Infrared Spectroelectrochemical Studies of Bis(1,2-dithiolene) Complexes of Transition Metals

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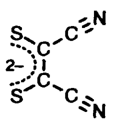
Infrared spectroelectrochemical studies have been conducted on the series of complexes $[M(mnt)_2]^{n-}$ (mnt = *cis*-1,2-dicyanoethylene-1,2-dithiolate; M = Fe or Au, $n = 1$; M = Co, Ni, Cu, Pd or Pt, $n = 2$). The ν(CN) values for related mono-, di-, and (for M = Cu or Au) tri-anions indicate that the extent of the metal contribution to the π orbital, which is delocalised over the mnt ligands, is directly comparable to that for the tri- and tetra-anionic forms of related tris(mnt) complexes, $[M(mnt)_3]^{n-}$ (n = 3 or 4). Previous ESR-based assignments of the singly occupied molecular orbital for $[M(mnt)_2]^{2-}$, M = Cu or Au, to predominantly metal (Cu)- or ligand (Au)-based orbitals are supported by the trends in ν(CN). For $[M(mnt)_2]^-$, M = Fe or Co, dimer formation and/or ligand association occurs to a significant extent in solution. While these reactions lead to irreversible electrochemical behaviour, well defined spectroelectrochemical results are obtained which are discussed in terms of the kinetics of the reaction and the electronic structure of the products.

Transition-metal complexes which support a range of accessible redox states are fundamental to a wide range of simple chemical and biological catalytic cycles. In many cases the ligand plays a crucial role in the redox chemistry, although the means by which this achieved is often far from clear. A key to the development of an understanding of these interactions is the study of redox-related complexes, particularly by structural and spectroscopic techniques. To this end, several techniques have been developed which allow the spectroscopic study of *in situ* electrogenerated complexes.[1,2] The application of these techniques increases the range of short-lived reactive complexes which may successfully be studied. Our work in this area has concentrated on the application of infrared spectroscopy to the elucidation of the changes which occur subsequent to the redox step.

cis-1,2-Dicyanoethylene-1,2-dithiolate [maleonitriledithiolate (mnt)] is a typical sulfur-donor chelate capable of forming a wide range of metal complexes, most of which are intensely coloured, stable, and rich in redox chemistry.[3-6] Complexes involving mnt as a ligand have been of intense interest since the early 1960s, much of the attention being focused on their electronic structure.[7-12] Central to this is the role of the mnt ligand itself in stabilising the metal in a series of unusual formal oxidation states. However, the assignment of these is ambiguous since this ligand can be formulated in both neutral and dianionic forms, suggesting that it acts as the redox centre and that the redox changes involve non-bonding sulfur or mnt π orbitals. Infrared spectroscopy is particularly appropriate for the study of mnt complexes since the CN groups, which are an integral part of the ligand, give rise to intense vibrational bands which are in general coupled only weakly to other vibrations of the molecule. A previous spectroelectrochemical investigation of tris(mnt) complexes showed that the wavenumbers of the ν(CN) bands are highly sensitive to the extent of π bonding of the mnt ligand and of the metal–ligand π interaction. The observation that ν(CN) is insensitive to the identity of the metal for the mono- and di-anionic forms of the tris(mnt) species was interpreted as being indicative of an insignificant metal–ligand π interaction. However, ν(CN) of the trianions showed a pronounced sensitivity to the identity of the metal, indicating a significant increase in the metal–ligand π interaction.[13] Further studies suggest that the metal sensitivity of ν(CN) is even greater for the tetranions.[14]



mnt

In this paper, infrared spectroelectrochemical results are reported for a range of bis(mnt) complexes. Although these have been intensively studied by various physical techniques,[4,6] the merit of the present work lies in the opportunity afforded to examine the infrared spectra of a wide range of redox-related complexes under identical conditions. The ν(CN) values thereby obtained are of importance since their metal dependence may be compared for bis- and tris-mnt complexes. Furthermore, for certain bis(mnt) complexes redox reactions have chemical consequences (ligand association/abstraction, dimerisation, polymerisation) and the elucidation of reactions of this type is a particular strength of spectroelectrochemistry which has received, until now, comparatively little attention.

