Cobalt(III) Tetraazamacrocyclic Complexes with Pendant Amino Groups: Synthesis, Structure and Electrochemical Properties

Bohdan Korybut-Daszkiewicz,*[a] Joanna Taraszewska,*[b] Katarzyna Zięba,[b] Krzysztof Woźniak,[c] and Daniel Kamiński[c]

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Two isomeric *cis*-2,9-bis(aminomethyl)-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (**1** and **2**) and two 2-aminomethyl-2-methyl-1,4,8,11-tetraazacyclotetradecane (**3** and **4**) cobalt(III) complexes have been prepared and characterised. During the synthesis of **2** a minor oxidation product **5** was formed. The structures of **3**, **4** and **5** have been determined by X-ray crystallography, and the UV/Vis spectra of **1**–**5** have been analysed. The average Co–N distances in **1** and **2** have been estimated from the correlation between the average Co–N bond lengths and position of the maximum absorption for hexaamine complexes given in literature. The electrochemical behaviour of **1**–**5** in neutral and acidic solutions has been studied by cyclic voltammetry. In complexes displaying electronic maxima at higher energy, cobalt(III) was reduced at more negative potentials. Small differences in the conformation of ligand between **3** and **4** explain the different behaviour of these complexes in acidic solutions.

Introduction

Compounds containing the sarcophagine group − consisting of the cyclam unit with a single diamine strap bridging the apical sites of the macrocycle[1] − belong to the most extensively studied Co^{III} macrocyclic hexaamine complexes. In these compounds the hexaaza ligand can completely surround the metal ion coordinated in an octahedral manner. Another approach is realised in pendant arm macrocycles, which usually occupy four equatorial sites around coordinated metal ion, and simultaneously, via pendant coordinating amine groups, are bound at one or both axial positions. The synthesis and physico-chemical properties of macrocyclic Co^{III} tetraamines with pendant amine groups have been extensively studied in recent years.[2−6] Recently Bernhardt et al.[7] synthesised the hexaamine with five secondary amine groups in the macrocyclic ring and one pendant primary amine group to give hexadenate octahedral complexes with Co^{III} and other cations. Macrocyclic Co^{III} tetraamines with one pendant amine group coordinated in one axial position and anion coordinated in the second axial position have also been extensively studied[8−12] Such complexes present a different ligand field environment to that found in the neutral hexaamine complexes.

Here we describe the synthesis, characterisation and electrochemical studies of Co^{III} *C*-functionalised cyclam derivatives containing two or one aminomethyl side arms that are able to interact with the metal ion in the central cavity. In two isomeric Co^{III} complexes of *cis*-2,9-bis(aminomethyl)-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (**1** and **2** respectively), the coordination of two pendant amino groups forces the ring to adopt a folded conformation. It was interesting to compare the behaviour of these complexes with their Ni^{II} analogues studied by us recently[13] and with other Co^{III} hexaamine complexes.

The crystallographic data for two isomeric Co^{III} complexes of 2-aminomethyl-2-methyl-1,4,8,11-tetraazacyclotetradecane (**3** and **4**) revealed that both complexes possess the *trans* configuration with the macrocyclic ring occupying the equatorial plane and the apical positions occupied by a pendant NH_2 group and a chloride ion in the *trans* configuration. They differ only in configuration at the secondary amine groups resulting in different conformations of the macrocyclic ring.

A goal of this study was to examine the influence of the macrocyclic ligand conformation on the properties of the synthesised complexes. The structures of the complexes studied are presented in Figure 1.

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[a] Institute of Organic Chemistry, Polish Academy of Sciences,
Kasprzaka 44/52, 01-224 Warszawa, Poland
Fax: (internat.) +48-(0)22 6326681
E-mail: bkd@icho.edu.pl
[b] Institute of Physical Chemistry, Polish Academy of Sciences,
Kasprzaka 44/52, 01-224 Warszawa, Poland
Fax: (internat.) +48-(0)22 6325276
E-mail: jota@ichf.edu.pl
[c] Department of Chemistry, University of Warsaw,
Pasteura 1, 02−093 Warszawa, Poland

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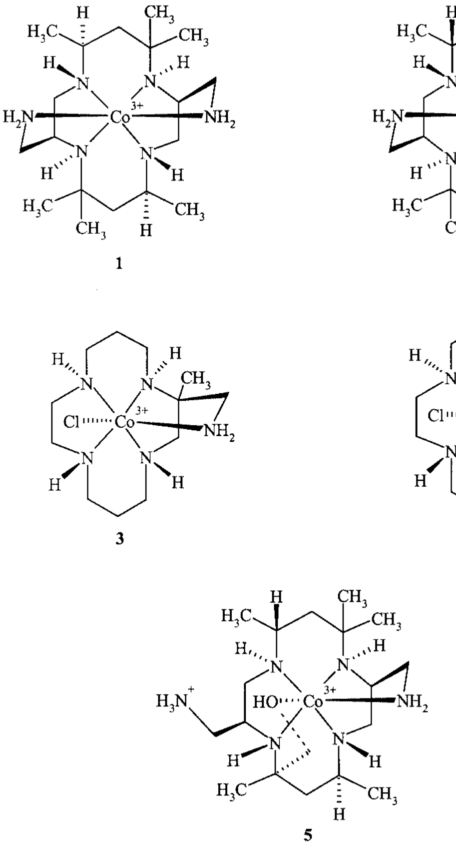

