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Anion Coordination Chemistry.
3.* Second-sphere Interaction between the Complex Anions Hexacyanoferrate(II) and Hexacyanocobaltate(III), with Polycharged Tetraazamacrocycles. Thermodynamic and Single Crystal X-ray Studies

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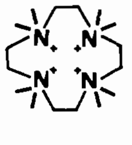
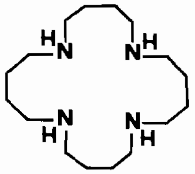
Abstract

The thermodynamic parameters $\Delta G°$, $\Delta H°$ and $\Delta S°$ for the supercomplex formation between the $[Fe(CN)_6]^{4-}$ and $[Co(CN)_6]^{3-}$ anions and the tetraprotonated species of the tetraazamacrocycle 1,6,11,16-tetraazacycloeicosane (L2) have been determined at 25 °C by potentiometric techniques and by direct microcalorimetry. The chemical model is very simple since only the 1:1 species $(H_4L2)[Fe(CN)_6]$ and $(H_4L2)[Co(CN)_6]^+$ are formed. Both species have favorable enthalpic and entropic contributions to their stability: $\Delta H° = -1.1$ kcal mol^{-1} and $\Delta S° = 13$ cal K^{-1} mol^{-1} for the first complex and $\Delta H° = -2.56$ kcal mol^{-1} and $\Delta S° = 2.3$ cal K^{-1} mol^{-1} for the second complex. The thermodynamic results have been interpreted in terms of hydrogen bond formation, electrostatic interactions and desolvation effect. The electrochemical behavior of $[Fe(CN)_6]^{4-}$ complexed by $[H_4L2]^{4+}$ has been studied by the cyclic voltammetry technique. The stability constant of the oxidized species $(H_4L2)[Fe(CN)_6]^+$ ($\log k_{ox} = 2.5$) has been obtained from the potentiometric stability constant of $(H_4L2)[Fe(CN)_6]$ and the redox potential shift of the complexed couple $(H_4L2)[Fe(CN)_6]/(H_4L2)[Fe(CN)_6]^+$ with respect to the uncomplexed couple $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$. To better investigate the influence of the electrostatic interaction the macrocyclic polyammonium receptor 1,1,4,4,7,7,10,10-octamethyl-1,4,7,10-tetraazacyclododecane tetrakis(iodide) (L1·4I) has been synthesized and characterized. The quaternarization of all nitrogen atoms prevents the formation of hydrogen bonds. Crystals of the compound $(L1)[Co(CN)_6]\cdot I\cdot 3H_2O$ are triclinic, space group $P1$, with $a = 12.091(3)$, $b = 11.696(2)$, $c = 11.484$ Å, $\alpha = 94.89(4)°$, $\beta = 102.75(4)°$, $\gamma = 92.55(3)°$, and $Z = 2$. Refinement of the atomic parameters by least-squares methods gave a final R factor of 0.061 ($R_w = 0.062$) for 4063 unique reflections with $I > 3\sigma(I)$. The structure consists of discrete macrocyclic $L1^{4+}$ cations, $[Co(CN)_6]^{3-}$, I^- anions, and water molecules. The interaction between the cation and anions is purely electrostatic and its strength is indicated by several close contacts between carbon atoms of the macrocyclic cation and cyanide nitrogens of the exacyanocobaltate(III) anion.

Introduction

Much attention has been paid to the coordination of anions [2–5]. Both physico-chemical properties and chemical reactivity of the anion are affected by its complexation [6–9]. Among the species able to strongly interact with anions, polyammonium macrocyclic compounds are promising candidates [10–14]. When the anionic species are metal complexes the term 'supercomplex' has been used to indicate the adduct formed between the anionic species and the receptor [7, 15]. The aim of the present work is to provide an insight into the nature of the second-sphere interaction between the complex anions hexacyanoferrate(II) and hexacyanocobaltate(III) with the macrocyclic polyammonium receptors 1,1,4,4,7,7,10,10-octamethyl-1,4,7,10-tetraazacyclododecane tetrakis(iodide) L1·4I and the fully protonated form of 1,6,11,16-tetraazacyclo-


L1


L2

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*Part 2 is ref. 1.

