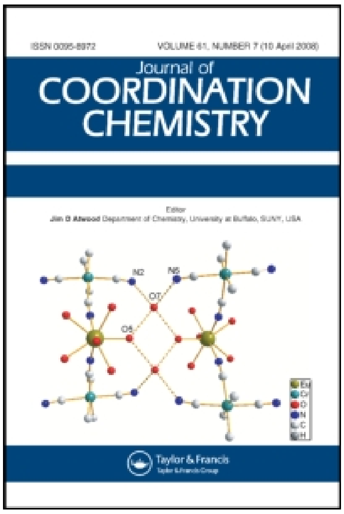

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INTERACTION BETWEEN TRINUCLEAR OXO-CENTRED COORDINATION COMPOUNDS OF TRANSITION METALS AND ORGANIC SOLVENTS[1]

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A number of oxo-centred trinuclear complexes have been obtained, of general formula $[M_3O(OOCR)_6L_3]X$ (R=H, CH_3; M=Cr(III), Fe(III); L=pyridine, 4-picoline; X=NO_3^-, ClO_4^-). The behaviour of these compounds in absolute methanol and in dimethylsulphoxide was investigated by the conductometric method. Dissociation constants of the complexes were determined. Molar conductivities and solvodynamic radii of the cations were also evaluated. It has been shown that the cations do not undergo solvation to any measurable extent.

KEY WORDS: Complexes, iron(III), chromium(III), dimethylsulphoxide, methanol, conductometry, solvation.

INTRODUCTION

Oxo-centred complexes of structure shown in Figure 1 have ben known for more than eighty years. However, for a long time their molecular formulae were written inadequately. Actual structures have been established by Welo,[3,4] Orgel[5] and by X-ray investigations.[6] A large number of such complexes with the $[M_3O(OOCR)_6L_3]^{n+}$ cation has been synthesized. Apart from species with the M_3O unit, consisting of trivalent atoms of the same kind, M^{III}, a number of complexes has been synthesized containing mixed-metal (e.g., Fe_2Cr, $FeCr_2$ etc.)[7,8] as well as mixed-valence species ($M_2^{III}M^{II}$, where M=Fe, Cr, Ru, Mn, Co, Ni etc.).[7-10] The essential components of these compounds are equilateral triangles of metal atoms with an oxygen atom at the centre, six edge-bridging carboxylato groups and three equatorial ligands, L (Fig. 1).

The O,O-ligands are usually mono- and di-carboxylic acids or amino acids. Increasing interest in metal-amino acid systems can be attributed to their potential as models for understanding biologically important molecules. The oxo-centred Fe_3O^{III} trinuclear species has been suggested as a useful model for the iron-storage complex ferritin.[11,12] Other have been tested for Cr-glucose tolerance factor activity or are known to catalyse epoxidation reactions.[13] The structures, chemical and physical properties of the triangular bridged metal complexes have been elegantly

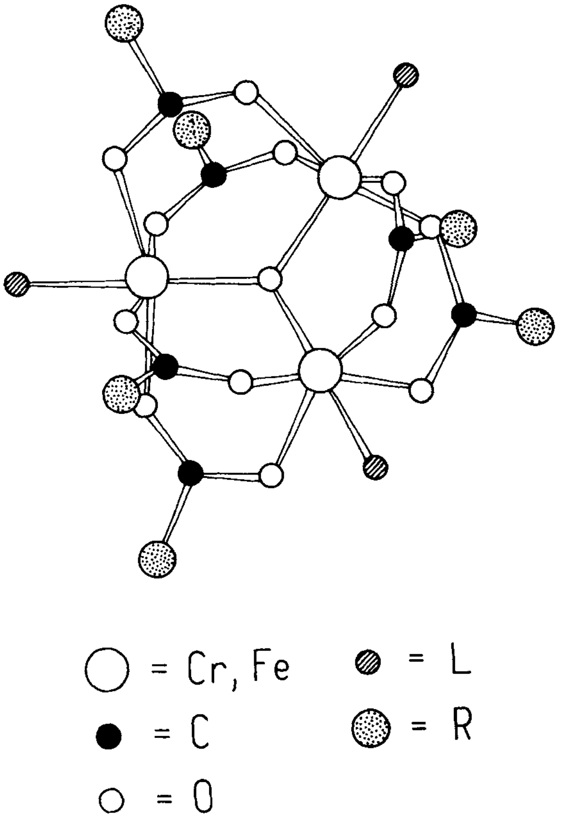

Figure 1 Structure of the $[M_3O(OOCR)_6L_3]^+$ complex ion, R=H, CH_3 etc; L=H_2O, pyridine, etc.