Figure 1. Schematic structures of studied complexes

Results and Discussion

Synthesis and Structure

Cobalt(III) complexes **1** and **2** were prepared by the reaction of free *cis*-2,9-substituted isomeric ligands with CoCl$_2$·6H$_2$O followed by aerial oxidation. The ^{1}H and ^{13}C NMR spectra of complexes **1** and **2** are consistent with that expected for the *cis*-fivefolded conformation of ligands − previously observed in their octahedral Ni^{II} complexes.[14]

During the synthesis of **2** (5,12-*trans*) an additional minor oxidation product **5** was formed and isolated by chromatography on a SP Sephadex C-25 column. X-ray analysis (Figure 2) revealed that complex **5** was formed by the oxidation of one of the geminal methyl groups attached to C-5 and located *trans* to the substituents at C-7 and C-10. The macrocyclic ring in complex **5** adopts a *trans*-III planar conformation with the 2-aminomethyl and 5-hydroxymethyl groups coordinated on opposite sides of the macrocycle. The remaining protonated 10-aminomethyl group occupies an equatorial position. A similar dioxygen oxidation of one of the *gem*-dimethyl substituents to a coordinated hydroxymethyl group in *C*-*meso*-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetrazacyclotetradecane have been reported by House et al.[15]

The *N*-isomeric cobalt(III) complexes **3** and **4** were similarly obtained and separated by chromatography on a Dowex 50WX2 cation-exchange column. Slow evaporation of acetonitrile−methanol (9:1) solutions gave crystals suitable for X-ray crystal analysis.

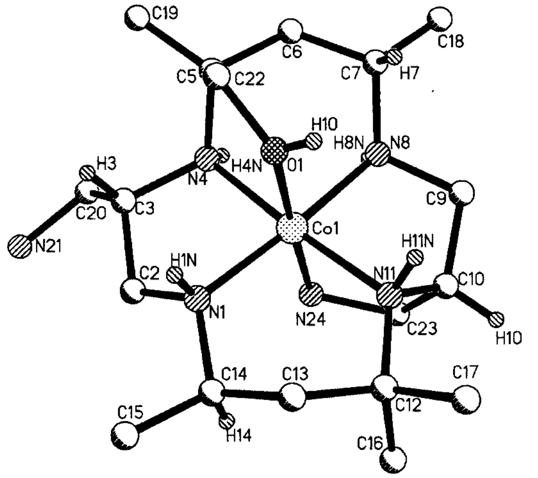

Figure 2. Molecular structure and labelling of atoms for the complex **5**; selected bond lengths (Å) are: Co(1)−O(1) 1.920(3), Co(1)−N(1) 1.957(4), Co(1)−N(4) 1.959(3), Co(1)−N(8) 1.983(3), Co(1)−N(11) 1.961(3), Co(1)−N(24) 1.936(4)

The molecular structures of cations **3** and **4** are shown in Figure 3 and 4, respectively. Both cations have irregular octahedral Co^{III} coordination spheres with the macro-cycle coordinated in a planar conformation and the pendant amino group in the apical position. The sixth coordination position is occupied by a chloride anion; *trans*-III (1*RS*,2*RS*,4*RS*,8*SR*,11*SR*) and *trans*-II (1*RS*,2*RS*,4*SR*,8*RS*,11*RS*) ligand configurations were established for **3** and **4**, respectively. The chloride anion in isomer **4** is coordinated on the same side of the macrocycle as three secondary amino group protons. The Co−Cl bond is longer [2.265(2) and 2.258(3) Å for two independent molecules] in the isomer **4** than in **3** [2.249(2) Å]. The two six-membered endomacrocyclic chelate rings in the cation **3** adopt the chair conformation, whereas one of them in isomer **4** [N(11)−N(1)] exists in the twist-boat conformation. The five-membered chelate rings exist in an envelope conformation in both isomers.

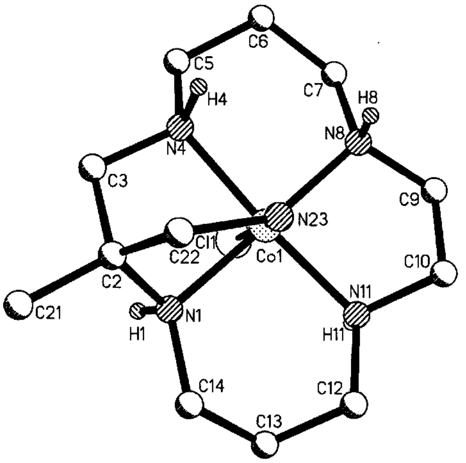

Figure 3. Molecular structure and labelling of atoms for the complex **3**; selected bond lengths (Å) are: Co(1)−Cl(1) 2.249(2), Co(1)−N(1) 1.961(6), Co(1)−N(4) 1.980(7), Co(1)−N(8) 1.965(7), Co(1)−N(11) 1.974(8), Co(1)−N(23) 1.972(6)