Experimental

The mnt dianion was prepared and isolated as the disodium salt, $Na_2(mnt)$, using a method[15] adapted from that described by Bähr and Schleitzer.[16] The complexes $[PPh_4]_2[Mn(mnt)_2]$, $[NBu_4]_2[\{Fe(mnt)_2\}_2]$, $[NEt_4]_2[M(mnt)_2]$ (M = Co, Ni, Cu, Pd or Pt), $[NBu_4]_2[Zn(mnt)_2]$ and $[NBu_4][Au(mnt)_2]$ were all prepared by literature methods[4,17-20] and shown to be pure by elemental analysis (C, H, N and S).

Tetra-*n*-butylammonium tetrafluoroborate $[NBu_4][BF_4]$ was prepared by neutralisation of the appropriate hydroxide (40% aqueous solution) with tetrafluoroboric acid. The product was recrystallised from methanol–water, and then dried under vacuum [100 °C, 0.1 Torr (*ca.* 13.3 Pa)] for 24 h before use. Dichloromethane for electrochemical work was allowed to stand over KOH for 24 h, dried by distillation from CaH_2 under nitrogen, and stored under nitrogen prior to use.

Electrochemical experiments (cyclic and a.c. voltammetry) were carried out by use of a Metrohm E506 potientiostat and E612 VA scanner. Platinum wires (exposed surface area *ca.* 9 mm^2) were used as working and counter electrodes while the reference was an Ag–AgCl system (Metrohm EA441/5) utilising

Table 1 Redox potentials of complexes $[M(mnt)_2]^{n-}$

M	Couple[a]/V $0/1^-$	$1^-/2^-$	$2^-/3^-$
Fe		−0.12	−0.96[b]
Co	+0.92[c]	+0.08	
Ni	+1.22	+0.25	
Cu	+1.28[d]	+0.31	−0.76
Pd	+1.13	+0.33	
Pt	+1.15	+0.23	
Au	+1.51	−0.54	−1.33[b]

[a] 0.2 mol dm^{-3} $[NBu^n_4][BF_4]$–CH_2Cl_2 and 20 °C; *E* in volts with respect to Ag–AgCl. All processes are fully reversible unless otherwise indicated. [b] Chemically irreversible; *E* refers to the potential at maximum cathodic current with scan speed of 200 mV s^{-1}. [c] Electrochemically reversible process but i_{peak} is about half that of the $1^-/2^-$ couple. [d] Chemically irreversible; *E* refers to the potential of maximum anodic current with scan speed of 200 mV s^{-1}.

Table 2 Wavenumbers of the ν(CN) bands for complexes $[M(mnt)_2]^{n-}$ [a]

M	$[M(mnt)_2]^-$	$[M(mnt)_2]^{2-}$	$[M(mnt)_2]^{3-}$
Mn		2180 (sh), **2190.0**	
Fe	2202 (sh), **2207.9**, 2219 (sh)[b]	**2194.9**, 2208 (sh)	
Co	2196 (sh), **2208.8**, 2221 (sh)[b]	**2192.5**	
Ni	**2211.3**, 2226 (sh)	**2194.9**, 2213 (sh)	
Cu	**2211.3**, 2222.8	2180 (sh), **2196.8**	2166 (sh), **2184.3**
Zn		2180 (sh), **2190.0**	
Pd	**2212.2**	**2197.8**, 2233 (sh)	
Pt	2204 (sh), **2215.1**	2189 (sh), **2199.7**	
Au	**2213.2**, 2226 (sh)	**2194.9**	**2183.3**

[a] Solution (CH_2Cl_2) infrared spectra; the most intense component of ν(CN) is given in boldface. [b] Dimer.

the same solvent and supporting electrolyte concentration as used to support the solute; all redox potentials are cited with respect to this electrode. The potential of the reference electrode was cross-referenced with respect to the ferrocene–ferrocenium redox couple as a calibrant (the oxidation of ferrocene was taken to occur at +0.50 V with respect to Ag–AgCl). The redox potentials of the complexes studied under the conditions outlined above are given in Table 1.

