Multinuclear NMR studies of some oxomolybdenum(VI) complexes with polyaminocarboxylates

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Abstract

[95]Mo and ^{13}C NMR spectra of aqueous solutions containing molybdate and either DTPA or TTHA at pH values between 2.0 and 9.5 reflect the presence of two complexes of 1:1 (MoL) and 2:1 (Mo_2L) stoichiometries for both ligands. All complexes give one broad [95]Mo signal at 60–70 ppm relative to free molybdate, with linewidth 380–890 Hz which increases when the pH decreases. The [95]Mo NMR parameters indicate that the metal center of the complexes consists of the MoO_3 species, which is confirmed by the presence of two ^{17}O NMR signals in the intensity ratio of 1:2 from the corresponding oxo ligands which are *trans* to the nitrogen and oxygen atoms of the ligand IDA-type moities that bind the metal center. The intensities and multiplicities of the ^{13}C signals of the complexes indicate that in the MoL complexes the metal center binds one of the terminal IDA-type moieties of the ligands, whereas in the Mo_2L complexes two metal centers bind the two terminal IDA-type moieties, yielding a very symmetric species. The intensities of the [95]Mo and ^{13}C signals give the pH dependence of the concentration of the free ligand, L, free molybdate, Mo, and the MoL and Mo_2L complexes. In general, for both 1:1 and 2:1 solution stoichiometries used, the free ligand and the two complexes are present between pH 2.0 and about 8, Mo only appears above pH 6 and at pH 9 only L and Mo occur. The pH dependence of the ^{13}C complexation shifts reflects the protonation state and sites of the ligand in the complexes. The binding of the MoO_3 center to two nitrogen atoms and one carboxylate oxygen of EDDA leads to two diastereomeric pairs of this complex, which are reflected in the presence of two sets of proton signals. Those spectra were assigned using two-dimensional COSY and *J*-resolved spectra. The vicinal coupling constants obtained were used to define the structures of the species present. Two-dimensional exchange spectra yielded the exchange mechanisms which operate in solution.

Introduction

Studies of the coordination chemistry of molybdenum in the Mo(VI) oxidation state are useful for understanding the mechanistic role of this metal in enzymatic [1–4] and industrial [5] catalysis, as well as in its biological transport processes [6].

Many solution complexation studies of Mo(VI) by aminocarboxylate ligands have been undertaken, including determination of stability constants [7–13], kinetic studies of complex formation [14] using polarography, potentiometry and UV, IR and Raman spectrophotometry. Structural studies in the solid state using X-ray diffraction methods have also been carried out [15, 16]. Various solution NMR studies of Mo(VI)–polyaminocarboxylate complexes have been reported, using [1]H [7, 17, 18], [13]C [19], [17]O [19, 20] and

[95]Mo [19] observation, while some Mo(V) complexes were also studied [21]. In this paper we complement previous NMR work of Reilley and co-workers [19], further studying the interaction of Mo(VI) with the ligands ethylenediaminediacetic acid (EDDA) and diethylenetriaminepentaacetic acid (DTPA) (Fig. 1) in aqueous solution at various pH values using ^{1}H, ^{13}C, ^{17}O and [95]Mo NMR. On the basis of the results obtained we studied for the first time the complexation of Mo(VI) by triethylenetetraaminehexaacetic acid (TTHA), 1,4,7-triazacyclononane ([9]aneN$_3$) and 1,4,7-triazacyclononane-*N,N′,N″*-triacetic acid (NOTA) (Fig. 1) also using ^{1}H, ^{13}C, ^{17}O and [95]Mo NMR spectroscopy.

Experimental

The ligands EDDA, DTPA and TTHA were obtained from Aldrich as the free acids. The macrocyclic chelates

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Therefore there are quite severe restrictions on the possible reactant concentrations to avoid any coupling between the binuclear complex formation and the subsequent electron transfer reaction. Other restrictions on these concentrations are imposed by the need of a sufficient excess of the Co(III) complex to have first-order conditions and by the need to avoid dimerization or oxidation of the iron(II) complex [13]. The final concentrations selected were 2×10^{-5} and 5×10^{-4} mol dm^{-3} for the iron and cobalt complexes, respectively.