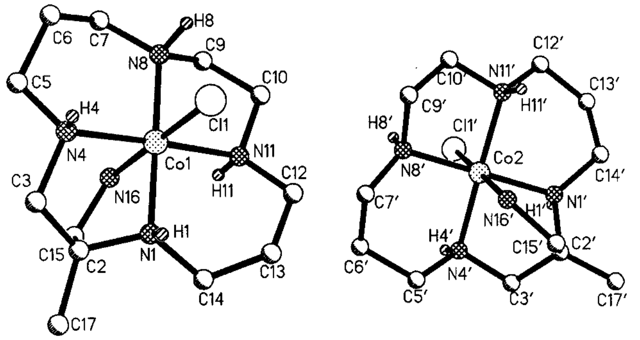

Figure 4. Molecular structure of the two independent cations of complex **4**; selected bond lengths (Å) are: Co(1)−Cl(1) 2.265(2), Co(1)−N(1) 1.942(7), Co(1)−N(4) 1.971(7), Co(1)−N(8) 1.971(8), Co(1)−N(11) 1.988(7), Co(1)−N(16) 1.96(1); Co(2)−Cl(1′) 2.258(3), Co(2)−N(1′) 1.967(7), Co(2)−N(4′) 1.977(7), Co(2)−N(8′) 1.974(7), Co(2)−N(11′) 1.993(7), Co(2)−N(16′) 1.984(8)

Solution Properties

Electronic Spectroscopy of Complexes

The aqueous solution UV/Vis electronic spectra of complexes **1−5** are presented in Table 1.

The spectra of complexes **1** and **2** exhibit two spin-allowed d−d transitions characteristic of low-spin d^6 ion in a pseudooctahedral ligand field. The transitions $^1T_{2g}\leftarrow{}^1A_{1g}$ and $^1T_{1g}\leftarrow{}^1A_{1g}$ in both complexes occur at lower energies than those in Co^{III} complexed with *cis*-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine (*cis*-diammac) and other Co^{III} hexaamine complexes.[4] The electronic spectrum of complex **1** displays electronic maxima at higher energies than those of **2**. Spectra of the complexes **3** and **4** exhibit three bands that are similar to those of other complexes of this type.[8,9,11,12] The appearance of the three bands is connected with the lower symmetry of the both complexes in comparison with hexaamine with two pendant NH_2 groups. The transition maxima occur at higher energies for **3** than for **4**. For complexes **1−4**, for each pH value, the electronic spectra were unchanged after 5 h, proving the lack of protonation of the amine groups in **1** and **2** and the lack of hydrolysis of the chloro-ligands in the complexes **3** and **4**.

For complex **5** in a neutral solution, the first band was observed as a shoulder at about 340 nm, due to overlap with a strong absorption band in the UV region. The second band appeared at 489 nm. In acidic medium the shoulder and the second band appeared at 338 nm and 469 nm, respectively. This indicates that in neutral solution the pendant amino group substitutes the hydroxy group in the coordination sphere of the central metal ion. In the acidic medium the amino group is protonated and the reverse process takes place.

A correlation has been reported[16] between the Co−N bond length and the position of the absorption maxima in $[Co(N)_6]$ complexes. Unfortunately, for the complexes **1** and **2** we have no crystallographic data. To estimate the average Co−N distance in these complexes we plotted (Figure 5) the λ_{max} values for $^1T_{2g}$ and $^1T_{1g}$ transitions against the average Co−N bond lengths for hexaamine complexes **6−12** taken from the literature (Table 1). The structures of complexes **6−12** are presented in Figure 6. The open circles and squares in Figure 5 are for complexes **1** and **2**, respectively. The estimated average Co−N distances from this correlation are 1.989 and 2.010 Å for **1** and **2**, respectively.

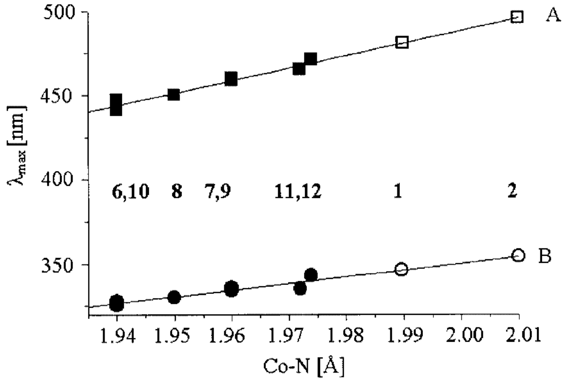

Figure 5. Plot of λ_{max} values against the average Co-N lengths for Co^{III} hexaamine complexes. Open circles and squares refer to complexes **1** and **2**, respectively. A- for $^1T_{1g}\leftarrow{}^1A_{1g}$ and B-for $^1T_{2g}\leftarrow{}^1A_{1g}$ transitions, respectively

Table 1. Electronic absorption spectra, formal potentials and average Co−N distances in cobalt(III) complexes