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eicosane L2. The two tetra-charged macrocycles have the same mass, the same charges but different size. Furthermore in the case of L1 the presence of only quaternary nitrogen atoms prevents the formation of hydrogen bonds in the adduct [1].

Experimental

Macrocycle Synthesis

All chemicals were reagent grade and were used without further purification.

1,1,4,4,7,7,10,10-Octamethyl-1,4,7,10-tetraazacyclododecane Tetrakis(iodide) L1·4I

1,2,2,6,6-Pentamethylpiperidine (PMP) was synthesized following the procedure reported in ref. 16. A solution (10 cm^3) of 13.2 g of CH_3I (93 mmol) in dry DMF was added, dropwise, at room temperature to a solution containing 1 g (5.8 mmol) of 1,4,7,10-tetraazacyclododecane and 7.25 g (46.4 mmol) of PMP dissolved in 50 cm^3 of dry DMF. A slightly exothermic reaction started contemporaneously with the addition. At the end of the addition a white product began to crystallize and the reaction mixture was left overnight to complete the crystallization. The product separated was collected, washed with ethylacetate and dried under vacuum at 50 °C. Recrystallization of this product from a water/acetone 1:1 mixture yielded 2 g (51%) of 1,1,4,4,7,7,10-heptamethyl-1,4,7,10-tetraazacyclododecane triodide monohydrated (**1**). *Anal.* Calc. for $C_{15}H_{39}N_4I_3O$: C, 26.80; H, 5.84; N, 8.33; I, 56.63. Found: C, 26.6; H, 5.9; N, 8.3; I, 56.7%. 1 g (1.5 mmol) of the partially N-methylated derivative (**1**), 0.47 g (3 mmol) of PMP and 0.85 g (6 mmol) of CH_3I were dissolved in 40 cm^3 of dry DMF and stored at room temperature for many days. A white powder separated on standing. The product was filtered off, washed with 1:1 DMF/diethyl ether mixture and dried under vacuum at 50 °C: yield 0.7 g (59%) of L1·4I. *Anal.* Calc. for $C_{16}H_{40}N_4I_4$: C, 24.14; H, 5.06; N, 7.03. Found: C, 24.1; H, 5.1; N, 7.0%. The chloride derivative of L1 was obtained by ionic exchange of the tetraiodide derivative with a Dowex 1 X 8 (100 mesh) resin in the chloride form.

The macrocycle 1,6,11,16-tetraazacycloeicosane L2 was prepared following the procedure described in ref. 17. The hydrolysis of the tetratosylated derivative L2·Ts_4 with sulphuric acid was improved by using more mild reaction conditions than those reported in ref. 17. The yield was increased up to 60% employing 75% sulphuric acid at 80 °C for 70 h.

Preparation of the Crystals

Good crystals of $(L1)[Co(CN)_6]\cdot I\cdot 3H_2O$, suitable for X-ray analysis were obtained by mixing water solutions of $K_3[Co(CN)_6]$ and L1·4I in 1:1 ratio. By slow evaporation at low temperature, colorless crystals of the above compound separated.

Materials

All potentiometric measurements were carried out in 0.15 mol dm^{-3} $NaClO_4$ (C. Erba ACS grade) purified according to the procedure already described [18]. Standardized CO_2-free solutions of NaOH, used in the potentiometric titrations, were prepared following the procedure described in ref. 19.

e.m.f. Measurements

The potentiometric titrations were carried out by using equipment (potentiometer, buret, stirrer, cell, microcomputer, etc.) that has been fully described [20]. The computer program SUPERQUAD [21] was used to process data and calculate the stability constants. Because the literature reported basicity constants of L2 were determined in different experimental conditions [22], we have determined them again in our experimental conditions in order to achieve a better overall accuracy. The values obtained, relative to the equilibrium (1)

$$[H_{(i-1)}L2]^{(i-1)+} + H^+ \rightleftarrows [H_iL2]^{i+} \qquad (1)$$

are the following: $\log K_1 = 11.65(3)$, $\log K_2 = 10.60(3)$, $\log K_3 = 8.34(3)$, $\log K_4 = 8.38(3)$. These values have been employed in the calculation of the stability constants.