described by Cannon and White.[7] From the evidence collected it follows that there has been little systematic study of the solution chemistry of the oxo-centred complexes. Another reason for undertaking this investigation into the behaviour of these complexes in non-aqueous media is the inspiring study of Snatzke and co-workers[14] who exploited polynuclear transition metal complexes, including the trinuclear oxo-centred ones, for the stereochemical exploration of a variety of chiral, naturally-occurring products. These studies were conducted in various non-aqueous solvents, such as nitromethane, dimethylsulphoxide, ethanol, etc. Appearance of circular dichroism within d—d bands has been attributed to ligand exchange of the complex against chiral groups. However, it is not exactly known which ligands can be exchanged. The exchange of bridging carboxylato ligands is impossible, at least with most of the chiral compounds studied. More probable is the exchange of monodentate ligands, L, in the coordination sphere.

Hence, it is not clear how the flexible chiral molecules can be forced to assume one preferred conformation. Our study of this problem began from observations of the interactions of these coordination compounds with pure organic solvents. In this contribution the effect has been studied of selected solvents on dissociation constants, ion mobility and solvodynamic radii of the cations. Measurements were made in two solvents, dimethylsulphoxide (DMSO) and mthanol. The former is an aprotic, polar solvent of high basicity, capable of solvating the cations.[15,16] On the other hand, methanol is an amphiprotic solvent[17] solvating both cations and anions.[18] Computer-aided calculations were performed using the previously reported computer programme[18-21] based on Pitts equation[22-25] with Ives' iterative procedure.[26]

EXPERIMENTAL

Reagents

Dimethylsulphoxide was purified first by removing water with molecular sieves (5Å) followed by shaking for a dozen or so hours with calcium hydride. After filtering off the hydride, the DMSO was twice distilled under reduced pressure on a 60-cm Vigreaux column under nitrogen. A middle fraction passing over at 90°C was collected and which had a conductivity of $7\text{–}8 \times 10^{-8}\,\mathrm{S\,cm^{-1}}$ (lit.[27] $2\text{–}3 \times 10^{-8}\,\mathrm{S\,cm^{-1}}$).

Methanol was first dried with anhydrous sodium sulphate, and then by the Grignard method, and distilled twice on a 50-cm Vigreaux column at a rate of $4\,\mathrm{cm^3\,min^{-1}}$.

The second distillation was carried out after addition of *ca* 0.4g of tartaric acid per litre of methanol.[28] A fraction boiling at 64.5 – 65.0°C was collected and whose conductivity was $3 \times 10^{-7}\,\mathrm{S\,cm^{-1}}$.

Preparation of the Coordination Compounds

The oxo-centred trinuclear complexes were prepared by a method described in the literature.[29] All compounds were characterised by elemental analysis as well as by i.r. spectra.

Measurements

The conductivity measurements were carried out as described elsewhere.[18] A digital conductivity meter (Philips PW-9526) with automatic temperature compensation was employed. A PW-9551/60 conductivity cell was used. All measurements were run at 25 ± 0.1°C.

Elemental analyses were performed on an EA 1108 elemental analyzer (Carlo Erba Instruments).

RESULTS AND DISCUSSION

The identity of the synthesized compounds was confirmed not only by the results of elemental analyses (Table 1), but also by i.r. spectra. Particularly informative were bands due to vibrations of the planar, D_{3h}, M_3O unit. With the formates, interpretation of the spectra was straightforward. On the other hand, the spectra of the acetate complexes were less simple due to the appearance of π(COO) and δ(OCO) bands.[29] This norwithstanding, a $655\,\mathrm{cm^{-1}}$ band in these spectra is assignable to $\nu_{as}(Cr_3O)$.

