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Outer-sphere coordination of polycyanometallate anions with polyammonium macrocycles: a spectrophotometric study

Anne Bayada [a], Geoffrey A. Lawrance [a,*], Marcel Maeder [a], Manuel Martinez [b], Brian W. Skelton [c], Allan H. White [c]

[a]*Department of Chemistry, The University of Newcastle, Callaghan 2308, Australia*
[b]*Department of Chemistry, University of Barcelona, Diagonal 647, 08028 Barcelona, Spain*
[c]*Department of Physical and Inorganic Chemistry, The University of Western Australia, Nedlands 6009, Australia*

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Abstract

The spectroscopic determination of the outer-sphere stability constants between polycyanometallate anions with cationic polyammonium macrocycles is reported. The interactions of anions $[M(CN)_n]^{m-}$ (M = Au(I), Ni(II), Co(III), Fe(II), Fe(III) and Mo(IV)) of differing geometry and charge are examined with dominantly diprotonated macrocycles. Electrostatic interactions play a major role in determining the strength of the outer-sphere interaction; however, log K_{os} values (range 1.7–3.9) are influenced in part by the topology of the anions and cations. The X-ray crystal structure of the trichloride diperchlorate dihydrate salt of the pentaprotonated macrocycle 10-methyl-1,4,8,12-tetraazacyclopentadecane-10-amine which crystallises in the $P\bar{1}$ space group with $a = 13.24(1)$, $b = 10.699(7)$, $c = 10.458(5)$ Å, $\alpha = 92.92(4)$, $\beta = 111.95(6)$, $\gamma = 109.45(7)°$ is also reported.

Keywords: Outer-sphere coordination; Polycyanometallate complexes; Anion complexes; Macrocyclic ligand complexes; Binding constants; Ion-pairing; Spectrophotometric titration

1. Introduction

Outer-sphere (or second shell) coordination between protonated polyamines and anions has attracted considerable attention recently [1–7]. Polyammonium macrocycles in particular are able to form charged, polyprotonated species even at pH > 7 and are capable of forming stable outer-sphere complexes with a range of inorganic and organic anions. These interactions have some interest for possible commercial applications. The selective binding and separation of gold, for example, can be achieved by froth floatation via the $Au(CN)_2^-$ anion with long chain derivatives of polyammonium macrocyclic receptors. These interactions have been examined by a number of physical methods in solution and by X-ray structure analyses.

Definition of the strength of interaction in solution comes with determination of the ion-pairing or outer-sphere stability constant, K_{os}. For anion–macrocyclic cation interactions in solution, stability constants have been measured largely by potentiometric and voltammetric methods. Spectrophotometric methods have been employed only to a limited extent because the spectral changes resulting from changes in the solvation shell are usually very small [8–10]. We have recently reported the outer-sphere stability constant for a bicyclic ammonium cation with a complex anion using a spectrophotometric method than can deal with these inherently small spectral changes [11]. The development of this method has enabled us to further investigate the interaction between a range of polycyanometallate anions with polyammonium macrocycles as anion receptors. As we reported earlier [11], spectrophotometric titrations can also provide structural information through the absorbance spectra, making it a useful complementary tool to the other methods of quantifying outer-sphere interactions.

In this paper we report on the spectrophotometric determination of the outer-sphere interaction between polycyanometallate anions of differing geometry and charge with several cationic polyammonium macrocycles. The pH regime for the study has been selected with a knowledge of macrocycle pK_a values to restrict the study to cation species with dominantly a 2^+ charge.

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*Corresponding author.

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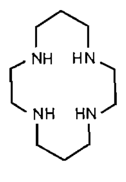
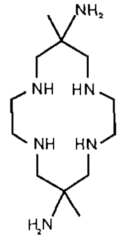
The relevant equilibrium is expressed in Eq. (1).

$$[M(CN)_n{}^{m-}]+[L\cdot H_2]^{2+} \overset{K_{os}}{\rightleftharpoons} [M(CN)_n{}^{m-}]\cdot[L\cdot H_2]^{2+} \quad (1)$$

where $n=2, 4, 6, 8$; $m=1$–4; M = Au(I), Ni(II), Co(III), Fe(II), Fe(III), Mo(IV); L = **1**–**4**. The nature of the interaction is largely electrostatic; however, hydrogen bonding as well as the geometry of the anion and the cation also plays a role in determining the strength of the interaction.