Electrochemical Measurements

CV studies were carried out by using the following apparatus: a potentiostat (Amel Model 552), pen recorder (Amel Model 862/A) and a three-electrode cell [23]. The working electrode was a platinum sphere, the auxiliary electrode was a platinum disk, and the reference electrode was a SCE.

Calorimetric Measurements

All calorimetric measurements were performed with an LKB BATCH Model 10700-2 microcalorimeter [24]. The heat of reaction was measured by mixing an aqueous solution of $K_4[Fe(CN)_6]$ or $K_3[Co(CN)_6]$ with a solution containing the tetraprotonated macrocycle L2. Under the reaction conditions (25 °C, $I = 0.15$ mol dm^{-3}) and employing the determined stability constants, the species present and their percentages at equilibrium before and after mixing were calculated by means of the DISPOL [25] computer program. The only species present at equilibrium before and after mixing were the tetra-protonated ligand $[H_4L2]^{4+}$ and the complex $(H_4L2)[M(CN)_6]^{n+}$ ($M = Fe^{2+}$, $n = 0$; $M = Co^{3+}$, $n = 1$). Blank experiments were carried out to correct for the enthalpy of dilution of the reactants.

TABLE I. Crystal and Refinement Data

Molecular formula	$CoC_{22}H_{46}N_{10}O_3I$
Molecular weight	684.51
a (Å)	12.091(3)
b (Å)	11.696(2)
c (Å)	11.484(2)
α (°)	94.89(4)
β	102.75(4)
γ	92.55(3)
V (Å^3)	1574.9
Z	2
Space group	$P\bar{1}$ [a]
D_{calc} (g cm^{-1})	1.44
Radiation	graphite monochromated Mo Kα (λ = 0.7107 Å)
Temperature (°C)	25
μ (cm^{-1})	15.4
Scan technique	$\theta/2\theta$
Scan speed (° min^{-1})	3.00
Scan width (°)	0.9 + 0.3 tang(θ)
Scan range (°)	$5.0 < 2\theta < 50.0$
Total no. ind. reflections	4273
Cutoff obs. data	$3\sigma(I)$
No. obs. reflections	4063
No. refined parameters	329
R [b]	0.061
R_w [c]	0.062

[a] Based on a centric distribution of E values and later confirmed by the structural determination. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$.

TABLE II. Positional Parameters (×10^4)[a]

Atom	x/a	y/b	z/c
Co	−2442(1)	−2503(1)	2612(1)
I	1809(1)	−2489(1)	1074(1)
N(1)	692(5)	4092(5)	2572(6)
C(2)	434(7)	2825(6)	2112(7)
C(3)	817(7)	2031(6)	3079(7)
N(4)	951(5)	832(5)	2558(5)
C(5)	1937(7)	759(6)	1968(7)
C(6)	3099(7)	942(7)	2849(8)
N(7)	4053(6)	1208(5)	2248(6)
C(8)	4001(7)	2357(6)	1724(7)
C(9)	4213(7)	3375(6)	2681(7)
N(10)	3775(5)	4460(5)	2173(6)
C(11)	2490(6)	4423(7)	1821(7)
C(12)	1938(6)	4466(6)	2903(7)
C(13)	217(8)	4348(7)	3653(8)
C(14)	81(7)	4764(7)	1586(8)
C(15)	−100(7)	405(7)	1628(8)
C(16)	1068(9)	59(7)	3566(8)
C(17)	5142(8)	1195(9)	3175(10)
C(18)	4061(9)	325(8)	1224(10)
C(19)	4202(8)	4662(7)	1065(8)
C(20)	4234(8)	5442(7)	3107(8)
C(21)	−2998(7)	−2728(7)	3998(7)
N(11)	−3317(6)	−2878(7)	4846(6)
C(22)	−1884(7)	−2330(6)	1209(7)
N(12)	−1573(6)	−2253(6)	360(6)
C(23)	−2285(7)	−884(8)	3033(7)
N(13)	−2178(7)	65(6)	3329(8)
C(24)	−2598(7)	−4124(7)	2221(8)
N(14)	−2691(7)	−5091(6)	2010(7)
C(25)	−950(7)	−2599(7)	3512(7)
N(15)	−50(7)	−2650(7)	4073(7)
C(26)	−3924(7)	−2382(7)	1687(7)
N(16)	−4798(7)	−2301(7)	1112(8)
O(w1)	3134(7)	5837(7)	5580(7)
O(w2)	6525(8)	2480(8)	1292(8)
O(w3)[b]	4061(13)	8498(13)	3812(13)
O(w4)[b]	1819(15)	7590(15)	6041(16)
O(w5)[b]	2251(14)	7911(14)	5215(15)