Kinetic measurements were always taken in fresh solutions, deaerated by bubbling with N_2. All the media studied were unbuffered, given that the reaction is pH independent in the range of $5 < pH < 9$ [16]. Under these working conditions the first-order kinetic plots were linear over at least three half-lives. The rate constants were found to be reproducible within a precision of about 5%.

The dependence of the pseudo-first-order rate constant with Co(III) complex concentration was also investigated. Results show a second-order rate law in all the electrolyte solutions used, first order with respect to each reactant, in agreement with previous results [13, 16]. An example is shown in Fig. 1 for 3 mol dm^{-3} sodium nitrate.

To investigate the confidence of our data, formation of the binuclear complex in aqueous solution was studied, with reactants at the concentrations specified above, in the presence of 0.15 mol dm^{-3} of $LiClO_4$. The rate constant obtained was 3.18×10^3 mol^{-1} dm^3 s^{-1} at 298.2 K. This compares well with the published value of 3.1×10^3 mol^{-1} dm^3 s^{-1} [13]. In all runs we carried
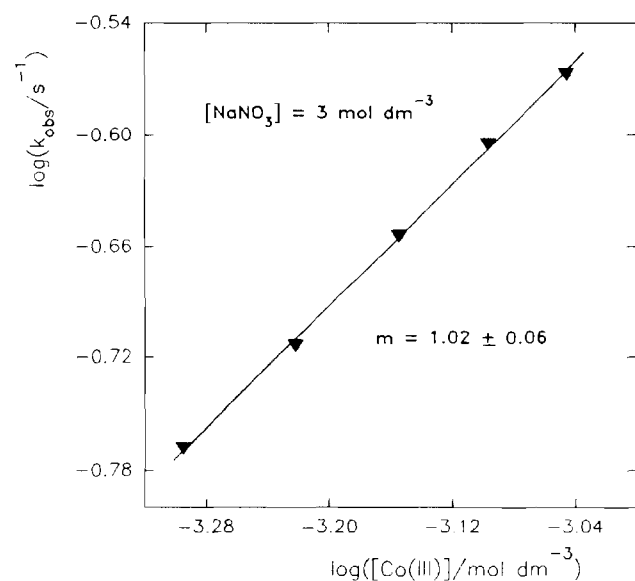
out, the formation reaction went to completion, with no sign of interference from the subsequent electron transfer step.

Electrochemistry

Electrochemical measurements were carried out to obtain information about the iron(II) center oxidation in the complex $Fe(CN)_5H_2O^{3-}$ (see below). The apparatus and electrodes used in this study have been described in a previous paper [17]. As the change in the nature and/or concentrations of supporting electrolytes produces variations in the liquid junction potential between the reference electrode and the solution, we have estimated the contributions coming from the variations in the liquid junction potentials using, as a starting point, the following expression

$$E_j = - \frac{RT}{F} \sum_i \int_\alpha^\beta \frac{t_i}{z_i} \, d(\ln a_i) \qquad (1)$$

where t_i is the transference number of ion i, z_i its charge and a_i its activity. In this expression addition is extended to all the ionic species present in the solution. However, in our working conditions the concentrations of the supporting electrolytes are much greater than those of the ions which come from the iron(II) complex. Therefore a good approach is to include in this sum only the ions produced by the background electrolyte. Assuming that the transference numbers are constant in the range of concentrations employed, the E_j values for sodium nitrate and calcium nitrate were calculated. In none of the cases were these values greater than 6 mV. The error in the experimental values of the standard formal potentials is about ± 5 mV. On this basis and considering that not all the transference numbers and activity values for the different salts are available in the literature, the $E^{\circ\prime}$ values used in 'Discussion' are not corrected from the liquid junction potential contributions. Besides, as will be seen later, these data will be used in a qualitative way.