(1)



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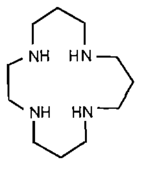

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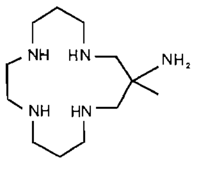

(4)

2. Experimental

2.1. Compounds

The macrocycles 6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine (**2**) and 10-methyl-1,4,8,12-tetraazacyclopentadecane-10-amine (**4**) were synthesised following the procedure described elsewhere [12,13]. The compounds 1,4,8,11-tetraazacyclotetradecane (**1**), 1,4,8,12-tetraazacyclopentadecane (**3**), $K_3Co(CN)_6$, $K_4Fe(CN)_6\cdot 3H_2O$ and $K_3Fe(CN)_6$ were all of Aldrich analytical reagent grade and were used without further purification. $K_4Mo(CN)_8\cdot 2H_2O$ was prepared as described in Ref. [14].

The dicyanoaurate(I) anion, $Au(CN)_2^-$, was prepared in the following manner. Gold(I) cyanide (27.9 mg, 0.125 mmol), potassium cyanide (77.9 mg, 1.20 mmol) and tetraethylammonium perchlorate (TEAP) (1.15 g, 4.99 mmol) were dissolved in water (50 ml) at pH = 8. The solution was stirred for approx. 1 h resulting in a 2.5×10^{-3} M solution of the dicyanoaurate(I), $Au(CN)_2^-$ in 0.1 M TEAP.

Potassium tetracyanonickelate(II), $K_2Ni(CN)_4$, was prepared essentially as described in Ref. [15].

2.2. Spectrophotometric titrations

The method employed has been described in detail recently elsewhere [11]. Absorption spectra were recorded on a Hitachi 220A spectrophotometer controlled by an IBM-compatible PC. The cell compartment was thermostatted to 25 °C and titrations were performed in the 1 cm absorption cell. An automated stepper-motor driven syringe, magnetic stirrer and pH electrode were also controlled by the computer. Data analysis was carried out using the program SPECFIT [16].

The pH of the polycyanometallate and ligand solutions was adjusted to 7–8 to ensure that the dominant species present was the diprotonated ligand$\cdot H_2{}^{2+}$ species. The ionic strength was maintained at 0.1 M with TEAP. In a typical experiment, 15 increments of 0.01 ml of a 2.0 M macrocyclic solution were added to 2.0 ml of the polycyanometallate. The concentrations used for the polycyanometallate solutions and wavelength range used are as follows: $Au(CN)_2^-$, 0.0025 M, 270–244 nm; $Ni(CN)_4^{2-}$, 0.005 M, 364–340 nm; $Co(CN)_6^{3-}$, 0.005 M, 350–260 nm; $Fe(CN)_6^{3-}$, 0.001 M, 460–330 nm; $Fe(CN)_6^{4-}$, 0.002 M, 365–310 nm; $Mo(CN)_8^{4-}$, 0.005 M, 450–320 nm. Depending on the wavelength range used, the absorption was measured at 10, 5 or 2 nm intervals. Titrations were repeated once.

2.3. Potentiometric titrations

Determination of the protonation constants of the ligand **4** was performed with a Metrohm 665 dosimat burette controlled by an IBM-compatible PC. The titration was carried out at 25 °C in aqueous solution of constant ionic strength (0.5 M KCl) under nitrogen. NBS buffers of pH 4 and 7 were used to calibrate the potentiometer. 95×0.002 ml increments of 0.4 M NaOH were added to 25.0 ml of a 5.77×10^{-4} M solution of $(4)\cdot 5HCl\cdot 2H_2O$. The program TITFIT [17] was used for analysis of the data and stability constants were obtained by iterative refinement.

2.4. Crystallography

2.4.1. Crystal data

$[H_5(4)]^{5+}\cdot 3Cl^-\cdot 2ClO_4^-\cdot 2H_2O \equiv C_{12}H_{34}Cl_5N_5O_{10}$, $M=585.7$; triclinic, space group $P\bar{1}$, $a=13.24(1)$, $b=10.699(7)$, $c=10.458(5)$ Å, $\alpha=92.92(4)$, $\beta=111.95(6)$, $\gamma=109.45(7)$°, $U=1270$ Å^3; D_c $(Z=2)$ 1.53 g cm^{-3}; μ (Mo Kα) 5.6 cm^{-1}; $F(000)$ 612. Specimen 0.43×0.16×0.34 mm.