[a] e.s.d.s given in parentheses. [b] Atoms with occupancy factor of 1/3.

Collection and Reduction of X-ray Intensity Data

A colorless crystal of approximate dimensions 0.15 × 0.22 × 0.30 mm was mounted on a Philips PW 1100 computer-controlled diffractometer and used for data collection. A summary of the crystallographic data is reported in Table I. Unit-cell dimensions were determined from the angular settings of 25 carefully centered reflections. Intensities were corrected for Lorentz, polarization, and absorption effects [26] (transmission factors ranged between 0.63 and 0.79). The intensities of three standard reflections were monitored every 120 min for stability control during data collection: the crystal did not show any systematic variation in the diffraction power.

Solution and Refinement of the Structure

On the basis of the centric distribution of E values the $P\bar{1}$ space group was assumed and later confirmed by the successful refinement of the structure. The structure was solved by the heavy-atom technique, with the use of Patterson and electron density syntheses. Refinement was performed by means of the full-matrix least-squares method. The function minimized was $\Sigma_w(|F_o| - |F_c|)^2$ with weights $w = a/\sigma^2(F)$, where a is an adjustable parameter. Anisotropic thermal parameters were refined for all non-hydrogen atoms. The hydrogen atoms of the macrocycle were included in calculated positions at 0.95 Å from the respective carbon atom and two different group isotropic thermal parameters were refined for methyl and methylene hydrogens which refined at the values 0.0563 and 0.0273 (U) respectively. One of the three water molecules of crystallization was found to be disordered over three different positions each with an occupancy factor of 1/3. The final difference Fourier showed only small peaks in the region of the water molecules and near the iodide anion. All calculations were performed on an IBM 4361/3 computer with the SHELX-76 set programs that use the analytical approximation for the atomic scattering factors and anomalous dispersion cor-

TABLE III. Thermodynamic Quantities for the Reaction between $[H_4L2]^{4+}$ and the anions: $[Co(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ [a]

Reaction	log *K*	ΔG° (kcal mol^{-1})	ΔH° (kcal mol^{-1})	ΔS° (cal mol^{-1} K^{-1})
$H_4L2^{4+} + [Fe(CN)_6]^{4-} = (H_4L2)[Fe(CN)_6]$	3.62(3)	−4.94(4)	−1.1(1)	13(1)
$H_4L2^{4+} + [Co(CN)_6]^{3-} = (H_4L2)[Co(CN)_6]^{+}$	2.38(3)	−3.25(4)	−2.56(6)	2.3(2)

[a] 25 °C in 0.15 mol dm^{-3} $NaClO_4$. Values in parentheses are the standard deviations on the last significant figure.

rections for all the atoms from ref. 27. Table II reports the list of the final atomic coordinates for non-hydrogen atoms with estimated standard deviations obtained from the least-squares inverse matrix. The molecular plots were produced by the program ORTEP [28].

