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Cascade complex formation by phosphate in the cobalt(II)/[30]aneN_{10} anaerobic system

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Abstract

The interaction of phosphate with the mono- and binuclear cobalt(II) complexes of [30]aneN_{10} (1,4,7,10,13,16,19,22,25,28-decaazacyclotriacontane) has been studied by potentiometry in 0.15 mol dm^{-3} $NaClO_4$ solution at 298.15 K under anaerobic conditions. The stable species $[CoH_2([30]aneN_{10})PO_4]^+$, $[CoH_4([30]aneN_{10})PO_4]^{3+}$, $[Co_2H([30]aneN_{10})PO_4]^{2+}$, $[Co_2H_2([30]aneN_{10})PO_4]^{3+}$ and $[Co_2H_3([30]aneN_{10})PO_4]^{4+}$, where the phosphate anion is directly bound to the metal ions or acts as a second sphere ligand, are formed and their stability constants have been determined. The results obtained allowed for the selection of suitable conditions for the study of dioxygen uptake.

Introduction

The ability of polyazacycloalkanes of the series $[3k]aneN_k$ ($k=7$–12) to form mono- and polynuclear complexes with transition metal ions in aqueous solution has been extensively argumented [1–3] and reviewed [4]. Due to the great number of nitrogen atoms in these ligands the formation of highly protonated complexes, both mono- and polynuclear, occurs. These species are characterized by highly positive charges and, therefore, strong coulombic attraction could be exerted, in principle, between them and anionic species present in solution, as found for the uncomplexed polyprotonated forms of these ligands [5]. This interaction could give rise either to the formation of mixed-ligand complexes in which both the macrocycle and the anion are involved in the first coordination sphere, or to the formation of second sphere complexes in which the anions are organized beyond the first coordination sphere. Alternatively, anions which present some appropriate groups could coordinate to metal ions and further interact via coulombic forces and/or hydrogen bonds with polyammonium groups of the protonated macrocycle. These complexes were labeled by Lehn as 'cascade' complexes [6].

A preliminary study on O_2 uptake by the dicobalt(II) complexes of [30]aneN_{10} (1,4,7,10,13,16,19,22,25,28-decaazacyclotriacontane) showed a different behavior in phosphate media than in the presence of other anionic species such as Cl^-, NO_3^-, ClO_4^-, borate [7]. This suggested that the two cobalt(II) ions located inside the macrocyclic cavity of [30]aneN_{10} could bind in turn to anionic groups giving rise to the formation of mixed-ligand complexes having a different reactivity toward molecular oxygen. Examples of such complexes have been reported [6, 8, 9] and in some cases the formation of dicobalt dioxygen species has been investigated [9].

We report here the results of a thermodynamic study on the formation of cascade-like species by the cobalt(II) complexes of [30]aneN_{10} in aqueous solution.

Experimental

E.m.f. measurements

All potentiometric measurements were carried out in 0.15 mol dm^{-3} $NaClO_4$ (C. Erba ACS grade) purified as previously reported [10], at 298.15 K. [30]ane$N_{10}\cdot 10HCl$ was obtained by means of the synthetic procedure reported in ref. 2. NaCl, KNO_3,

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$Na_2B_4O_7$ and Na_2HPO_4 (Suprapur grade) were purchased from Merck. Cobalt(II) chloride stock solution was prepared in doubly distilled water and the concentration of the metal ion was determined by standard gravimetric methods. The potentiometric titrations were carried out by using equipment and methods that have already been described [11]. NaOH and HCl O_2/CO_2-free solutions used in the titrations were prepared and stored in an argon atmosphere by adapting the procedure reported in ref. 12. All solutions used were exhaustively deaerated by an argon flow and kept under the same atmosphere during the measurements. For the mixed-ligand system Co^{2+}/[30]aneN_{10}/PO_4^{3-}, in order to reach the equilibrium in the complex formation reactions, several minutes were allowed to elapse between each e.m.f. reading. Moreover, several measurements were made both in formation and in dissociation (from acidic to alkaline solution and vice versa) in order to test for reversibility of the reactions.

Anaerobic complexation of Co^{2+} by [30]aneN_{10} had already been studied [3] and it has been further considered here in the presence of a large excess of the ligand (up to $R=[Co^{2+}]/[L]=0.2$) by means of the procedure already reported [3]. The logarithm of the equilibrium constants for the formation of the observed mononuclear complexes in 0.15 mol dm^{-3} $NaClO_4$ at 298.15 K are: $\log K=29.88(8)$ for $Co^{2+}+L+2H^+=CoH_2L^{4+}$ and $\log K=36.87(6)$ for $Co^{2+}+L+3H^+=CoH_3L^{5+}$; values in parentheses are standard deviation on the last significant figure.