2.4.2. Structure determination

A unique room-temperature diffractometer data set ($T\sim295$ K; $2\theta_{max}=50$°, $2\theta/\theta$ scan mode; monochromatic Mo Kα radiation, $\lambda=0.7107(3)$ Å independent reflections, 3373 with $I>3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement without absorption correction. Anisotropic thermal parameters were refined for all non-hydrogen atoms, $(x, y, z, U_{\text{iso}})_{\text{H}}$ being constrained at estimated values. Conventional residuals on $|F|$ at convergence, R, R_w, were 0.078, 0.093 (statistical weights derivative of $\sigma^2(I)=\sigma^2(I_{\text{diff}})+0.0005\ \sigma^4(I_{\text{diff}})$). Neutral atom complex scattering factors were employed with computation using the XTAL 3.0 program system [18]. A list of atom coordinates appears in Table 1, with bond distances and bond angles collected in Table 2. Cation torsional angles and hydrogen bonding interactions appear in Tables 3 and 4, respectively. The skeletal numbering is given in the view of the molecular cation presented in Fig. 1.

2.4.3. *Abnormal features/variations in procedure*

Ligand carbon and nitrogen atoms were distinguished on the basis of refinement behaviour; difference map residues were suggestive of all ligand nitrogen atoms being fully populated and they were modelled as such.

Table 1
Atom coordinates for $[H_5(4)]^{5+}\cdot 3Cl^-\cdot 2ClO_4^-\cdot 2H_2O$

Atom	x	y	z	U_{eq} (Å^2)
Cl(1)	0.2647(2)	0.6733(2)	0.0120(2)	0.0553(9)
O(11)	0.3485(7)	0.8033(8)	0.0383(9)	0.1490(5)
O(12)	0.2031(7)	0.6223(9)	−0.1315(7)	0.1270(5)
O(13)	0.1919(9)	0.6930(1)	0.0700(1)	0.1860(7)
O(14)	0.3230(1)	0.5960(1)	0.0760(1)	0.2100(1)
Cl(2)	0.5304(1)	0.7254(2)	0.1843(2)	0.0386(7)
O(21)	0.4211(4)	0.6750(6)	0.6901(5)	0.0680(3)
O(22)	0.5237(7)	0.6487(9)	0.9132(7)	0.1680(5)
O(23)	0.6198(6)	0.7230(1)	0.7803(7)	0.1340(5)
O(24)	0.5577(7)	0.8562(8)	0.8680(1)	0.1490(6)
Cl(3)	0	0.5	0.5	0.0610(2)
Cl(4)	0	0	0.5	0.0350(1)
Cl(5)	−0.1002(1)	−0.1554(2)	0.0645(2)	0.0474(8)
Cl(6)	0.5182(1)	−0.1662(2)	0.4371(2)	0.0472(8)
C(1)	0.1412(5)	0.2725(6)	0.3111(6)	0.0300(3)
N(1)	0.1814(5)	0.3584(5)	0.2150(5)	0.0410(3)
C(11)	0.0065(5)	0.2107(7)	0.2414(7)	0.0390(3)
C(2a)	0.1912(5)	0.3733(6)	0.4498(6)	0.0320(3)
N(3a)	0.1403(4)	0.3195(5)	0.5513(5)	0.0280(2)
C(4a)	0.2251(6)	0.3737(6)	0.7039(6)	0.0360(3)
C(5a)	0.3280(6)	0.3283(7)	0.7508(6)	0.0390(3)
C(6a)	0.2938(5)	0.1803(7)	0.7577(7)	0.0370(3)
N(7a)	0.3973(4)	0.1410(6)	0.8017(5)	0.0370(2)
C(8a)	0.3725(6)	−0.0025(8)	0.8133(7)	0.0490(4)
C(2b)	0.1978(5)	0.1693(6)	0.3403(6)	0.0290(3)
N(3b)	0.1580(4)	0.0554(5)	0.2236(5)	0.0320(2)
C(4b)	0.2182(6)	−0.0431(7)	0.2669(7)	0.0380(3)
C(5b)	0.1641(5)	−0.1358(6)	0.3489(7)	0.0350(3)
C(6b)	0.2405(5)	−0.2074(6)	0.4324(7)	0.0360(3)
N(7b)	0.3323(4)	−0.1220(5)	0.5731(6)	0.0370(2)
C(8b)	0.2851(6)	−0.1069(7)	0.6785(7)	0.0440(3)
O(1)	0.9467(5)	0.4722(6)	0.8172(7)	0.0860(3)
O(2)	0.4160(5)	0.5245(6)	0.3858(7)	0.0880(3)

Table 2
Bond lengths and angles for $[H_5(4)]^{5+}\cdot 3Cl^-\cdot 2ClO_4^-\cdot 2H_2O$