Results and Discussion

One of the main tasks of the present work is the accurate measurement of the enthalpy of supercomplex formation. For this reason we have chosen polyammonium receptors able to yield simple, 'clean' systems with the anionic complexes $[Fe(CN)_6]^{4-}$ and $[Co(CN)_6]^{3-}$. For the macrocycle L2, because of the long hydrocarbon chains connecting the adjacent nitrogen atoms, the protonation constants are such (see 'Experimental') that in a wide pH range the only species present is the fully protonated, tetracharged $[H_4L2]^{4+}$. In the case of L1 the quaternarization of all the nitrogen atoms present has lead to the tetracharged $L1^{4+}$ cation. Unfortunately in the latter case, the very low solubility of the adduct with the anions investigated, prevents the measurements of the thermodynamic quantities associated with the formation of the 'supercomplexes'. In Table III the thermodynamic quantities ΔG°, ΔH° and ΔS° relative to the supercomplex formation equilibria between $[Fe(CN)_6]^{4-}$, $[Co(CN)_6]^{3-}$ and $[H_4L2]^{4+}$ have been reported. The chemical model is very simple, since only the 1:1 species is formed. The anion $[Fe(CN)_6]^{4-}$ forms a more stable complex than $[Co(CN)_6]^{3-}$, this is not surprising because electrostatic interactions of the former anionic guest with the tetra-charged $[H_4L2]^{4+}$ host are enforced compared to $[Co(CN)_6]^{3-}$, owing to the reduced negative charge of the latter anion. To our knowledge this is the first report on the calorimetrically determined enthalpy of formation of complexed species having azamacrocycle as second-sphere ligand. Thermodynamic results (see Table III) show that both complexes have favorable enthalpic and entropic contributions to their stability. The favorable enthalpic contribution is made up by two opposite main terms: an endothermic effect due to the removal of water molecules solvating the ions involved in the complex formation and an exothermic effect due to the formation of hydrogen bonds ($-C{=}N\cdots H-N^{+}$) between the cyanide groups and the hydrogen atoms of the protonated nitrogen atoms of the macrocycle. This demonstrates that the formation of hydrogen bonds in the supercomplexed species is an important contribution to the overall stability of the species itself. In the case of the more stable complex $(H_4L2)[Fe(CN)_6]$ the stability is mainly due to a very favorable entropic term, the enthalpic contribution being small, and in any case, less favorable than that of the weaker complex $(H_4L2)[Co(CN)_6]^{+}$. The complete charge neutralization, which takes place in the former complex and the consequent desolvation effect can explain the very favorable entropic term (see Table III) [29]. The electrochemical behavior of the $[Fe(CN)_6]^{4-}$ anion complexed by the L2 polyammonium receptor has been studied. The redox potential of the neutral complex $(H_4L2)[Fe(CN)_6]$ has been determined by cyclic voltammetry in aqueous solution of 0.15 mol dm^{-3} KCl at 25 °C. The couple $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ is reversible also in the complexed form and its redox potential is shifted toward more anodic values ($E_{1/2} =$ 0.190 V for the free anion and $E_{1/2} = 0.255$ V for the complexed anion). The redox potential shift, involved in the transfer of *n* electrons between the two complexes, is related to the ratio of the stability constants of the reduced and oxidized forms by the relationship $E_{1/2} = (RT/nF)(\ln K_{red} - \ln K_{ox})$ provided that the transfer is reversible and no change in the first coordination sphere occurs [30]. The previous conditions are matched in our case, and the equilibrium constant for the reaction (2) can be obtained from the stability constant, potentiometrically determined, of $(H_4L2)[Fe(CN)_6]$ ($\log K =$ 3.62, see Table III) and the redox potential shift determined by cyclic voltammetry (0.065 V). The calculated value is $\log K_{ox} = 2.5$, smaller than 3.62 which is the value found for $\log K_{red}$ (see Table III). Indeed the oxidized species $[Fe(CN)_6]^{3-}$ is expected to interact less strongly with the $[H_4L2]^{4+}$ cation than the reduced, more charged, $[Fe(CN)_6]^{4-}$ anion. Furthermore the values calculated for the logarithm of the stability constant of $(H_4L2)[Fe(CN)_6]^{+}$ (2.5) is very similar to that of the equally charged

$$[Fe(CN)_6]^{3-} + H_4L2^{4+} \rightleftharpoons (H_4L2)[Fe(CN)_6]^{+} \qquad (2)$$