Complex	E_f [V] vs. MCE	λ_{max}, nm (ε, $dm^3mol^{-1}cm^{-1}$)	$Co-N_{av}$ [Å]	Ref.
1	−0.52	346(92); 481(98)	1.989	this work
2	−0.48	354(121); 496(118)	2.010	this work
3	−0.43	362(94); 454(38); 534(61)	–	this work
4	−0.37	365(118); 461(53.5); 550(85)	–	this work
5	−0.42	338(167); 489(78)	–	this work
6	−0.85	328; 447	1.94	[4]
7	−0.72	334; 459	1.96	[4]
8	−0.86	330; 450	1.95	[4]
9	−0.76	336; 460	1.96	[4]
10	−0.83	325; 441	1.94	[4]
11	−0.71	343; 471	1.974	[4]
12	−0.64	335; 465	1.972	[7]
13	−0.49	350; 516	–	[9]

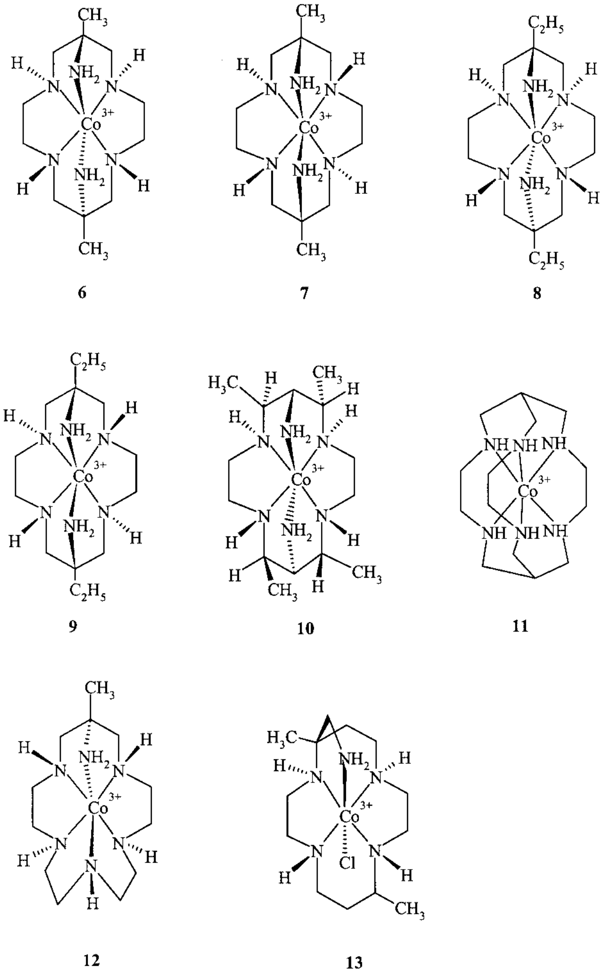

Figure 6. Schematic structures of Co^{III} hexaamine complexes **6−11**,[4] **12**[7] and chloro-pentaamine complex **13**[9]

Redox Properties of Complexes and Acid−Base Equilibria

The voltammetric behaviour of **1−4** was studied in aqueous solutions containing 0.1 M NaCl as the supporting electrolyte. The redox process Co^{III}/Co^{II} in all complexes was reversible or quasi-reversible. The values of formal potentials E_f, calculated as midpoints between the corresponding cathodic and anodic peaks, are −0.52, −0.48, −0.43 and −0.37 V for complexes **1−4**, respectively.

In **1** the ratio i_c/i_a was less than 1 which suggests that the larger Co^{II} ion cannot be well accommodated in the macrocyclic cage and the complex starts decomposing. This is supported by the smaller estimated average Co−N distance for **1** compared with **2**. On the C.V. curves recorded at higher scan rates (1 V s^{-1}) the ratio i_c/i_a was 1.

In comparison with other hexaamine complexes,[4] the redox potentials of the complexes **1** and **2** are shifted to less negative values. Replacement of one -NH$_2$ group by chloride causes a further positive shift. Comparison of the spectrophotometric and electrochemical parameters for **1−5** with those from literature revealed a very good correlation between E_f and λ_{max} (Figure 7). Consequently, for complexes displaying electronic maxima at higher energy, Co^{III} is reduced at more negative potentials. A similar correlation was found for Ni^{II} hexaamine complexes by Gavrish and Lampeka.[17]

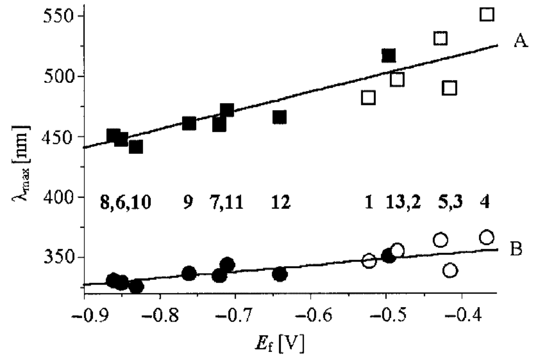

Figure 7. Plots of λ_{max} against formal potentials E_f for Co^{III} complexes **6−13**. Open circles and squares refer to complexes **1−5;** A for $^1T_{1g} \leftarrow {}^1A_{1g}$ and B for $^1T_{2g} \leftarrow {}^1A_{1g}$ transitions, respectively

The presence of a charged Cl$^-$ donor instead of neutral primary amine group clearly changes both the charge and electronic effects in the complex. As the average Co−N distances in **3** and **4** are similar, the main reason for the difference in E_f values is that the Co−Cl distances are ca. 2.249(2) Å in **3**, and 2.265(2) and 2.258(3) Å in **4**. The longer Co−Cl distance in **4** diminishes the electronic density on the central ion and facilitates reduction of the Co^{III} complex. The shorter Co−NH$_2$ distance in complex **4** than in **3** seems to play a minor role.