Bond distances (Å)		Bond angles (°)	
Cl(1)–O(11)	1.398(8)	O(11)–Cl(1)–O(12)	110.4(6)
Cl(1)–O(12)	1.389(6)	O(11)–Cl(1)–O(13)	103.6(6)
Cl(1)–O(13)	1.38(1)	O(11)–Cl(1)–O(14)	106.8(6)
Cl(1)–O(14)	1.34(1)	O(12)–Cl(1)–O(13)	110.7(6)
Cl(2)–O(21)	1.439(4)	O(12)–Cl(1)–O(14)	111.3(7)
Cl(2)–O(22)	1.361(9)	O(13)–Cl(1)–O(14)	113.7(8)
Cl(2)–O(23)	1.36(1)	O(21)–Cl(2)–O(22)	110.6(4)
Cl(2)–O(24)	1.359(9)	O(21)–Cl(2)–O(23)	110.0(4)
C(1)–N(1)	1.518(9)	O(21)–Cl(2)–O(24)	110.3(5)
C(1)–C(11)	1.532(8)	O(22)–Cl(2)–O(23)	109.8(6)
C(1)–C(2a)	1.534(9)	O(22)–Cl(2)–O(24)	109.3(6)
C(1)–C(2b)	1.51(1)	O(23)–Cl(2)–O(24)	106.7(6)
C(2a)–N(3a)	1.50(1)	N(1)–C(1)–C(11)	107.3(5)
N(3a)–C(4a)	1.508(7)	N(1)–C(1)–C(2a)	103.9(5)
C(4a)–C(5a)	1.52(1)	N(1)–C(1)–C(2b)	110.6(6)
C(5a)–C(6a)	1.51(1)	C(11)–C(1)–C(2a)	113.1(6)
C(6a)–N(7a)	1.48(1)	C(11)–C(1)–C(2b)	114.1(5)
N(7a)–C(8a)	1.49(1)	C(2a)–C(1)–C(2b)	107.5(5)
C(8a)–C(8b)	1.531(8)	C(1)–C(2a)–N(3a)	113.8(5)
C(2b)–N(3b)	1.480(8)	C(2a)–N(3a)–C(4a)	114.1(4)
N(3b)–C(4b)	1.51(1)	N(3a)–C(4a)–C(5a)	114.7(6)
C(4b)–C(5b)	1.52(1)	C(4a)–C(5a)–C(6a)	113.6(5)
C(5b)–C(6b)	1.52(1)	C(5a)–C(6a)–N(7a)	111.4(5)
C(6b)–N(7b)	1.503(7)	C(6a)–N(7a)–C(8a)	116.5(5)
N(7b)–C(8b)	1.48(1)	N(7a)–C(8a)–C(8b)	114.8(6)
		C(1)–C(2b)–N(3b)	117.6(4)
		C(2b)–N(3b)–C(4b)	112.8(4)
		N(3b)–C(4b)–C(5b)	110.6(7)
		C(4b)–C(5b)–C(6b)	113.6(6)
		C(5b)–C(6b)–N(7b)	112.7(6)
		C(6b)–N(7b)–C(8b)	114.3(5)
		C(8a)–C(8b)–N(7b)	114.4(6)

Table 3
Cation torsion angles (°). Atoms are denoted by number only; the two values in each entry are for sections a, b respectively (see Fig. 1). *N* is italicized

Atoms	Angle	
2–1–2–*3*	−76.1(7),	176.3(5)
1–2–*3*–4	147.7(6),	−178.1(6)
2–*3*–4–5	−67.2(7),	78.1(6)
3–4–5–6	−70.1(8),	−162.6(5)
4–5–6–*7*	179.1(6),	83.8(8)
5–6–*7*–8	179.3(6),	73.4(8)
6–*7*–8–9	58.5(10),	171.2(6)
7–8–8–*7*	77.5(9)	

The cation in general was well-defined; perchlorate thermal motion was very high, possibly a foil for unresolved disorder, and probably the chief source of the high residual. Difference map residues were modelled as water molecule oxygen atoms; thermal motion was such as not to permit resolution of associated hydrogen atoms. On the basis of refinement behaviour, all atom sites seem fully occupied.