Electrochemical measurements were carried out at an $Fe(CN)_5H_2O^{3-}$ complex concentration of 7.5×10^{-4} mol dm^{-3} using $LiNO_3$, $Mg(NO_3)_2$, $Ca(NO_3)_2$ and $Sr(NO_3)_2$ at different concentrations as background electrolytes. In the cases of sodium and potassium nitrate salts, the stability of the resultant $Fe(CN)_5H_2O^{2-}$ species is not sufficient to see the cathodic wave adequately in the voltammogram. Therefore, the $E^{\circ\prime}$ values for these supporting electrolytes could not be measured.

Fig. 1. Plot of $\log(k_{obs}$ (s^{-1})) against $\log([Co(III)]$ (mol dm^{-3})) for the binuclear complex formation in $NaNO_3$ 3 mol dm^{-3} at 298.2 K.

Results and discussion

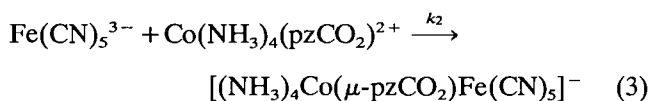Table 1 shows the rate constant values at 298.2 K for all the concentrated electrolyte solutions studied.
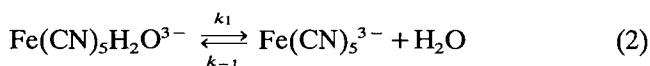
TABLE 1. Second-order rate constants at 298.2 K for the binuclear complex formation in the different concentrated electrolyte solutions

[Salt] (mol dm^{-3})	$10^{-2} \times k_f$ (mol^{-1} dm^3 s^{-1})					
	KNO$_3$	NaNO$_3$	LiNO$_3$	Mg(NO$_3$)$_2$	Ca(NO$_3$)$_2$	Sr(NO$_3$)$_2$
0.25				8.40	1.05	1.10
0.50	13.6	13.8		4.91	6.57	6.99
1.00	9.42	9.97	7.57	2.22	3.45	3.57
1.50	5.78			1.21	2.02	2.28
2.00	4.40	5.56	4.17	0.76	1.47	1.70
2.50	3.63			0.50	1.15	1.34
3.00		3.36	3.04	0.34	0.91	1.00
4.00		2.67	2.17			
5.00		1.83	1.68			
6.00		1.42	1.28			

k_f(LiClO$_4$ 0.15 mol dm^{-3}) = 3.18×10^3 mol^{-1} dm^3 s^{-1} at 298.2 K.
ΔH^*(LiClO$_4$ 0.15 mol dm^{-3}) = 74±2 kJ mol^{-1} at 298.2 K.
ΔS^*(LiClO$_4$ 0.15 mol dm^{-3}) = 70±10 J mol^{-1} K^{-1} at 298.2 K.

The highest potassium nitrate concentration used was 2.5 mol dm^{-3} because of its solubility limit. One can see from this Table that there is a specific salt effect, in the sense that the influence of the electrolyte concentration on the rate constants depends not only on the ionic strength of the medium, but also on the nature of the salt present in it. To rationalize experimental results, the possible mechanisms followed by the reaction studied will be taken into account first.

The second-order rate law observed experimentally can be explained by a limiting dissociative mechanism, D.

$$Fe(CN)_5H_2O^{3-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Fe(CN)_5^{3-} + H_2O \quad (2)$$

$$Fe(CN)_5^{3-} + Co(NH_3)_4(pzCO_2)^{2+} \overset{k_2}{\longrightarrow}$$

$$[(NH_3)_4Co(\mu\text{-}pzCO_2)Fe(CN)_5]^- \quad (3)$$

The following interchange dissociative mechanism, I_D, is also in agreement with a second-rate law.