The behaviour of Co^{III} in complexes **1−3**, in acidic solutions was similar. Up to the lowest value, pH 1, Co^{III} was reduced at the same potential as in neutral solutions and the reduction currents remained constant, indicating that the pendant NH$_2$ groups are not protonated. Upon lowering of pH from 7 to 1, the redox process Co^{III}/Co^{II} in **1** and **2** become less reversible ($\Delta E \approx 100$ mV) and the anodic peaks continuously diminished. In **3** up to pH 2.5, the redox process was quasi-reversible with $i_{pa}/i_{pc} = 1$. At lower pHs the anodic current started to diminish due to the protonation of the NH$_2$ group. The presence of two axial protons from the secondary amino groups in the macrocyclic ring in the neighbourhood of the protonated NH$_3^+$ group may explain why Co^{II} cannot coordinate either a H$_2$O molecule or a Cl$^-$ anion. Therefore, this complex is electrochemically inactive. Similarly, the lack of the oxidation of Co^{II} in the protonated form of **2** may be connected with the presence of many methyl groups in the macrocyclic ring, which prevent access of axial ligands.

With increasing solution acidity, the behaviour of the complex **4** was different than that of **3** (Figure 8), indicating that even small differences in structure can significantly influence the electrochemistry. With decreasing pH, the reduction potential of Co^{III} shifts towards less negative values. However, the height of the peak remains constant, which means that the −NH$_2$ group in this complex is not protonated. The shift of the Co^{III} reduction potential may be connected with the competition between protons from solution and the metal centre for chloride ion, which is at

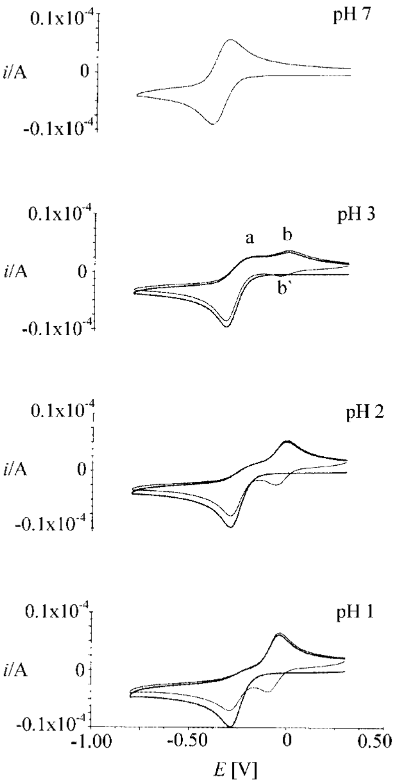

Figure 8. Cyclic voltammograms of 5×10^{-4} M of complex **4** recorded at the GC-20 electrode in aqueous 0.1 M NaCl solution at various pH, scan rate 0.05 V s^{-1}

a longer distance than in **3**. This weakens its coordination ability and decreases the charge density on Co^{III}, making the reduction process easier.

In the anodic scan at pH 3, the anodic peak *a* diminishes as in the other complexes and a new anodic peak *b* appears at about 0.0 V. The product formed at this potential is subsequently reversibly reduced at a potential of peak *b′* in the second scan. The heights of peaks *b* and *b′* increase with lowering pH. The formal potential $E_f = -0.07$ V of this process is similar to that corresponding to the redox process Co^{III}/Co^{II} in $[Co^{III}$-cyclam$Cl_2]Cl$[9] (about −0.11 V). Therefore, we can assume that, after protonation of the NH_2 group, Co^{II} in **4** coordinates the Cl^- ion and the second pair of peaks is connected with the Co^{III}/Co^{II} redox process from complex **4** with two chloride ions coordinated to the metal centre. In an experiment performed in 0.1 M $HClO_4$ solution the second pair of peaks appeared at positive potentials (E_f about +0.11 V), which suggests that, after protonation of the -NH_2 group, the ligand at the second apical position was replaced by a water molecule.

In **5**, the reduction potential of Co^{III} is shifted with decreasing pH towards less negative values. For example, from −0.46 V at pH 7 to −0.31 V at pH 1. This is in agreement with the postulated substitution of the coordinated hydroxy group in a neutral solution by the pendant -NH_2 group, protonation of it at low pH values, and subsequent replacement by the OH group.