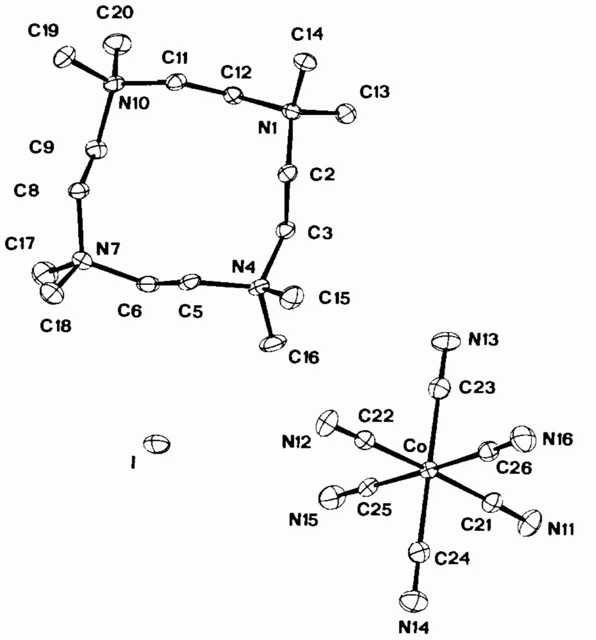

Fig. 1. ORTEP drawing of macrocyclic cation $L1^{4+}$ and of the anions hexacyanocobaltate(III) and iodide. The thermal ellipsoids are drawn at 30% probability.

species $(H_4L2)[Co(CN)_6]^+$ (2.38, see Table III). The previous considerations further confirm the importance of the electrostatic contribution to the overall stability of the supercomplexed species. The comparison of the stabilities of the supercomplexes investigated with those of the species with the same stoichiometries but with much larger azamacrocycles (see refs. 1, 15) indicates that the values found are all very comparable with no significant difference.

To better investigate the influence of the electrostatic contribution to the supercomplex formation the octamethylated, tetracharged macrocyle $L1^{4+}$ was synthesized and the solid structure of its adduct with $[Co(CN)_6]^{3-}$ anion was determined.

TABLE IV. Significant Contact Distances and Hydrogen Bonds (Å)

I---C(5)	3.84	I---C(11)[a]	3.86
I---C(14)[a]	3.91	I---C(2)[b]	4.02
I---C(14)[b]	4.08	I---N(16)[c]	4.09
N(11)---C(3)[d]	3.46	N(11)---C(6)[d]	3.29
N(11)---C(9)[d]	3.34	N(11)---C(12)[c]	3.48
N(12)---C(2)[b]	3.45	N(12)---C(5)[b]	3.28
N(12)---C(8)[b]	3.34	N(12)---C(11)[b]	3.37
N(15)---C(13)[d]	3.45	N(16)---C(18)[e]	3.43
I···O(w2)[f]	3.72	I···O(w3)[a]	3.74
N(13)···O(w4)[g]	2.77	N(13)···O(w5)[g]	2.80
N(14)···O(w2)[h]	2.94	N(15)···O(w4)[a]	2.81
N(15)···O(w5)[a]	2.82	N(16)···O(w2)[b]	3.06
O(w1)···O(w4)	2.74	O(w1)···O(w5)	2.72

Symmetry related by: [a]$x, -1+y, z$; [b]$-x, -y, -z$; [c]$1+x, y, z$; [d]$-x, -y, 1-z$; [e]$-1+x, y, z$; [f]$1-x, -y, -z$; [g]$-x, 1-y, 1-z$; [h]$-1+x, -1+y, z$.

Description of the Structure of $(L1)[Co(CN)_6]\cdot I\cdot 3H_2O$

The crystal structure of the compound consists of discrete $L1^{4+}$ cations and $[Co(CN)_6]^{3-}$ and I^- anions which are shown in Fig. 1. The unit cell contents are shown in Fig. 2. The interaction between the cation and the two anions is merely electrostatic and its strength is indicated by several close contacts between the cyanide nitrogens of the exacyanocobaltate(III) anion, the iodide anion and carbon atoms of the macrocyclic ring as reported in Table IV. From the inspection of Table IV it can be observed that only the nitrogen atoms of the cyanide groups less involved in close contacts with the macrocycle are available for hydrogen bond interactions with the water molecules. Bond lengths and angles involving the non-hydrogen atoms are reported