All potentiometric data were treated by means of the computer program SUPERQUAD [14] to obtain the stability constants here reported.

Treatment of e.m.f. data

The formation of mixed-ligand complexes was observed only in the presence of phosphate. For this system, Co^{2+}/[30]aneN_{10}/PO_4^{3-}, four titrations were performed and the relevant e.m.f. data were processed by means of the same computer program [13] to calculate the equilibrium constants (Table 1). The protonation constants, used in the calculations, of [30]aneN_{10} are from ref. 2 and those of PO_4^{3-} from ref. 14, which also reports the equilibrium constants for the interaction of phosphate with [30]aneN_{10}. The equilibrium constants for the formation of dicobalt(II) complexes of [30]aneN_{10} came from ref. 3, while those for the mononuclear ones are reported above. Complexation of cobalt(II) by phosphate, under the experimental conditions here employed, has also been considered*. In a first trial of calculation the values of the equilibrium constants, previously determined, for the known species were fixed and only those for the equilibria involving [30]aneN_{10}/PO_4^{3-} cobalt(II) complexes were refined. This procedure gave a set of values for the formation constants of the species $[Co_2H([30]aneN_{10})PO_4]^{2+}$, $[Co_2H_2([30]aneN_{10})PO_4]^{3+}$, $[Co_2H_3([30]aneN_{10})PO_4]^{4+}$, $[CoH_2([30]aneN_{10})PO_4]^{+}$ and $[CoH_4([30]aneN_{10})PO_4]^{3+}$. Subsequently the e.m.f. data of these measurements were merged with those obtained in the absence of phosphate, and the new set of data was used to refine the values of the formation constants of all the cobalt(II) complexes. No significant variations on the values of these constants were found with respect to both the previous values obtained in the absence of phosphate and the new values determined in the presence of phosphate. The last refinements, to calculate the equilibrium constants reported in Table 1, were made, by using only the e.m.f. data obtained in the presence of phosphate.

Results and discussion

Potentiometric studies on the system cobalt(II)/[30]aneN_{10} in the presence of different amounts of chloride, nitrate, perchlorate, borate and phosphate, under anaerobic conditions, revealed that only phosphate acts as secondary ligand, giving rise to the formation of both mono- and binuclear cobalt(II) complexes. The stability constants of these species are presented in Table 1. Figures 1 and 2 show the distribution of the complexed species formed as a function of pH in the mixed-ligand system, calculated for solutions containing 1×10^{-3} mol dm^{-3} [30]aneN_{10}, 5×10^{-2} mol dm^{-3} phosphate and 2×10^{-3} mol dm^{-3} (Fig. 1) or 2×10^{-4} mol dm^{-3} (Fig. 2) cobalt(II). As can be seen from Fig. 1, for 2:1 Co^{2+}:[30]aneN_{10} molar ratios dicobalt(II) cascade complexes prevail in the pH range 5.5–10.5, while at higher pHs $[Co_2([30]aneN_{10})OH]^{3+}$

TABLE 1. Logarithms of the stability constants of the mixed-ligand complexes formed in the system $Co^{2+}/L/PO_4^{3-}$ (L = [30]aneN_{10}) in 0.15 mol dm^{-3} $NaClO_4$ at 298.15 K

Reaction	log *K*
$2Co^{2+}+L+PO_4^{3-}+H^+$	35.43(7)[a]
$2Co^{2+}+L+PO_4^{3-}+2H^+$	43.98(3)
$2Co^{2+}+L+PO_4^{3-}+3H^+$	49.96(3)
$Co^{2+}+L+PO_4^{3-}+2H^+$	35.22(9)
$Co^{2+}+L+PO_4^{3-}+4H^+$	51.52(9)
$Co^{2+}+CoH_2LPO_4^{+}$	8.8
$Co_2L^{4+}+HPO_4^{2-}$	2.1
$[Co_2L(HPO_4)]^{2+}+H^+$	8.5
$[Co_2HL(HPO_4)]^{3+}+H^+$	6.0

[a] Values in parentheses are standard deviations in the last significant figure.

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*The stability constant for the equilibrium $Co^{2+}+PO_4^{3-}+H^+=CoHPO_4$ ($\log K=13.70$) has been determined by potentiometric titration in 0.15 mol dm^{-3} $NaClO_4$ at 298.15 K.