Conclusion

Structural properties such as ring size and conformation of the ligands studied by us are very selective in the stabilisation of the Co^{II} cations. The effect of the ring size was particularly evident in the case of Co^{II} in the complex **1**. This complex decomposed because Co^{II} could not be well accommodated in the macrocyclic cavity. The redox process in hexaamine complexes **1** and **2** was recorded at more negative potentials than in the complexes **3** and **4** with an axially coordinated Cl donor instead of a neutral primary amine group. The longer Co−Cl distance in complex **4** facilitated the reduction of Co^{III}. Small differences in the ligand conformation between **3** and **4** caused different behaviour of these complexes in acidic solutions.

Experimental Section

Syntheses: The preparation of 2-aminomethyl-2-methyl-1,4,8,11-tetraazacyclotetradecane and isomeric (2*RS*,5*RS*,9*RS*,12*RS*)- and (2*RS*,5*SR*,9*RS*,12*RS*)-2,9-bis(aminomethyl)-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecanes has been described elsewhere.[14]

Instrumentation: Cyclic voltammograms of complexes **1−5** were measured at a glassy carbon (GC-20) electrode, with a Pt plate as the counter electrode. The reference electrode, a 1 M NaCl aqueous calomel electrode (MCE), was connected to the electrolytic cell via an intermediate vessel filled with the solution under investigation. Solutions were deaerated by flushing with pure argon. An Autolab (EcoChemie) measuring system was used. Electronic spectra were recorded using a Cary 1 (Varian) spectrophotometer. The NMR spectra were obtained on a Bruker AM 500 spectrometer.

(2*RS*,5*RS*,9*RS*,12*RS*)-2,9-Bis(aminomethyl)-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecanecobalt(III) Trichloride (1): A solution of free ligand (0.34 g, 0.001 mol) in methanol (10 cm^3) was added to a solution of $CoCl_2{\cdot}6H_2O$ (0.24 g, 0.001 mol) in methanol (20 cm^3) and aerated overnight, diluted with water (100 cm^3) and absorbed on the SP Sephadex C-25 column. The column was eluted with a 0.1 M solution of sodium sulfate. The single orange band was collected, absorbed on a Dowex 50WX2 cation-exchange column (H^+ form) that was washed with 1 M HCl and eluted with 3 M HCl. An orange eluate was evaporated to dryness and the residue dissolved in a methanol−acetonitrile mixture. Upon evaporation of methanol, orange crystals were obtained. Yield 0.34 g (70%). $C_{18}H_{42}Cl_3CoN_6{\cdot}2H_2O$ (543.9): calcd. C 39.8, H 8.5, Cl 19.6, N 15.5; found C 39.9, H 8.7, Cl 20.1, N 15.8. ^1H NMR (500.13 MHz, D_2O + DCl): δ = 1.41 (s) and 1.44 (s, 7,14-CH_3), 1.37 (d, 5,12-CH_3), 3.05 (m, 5,12-CH), 2.59 (d) and 3.06 (m, 2,9-CH_2NH_2), 3.54 (m, 2,9-CH), 1.73 (m) and 1.75 (m, 6,13-CH_2) 3.08 (m) and 3.18 (m, 3,10-CH_2), 4.70 (1,8-NH), 5.93 (4,11-NH), 4.92 and 5.49 (NH_2) ppm. ^{13}C NMR (125.8 MHz, D_2O +DCl): δ = 28.0 and 30.8 (7,14-CH_3), 22.0 (5,12-CH_3), 46.9 (2,9-CH_2NH_2), 66.1 (2,9-C), 60.2 (3,10-C), 59.9 (5,12-C), 47.9 (6,13-C), 59.0 (7,14-C) ppm.

(2*RS*,5*SR*,9*RS*,12*RS*)-2,9-Bis(aminomethyl)-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecanecobalt(III) Trichloride (2) and 2-Aminomethyl-9-ammoniummethyl-7-hydroxymethyl-5,7,12,14,14-pentamethyl-1,4,8,11-tetraazacyclotetradecanecobalt(III) Tetrachloride (5): These complexes were obtained from the

(2*RS*,5*SR*,9*RS*,12*RS*) isomer of the macrocyclic ligand by the same procedure. The minor red ligand oxidation product **5** was isolated as the first band eluted from a SP Sephadex C-25 column. Yield 60% and 8% of **2** and **5**, respectively.

Complex 2: $C_{18}H_{42}Cl_3CoN_6{\cdot}3H_2O$ (561.9): calcd. C 38.5, H 8.6, Cl 18.9, N 14.9; found C 38.9, H 8.2, Cl 18.6, N 14.6. ^1H NMR (500.13 MHz, D_2O): δ = 1.35 (s), 1.42 (s), 1.43 (s) and 1.47 (s, 7,14-CH_3), 1.27 (d) and 1.37 (d, 5,12-CH_3), 3.05 (m) and 3.20 (m, 5,12-CH), 2.71 (d), 3.00 (bd) and 2.66 (d), 3.00 (bd, 2,9-CH_2NH_2), 3.53 (t) and 3.59 (t, 2,9-CH), 1.56 (d), 2.16 (dd) and 1.62 (dd), 1.68 (dd, 6,13-CH_2) 3.29 (d), 3.14 (m) and 2.73 (d), 3.12 (m, 3,10-CH_2) ppm. ^{13}C NMR (125.8 MHz, D_2O): δ = 25.3, 27.8, 31.5 and 35.4 (7,14-CH_3), 21.2 and 22.3 (5,12-CH_3), 46.1 and 48.6 (2,9-CH_2NH_2), 64.8 and 64.8 (2,9-C), 50.8 and 61.3 (3,10-C), 52.9 and 59.8 (5,12-C), 45.2 and 47.7 (6,13-C), 59.8 and 61.1 (7,14-C) ppm.

