Inorganica Chimica Acta, 204 (1993) 221-225

Thermodynamic study of the interaction of long open-chain polyazaalkanes with cobalt(II) and nickel(II) ions

Andrea Bencini, Antonio Bianchi*, Vieri Fusi, Piero Paoletti*, Barbara Valtancoli
Department of Chemistry, University of Florence, via Maragliano 75/77, 50144 Florence (Italy)

Antonio Andres, Juan Aragó and Enrique Garcia-España*
Department of Inorganic Chemistry, University of Valencia, C/Dr. Moliner 50, 46100 Burjassot (Valencia) (Spain)

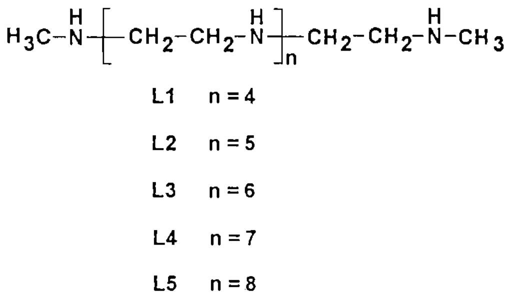
(Received July 2, 1992; revised September 28, 1992)

Abstract

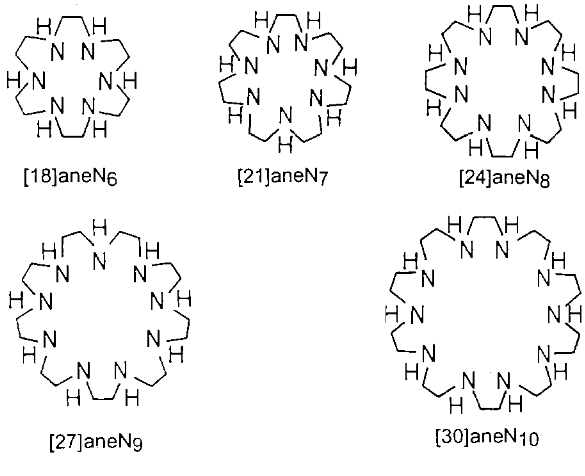
Complexation equilibria between the open-chain terminally methylated polyamines 1,14-bis(methylamino)-3,6,9,12-tetraazatetradecane (L1), 1,17-bis(methylamino)-3,6,9,12,15-pentaazaheptadecane (L2), 1,20-bis(methylamino)-3,6,9,12,15,18-hexaazaicosane (L3) and 1,23-bis(methylamino)-3,6,9,12,15,18,21-heptaazatricosane (L4) with Co^{2+} and Ni^{2+} have been studied by means of potentiometric and spectrophotometric methods in 0.15 mol dm^{-3} $NaClO_4$ aqueous solution at 298.15 K. The stability constants for the complexes formed have been determined from e.m.f. data. All these ligands form mononuclear ML^{2+} complexes of similar stability with Co^{2+} and Ni^{2+}. Binuclear Co_2L4^{4+}, Ni_2L3^{4+} and Ni_2L4^{4+} are also formed. The equilibrium constants of the complexes of L1–L4, which are the open-chain counterparts of the macrocyclic ligands [3k]aneN_k (k = 6–9), reveal that only [18]aneN_6 with Co^{2+} and Ni^{2+}, and [21]aneN_7 with Co^{2+} present enhanced stability (macrocyclic effect) with respect to L1–L4. However this effect has not been observed for binuclear complexes.

Introduction

Recently we have reported on the synthesis [1] and the coordinating ability toward Cu^{2+} [1], Zn^{2+} and Cd^{2+} [2] ions of the open-chain terminally methylated polyamines 1,14-bis(methylamino)-3,6,9,12-tetraazatetradecane (L1), 1,17-bis(methylamino)-3,6,9,12,15-pentaazaheptadecane (L2), 1,20-bis(methylamino)-3,6,9,12,15,18-hexaazaicosane (L3), 1,23-bis(methylamino)-3,6,9,12,15,18,21-heptaazatricosane (L4) and 1,26-bis(methylamino)-3,6,9,12,15,18,21,24-octaazahexacosane (L5) (Scheme 1), which can be considered appropriate open-chain counterparts [1] of the macrocyclic ligands [3k]aneN_k (k = 6–10) [3] (Scheme 2). In these papers it was shown that the metal coordination chemistry of these ligands is essentially the same as that of their cyclic [3k]aneN_k counterparts. However, it was noticed that for each one of the studied metal ions, there is a determined ligand from which the stability of the mononuclear complexes of the open-chain ligands starts being higher than that of the


$H_3C-\overset{H}{N}-\left[CH_2-CH_2-\overset{H}{N}\right]_n-CH_2-CH_2-\overset{H}{N}-CH_3$

Scheme 1.