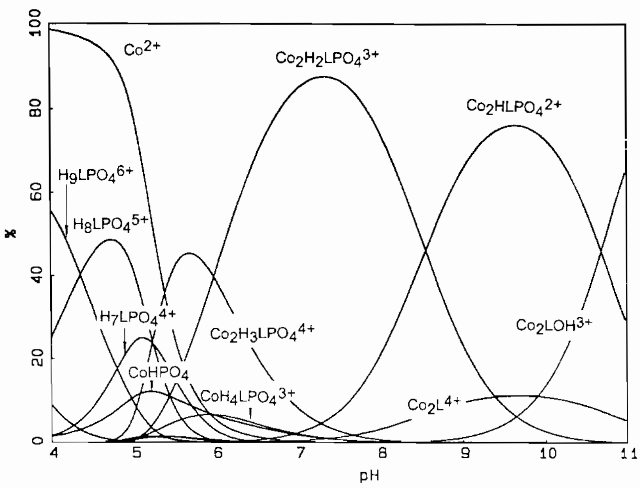

Fig. 1. Calculated distribution of the complexed species formed as a function of pH in the system Co^{2+}/[30]aneN_{10} (L)/phosphate. Co^{2+} 2×10^{-3} mol dm^{-3}, [30]aneN_{10} 1×10^{-3} mol dm^{-3}, phosphate 5×10^{-2} mol dm^{-3}.

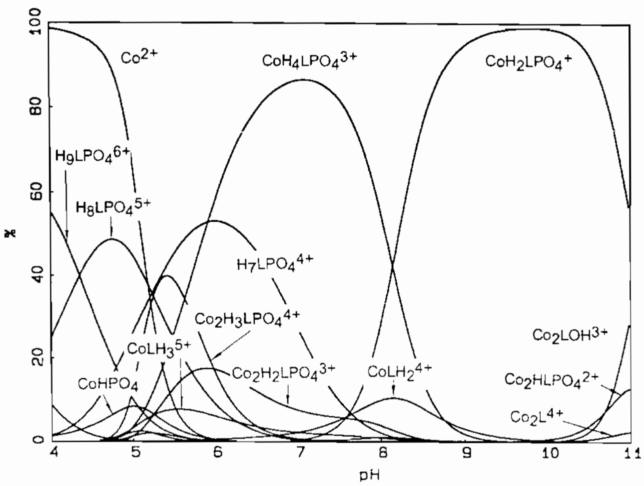

Fig. 2. Calculated distribution of the complexed species formed as a function of pH in the system Co^{2+}/[30]aneN_{10} (L)/phosphate. Co^{2+} 2×10^{-4} mol dm^{-3}, [30]aneN_{10} 1×10^{-3} mol dm^{-3}, phosphate 5×10^{-2} mol dm^{-3}.

is the major species. Under these experimental conditions only a small amount of the mononuclear species $[CoH_4([30]aneN_{10})PO_4]^{3+}$ is formed around pH 6. On the contrary, in the presence of a large excess of [30]aneN_{10} (Fig. 2) mononuclear cascade complexes are the prevailing species in solution.

In more acidic solutions the complexes bear severe protonation with release of Co^{2+} and formation of phosphate adducts of the polyammonium cations (Figs. 1 and 2).

If the stepwise protonation constants of $PO_4{}^{3-}$ are considered ($\log K_1 = 11.54$, $\log K_2 = 6.72$, $\log K_3 = 2.11$) [15] we note that the species $HPO_4{}^{2-}$ largely predominates in solution between pH 7 and 11. Therefore it seems reasonable that, at least in this pH range, $HPO_4{}^{2-}$ is the species involved in the coordination to the cobalt(II) macrocyclic complexes. Consequently, the mono- and diprotonated dicobalt(II) cascade complexes could be formulated as $[Co_2([30]aneN_{10})HPO_4]^{2+}$ and $[Co_2(H[30]aneN_{10})HPO_4]^{3+}$, respectively. Furthermore the value of the equilibrium constant for the binding of a proton to $[Co_2([30]aneN_{10})HPO_4]^{2+}$ ($\log K = 8.24$, Table 1) is markedly higher than the second protonation constant of $PO_4{}^{3-}$ suggesting again the protonation of the macrocycle and the formation of the species $[Co_2(H[30]aneN_{10})HPO_4]^{3+}$. At lower pHs $[Co_2(H[30]aneN_{10})HPO_4]^{3+}$ produces, by addition of a further proton, the triprotonated dicobalt(II) complex (Fig. 1). Hypotheses about the location of the third proton in this species are not conclusive. The predominant species formed at these pH values (pH ~ 6) in the absence of phosphate is $[Co_2(H_2[30]aneN_{10})]^{6+}$ which could interact with $HPO_4{}^{2-}$ to yield the triprotonated cascade complex. On the other hand, at the same pHs phosphate is mainly present in the $H_2PO_4{}^{-}$ form. Furthermore the equilibrium constant ($\log K = 5.84$, Table 1) for the addition of a proton to $[Co_2(H[30]aneN_{10})HPO_4]^{3+}$ is fairly similar to both the second protonation constant of $HPO_4{}^{2-}$ (ref. 14) and the protonation constant of the dicobalt(II) macrocyclic complex [3].