Complex 5: $C_{18}H_{43}Cl_4CoN_6O{\cdot}2H_2O$ (596.4): calcd. C 36.3, H 7.9, N 14.1; found C 36.6, H 7.9, N 13.6. ^1H NMR (500.13 MHz, D_2O): δ = 1.34 (s), 1.41 s, 1.58 (s) (7,14-CH_3), 1.34 and 1.50 (d, 5,12-CH_3), 3.35 (s, 7-CH_2OH) ppm. ^{13}C NMR (125.8 MHz, D_2O): δ = 20.0, 20.6, 21.3, 25.1, 32.5 (CH_3), 43.0, 47.8, 49.2, 52.1, 53.1, 55.4, 56.9, 57.1, 57.5, 59.7, 62.1, 70.5, 71.3 ppm.

Isomeric 2-Aminomethyl-2-methyl-1,4,8,11-tetraazacyclotetradecanecobalt(III) Trichlorides (3 and 4): A solution of 2-aminomethyl-2methyl-1,4,8,11-tetraazacyclotetradecane (1.0 g, 0.004 mol) in methanol (40 cm^3) was added to solution of $CoCl_2{\cdot}6H_2O$ (1.0 g, 0.004 mol) in methanol (60 cm^3) and aerated overnight, acidified with concentrated HCl (1 cm^3), diluted with water (500 cm^3) and then absorbed on a Dowex 50WX2 cation-exchange column (H^+ form). The column was washed with 1 M HCl and eluted with 2 M HCl. Two deep red bands were separated and the solvents evaporated to dryness. The residues were dissolved in small volumes of methanol and diluted with acetonitrile. Upon evaporation deep red crystals were obtained from both fractions. Yield 0.7 g (41%) of **3** (first fraction) and 0.6 g (35%) of **4** (second fraction).

Complex 3: $C_{12}H_{29}Cl_3CoN_5{\cdot}2H_2O$ (444.72): calcd. C 32.4, H 7.4, Cl 23.9, N 15.8; found C 32.1, H 7.4, Cl 24.5, N 15.8. ^1H NMR (500.13 MHz, D_2O + DCl): δ = 1.36 (s, 2-CH_3), 2.78 (m) and 2.86 (m, pendant-CH_2), 4.00 (m), 4.04 (m, NH_2), 6.52 (1-NH), 2.95 (3-CH, ax), 3.00 (3-CH, eq.), 5.56 (4-NH), 3.19 (5-CH, ax), 2.48 (5-CH, eq.), 1.97 (6-CH, ax), 2.05 (6-CH, eq.), 2.67 (7-CH, ax), 2.96 (7-CH, eq.), 6.00 (8-NH), 2.58 (9-CH, ax), 3.06 (9-CH, eq.), 2.56 (10-CH, ax), 3.01 (10-CH, eq.), 6.12 (11-NH), 2.65 (12-CH, ax), 2.85 (12-CH, eq.), 1.82 (13-CH, ax), 2.20 (13-CH, eq.), 2.30 (14-CH, ax), 2.93 (14-CH, eq.) ppm. ^{13}C NMR (125.8 MHz, D_2O +DCl): δ = 16.5 (2-CH_3), 48.8 (pendant-CH_2), 71.4 (2-C), 63.7 (3-C), 48.9 (5-C), 29.2 (6-C), 51.0 (7-C), 54.3 (9-C), 55.9 (10-C), 50.6 (12-C), 28.8 (13-C), 46.1 (14-C) ppm, assignments established on the basis of $^1H-^1H$ and $^1H-^{13}C$ correlation experiments.

Complex 4: $C_{12}H_{29}Cl_3CoN_5{\cdot}H_2O$ (426.70): calcd. C 33.8, H 7.3, Cl 24.9, N16.4; found C 33.6, H 7.3, Cl 25.2, N 16.1. ^1H NMR (500.13 MHz, D_2O + DCl): δ = 1.33 (s, 2-CH_3), 2.67 (m) and 2.88 (m, pendant-CH_2), 3.97 (m, NH_2), 6.27 (bd, 1-NH), 3.34 (m, 3-CH, ax), 2.69 (m, 3-CH, eq.), 6.47 (bt, 4-NH), 2.58 (5-CH, ax), 2.94 (5-CH, eq.), 1.83 (6-CH, ax), 2.17 (bd, 6-CH, eq.), 2.90 (7-CH_2), 6.28 (8-NH), 2.67 (m, 9-CH, ax), 2.98 (m, 9-CH, eq.), 2.45 (m, 10-CH, ax), 3.09 (m, 10-CH, eq.), 5.89 (bt, 11-NH), 2.59 (12-CH, ax), 2.91 (12-CH, eq.), 2.09 (m, 13-CH, ax), 2.25 (m, 13-CH, eq.), 2.53 (14-CH, ax), 2.88 (14-CH, eq.) ppm. ^{13}C NMR