Scheme 2.

---

*Authors to whom correspondence should be addressed.

0020-1693/93/$6.00

macrocyclic ones. This fact was related to the relative ligand–metal sizes as well as to the preferred coordination geometry of the different metals studied. The binuclear complexes of the open-chain ligands were, in all cases, more stable than those of their cyclic counterparts. Therefore it was concluded that for these ligands with a high degree of flexibility a 'macrocyclic effect' [4] was no longer present.

To get further insight into these coordination tendencies, we have extended the study to the interaction of L1–L4 with the metal ions Co^{2+} and Ni^{2+}.

Experimental

Reagents

The synthesis of ligands L1–L4 was carried out as previously reported [1]. Stock solutions of cobalt(II) and nickel(II) chlorides were prepared in doubly distilled water and the concentration of the metal ions determined by standard gravimetric methods. CO_2-free NaOH and HCl solutions used in the titrations were prepared as described in ref. 5. $NaClO_4$ (C.Erba ACS Grade) was purified accordingly to a previously reported procedure [6].

E.m.f. measurements

The potentiometric titrations were carried out in 0.15 mol dm^{-3} $NaClO_4$ by using equipment that has already been described [7]. The reference electrode was an Ag/AgCl electrode in saturated KCl solution. The glass electrode was calibrated as a hydrogen concentration probe by titration of known amounts of HCl with CO_2-free NaOH solutions and determining the equivalent point by the Gran's method [8], which gives the standard potential $E°$, and the ionic product of water K_w. All solutions used were exhaustively deaerated by an argon flow and kept under the same atmosphere during the measurements. At least three titration curves for each system investigated were used. In order to reach the equilibrium in these complex formation reactions, several minutes were allowed between each e.m.f. reading. Moreover, several measurements were made both in formation and in dissociation (from acid to alkaline solutions and vice versa) in order to test for reversibility of the reactions. The computer program SUPERQUAD [9] was used to process e.m.f. data and calculate the stability constants. The values of the protonation constants of L1–L4 used in the calculation have already been reported [1].

Spectrophotometric measurements

The electronic spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer equipped with 1-cm cells thermostated at 298 K. Solutions of the Ni^{2+} complexes were prepared by mixing the appropriate quantities of Ni^{2+} stock solution, L1–L4 hydrochlorides and standardized NaOH solution, calculated by means of the equilibrium data here reported.

Results and discussion

The logarithms of the stability constants for the complexes of L1–L4 with Co^{2+} and Ni^{2+}, determined in 0.15 mol dm^{-3} $NaClO_4$ solution at 298.15 K, are reported in Tables 1 and 2. All the ligands form mononuclear ML^{2+} species with both metal ions. The largest ligands form also binuclear M_2L^{4+} species with Co^{2+} (L4) and Ni^{2+} (L3, L4).

The variation of the stability constants of the mononuclear CoL^{2+} and NiL^{2+} species does not present any clear tendency along the series (Fig. 1), according to the trend already observed for Cu^{2+} [1], Zn^{2+} and Cd^{2+} [2]. Both Co^{2+} and Ni^{2+} complexes present a high tendency to form protonated species with L1–L4 (Tables 1 and 2). The number of protonated species formed increases with the number of nitrogen atoms of the ligands. The analysis of the protonation constants of the complexes is often of interest to infer coordination numbers. The equilibrium constants for the first protonation of $CoL1^{2+}$ and $NiL1^{2+}$ (log $K=5.87$ and 5.93, respectively) are much lower than that for the third protonation of the free ligand (log $K=8.88$ [1]) suggesting that the protonation takes place on an already coordinated nitrogen atom. Therefore, all six donor atoms of L1 would participate in the coordination to both metal ions. However, the first protonation constants for the complexes of both metal ions with the remaining ligands (L2–L4) [1] are much higher, indicating the presence of, at least, one non-coordinated nitrogen atom in all of them. All these data, together with the almost steady value of the formation constants for the ML^{2+} species along the series and the features of the electronic spectra for the Ni^{2+} complexes, suggest that all the ligands here considered involve, at least in the formation of unprotonated mononuclear complexes, six of their donor atoms to complete the coordination sphere of Ni^{2+} and Co^{2+}.