The well-defined band at $315\,\mathrm{cm^{-1}}$ is due to the out-of-plane movement of the central oxygen, $\delta_{sym}(Cr_3O)$. Analogous bands in iron (III) complexes appear,

Table 1 Elemental analyses for the complexes

Complex	Calculated (%) C	H	N	Found (%) C	H	N
$[Fe_3O(CH_3COO)_6(Py)_3]NO_3$	38.74	3.97	6.69	37.88	3.98	6.47
$[Fe_3O(CH_3COO)_6(Py)_3]ClO_4$	37.08	3.80	4.80	36.80	3.75	4.55
$[Fe_3O(CH_3COO)_6(4\text{-}Pic)_3]NO_3$	40.98	4.47	6.37	40.08	4.85	6.27
$[Fe_3O(CH_3COO)_6(4\text{-}Pic)_3]ClO_4$	39.31	4.29	4.58	38.90	4.01	4.67
$[Cr_3O(CH_3COO)_6(Py)_3]NO_3$	39.28	4.03	6.78	39.95	3.95	6.50
$[Cr_3O(CH_3COO)_6(Py)_3]ClO_4$	37.58	3.85	4.87	36.80	3.75	4.59
$[Cr_3O(CH_3COO)_6(4\text{-}Pic)_3]NO_3$	41.53	4.53	6.45	41.92	4.50	6.29
$[Cr_3O(CH_3COO)_6(4\text{-}Pic)_3]ClO_4$	39.81	4.34	4.64	39.03	4.19	4.48
$[Cr_3O(HCOO)_6(Py)_3]ClO_4$	32.38	2.72	5.39	32.25	2.68	5.25
$[Cr_3O(HCOO)_6(4\text{-}Pic)_3]ClO_4$	35.11	3.32	5.12	34.92	3.25	5.21

respectively, at 605 and 295 cm^{-1}.[30,31] Illustrative examples of certain sections of the spectra are shown in Figure 2.

During the investigation of methanolic solutions of the Fe(III) complexes they soon became turbid. For this reason the Fe(III) cmpounds were investigated exclusively in DMSO. The results of conductometric measurements are listed in Tables 1, 2 and 4. Limiting conductivities, Λ_0, of the complexes were obtained in the first approximation by extrapolation of the expression, $\Lambda = f(\sqrt{c})$. Their accurate values were subsequently computed using a programme based on the Pitts' equation. The degrees of dissociation, α, and the mean activity coefficients, $f\pm$, were also calculated from this equation. Limiting conductivities of the complex cations, λ^0_+, were determined from the Kohlrausch law of independent ion migration. Analogous magnitudes for the anions were taken from the literature. In dimethylsulphoxide, the limiting conductivities of the nitrate, $\lambda^0_{NO_3^-}$, and perchlorate, $\lambda^0_{ClO_4^-}$, ions are respectively 27[32] and 24.8,[19] whilst in methanol they are 61.13[33] and 67.07.[18] The values of the limiting conductivities are summarised in Table 5.

As can be seen, the conductivity mobility of the cations in methanol is on the average four times as high as in DMSO. This it distinctly depends on solvent viscosity. The viscosity of DMSO is 1.99 cP, being 3.6 times as high as that of methanol 0.55 cP.

There is also a close relationship between ion mobility and size of solvent molecules. Again, the molecular volume of DMSO is 118Å^3 as compared with 67.6Å^3 for methanol.[18] It can thus be concluded that the complex cations behave in both solvents as bulky organic cations, such as tetrabutylammonium, tetraphenylarsonium and others.[34-36]

The ionic conductivity values were then utilised for calculation of the solvodynamic radii of the cations from the Stokes equation.[37] The results were compared with those obtained from X-ray measurements. Values were around 5Å. By utilising the Robinson and Stokes correction coefficient (*1*) for calculation of the solvodynamic radii of the cations, values matching crystallographic ones were obtained.

$$r_{ef} = \frac{0.82}{\lambda^0_+ \cdot \eta_0} \times \frac{r_c}{r_s} \tag{1}$$