Table 4
Hydrogen bonding interactions (Å)

Atoms	Distance (Å)
(i) Those involving the cation	
(a) chloride···H_N (Cl···H, <2.7 Å)	
Cl(3)···H(3aB) (N(3a))	2.1$_9$ (3.036(6))
Cl(4)···H(3aA) (N(3a))	2.2$_9$ (3.204(5))
Cl(5)···H(1c^i) (N(1^i))	2.1$_9$ (3.141(6))
Cl(5)···H(3bA^i) (N(3b^i))	2.3$_1$ (3.155(6))
Cl(5)···H(3bB) (N(3b))	2.2$_3$ (3.128(5))
(b) water oxygen···H_N (O···H, <2.5 Å)	
O(1)···H(1b^{ii}) (N(1^{ii}))	1.9$_0$ (2.82(1))
O(2)···H(1a) (N(1))	1.9$_1$ (2.801(7))
(c) perchlorate oxygen···H_N (O···H, <2.5 Å)	
O(11)···H(7a^{ii}) (N(7a^{ii}))	2.4$_2$ (2.97(1))
O(21)···H(7bB^{ii}) (N(7b^{iii}))	2.0$_6$ (2.913(9))
O(22)···H(7aA^{iv}) (N(7a^{iv}))	2.4$_3$ (3.23(1))
(ii) Water···water, perchlorate (O···O, <3 Å)	
O(1)···O(13^{ii})	2.75(1)
O(2)···O(23^{ii})	2.89(1)
O(2)···O(2^{ii})	2.81(1)

Transformations of the asymmetric unit: $^{i}(\bar{x}, \bar{y}, \bar{z})$; $^{ii}(1+x, 1+y, 1+z)$; $^{iii}(x, 1+y, z)$; $^{iv}(1+x, 1+y, 2+z)$.

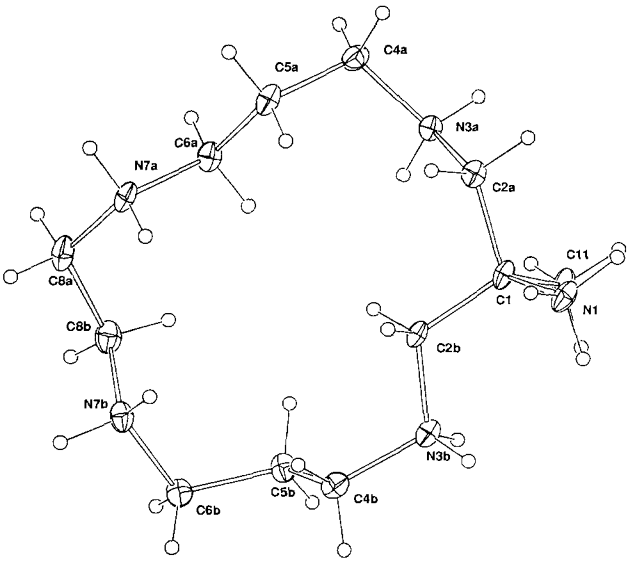

Fig. 1. Projection of the cation of $[H_5(4)]\cdot Cl_3\cdot(ClO_4)_2\cdot 2H_2O$; 20% probability level thermal ellipsoids are shown for the non-hydrogen atoms, hydrogen atoms having an arbitrary radius of 0.1 Å.

Table 5
Logarithms of the stability constants for the interaction between the diprotonated macrocyclic ligands and polycyanometallate anions at 25 °C and 0.1 M

$M(CN)_n^{m-}$	**1**	**2**	**3**	**4**
$Au(CN)_2^-$	3.1(±0.13)	2.7(±0.07)	2.5(±0.03)	1.7(±0.03)
$Ni(CN)_4^{2-}$	2.9(±0.03)	2.3(±0.03)	2.5(±0.04)	2.2(±0.03)
$Co(CN)_6^{3-}$	3.1(±0.04)	2.2(±0.03)	2.6(±0.09)	1.8(±0.03)
$Fe(CN)_6^{3-}$	3.2(±0.09)	2.3(±0.03)		
$Fe(CN)_6^{4-}$	3.9(±0.03)	2.5(±0.04)	3.2(±0.09)	2.3(±0.12)
$Mo(CN)_8^{4-}$	3.3(±0.14)		2.7(±0.05)	

Table 6
Logarithms of protonation constants for macrocyclic ligands determined potentiometrically

Equilibria	**1** [19]	**2** [20]	**3** [19]	**4**
$L+H \rightleftharpoons LH$	11.5	11.0	11.1	11.0(±0.07)
$LH+H \rightleftharpoons LH_2$	10.5	9.9	10.3	9.5(±0.08)
$LH_2+H \rightleftharpoons LH_3$	<2	6.3	5.2	6.1(±0.08)
$LH_3+H \rightleftharpoons LH_4$	<2	5.5	3.6	3.6(±0.09)
$LH_4+H \rightleftharpoons LH_5$		2.9		<2
$LH_5+H \rightleftharpoons LH_6$		<2		

3. Results and discussion

The stability constants determined for the outer-sphere complexation between the diprotonated macrocycles **1**–**4** with polycyanometallate anions of differing geometry and charge are presented in Table 5. The protonation constants for the macrocycles involved in this study are shown in Table 6, and permit generation of the diprotonated macrocycles in the pH range 7–8.