By means of similar considerations the diprotonated complex $[CoH_2([30]aneN_{10})PO_4]^{+}$ could be formulated as $[Co(H[30]aneN_{10})HPO_4]^{+}$. On the other hand the location of the protons in the tetraprotonated mononuclear complex cannot be inferred, at least one proton being bound to the phosphate group.

As far as the involvement of phosphate in the coordination to Co^{2+} is considered, we can note that [30]aneN_{10}, and even more its protonated forms, do not present enough donor atoms to complete the first coordination sphere of two Co^{2+} ions, and consequently, in binuclear complexes, phosphate should be directly bound to the metal ions. Furthermore, the stability constants for the binding of $HPO_4{}^{2-}$ to $[Co_2([30]aneN_{10})]^{4+}$ ($\log K = 2.1$, Table 1) is quite similar to that for the coordination of $HPO_4{}^{2-}$ to the free metal ion ($\log K = 2.16$ under our experimental conditions) suggesting coordination to a single metal center (proposed structure in Fig. 3). When these complexes involve protonated forms of the ligands the mixed-ligand species could be over-stabilized by hydrogen bonds between the anion and polyammonium groups of the macrocycle. In the case of the mononuclear complexes, even in the protonated species, an exceedingly large number of nitrogen atoms is available for coordination to the Co^{2+} ion and then it seems likely that $PO_4{}^{3-}$ and/or $HPO_4{}^{2-}$ act, more or less directly, as second sphere ligands (proposed structure in Fig. 4).

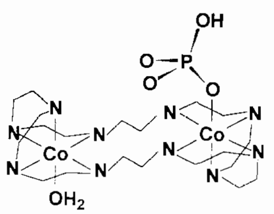

Fig. 3. Proposed structure for binuclear Co^{2+}/[30]aneN_{10}/phosphate cascade complexes.

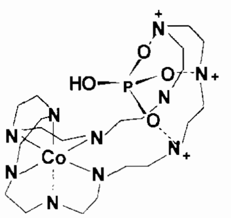

Fig. 4. Proposed structure for mononuclear Co^{2+}/[30]aneN_{10}/phosphate second sphere complexes.

Conclusions

Characterization of the species formed in the system Co(II)/[30]aneN_{10} in the presence and absence of phosphate, in a large range of metal to ligand molar ratios, has been accomplished by potentiometric study. The formation of highly stable Co(II)/[30]aneN_{10}/phosphate cascade species is the main feature of this system. In these complexes phosphate can act both as a secondary ligand, directly bound to cobalt(II), or as a second sphere ligand. In any case the over-stabilization produced by phosphate coordination should protect the metal ion from further binding molecules. Due to the variety of the species formed, and to their characteristics, O_2 activation in such a system has been an intriguing problem [15]. The results here obtained under anaerobic conditions have made possible the selection of suitable conditions for the study of dioxygen uptake.

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References

1 M. Micheloni, P. Paoletti and A. Bianchi, *Inorg. Chem., 24* (1985) 3702; A. Bianchi, S. Mangani, M. Micheloni, V. Nanini, P. Orioli, P. Paoletti and B. Seghi, *Inorg. Chem., 23* (1984) 1182; A. Bencini, A. Bianchi, E. Garcia-España, M. Giusti, M. Micheloni and P. Paoletti, *Inorg. Chem., 26* (1987) 681; A. Bencini, A. Bianchi, E. Garcia-España, M. Micheloni and P. Paoletti, *Inorg. Chem., 27* (1988) 176; A. Bencini, A. Bianchi, E. Garcia-España, S. Mangani, M. Micheloni, P. Orioli and P. Paoletti, *Inorg. Chem., 27* (1988) 1104; A. Bencini, A. Bianchi, P. Dapporto, E. Garcia-España, M. Micheloni and P. Paoletti, *Inorg. Chem., 28* (1989) 1188; A. Bencini, A. Bianchi, M. Castelló, M. Di Vaira, J. Faus, E. Garcia-España, M. Micheloni and P. Paoletti, *Inorg. Chem., 28* (1989) 347; A. Bencini, A. Bianchi, M. Castelló, P. Dapporto, J. Faus, E. Garcia-España, M. Micheloni, P. Paoletti and P. Paoli, *Inorg. Chem., 28* (1989) 3175; A. Bencini, A. Bianchi, P. Dapporto, E. Garcia-España, V. Marcelino. M. Micheloni, P. Paoletti and P. Paoli, *Inorg. Chem., 29* (1990) 1716; A. Bencini, A. Bianchi, P. Dapporto, E. Garcia-España, M. Micheloni, P. Paoletti and P. Paoli, *J. Chem. Soc., Chem. Commun.*, (1990) 1382.