$$Fe(CN)_5H_2O^{3-} + Co(NH_3)_4(pzCO_2)^{2+} \overset{K_0}{\rightleftharpoons}$$

$$(NH_3)_4Co(pzCO_2)^{2+}...H_2OFe(CN)_5^{3-} \quad (4)$$

$$(NH_3)_4Co(pzCO_2)^{2+}...H_2OFe(CN)_5^{3-} \overset{k_3}{\longrightarrow}$$

$$[(NH_3)_4Co(\mu\text{-}pzCO_2)Fe(CN)_5...H_2O]^- \quad (5)$$

$$[NH_3)_4Co(\mu\text{-}pzCO_2)Fe(CN)_5...H_2O]^- \overset{fast}{\longrightarrow}$$

$$[(NH_3)_4Co(\mu\text{-}pzCO_2)Fe(CN)_5]^- + H_2O \quad (6)$$
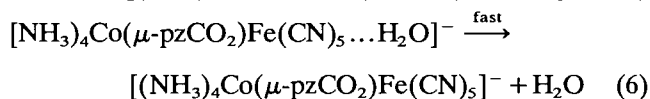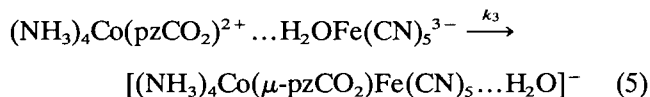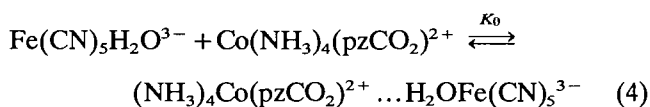
Applying the steady state approximation, the rate law of the D mechanism would be

$$v = \frac{k_1k_2[Fe(CN)_5H_2O^{3-}][Co(NH_3)_4(pzCO_2)^{2+}]}{k_{-1}[H_2O] + k_2[Co(NH_3)_4(pzCO_2)^{2+}]} \quad (7)$$

and for the interchange dissociative mechanism

$$v = \frac{k_3K_0[Fe(CN)_5H_2O^{3-}][Co(NH_3)_4(pzCO_2)^{2+}]}{1 + K_0[Co(NH_3)_4(pzCO_2)]^{2+}} \quad (8)$$

Considering that water concentration remains constant during the reaction and assuming that water and pyrazinecarboxylate have a similar efficiency as attacking ligands, eqn. (7) is reduced to a simple second order form (eqn. (9)).

$$v = \frac{k_1k_2}{k_{-1}} [Fe(CN)_5H_2O^{3-}][Co(NH_3)_4(pzCO_2)^{2+}] \quad (9)$$

On the other hand, under our working conditions $K_0[Co(NH_3)_4(pzCO_2)^{2+}] \ll 1$ given that, on the basis of the primitive model, in concentrated electrolyte solutions (ionic strength up to 0.5 mol dm^{-3}) $K_0 \approx 5$ mol^{-1} dm^3. Thus, eqn. (8) would also be reduced to a second-order rate law of the form

$$v = k_0k_3[Fe(CN)_5H_2O^{3-}][Co(NH_3)_4(pzCO_2)^{2+}] \quad (10)$$

Therefore, kinetic data cannot, at first, help to elucidate which mechanism is followed by the reaction. Previous articles have considered a relative lack of variance among the specific rates of attack of a number of entering ligands on Fe(CN)$_5$H$_2$O^{3-} as an indication of a predominantly dissociative mechanism [8, 18–20]. On the other hand, the large and positive values of ΔV^* and ΔS^* [7, 16] for the process under study are characteristic of a dissociative mechanism [21]. Table 2 summarizes the activation volume data for various dissociative, D, reactions involving pentacyanoferrate(II) complexes and that for the reaction studied. From this Table, one can see the similarity in sign and magnitude of the ΔV^* values for all reactions. It is also interesting to point out that the experimental trends observed for the rate constants of dissociative reactions Fe(CN)$_5$L^{n-} + L′ in concentrated electrolyte solutions are similar to those found in this work [7]. In fact, for these processes the reaction rate decreases when in-

TABLE 2. Volumes of activation in aqueous solution at 298.2 K for various dissociative reactions at pentacyanoferrate(II) complexes

Reaction	ΔV^* (cm^3 mol^{-1})	Reference
Fe(CN)$_5$(3,5-Mepy)$^{3-}$ + CN$^-$	23.1±1.6	22
Fe(CN)$_5$(3-CNpy)$^{3-}$ + CN$^-$	20.6±1.3	22
Fe(CN)$_5$(4-CNpy)$^{3-}$ + CN$^-$	20.6±1.2	22
Fe(CN)$_5$(2-Mepy)$^{3-}$ + CN$^-$	19.4±1.5	22
Fe(CN)$_5$(3,5-Me$_2$py)$^{3-}$ + pz	21.2±1.0	22
Fe(CN)$_5$H$_2$O^{3-} + Co(NH$_3$)$_4$(pzCO$_2$)$^{2+}$	23.1±1.6	16