Infrared spectra were recorded by use of a Bruker IFS 113V Fourier-transform interferometer equipped with a liquid-nitrogen-cooled MCT detector and Ge-coated KBr beamsplitter. The IRRAS cell used has been described elsewhere.[21] The wavenumbers of the bands due to ν(CN) are given in Table 2.

All solutions were degassed with dry oxygen-free nitrogen before use and maintained under a nitrogen atmosphere throughout all experimentation. Sample concentrations for infrared spectroelectrochemistry were less than 5 × 10^{-2} mol dm^{-3}.

Results

(*i*) *Iron and Cobalt*.—The iron and cobalt bis(mnt) complexes are known to undergo in solution monomer–dimer equilibria which are highly dependent upon the charge on the anion, the co-ordinating power of the solvent, and the presence of co-ordinating ligands.[22,23] The tendency of dianions to give monomers[24] and monoanions to form dimers is also apparent in the solid state.[25]

The spectral changes in the ν(CN) region which result from the oxidation of $[Co(mnt)_2]^{2-}$ at a concentration of *ca.* 3 × 10^{-3} mol dm^{-3} are marked by a well defined isosbestic point [Fig. 1(*a*)]. This implies that, on the 40 s time-scale of the experiment, the products are formed without the generation of intermediate species. Since, under the conditions of the experiment, the oxidation product is known[26] to be the dimer, $[\{Co(mnt)_2\}_2]^{2-}$, the reaction proceeds with dimer formation being either very fast or very slow on the time-scale of the overall oxidation. Since estimates of the rate of dimer formation from voltammetric studies[27] indicate a half-life of much less than 1 min, the observation that the spectrum of the product does not change over 10 min is inconsistent with the alternative of requiring a comparatively slow rate of dimerisation. Therefore the spectral features arise from $[\{Co(mnt)_2\}_2]^{2-}$, the concentration of monomeric $[Co(mnt)_2]^-$ being insufficient to be detected spectroscopically. This interpretation is supported by the observation that the rate of re-reduction is slow relative to that of the initial oxidation. The re-reduction step proceeds with quantitative regeneration of the starting material. The associated spectra [Fig. 1(*b*)] exhibit a near isosbestic point which is significantly poorer than that of the oxidation step. This observation is consistent with the build-up of small concentrations of other species, such as $[\{Co(mnt)_2\}_2]^{3-}$ during the redox step.

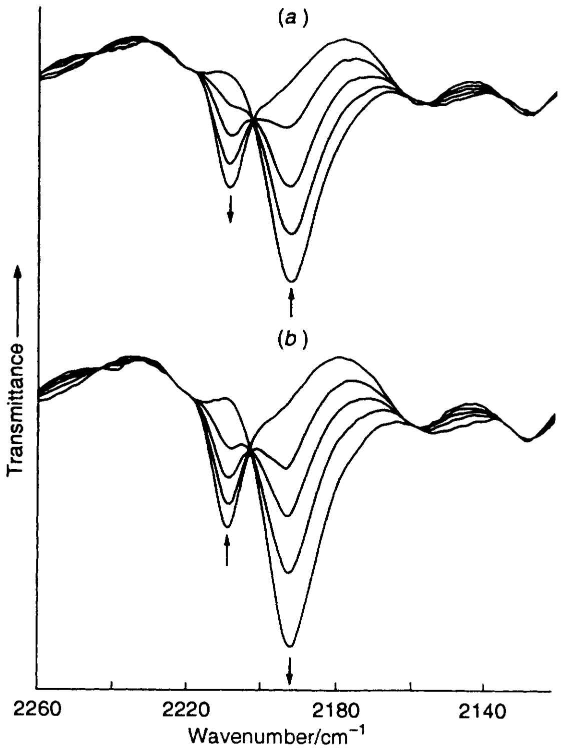


Fig. 1 Infrared spectroelectrochemistry of the oxidation (*a*) and re-reduction (*b*) of $[Co(mnt)_2]^{2-}$ in dichloromethane (resolution 0.5 cm^{-1}, 293 K, *ca.* 1 × 10^{-2} mol dm^{-3}, time between spectra *ca.* 10 s)

Dimer formation appears to have only a small effect on the band due to ν(CN). The oxidation product gives rise to a strong band at 2208.8 cm^{-1}, with weak shoulders at 2196 and 2221 cm^{-1}. Experiments conducted on solutions having lower initial concentrations of $[Co(mnt)_2]^{2-}$ give rise to electrogenerated species with a ν(CN) band at a slightly lower wavenumber (2207 cm^{-1}) and the spectra no longer exhibit clearly defined isosbestic points for the oxidation process. This may be due to partial dissociation of the dimer, reflecting the magnitude of the equilibrium product.