The anion geometries range from linear, $Au(CN)_2^-$, through square planar, $Ni(CN)_4^{2-}$, octahedral $Co(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$ to dodecahedral, $Mo(CN)_8^{4-}$. In the dicyanoaurate(I) anion, $Au(CN)_2^-$, the Au(I) ion has a free ion radius of 1.37 Å. Bound to cyanide ion, the Au–C bond length is 1.97 Å and the C≡N bond length is 1.15 Å. Using the van der Waals radius for nitrogen in cyanide as 1.60 Å, the overall length of the anion is 9.44 Å [21]. The anion can therefore be considered as a cylinder of this length and of radius approximately 1.60 Å. A similar approach can be used to describe the geometries of the other anions used in this study. The $Co(CN)_6^{3-}$, $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$ and $Mo(CN)_8^{4-}$ ions can all be considered as spheres with calculated radii of approximately 4.64, 4.63, 4.69 and 4.91 Å, respectively [21].

It can be observed that for anions of similar geometry and size, such as $Co(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$, the stability constant for the interaction with each dicharged cation is significantly higher for the higher charged $Fe(CN)_6^{4-}$ anion. The interaction with the $Fe(CN)_6^{3-}$ anion is comparable to that of the $Co(CN)_6^{3-}$ anion of the same charge. This indicates that electrostatic interactions play an important role in determining the strength of outer-sphere complexation. The square planar $Ni(CN)_4^{2-}$ ion and the linear $Au(CN)_2^-$ ion both have lower charges and are therefore expected to show a weaker interaction based on electrostatic grounds. Their shapes, however, are not spherical and these ions can interact in a more intimate way. For example, the linear $Au(CN)_2^-$ anion can have a much closer 'side-on' approach compared to the other larger anions investigated. Such arguments can account for why the stability constants of these ions are larger than expected on the basis of charge alone. The $Fe(CN)_6^{4-}$ ion has a stronger interaction in comparison to the $Mo(CN)_8^{4-}$ ion of the same charge. Once again the size of the anion also plays an important role, as the smaller $Fe(CN)_6^{4-}$ ion has a higher surface charge density and may approach closer to the cation. Fig. 2 shows the observed trends in stability with the range of macrocycles and polycyanometallates used.

The geometry of the cations also plays a role in the strength of the interaction. A comparison between the unsubstituted and substituted pairs of macrocycles **1**/**2** and **3**/**4** indicates that the pendant methyl and amine groups influence the strength of the interaction by causing some steric hindrance, seen in some slight decrease in stability. Indeed, it has been shown that compatible topology between the receptor and substrate plays an important role in determining the strength of the interaction [6,7], and this is reinforced in these systems. Studies have shown that the first two protonations of the free polyamine involves the secondary ring protons. Because of the similar structures of all macrocycles in this study, the same protonation scheme can be assumed and at pH 7–8 the pendant primary amines are not protonated. The unprotonated primary amine group still has the capacity to form hydrogen bonds in a way similar to a water molecule; however, this effect appears to be of minor importance in comparison to the steric effects caused by the groups.

The macrocycle $H_5(\mathbf{4})$ adopts in the solid-state, as the mixed trichloride diperchlorate salt, a disordered geometry for the ring unlike that observed when complexed to metal ions, with the protons on the ring nitrogens all *exo* to the macrocyclic ring (Fig. 1 and Table 3). This differs considerably from the geometry of the analogue $H_2(\mathbf{2})$ in a number of crystal structures [22,23], where the macrocycle usually displays inversion symmetry with a geometry where the nitrogens display *endo* arrangement like that observed when bound as a tetradentate ligand to metal ions. The structure of $[H_5(\mathbf{4})]^{5+}$ as the mixed chloride perchlorate hydrate displays hydrogen bonding interactions of varying significance (Table 4). There is a strong interaction between oxygens of the waters of crystallisation and the exposed protonated pendant primary amine, with the O···HN distance near 1.9 Å, indicating the potential capacity of the pendant amine for participation in second coordination sphere binding. Both chloride and perchlorate oxygen interactions are directed towards mainly protonated secondary amines in the macrocyclic ring, with Cl···HN distances in the former in the range