Table 2. Crystal data and structure refinement details for complexes **3**, **4** and **5**

Compound	**3**	**4**	**5**
Empirical formula	$C_{12}H_{29}Cl_3CoN_5{\cdot}2H_2O$	$2C_{12}H_{29}Cl_3CoN_5{\cdot}1.5H_2O$	$C_{18}H_{43}Cl_4CoN_6O{\cdot}H_2O$
Molecular mass	444.72	844.40	578.33
Temperature [K]	293(2)	293(2)	293(2)
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system, space group	Orthorhombic, *Pccn*	Monoclinic, *P*2₁/*c*	Monoclinic, *P*2₁/*n*
Unit cell dimensions			
a [Å]	18.230(4)	14.855(3)	8.0523(16)
b [Å]	13.650(3)	10.472(2)	19.465(4)
c [Å]	15.770(3)	24.955(5)	17.532(4)
β [°]	90	97.68(3)	95.47(3)
Volume [$Å^3$]	3924.2(14)	3847.2(13)	2735.4(9)
Z	8	8	4
Calculated density [$g{\cdot}cm^{-3}$]	1.505	1.458	1.404
Absorption coefficient [mm^{-1}]	1.30	1.31	1.04
F(000)	1872	1772	1224
Crystal size [mm]	0.2 × 0.2 × 0.4	0.1 × 0.1 × 0.2	0.1 × 0.3 × 0.5
Θ range for data collection [°]	3.19 to 21.00	3.38 to 22.00	3.45 to 21.00
Limiting indices	$-18 \le h \le 18$	$-15 \le h \le 11$	$-6 \le h \le 8$
	$-13 \le k \le 13$	$-10 \le k \le 11$	$-18 \le k \le 19$
	$-8 \le l \le 15$	$-26 \le l \le 26$	$-16 \le l \le 17$
Reflections collected/unique	14029/2073	15455/4681	9775/2906
	R(int) = 0.0627	*R*(int) = 0.1182	*R*(int) = 0.0298
Completeness to Θ = 21.00	98.6%	99.3%	99.0%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2073/0/337	4681/0/625	2906/0/461
Goodness-of-fit on F^2	1.197	0.907	1.053
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0659	*R*1 = 0.0639	*R*1 = 0.0406
	*wR*2 = 0.1420	*wR*2 = 0.1464	*wR*2 = 0.1085
R indices	*R*1 = 0.0673	*R*1 = 0.1221	*R*1 = 0.0448
(all data)	*wR*2 = 0.1427	*wR*2 = 0.1629	*wR*2 = 0.1115
Largest diff. peak and hole [$e{\cdot}Å^{-3}$]	0.495 and −0.270	0.801 and −0.426	0.666 and −0.257

(125.8 MHz, D_2O +DCl): δ = 17.4 (2-CH_3), 49.1 (pendant-CH_2), 72.2 (2-C), 64.0 (3-C), 53.1 (5-C), 25.8 (6-C), 47.1 (7-C), 54.7 (9-C), 56.6 (10-C), 51.0 (12-C), 29.6 (13-C), 42.8 (14-C) ppm, assignments established on the basis of $^1H-^1H$ and $^1H-^{13}C$ correlation experiments.

X-ray Crystallography: Crystal structure data for**3**, **4** and **5** are given in Table 2, together with refinement details. All measurements of crystal were performed on a Kuma KM4CCD κ-axis diffractometer with graphite-monochromated Mo-K_α radiation. The crystal was positioned at 65 mm from the KM4CCD camera. For complex **3**: 4 runs of 575 frames each were measured at 0.2° intervals with a counting time of 37 s. For complex **4**: 4 runs of 153 frames each were measured at 0.75° intervals with a counting time of 30 s. For complex **5**: 4 runs of 153 frames each were measured at 0.75° intervals with a counting time of 30 s. The data were corrected for Lorentz and polarisation effects. No absorption correction was applied. Data reduction and analysis were carried out with the Kuma Diffraction (Wrocław) programs (KM4CCD and KM4RED).

The structures were solved by direct methods[18] and refined using SHELXL.[19] The refinement was based on F^2 for all reflections except those with very negative F^2. Weighted R factors wR and all goodness-of-fit S values are based on F^2. Conventional R factors are based on F with F set to zero for negative F^2. The $F_o^2 > 2s(F_o^2)$ criterion was used only for calculating R factors and is not relevant to the choice of reflections for the refinement. The R factors based on F^2 are about twice as large as those based on F. Most hydrogen atoms were located from differential maps and refined isotropically but some were fixed at ideal geometrical positions. For **4**, we were unable to find one hydrogen atom belonging to the disordered water molecule. One of the water molecules in **4** occupies a special position. Refinement of the solvent molecules is slightly worse. Scattering factors were taken from Tables 6.1.1.4 and 4.2.4.2 in ref.[20]

CCDC-187666, CCDC-187667 and CCDC-187668 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/etrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

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