3,5-Mepy = 3,5-methylpyridine; 3,5-Me$_2$py = 3,5-dimethylpyridine; 3-CNpy = 3-cyanopyridine; 4-CNpy = 4-cyanopyridine; pz = pyrazine; pzCO$_2$ = pyrazinecarboxylate.

creasing the electrolyte concentration and this decrease is larger for bivalent cation salts than for monovalent cation salts. The above comments can be taken as indicative that the binuclear complex formation studied follows predominantly a D mechanism, an idea also proposed by other authors [16]. On this basis, $k_f = (k_1 k_2)/k_{-1}$ and the observed salt effects would be the result of the electrolyte influence on each of the terms which contribute to k_f.

k_2 refers to an approaching process between two species of opposite charge. Taking into account a primitive model [23], which considers only coulombic interactions, it is possible to investigate the dependence of this process on electrolyte concentration. Results show that for ionic strengths higher than 1 mol dm^{-3} the approaching process is not dependent on ionic strength. This is in agreement with the idea advanced earlier that changes in coulombic interactions are not important in concentrated electrolyte solutions [24–26]. On this basis, the decrease of the rate constant with salt concentration would be mainly due to the electrolyte influence on the formation of the $Fe(CN)_5^{3-}$ species.

At first thought, the formation of the species $Fe(CN)_5^{3-}$ could be favoured when salt concentration increases. This process is accompanied by the release of a water molecule from the inner coordination sphere of the iron(II) center to the bulk and this release would be easier if the water activity in the bulk is small. In this respect, water activity decreases by increasing electrolyte concentration for all the salts used [27]. The fact that the trend observed is the opposite means that this is not the factor which determines the experimental salt effects.

For the species $Fe(CN)_5^{3-}$ to be formed, it is necessary to break the bond $Fe–OH_2$. The dissociative character of the substitution reactions at $Fe(CN)_5 L^{n-}$ complexes has been explained on the basis of the special characteristics of the cyanide ligands. These strong field ligands weaken the $Fe–L$ bond and favour a dissociative mechanism. For this mechanism, the determining step of the reaction is the breaking of the $Fe–L$ bond, therefore factors which make the release of the L ligand more difficult will diminish the rate of the reaction. When an electrolyte is present in the medium, and considering the negative charge of the $Fe(CN)_5 H_2 O^{3-}$ complex, it would be expected that the main effects come from the cation of the salt. Besides, all the electrolytes used have a common anion. Therefore below attention will be paid to the nature of the cation present in the medium. Taking into account the electronic density on the cyanide ligands, it seems reasonable to expect that cations interact preferentially with the iron complex in the vicinity of these ligands [28]. Because of the electrostatic interactions, the presence of the cations would diminish the electronic density on the

iron(II) metal center, reinforcing the $Fe–OH_2$ bond and therefore, making the release of the water molecule more difficult. Considering that these interactions will increase when increasing the polarization power of the cation, these trends would be expected: $k_{Li^+} < k_{Na^+} < k_{K^+}$ and $k_{Sr^{2+}} < k_{Ca^{2+}} < k_{Mg^{2+}}$, with k(monovalent cation salt) > k(bivalent cation salt) for a given ionic strength. The trend observed is similar with the exception that $k_{Na^+} > k_{K^+}$ (more about this later). One way to investigate the validity of the above idea could be to study the oxidation of the iron(II) center in the species $Fe(CN)_5 H_2 O^{3-}$ in the same electrolyte solutions. If the presence of the cations, through electrostatic interactions, decreases the electronic density on the iron(II) center, the oxidation of $Fe(CN)_5 H_2 O^{2-/3-}$ would be more difficult. In other words, the formal potential of the couple would increase. The standard formal potentials at 298.2 K, obtained by using cyclic voltammetry, are listed in Table 3. This Table shows that the oxidation process is more difficult when increasing the electrolyte concentration. The lack of values corresponding to sodium and potassium nitrate is due to the irreversibility of the system in these media (see 'Experimental'). Figure 2 shows a plot of $\ln(k_f)$ against $E^{\circ\prime}$. A good linear correlation is observed, that seems to indicate that the same cation–solute interactions are responsible for the variations in the reaction rate and in the standard formal potentials of the couple $Fe(CN)_5 H_2 O^{2-/3-}$ in the same salt solutions.