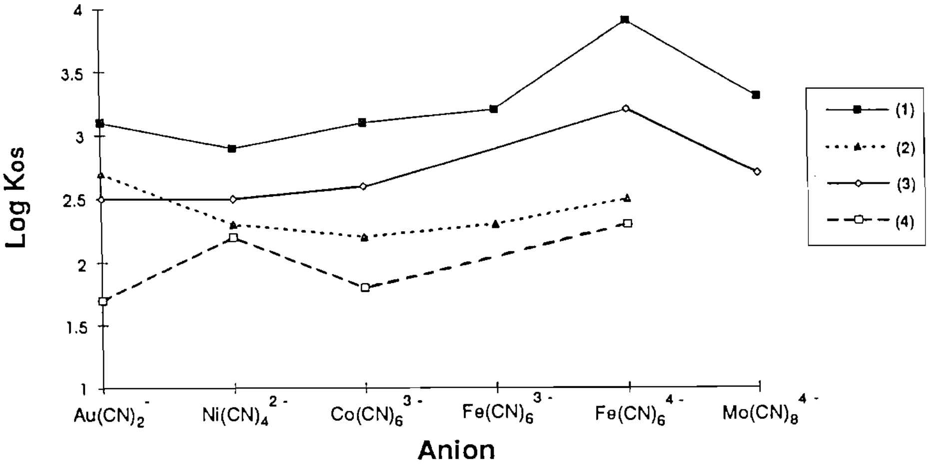

Fig. 2. Plot of the logarithms of the stability constants for the outer-sphere interactions of the diprotonated macrocycles **1**–**4** with the polycyanometallate anions.

2.2–2.3 Å and O···HN distances in the latter between 2.05 and 2.45 Å. The perchlorate O···HN distances are on average 0.2 Å shorter than in the perchlorate salt of $[H_4(\mathbf{2})]^{4+}$ [23], the difference possibly related to the *exo* structure in $[H_5(\mathbf{4})]^{5+}$ compared to the *endo* structure in $[H_4(\mathbf{2})]^{4+}$. The Cl···HN interactions appear weaker than interactions involving $[H_4(\mathbf{2})]^{4+}$ and $Fe(CN)_6^{3-}$ [22], which is consistent with the relatively strong ion-pairs formed in solution with the polycyanometallates. These interactions with the macrocycle are clearly stronger than general hydrogen bonding interactions between water molecules and perchlorate anions.

The observed stabilities for the protonated ligands **2** and **4** when involved in binding complex anions may also be related to the different 'shapes' of the cations in the solid-state. Although the solid-state geometry does not indicate geometry in solution, the 'common' shape of **2** in both the free ligand and in the complexes suggests that the symmetrical *endo* arrangement may persist in this case, at least in solution. This implies that **2** has a 'compact' shape in solution that is more appropriate than that of **4** for strong outer-sphere binding to the anions used in this study. As a consequence, the stability constants are higher for the ligand **2** as a smaller change in solvation energy is expended on binding than in **4**, where reorganisation in order to achieve the desired 'shape' required for maximum cation–anion interaction may be required.

As the macrocyclic ring is increased from 14-membered to 15-membered a decrease in stability is observed. This can be attributed to an increased dispersion of positive charge with a larger ring size. This trend has also been observed by Bencini and co-workers [7] who have investigated the interaction of polyprotonated forms of $[3k]aneN_k$ ($k=7$–12) macrocycles with $Fe(CN)_6^{4-}$, $Co(CN)_6^{3-}$ and $Pt(CN)_4^{2-}$ by potentiometry.

Fig. 3 shows the molar absorption spectra of the outer-sphere complex formed between $Co(CN)_6^{3-}$ and the macrocycle $H_2(\mathbf{4})$. The outer-sphere complex formed has a higher molar absorptivity than the initial hexacyanocobaltate(III) anion. This finding is similar to that reported earlier [11], where we also found an increase in absorption upon outer-sphere complexation to a bicyclic ammonium cation. This can be explained in terms of the relaxation of the Laporte selection rule whereby outer-sphere complexation distorts the centre of symmetry that is present in the $Co(CN)_6^{3-}$ ion alone, providing some absorption increase [24].