Here r_{ef} is the effective radius of the cation, (Å), r_c/r_s is the correction coefficient, λ^0_+

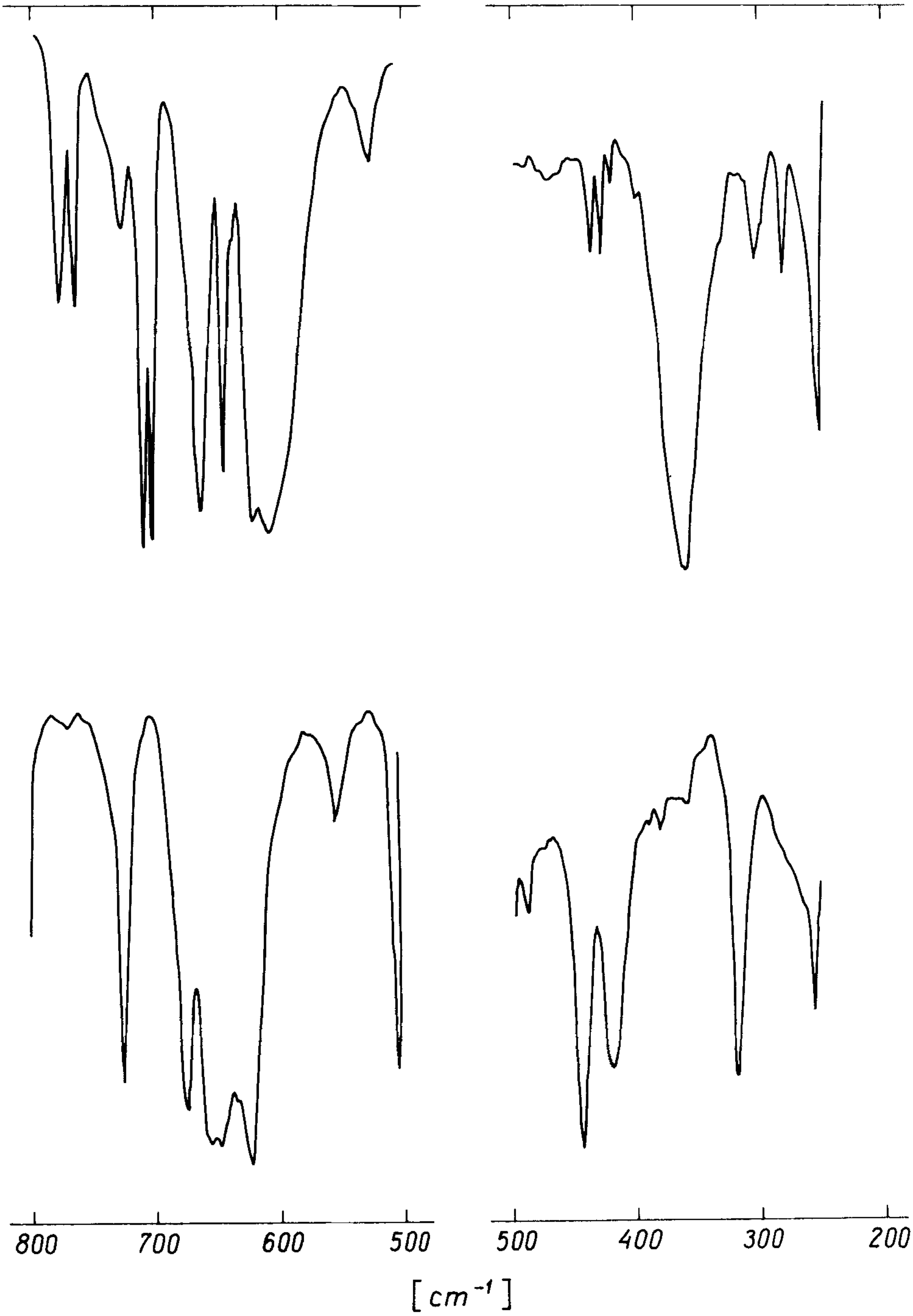

Figure 2 Infrared spectra of (upper) $[Fe_3O(CH_3COO)_6Py_3]NO_3$ and (lower) $[Cr_3O(CH_3COO)_6(4\text{-}pic)_3]ClO_4$.