In order to confirm that the shifts observed for ν(CN) are consistent with those which would occur on increasing the co-ordination number of the metal atom, the oxidation of $[Co(mnt)_2]^{2-}$ was performed in the presence of a co-ordinating ligand. Voltammetric studies of the oxidation of $[Co(mnt)_2]^{2-}$ in the presence of pyridine indicate that there is negligible pyridine co-ordination to the dianion but strong co-ordination to the monoanion.[26] Consistent with this the band due to ν(CN) of $[Co(mnt)_2]^{2-}$ is unaffected by the presence of pyridine (py) whereas the spectrum of the oxidation product is substantially different therefrom, with the growth of a new peak at 2197 cm^{-1}, with shoulders at 2204 and 2209 cm^{-1}. These spectral features are assigned to $[Co(mnt)_2(py)_2]^-$ on the basis of the reported equilibrium products.[26] Re-reduction led to quantitative regeneration of the starting material. Neither the oxidation nor the reduction proceeds *via* well defined isosbestic points, suggesting that at least one of the rate constants in each direction (*i.e.* rate of gain or loss of either the first or second pyridine molecule) is comparable to the rate of electrosynthesis. Comparison of the spectra of $[\{Co(mnt)_2\}_2]^{2-}$ and $[Co(mnt)_2(py)_2]^-$ shows that adduct formation (either by dimerisation or by the introduction of a co-ordinating ligand) leads to a lower wavenumber for ν(CN). This may be explained in terms of greater charge build-up on the metal, leading to increased back donation into the ligand π orbitals. The larger electron density of the ligand π* orbitals, antibonding with respect to C≡N, results in a weakening of the CN bond and thus to a lowering of ν(CN).

Whereas dimer formation is less favoured for $[Fe(mnt)_2]^-$ than for the corresponding cobalt complex (as inferred from the relative magnitudes of their stability constants in weakly co-ordinating solvents[26]), both complexes exhibit similar behaviour in dichloromethane. The oxidation of $[Fe(mnt)_2]^{2-}$ proceeds *via* several well defined isosbestic points which are apparent only after the second spectrum recorded after switching the potential to +0.4 V. During the initial period of the oxidation a broad feature is removed from the spectrum at a rate much faster than that of the bands due to $[Fe(mnt)_2]^{2-}$. The broad band may be due either to a surface-adsorbed species, which reduces the reflectivity of the electrode, or to a contaminant. On returning the potential to −0.6 V the starting complex is regenerated quantitatively. No isosbestic points are apparent in the spectra recorded through the course of this reaction and the spectral features associated with both the dianion and the monoanion/dimer have band profiles which change during the transformation. The concentration of short-lived species formed in the reoxidation of $[\{Fe(mnt)_2\}_2]^{2-}$ appears greater than was observed for the corresponding cobalt complex. The band due to ν(CN) of $[\{Fe(mnt)_2\}_2]^{2-}$ consists of a strong component at 2207.9 cm^{-1} with shoulders at 2202 and 2219 cm^{-1}, and the rate of oxidation is qualitatively faster than that of re-reduction. The values of ν(CN) for the strongest band of the oxidation products of cobalt and iron complexes are similar to one another and, in keeping with the changes to ν(CN) attendant upon adduct formation, occur at the bottom of the range of ν(CN) values for monoanions in general.