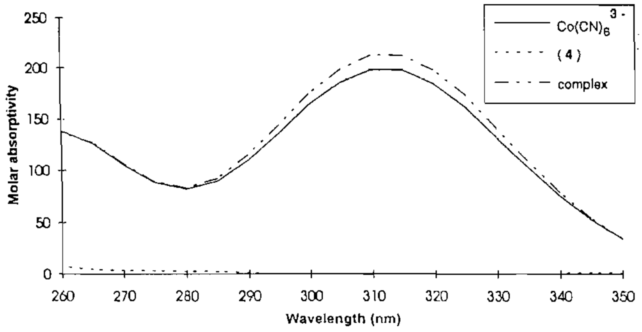

Fig. 3. Molar absorptivity of $Co(CN)_6^{3-}$, $H_2(\mathbf{4})$ and calculated molar absorptivity for the outer-sphere complex.

Fig. 4 compares the spectral changes observed at 315 nm during the titration to those calculated from the SPECFIT program. It also shows the changes expected for dilution alone, if there was no interaction between the anion and macrocycle. It is clear that although the changes appear to show a decrease in absorbance there is in fact an increase relative to the dilution curve which implies that there is complexation occurring, with the complex having a higher absorptivity than the parent hexacyanide. Fig. 5 also reveals the concentration profile for this titration. Here is can be observed that there is only a relatively small percentage of complex formation upon addition of the ligand. This is consistent with the inherently weak nature of outer-sphere complexation in aqueous solution.

Hydrogen bonding can also contribute to the strength of the outer-sphere interaction. There have been numerous solid-state studies examining the hydrogen bonding involved with outer-sphere complexed species. Bernhardt et al. [23], for instance, have reported the crystal structure of $[H_4L][Fe(CN)_6]$ where L is **2**. Significant

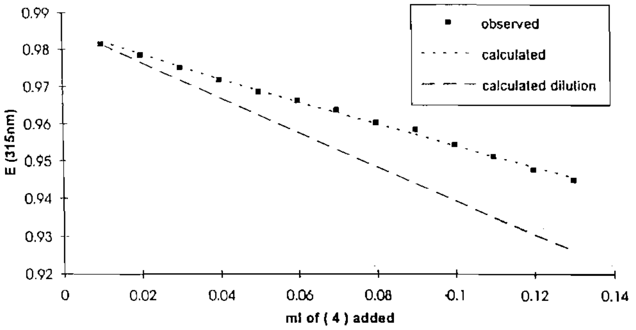

Fig. 4. Spectral changes at 315 nm for the titration of $Co(CN)_6^{3-}$ with $H_2(\mathbf{4})$.

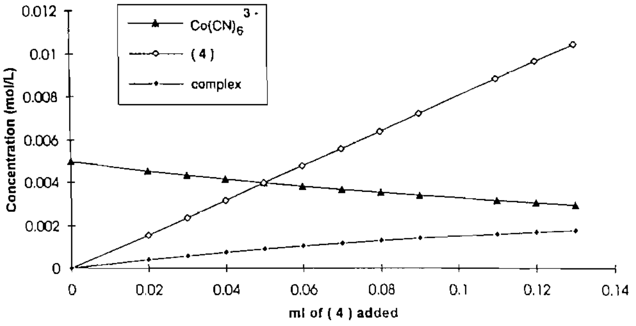

Fig. 5. Concentration profiles for the titration of $Co(CN)_6^{3-}$ with $H_2(\mathbf{4})$.

hydrogen-bonding interactions were observed at the terminal NH_3^+ groups; however, hydrogen bonds involving the secondary (ring) nitrogens and water molecules also exist. If these interactions also exist in solution, then they can contribute to the strength of the interaction. Bencini et al. [7] have also reported the crystal structure of the $(H_{10}[30]aneN_{10})[Pt(CN)_4]_5 \cdot 2H_2O$ complex and have suggested that, in solution, complex formation partially disrupts the hydrogen bonding to the solvent of both receptors and anion and creates new hydrogen bonds. This enthalpic contribution favours the formation of the outer-sphere species. Although electrostatic contributions play an important role in determining the strength of the outer-sphere interaction, in addition one must also consider the effects of hydrogen bonding as well as the topology of the substrates and receptors.

The spectrophotometric method reported herein and described in some detail elsewhere [11] for quantifying the outer-sphere interaction between polycyanometallates and polyammonium macrocycles offers an alterative method to the already established potentiometric and voltammetric methods. As we previously reported [11], the advantages of such a method include: (a) no need for a deprotonation equilibrium; (b) investigations at high and low pH are possible; (c) no restriction to aqueous solution applies; (d) structural information about the adducts can be obtained from the absorption spectra. The method can therefore have wide application in investigating the strength of interaction between both inorganic and organic anions as well as other cationic receptors.

Acknowledgement

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