Table 2 Molar conductivity (S cm^2 mol^{-1}) and complex concentration (mol dm^{-3}) in DMSO at 25°C

[Fe$_3$O(CH$_3$COO)$_6$Py$_3$]NO$_3$		[Fe$_3$O(CH$_3$COO)$_6$Py$_3$]ClO$_4$		[Fe$_3$O(CH$_3$COO)$_6$(4-Pic)$_3$]NO$_3$		[Fe$_3$O(CH$_3$COO)$_6$(4-Pic)$_3$]ClO$_4$	
C·10^4	Λ	C·10^4	Λ	C·10^4	Λ	C·10^4	Λ
5.02	35.23	5.02	31.18	4.66	31.03	5.05	31.46
10.30	34.17	10.00	30.38	9.38	29.08	9.99	30.91
15.40	33.64	14.80	29.98	13.60	27.81	15.20	30.51
20.10	33.28	22.00	29.19	18.20	26.55	20.30	29.93
33.80	32.10	30.20	28.88	28.10	24.82	30.90	29.52
40.70	31.82	39.20	28.68	37.30	23.12	38.00	29.80
50.30	31.90	50.00	28.38	45.20	22.10	50.50	28.69
60.40	31.21	60.00	27.89	53.70	20.61	60.00	28.72

Table 3 Molar conductivity (S cm^2 mol^{-1}) and complex concentration (mol dm^{-3}) in DMSO at 25°C

[Cr$_3$O(CH$_3$COO)$_6$Py$_3$]ClO$_4$		[Cr$_3$O(CH$_3$COO)$_6$(4-Pic)$_3$]ClO$_4$		[Cr$_3$O(HCOO)$_6$Py$_3$]ClO$_4$		[Cr$_3$O(HCOO)$_6$(4-Pic)$_3$]ClO$_4$	
C·10^4	Λ	C·10^4	Λ	C·10^4	Λ	C·10^4	Λ
5.24	30.83	5.18	31.15	2.84	34.96	3.09	32.41
10.10	30.48	10.40	30.70	5.68	30.25	6.00	32.15
15.10	30.35	15.30	30.42	8.27	30.47	8.96	32.00
20.20	29,85	20.50	30.12	10.70	30.03	11.20	31.91
29.70	28.82	30.90	29.72	16.60	28.83	17.10	31.65
40.20	28.61	41.10	29.25	21.50	28.41	22.50	31.50
50.60	27.88	50.50	29.02	27.00	28.16	28.40	31.32
60.70	27.94	60.80	28.75	38.90	27.48	41.40	31.00

Table 4 Molar conductivity (S cm^2 mol^{-1}) and complex concentration (mol dm^{-3}) in methanol at 25°C

				[Cr$_3$O-					
-(CH$_3$COO)$_6$Py$_3$]NO$_3$		-(CH$_3$COO)$_6$(4-Pic)$_3$]NO$_3$		-(CH$_3$COO)$_6$(4-Pic)$_3$]ClO$_4$		-(HCOO)$_6$Py$_3$]ClO$_4$		-(HCOO)$_6$(4-Pic)$_3$]ClO$_4$	
C·10^4	Λ	C·10^4	Λ	C·10^4	Λ	C·10^4	Λ	C·10^4	Λ
2.59	91.51	2.65	86.04	2.43	92.32	2.50	95.02	2.60	89.52
5.15	88.74	5.25	84.95	4.38	90.40	5.07	93.21	5.29	86.01
7.84	87.25	7.16	83.38	7.33	88.61	7.79	91.52	7.47	84.20
10.20	85.58	10.40	79.71	9.85	88.05	10.00	90.20	10.00	81.52
15.40	85.07	15.70	79.62	14.40	86.16	15.20	87.51	15.50	77.50
20.68	83.50	21.10	78.72	19.20	84.58	19.90	85.50	20.90	74.26
25.40	81.90	25.80	77.98	24.00	83.68	25.00	84.21	25.80	71.55
28.30	81.27	27.40	77.77	27.80	82.59	30.20	82.22	30.90	69.63