(*ii*) *Nickel, Palladium and Platinum.*—For each metal the bis(mnt) dianion undergoes two oxidation steps, each of which is chemically and electrochemically reversible.[4] The product of the first step is known to be sufficiently stable to permit its isolation.[20,28,29] Crystal structures are available for the nickel mono- and di-anionic complexes and these show that there is little structural change associated with their interconversion.[29,30] Accordingly, interconversion between the di- and mono-anion in a spectroelectrochemical experiment proceeds quantitatively as is exemplifed by the palladium complex (Fig. 2). The presence of an isosbestic point in the spectra suggests that there is direct interconversion between the mono- and di-anions, with no significant build-up in concentration of intermediate species. For all three complexes the band due to ν(CN) decreases in intensity and increases in wavenumber by 15 ± 1 cm^{-1} on oxidation to the monoanion.

Oxidation of monoanionic bis(mnt) complexes to the corresponding neutral species is marked by broad irreversible increases in absorbance in concert with a decrease in intensity of the ν(CN) band of the monoanion. Lowering of the temperature to −25 °C failed to improve the quality of the spectra. Despite the reversibility of the electrochemistry, in no case was it possible to identify spectral features due to simple neutral bis(mnt) complexes.

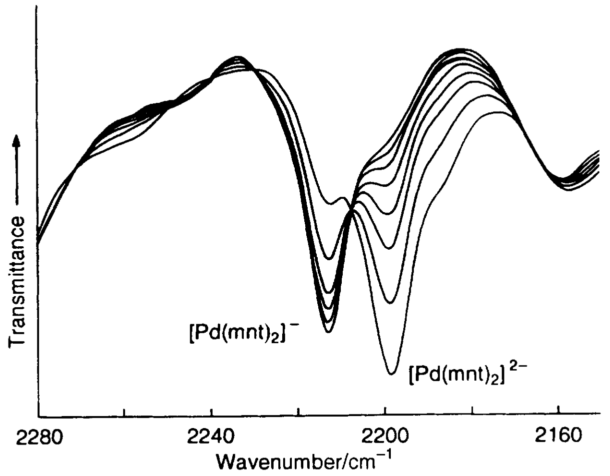


Fig. 2 Infrared spectroelectrochemistry of the oxidation of $[Pd(mnt)_2]^{2-}$ in dichloromethane (resolution 0.5 cm^{-1}, *ca.* 2 × 10^{-2} mol dm^{-3}, 293 K, time between spectra *ca.* 15 s)

(*iii*) *Copper and Gold.*—There is electrochemical evidence supporting the existence of four redox-linked forms, ranging from the neutral to the trianionic, of copper as well as gold bis(mnt) complexes. All the redox processes, apart from the oxidation of $[Cu(mnt)_2]^-$ to the neutral species and the reduction of the gold dianionic complexes to the trianion, are reversible. Formulation of the ligand as a dianion implies that the metal has a formal oxidation state of +3 for $[M(mnt)_2]^-$. For the Group 11 elements this corresponds to a d^8 electron configuration, which is expected to have a strong preference for square-planar co-ordination. The crystal structure of $[M(mnt)_2]^-$, M = Cu or Au, shows indeed that the anion is essentially planar.[31,32] The similarity of solution (CH_2Cl_2) and solid-state (KBr disc) spectra suggest that this stereochemistry is retained in solution. For both the copper and gold salts, the monoanionic form gives rise to two well defined bands due to ν(CN) with separations of 11.5 (Cu) and 12.5 (Au) cm^{-1}. In both cases the lower-wavenumber component is approximately twice as intense as its accompanying band. On reduction to the dianion the spectrum is dominated by a single band of increased intensity and lower wavenumber. For copper, the dianion is the most stable form of the complex and crystal structures indicate the retention of square-planar co-ordination, but with significantly increased Cu–S distances [2.275(1) Å][33] compared to that of the monoanion [2.166(5) Å].[31] The electrochemical reversibility (including the observation that $E_{pa} - E_{pc}$ is the same as that of the ferrocene–ferrocenium couple recorded under the same conditions) exhibited for the mono-/di-anion couple by the copper complex indicates that no structural change which alters significantly the reoxidation potential occurs as a result of the electron transfer. Since the electronic and molecular structures of the mnt complexes are strongly coupled, $[Cu(mnt)_2]^{2-}$ is therefore also inferred to be planar in solution, consistent with the solid-state structures. A similarly well defined electrochemical response is obtained for the di-/tri-anion couple which suggests that $[Cu(mnt)_2]^{3-}$ also is planar in solution. It is interesting that electrochemical studies of the complexes of Cu^I and Cu^{II} with 1,4,8,11-tetrathiacyclotetradecane suggest that conformational equilibria are associated with the redox step.[34] These different observations may be due to different electronic and/or steric interactions with the ligand.