The fact that $k_{K^+} < k_{Na^+}$ could be related to the special characteristics of this ion. Potassium ion belongs to a different class in the Nightingale classification [29]. This ion breaks water structure, whereas sodium, lithium, magnesium, calcium and strontium ions promote water structure. So, in the case of potassium other kinds of interactions (structural) could be present. Indeed, these effects have been used to explain the different behavior shown by potassium salts in the study

TABLE 3. Standard formal potentials of $Fe(CN)_5 H_2 O^{2-/3-}$ at 298.2 K in various concentrated electrolyte solutions

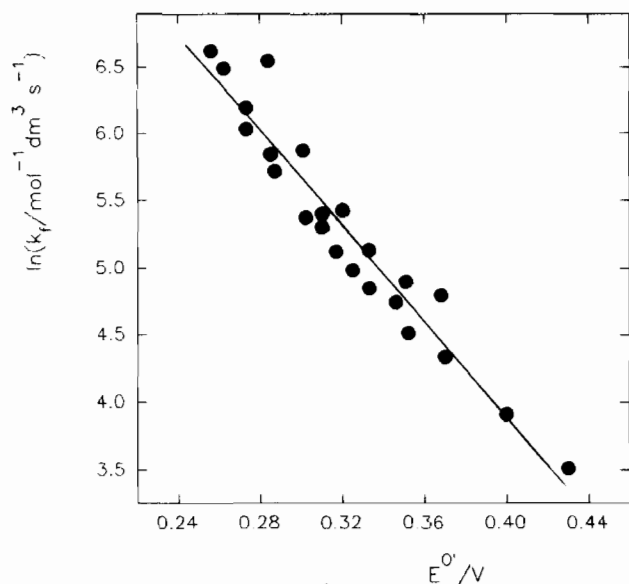| LiNO$_3$						
[Salt] (mol dm^{-3})	1.0	2.0	3.0	4.0	5.0	6.0
$E^{\circ\prime}$ (V)	0.256	0.273	0.287	0.302	0.317	0.333
Mg(NO$_3$)$_2$						
[Salt] (mol dm^{-3})	0.5	1.0	1.5	2.0	2.5	3.0
$E^{\circ\prime}$ (V)	0.273	0.310	0.338	0.370	0.400	0.430
Sr(NO$_3$)$_2$						
[Salt] (mol dm^{-3})	0.5	1.0	1.5	2.0	2.5	3.0
$E^{\circ\prime}$ (V)	0.262	0.285	0.310	0.325	0.346	0.352
Ca(NO$_3$)$_2$						
[Salt] (mol dm^{-3})	0.5	1.0	1.5	2.0	2.5	3.0
$E^{\circ\prime}$ (V)	0.284	0.301	0.320	0.333	0.351	

Fig. 2. Plot of $\ln(k_f\ (\text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}))$ against $E^{o\prime}$ (V) at 298.2 K for the binuclear complex formation.

of various reactions in concentrated electrolyte solutions [30].