2 A. Bencini, A. Bianchi, E. Garcia-España, M. Giusti, S. Mangani, M. Micheloni, P. Orioli and P. Paoletti, *Inorg. Chem., 26* (1987) 1243.

3 A. Bencini, A. Bianchi, E. Garcia-España, M. Micheloni and P. Paoletti, *Inorg. Chem., 28* (1989) 2480.

4 A. Bianchi, M. Micheloni and P. Paoletti, *Coord. Chem. Rev., 110* (1991) 17; A. Bencini, A. Bianchi, P. Paoletti and P. Paoli, *Coord. Chem. Rev., 120* (1992) 51.

5 E. Garcia-España, M. Micheloni, P. Paoletti and A. Bianchi, *Inorg. Chim. Acta, 102* (1985) L9; A. Bianchi, E. Garcia-España, S. Mangani, M. Micheloni, P. Orioli and P. Paoletti, *J. Chem. Soc., Chem. Commun.*, (1987) 729; A. Bencini, A. Bianchi, E. Garcia-España, M. Giusti, S. Mangani, M. Micheloni, P. Orioli and P. Paoletti, *Inorg. Chem., 26* (1987) 3902; A. Bencini, A. Bianchi, P. Dapporto, E. Garcia-España, M. Micheloni, P. Paoletti and P. Paoli, *J. Chem. Soc., Chem. Commun.*, (1990) 753; J. Aragó, A. Bencini, A. Bianchi, A. Domenech and E. Garcia-España, *J. Chem. Soc., Dalton Trans.*, (1992) 319.

6 J.-M. Lehn, *Pure Appl. Chem., 52* (1980) 2441.

7 S. Cabani, N. Ceccanti and M. R. Tinè, *Pure Appl. Chem., 63* (1991) 1455.

8 P. K. Coughlin, J. C. Dewan, S. J. Lippard, E. Watanabe and J.-M. Lehn, *J. Am. Chem. Soc., 101* (1979) 265; P. K. Coughlin, S. J. Lippard, A. E. Martin and J. E. Bulkowski, *J. Am. Chem. Soc., 102* (1980) 7617; Y. Agnus, R. Louis, J.-P. Gisselbrecht and R. Weiss, *J. Am. Chem. Soc., 106* (1984) 93.

9 R. J. Motekaitis, A. E. Martell, J.-P. Lecomte and J.-M. Lehn, *Inorg. Chem., 22* (1983) 609; A. E. Martell and R. Motekaitis, *J. Am. Chem. Soc., 110* (1988) 8059; B. Szpoganicz, R. Motekaitis and A. E. Martell, *Inorg. Chem., 29* (1990) 1467; R. Motekaitis and A. E. Martell, *Inorg. Chem., 30* (1991) 695.

10 M. Micheloni, P. M. May and D. R. Williams, *J. Inorg. Nucl. Chem., 40* (1978) 1209.

11 A. Bianchi, L. Bologni, P. Dapporto, M. Micheloni and P. Paoletti, *Inorg. Chem., 23* (1984) 1201.

12 M. Micheloni, A. Sabatini and A. Vacca, *Inorg. Chim. Acta, 25* (1977) 41.

13 P. Gans, A. Sabatini and A. Vacca, *J. Chem. Soc., Dalton Trans.*, (1985) 1195.

14 A. Bencini, A. Bianchi, E. Garcia-España, E. C. Scott, L. Morales, B. Wang, M. P. Mertes, K. B. Mertes and P. Paoletti, *Bioorg. Chem., 20* (1992) 8.

15 S. Cabani, N. Ceccanti, M. R. Tinè, A. Bencini, A. Bianchi and P. Paoletti, *J. Chem. Soc., Dalton Trans.*, in press.