Although reduction of $[Cu(mnt)_2]^{2-}$ to the trianion is

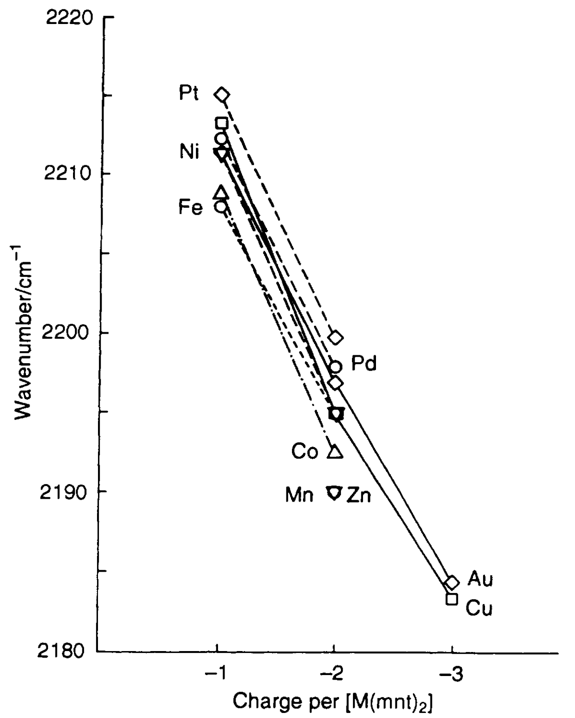


Fig. 3 The wavenumber of the principal component of the band due to ν(CN) plotted against the charge per [M(mnt)$_2$]

electrochemically reversible, the corresponding process for the gold complex is electrochemically irreversible. Spectroelectrochemical results indicate that the reduction to [Au(mnt)$_3$]$^{3-}$ is chemically reversible. While the similarity between the spectral changes which occur for the gold and copper complexes on reduction to the trianionic forms may suggest that they have similar structural chemistry, this inference needs to be treated with caution since the bands due to ν(CN) give limited information on distortion of the structure as a whole. Both the electrochemical and spectroelectrochemical results are consistent with both [Au(mnt)$_2$]$^-$ and [Au(mnt)$_2$]$^{2-}$ having similar structures in solution. Based on previous crystallographic and the present spectroscopic results, the geometries are likely to be planar. Although the oxidation of [Au(mnt)$_2$]$^-$ is electrochemically reversible, we were unable to stabilise the neutral complex sufficiently to obtain its spectrum.

(*iv*) *Manganese and Zinc*.—Neither the bis(mnt) complexes of manganese or zinc undergo well defined oxidation or reduction (either reversible or irreversible). For the purpose of comparison, the spectra of their respective dianions were collected under standard spectroelectrochemical conditions.

Discussion

A striking feature of the vibrational spectroscopy of the mono- and di-anionic forms of tris(mnt) complexes is the virtual total insensitivity of ν(CN) to the identity of the metal.[13] However, the ν(CN) bands of the mono- and di-anions of bis(mnt) complexes exhibit appreciable sensitivity to the identity of the metal (Fig. 3). In this respect, the mono- and di-anionic bis(mnt) complexes bear a closer resemblance to the tri- and tetra-anionic[13,14] tris(mnt) species, for which ν(CN) is sensitive to the identity of the metal, than to the analogous mono- and di-anions. The comparison is substantiated by the representation of the mnt ligand as a dianion and the resulting formulation of identical formal oxidation states for the mono- and di-anionic bis(mnt) complexes and tri- and tetra-anionic tris(mnt) complexes. Within this formalism the oxidation state of the metal, rather than the overall charge of the complex, is the most important factor in determining the extent of metal–ligand π interaction for mnt complexes of different stoichiometry.