References

1 J. Burgess and E. Pelizzetti, *Gazz. Chim. Ital.*, *118* (1988) 803.
2 J. Burgess and E. Pelizzetti, *Prog. React. Kinet.*, *17* (1992) 1.
3 M. L. Moyá, A. Barrios, M. M. Graciani, R. Jiménez, E. Múñoz, F. Sánchez and J. Burgess, *Transition Met. Chem.*, *16* (1991) 165.
4 I. Tejera, A. Rodríguez, F. Sánchez, M. L. Moyá and J. Burgess, *J. Chem. Soc., Faraday Trans.*, *87* (1991) 2573.
5 I. Tejera, R. Jiménez, A. Rodríguez, F. Sánchez and M. L. Moyá, *React. Kinet. Catal. Lett.*, *46* (1992) 427.
6 A. Barrios, M. M. Graciani, R. Jiménez, E. Múñoz, F. Sánchez, M. L. Moyá, S. Alshehri and J. Burgess, *Transition Met. Chem.*, *17* (1992) 231.
7 A. Al.Alousy, S. Alshehri, J. Burgess, M. M. Graciani, M. L. Moyá, E. Múñoz, A. Rodríguez and F. Sánchez, *Transition Met. Chem.*, in press.
8 H. E. Toma, J. M. Malin and E. Giesbrecht, *Inorg. Chem.*, *12* (1973) 2084.
9 D. B. Soria, V. Hidalgo and N. Katz, *J. Chem. Soc., Dalton Trans.*, (1982) 1555.
10 E. A. Abu-Gharib, R. Ben Ali, M. J. Blandamer and J. Burgess, *Transition Met. Chem.*, *12* (1989) 371.
11 A. Haim, *Prog. Inorg. Chem.*, *30* (1964) 273.
12 H. E. Toma, *J. Inorg. Nucl. Chem.*, *37* (1975) 785.
13 J. Malin, D. Ryan and V. O'Halloran, *J. Am. Chem. Soc.*, *100* (1978) 2097.
14 H. E. Toma and C. Creutz, *Inorg. Chem.*, *16* (1977) 545.
15 M. Galán, M. Domínguez, R. Andreu, M. L. Moyá, F. Sánchez and J. Burgess, *J. Chem. Soc., Faraday Trans.*, *86* (1990) 937.
16 P. Guardado and R. Van Eldik, *Inorg. Chem.*, *19* (1990) 3473.
17 E. Roldán, M. Domínguez and D. González-Arjona, *Comput. Chem.*, *10* (1986) 187.
18 H. E. Toma and J. M. Malin, *Inorg. Chem.*, *12* (1973) 2080.
19 Z. Bradic, M. Pribanic and A. Asperger, *J. Chem. Soc., Dalton Trans.*, (1975) 353.
20 I. Murati, P. Dusanka, A. Sustra and A. Asperger, *J. Chem. Soc., Dalton Trans.*, (1978) 500.
21 R. G. Wilkins, *Kinetics and Mechanisms of Reactions of Transition Metal Complexes*, VHC, Weinheim–Cambridge, 2nd edn., 1991, Ch. 4.
22 M. J. Blandamer and J. Burgess, *Pure Appl. Chem.*, *55* (1983) 55.
23 R. M. Fuoss, *J. Am. Chem. Soc.*, *110* (1978) 5576.
24 M. H. Dunn and J. J. Kozak, *J. Chem. Phys.*, *76* (1986) 984.
25 A. I. Khokhlova and L. P. Shishin, *Russ. J. Phys. Chem.*, *57* (1983) 1653.
26 H. Bruhn, S. Nigan and J. F. Holzwarth, *Faraday Discuss. Chem. Soc.*, *74* (1982) 129.
27 R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, Butterworths, London, 1959.
28 (a) M. L. Moyá, A. Rodríguez and F. Sánchez, *Inorg. Chim. Acta*, *188* (1991) 185; (b) M. L. Moyá, A. Rodríguez and F. Sánchez, *Inorg. Chim. Acta*, *197* (1992) 227; (c) L. W. Warner, M. F. Hoq, T. K. Myser, W. W. Henderson and R. E. Shepherd, *Inorg. Chem.*, *25* (1986) 1911.
29 R. H. Stokes and R. Mills, *Viscosity of Electrolytes and Related Properties*, Pergamon, London, 1965.
30 A. Rodríguez, M. Bejarano, E. Fernández-Boy, M. M. Graciani, F. Sánchez and M. L. Moyá, *J. Chem. Soc., Faraday Trans.*, *88* (1992) 591, and refs. therein.