Table 5 Limiting molar conductivities, λ_+^0 (S cm^2 mol^{-1}), and solvodynamic effective radii, r_{eff}[Å] in DMSO and methanol

	DMSO		Methanol	
Complex	λ_+^0	r_{eff}[Å]	λ_+^0	r_{eff}[Å]
$[Fe_3O(CH_3COO)_6Py_3]^+$	8.0	5.23		
$[Fe_3O(CH_3COO)_6(4\text{-}Pic)_3]^+$	7.8	5.19		
$[Cr_3O(CH_3COO)_6Py_3]^+$	7.4	5.06	33.9	5.25
$[Cr_3O(CH_3COO)_6(4\text{-}Pic)_3]^+$	7.3	5.10	29.2	5.10
$[Cr_3O(HCOO)_6Py_3]^+$	8.8	5.26	34.7	5.07
$[Cr_3O(HCOO)_6(4\text{-}Pic)_3]^+$	8.1	5.30	30.9	5.16

Table 6 Limiting molar conductivities, Λ_0 (S cm^2 mol^{-1}), dissociation constants, K_d, maximum approximation parameters, $\mathring{a}$[Å], degree of dissociation, α, and activity coefficients, $f\pm$, of the complexes at 25°C

	Λ_0	K_d	$\mathring{a}$	α	$f\pm$
Complex	DMSO				
$[Fe_3O(CH_3COO)_6Py_3]NO_3$	36.2	0.07	5.5	0.98	0.8
$[Fe_3O(CH_3COO)_6(4\text{-}Pic)_3]NO_3$	34.9	0.10	6.5	0.99	0.9
$[Fe_3O(CH_3COO)_6Py_3]ClO_4$	31.6	0.07	5.5	0.98	0.8
$[Fe_3O(CH_3COO)_6(4\text{-}Pic)_3]ClO_4$	32.5	0.12	6.5	0.97	0.8
$[Cr_3O(CH_3COO)_6Py_3]ClO_4$	32.5	0.07	6.5	0.97	0.8
$[Cr_3O(CH_3COO)_6(4\text{-}Pic)_3]ClO_4$	32.1	0.07	7.0	0.99	0.8
$[Cr_3O(HCOO)_6Py_3]ClO_4$	33.6	0.02	6.0	0.93	0.8
$[Cr_3O(HCOO)_6(4\text{-}Pic)_3]ClO_4$	32.9	0.02	6.0	0.93	0.8
	Methanol				
$[Cr_3O(CH_3COO)_6Py_3]NO_3$	95.0	0.04	6.5	0.97	0.8
$[Cr_3O(CH_3COO)_6(4\text{-}Pic)_3]NO_3$	92.1	0.03	6.5	0.96	0.8
$[Cr_3O(CH_3COO)_6(4\text{-}Pic)_3]ClO_4$	94.7	0.08	8.0	0.99	0.9
$[Cr_3O(HCOO)_6Py_3]ClO_4$	101.5	0.02	6.0	0.80	0.8
$[Cr_3O(HCOO)_6(4\text{-}Pic)_3]ClO_4$	98.0	0.02	6.5	0.74	0.8

is the limiting molar conductivity of the ion (S cm^2 mol^{-1}) and η_0 is the viscosity of solvent, (P).

Calculated values of the radii are given in Table 5. As seen, the radii measured in both solvents are comparable. This means that different properties of the solvents have no influence on the nature of the interaction between the complex cation and solvent. Also, the radii calculated from (*1*) and those derived from X-ray measurements are comparable. It can thus be concluded that the complex cations do not undergo solvation to any measurable extent. They are, however, largely dissociated, as indicated by the dissociation constants (Table 6), which are high.

Both series of salts behave in the two solvents as highly dissociated electrolytes. Further, the dissociation constants in these solvents are comparable, as are the maximum approximation parameters, $\mathring{a}$, degrees of dissociation, α, and activity coefficients, $f\pm$. Accordingly, the two solvents do not exhibit differentiating features relative to the coordination compounds considered. Our further studies reveal, however, that not all the oxo-centred trinuclear complexes behave as the aforementioned ones in nonaqueous media. A following contribution will deal with these problems.

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