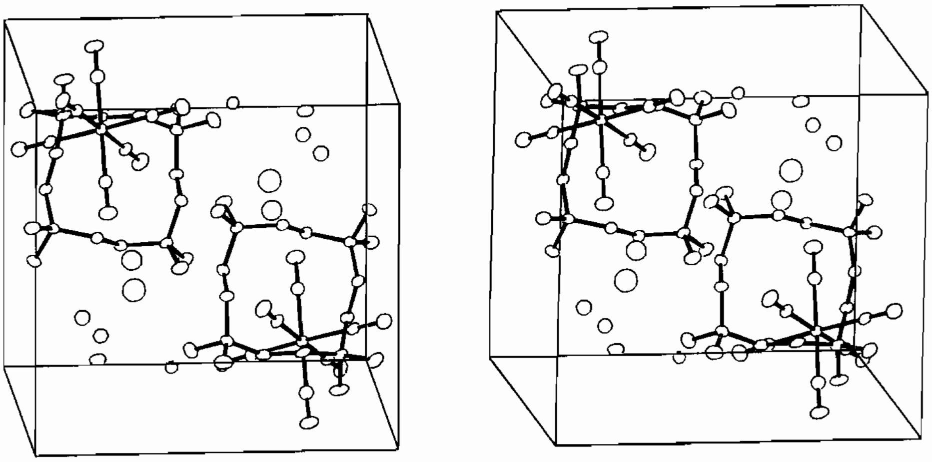

Fig. 2. Stereoview of the unit cell contents of the compound $(L1)[Co(CN)_6]\cdot I\cdot 3H_2O$.

TABLE V. Bond Distances (Å), Angles (°) and Torsion Angles (°)[a]

Distances

N(1)–C(2)	1.525(9)	N(1)–C(12)	1.505(9)	N(1)–C(13)	1.493(9)
N(1)–C(14)	1.511(9)	C(2)–C(3)	1.516(10)	C(3)–N(4)	1.508(9)
N(4)–C(5)	1.498(9)	N(4)–C(15)	1.503(10)	N(4)–C(16)	1.515(9)
C(5)–C(6)	1.534(11)	C(6)–N(7)	1.503(10)	N(7)–C(8)	1.516(9)
N(7)–C(17)	1.500(11)	N(7)–C(18)	1.500(11)	C(8)–C(9)	1.522(10)
C(9)–N(10)	1.511(9)	N(10)–C(11)	1.514(9)	N(10)–C(19)	1.507(10)
N(10)–C(20)	1.449(10)	C(11)–C(12)	1.532(10)		
Co–C(21)	1.893(9)	Co–C(22)	1.901(8)	Co–C(23)	1.905(9)
Co–C(24)	1.901(9)	Co–C(25)	1.884(9)	Co–C(26)	1.888(9)
C(21)–N(11)	1.147(10)	C(22)–N(12)	1.129(9)	C(23)–N(13)	1.125(10)
C(24)–N(14)	1.132(10)	C(25)–N(15)	1.142(10)	C(26)–N(16)	1.128(10)

