-metal complexes reflects the greater overlap of the more radially expansive 4d and 5d metal orbitals with the ligand π_v orbital. Based on the arguments outlined above the rhenium complex would be expected to give the lowest value of ν(CN) since in this case the occupancy of $5e'$ is greatest, contrary to that observed (Fig. 6). It is unclear whether the differing behaviour of the second- and third-row transition metals is due to different orbital interactions or to changes in the electronic structure in response to changes in the molecular structure.

The increased sensitivity of ν(CN) to the identity of the metal apparent for the trianions develops further for the tetraanions. For the tris(mnt) complexes of V, Mo and Re the range of ν(CN) values increases from 0.5 cm^{-1} for the mono- and di-anions to 10.6 and 31 cm^{-1} for the tri- and tetra-anions respectively (Fig. 6). Furthermore the effect on ν(CN) of reduction becomes larger as the negative charge on the complex increases, consistent with an increasing ligand π_v orbital contribution to $5e'$.

Conclusion

The acquisition of IR spectra from the highly reduced end-members of the tris(mnt) complexes has permitted further examination of the pronounced 'turn on' of the metal–ligand π interaction which occurs for these complexes as a result of reduction of the dianions. It is clear from the relatively few number of cases available for the tetraanions that the sensitivity of ν(CN) to the identity of the metal is even more pronounced than is the case for the trianions. The contribution of the ligand π_v orbital to the molecular orbitals has been used to explain the differences in the ν(CN) values of the first-row transition-metal complexes, however similar arguments fail to account for the behaviour of corresponding second- and third-row transition metals.

An important aspect of this work is the application of modulation spectroelectrochemical techniques to the examination of highly reactive co-ordination compounds. This approach provides greater control over the time spent in the oxidation/reduction stages of the experiment and permits fine-tuning of the spectroelectrochemical experiment in a way which is not available for bulk electrosynthetic techniques and which broadens the range of systems for which spectroscopic results may be obtained reliably. This has been demonstrated by the examination of the IR spectra of the highly reduced end-members of the tris(mnt) complexes of V, Re and Mo.

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