For [M(mnt)$_2$]$^-$ the ν(CN) values increase as the group is descended (*viz.* Ni, Pd, Pt; Cu, Au). Since a decrease of the π-electron density of the ligand leads to an increase in ν(CN), this implies that there is less metal participation in ligand π-acceptor orbitals and/or more in ligand π-donor orbitals for the heavier transition metals. The latter alternative is expected to be dominant given the greater radial extent of the 4d and 5d orbitals and the electronic structure of the mnt ligand. For the dianions, however, the sequence of ν(CN) values for the complexes of Ni, Pd, and Pt is preserved, whereas the order for those of Cu and Au is reversed. Furthermore, this ordering of ν(CN) (Cu > Au) is maintained for their respective trianions. These observations can be related to the identity of the HOMO (highest occupied molecular orbital) for the different complexes. For convenience, the MO diagram for [Ni(edt)$_2$]$^{2-}$ (D_{2h} symmetry, edt = ethylenedithiolate $S_2C_2H_2{}^{2-}$), which is given as Fig. 1 of ref. 35, will be used. For the monoanions of the Group 10 and 11 metals the HOMO is $2b_{3g}$, a metal d_{xz} orbital which interacts with the $b_{3g}(\pi)$ orbital of the ligand. For the Group 10 metals the orbital is singly occupied and ESR measurements[36] are in keeping with this assignment. The [M(mnt)$_2$]$^{2-}$ complexes, M = Ni, Pd or Pt, are diamagnetic (the HOMO remains the $2b_{3g}$ orbital), but ESR spectroscopy of the corresponding copper and gold complexes suggests that the HOMO is different in these two cases. For [Cu(mnt)$_2$]$^{2-}$ the unpaired electron is localised on the metal atom (d_{xy}) in the b_{1g} orbital,[37] whereas for [Au(mnt)$_2$]$^{2-}$ the electron is predominantly localised on the ligand ($2b_{2g}$ or $2a_u$) orbitals.[38] Consistent with this interpretation there is a larger drop of ν(CN) associated with reduction of the monoanion to the dianion for the gold complex (18 cm^{-1}) than for the platinum complex (15 cm^{-1}), and the trend of ν(CN) as the group is descended is reversed.

Of the complexes which give stable monoanions, only those of iron and cobalt are susceptible to dimer formation. In both cases the dimerisation process, occurring as a result of the oxidation reaction, is fast compared to the rate of electron transfer under our conditions. The reduction of the dimer, however, proceeds with the build-up of at least one intermediate species. The bands due to ν(CN) for mono- and di-meric bis(mnt) complexes exhibit only slight differences, highlighting the difficulties associated with distinguishing dimer formation on the basis of infrared spectroscopy alone. For the examination of these processes UV/VIS spectroscopy has proved to be a more informative technique.[23]

Despite the electrochemical reversibility of the oxidations of several of the anions, in no case was it possible to obtain the infrared spectra of a neutral complex. Similar behaviour was noted for the neutral tris(mnt) complexes.[13] It is likely that the decomposition of [M(mnt)$_2$] is highly concentration-dependent and that this is the reason for the discrepancy between the electrochemical and spectroelectrochemical results.

Conclusion

Trends in the wavenumbers of the bands due to ν(CN) of bis(mnt) complexes are well explained in terms of the MO description, as long as the identity of the HOMO can be established. In cases where the HOMO is $2b_{3g}$ the trend is for ν(CN) to decrease as the group to which the metal belongs is descended. This can be interpreted as reflecting the greater π-acceptor character of the heavier transition metals when co-ordinated to sulfur-donor ligands. The different character of the HOMO for [M(mnt)$_2$]$^{2-}$, M = Cu or Au, suggested by ESR studies, is reflected by the change in the trend of ν(CN) values. It is interesting that the change in character of the HOMO has only a slight effect on the value of ν(CN).

For both [M(mnt)$_2$]$^{n-}$, n = 1 or 2, and [M(mnt)$_3$]$^{n-}$, n = 3 or 4, the value of ν(CN) depends on the identity of the metal suggesting that there is significant π interaction between the ligand and the metal. Comparison of the results for the bis- and tris-mnt complexes suggests that this interaction depends more on the formal oxidation state of the metal (treating the mnt ligand as a dianion) than on the overall charge on the complex.

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