Angles

C(12)–N(1)–C(2)	114.3(6)	C(13)–N(1)–C(2)	109.7(6)
C(13)–N(1)–C(12)	108.0(6)	C(14)–N(1)–C(2)	106.3(6)
C(14)–N(1)–C(12)	110.1(6)	C(14)–N(1)–C(13)	108.3(6)
C(3)–C(2)–N(1)	112.6(6)	N(4)–C(3)–C(2)	111.9(6)
C(5)–N(4)–C(3)	113.2(6)	C(15)–N(4)–C(3)	110.0(6)
C(15)–N(4)–C(5)	107.4(6)	C(16)–N(4)–C(3)	107.4(6)
C(16)–N(4)–C(5)	111.1(6)	C(16)–N(4)–C(15)	107.5(6)
C(6)–C(5)–N(4)	113.8(6)	N(7)–C(6)–C(5)	113.0(7)
C(8)–N(7)–C(6)	114.2(6)	C(17)–N(7)–C(6)	107.1(7)
C(17)–N(7)–C(8)	109.4(7)	C(18)–N(7)–C(6)	111.5(7)
C(18)–N(7)–C(8)	105.7(7)	C(18)–N(7)–C(17)	108.9(7)
C(9)–C(8)–N(7)	112.8(6)	N(10)–C(9)–C(8)	111.7(6)
C(11)–N(10)–C(9)	112.8(6)	C(19)–N(10)–C(9)	110.9(6)
C(19)–N(10)–C(11)	107.1(6)	C(20)–N(10)–C(9)	107.3(6)
C(20)–N(10)–C(11)	110.7(6)	C(20)–N(10)–C(19)	108.1(6)
C(12)–C(11)–N(10)	113.1(6)	C(11)–C(12)–N(1)	113.2(6)
C(22)–Co–C(21)	178.2(3)	C(23)–Co–C(21)	90.6(3)
C(24)–Co–C(21)	88.5(3)	C(25)–Co–C(21)	89.4(3)
C(26)–Co–C(21)	91.8(3)	C(23)–Co–C(22)	91.2(3)
C(24)–Co–C(22)	89.7(3)	C(25)–Co–C(22)	90.5(3)
C(26)–Co–C(22)	88.4(3)	C(24)–Co–C(23)	179.0(4)
C(25)–Co–C(23)	88.7(3)	C(26)–Co–C(23)	90.5(4)
C(25)–Co–C(24)	90.9(3)	C(26)–Co–C(24)	89.9(4)
C(26)–Co–C(25)	178.6(3)	Co–C(21)–N(11)	178.5(8)
Co–C(22)–N(12)	178.0(7)	Co–C(23)–N(13)	177.2(8)
Co–C(24)–N(14)	178.8(8)	Co–C(25)–N(15)	178.9(8)
Co–C(26)–N(16)	178.3(8)		

Torsion angles

N(1)–C(2)–C(3)–N(4)	-159.6	C(2)–C(3)–N(4)–C(5)	69.6
C(3)–N(4)–C(5)–C(6)	69.5	N(4)–C(5)–C(6)–N(7)	-163.3
C(5)–C(6)–N(7)–C(8)	66.8	C(6)–N(7)–C(8)–C(9)	68.1
N(7)–C(8)–C(9)–N(10)	-160.6	C(8)–C(9)–N(10)–C(11)	69.4
C(9)–N(10)–C(11)–C(12)	69.4	N(10)–C(11)–C(12)–N(1)	-163.4
C(11)–C(12)–N(1)–C(2)	66.6	C(12)–N(1)–C(2)–C(3)	68.3

[a] e.s.d.s given in parentheses.

in Table V. The $[Co(CN)_6]^{3-}$ anion shows only slight deviations from the ideal O_h symmetry; the mean Co–C distance of 1.895(9) Å is in agreement with the analogous distance found in the crystal structure of $(H_8L)[Co(CN)_6]_2Cl_2 \cdot 10H_2O$ (L = 1,4,7,10,13,16,19,22,25,28-decaazacyclotriacontane) [31]. The other distances in the complex anion and in the macrocycle agree with literature values. It is worth noting that all the C–N–C and N–C–C angles involving the atoms of the cyclic framework of the cation are all noticeably greater than 109.28° (see Table V) implying the existence of conformational strain within the macrocyclic ring (*vide infra*). In the charged macrocycle the four nitrogen atoms deviate only 0.025 Å from the least-squares plane through them and are linked by ethylenic chains in chair conformation with the carbon atoms located alternately above and below the mean plane from which they are symmetrically displaced. Such *trans* conformation is revealed by the values of the torsion angles about the C–C bonds (see Table V) and is indicative of the macrocycle stiffening due to the electrostatic repulsions between the positively charged quaternary nitrogens. It is interesting to note that a similar stiff macrocyclic configuration was invoked to explain the thermodynamic results of the last step of protonation of some tetraazamacrocycles [32]. The three water molecules of crystallization are involved in hydrogen bonds between themselves and with some of the cyanide nitrogen atoms (see Table IV).

Supplementary Material

Tables of thermal parameters, calculated positions of hydrogen atoms (4 pages); a listing of observed and calculated structure factors (20 pages) are available from the authors on request.

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