The electronic spectral data for the nickel(II) complexes of L1–L4 in solution, obtained in the range 300–1200 nm, are reported in Table 3. All the complexes here studied present three-band electronic spectra typical for octahedral high-spin nickel(II) chromophores. The spectral bands for the $NiHL1^{3+}$ species are significantly shifted towards low energies with respect to the unprotonated $NiL1^{2+}$ complex. This reduced ligand field interaction accords with the detachment of one

TABLE 1. Logarithms of the stability constants for the formation of Co^{2+} complexes of ligands L1–L4 in 0.15 mol dm^{-3} $NaClO_4$ aqueous solution at 298.15 K

Reaction	log *K*			
	L1	L2	L3	L4
$Co^a + L = CoL$	14.756(7)[b]	13.99(4)	14.05(3)	15.68(5)
$Co + L + H = CoHL$	20.63(1)	22.39(2)	23.84(2)	25.08(3)
$Co + L + 2H = CoH_2L$	26.21(3)	27.60(3)	30.45(1)	32.15(4)
$Co + L + 3H = CoH_3L$			35.92(3)	37.99(2)
$CoH_3L + H = CoH_4L$				
$CoL + H = CoHL$	5.87	8.40	9.79	9.40
$CoHL + H = CoH_2L$	5.58	5.21	6.61	7.07
$CoH_2L + H = CoH_3L$			5.47	5.84
$2Co + L = Co_2L$				21.69(3)
$2Co + L + H_2O = Co_2L(OH) + H$				13.31(7)
$2Co + L + 2H_2O = Co_2L(OH)_2 + 2H$				3.80(6)
$Co_2L + OH = Co_2L(OH)$				5.35
$Co_2L(OH) + OH = Co_2L(OH)_2$				4.22

[a] Charges have been omitted. [b] Values in parentheses are standard deviations in the last significant figure.

TABLE 2. Logarithms of the stability constants for the formation of Ni^{2+} complexes of ligands L1–L4 in 0.15 mol dm^{-3} $NaClO_4$ aqueous solution at 298.15 K

Reaction	log *K*			
	L1	L2	L3	L4
$Ni^a + L = NiL$	18.24(1)[b]	16.64(4)	17.47(2)	17.08(4)
$Ni + L + H = NiLH$	24.17(1)	25.55(3)	27.80(1)	27.63(3)
$Ni + L + 2H = NiLH_2$	28.94(2)	31.35(2)	34.49(1)	35.81(2)
$Ni + L + 3H = NiLH_3$			39.38(1)	41.34(1)
$Ni + L + 4H = NiLH_4$			43.38(1)	45.78(2)
$NiL + H = NiHL$	5.93	8.91	10.33	9.86
$NiHL + H = NiH_2L$	4.77	5.80	6.69	8.18
$NiH_2L + H = NiH_3L$			4.89	5.53
$NiH_3L + H = NiH_4L$			4.00	4.44
$2Ni + L = Ni_2L$			24.87(1)	27.20(3)
$2Ni + L + H = Ni_2HL$			31.05(3)	33.23(5)
$Ni_2L + H = Ni_2HL$			6.18	6.03

[a] Charges have been omitted. [b] Values in parentheses are standard deviations in the last significant figure.

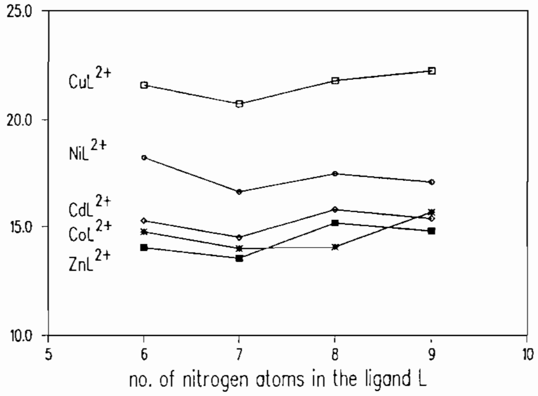


Fig. 1. Stability of L1–L4 complexes as a function of the number of nitrogen atoms in the ligands. log*K* values refer to 0.15 mol dm^{-3} $NaClO_4$ aqueous solution at 298.15 K.

TABLE 3. Electronic spectral data for nickel(II) complexes of L1–L4 ligands

Compound	λ_{max} $(\epsilon)^a$		
$(NiL1)^{2+}$	890 (18.9)	544 (11.1)	354 (18.7)
$(NiHL1)^{3+}$	939 (15)	570 (9)	357 (16)
$(NiL2)^{2+}$	898 (16.8)	544 (9.3)	357 (16.5)
$(NiHL2)^{3+}$	898 (17)	548 (9)	357 (16)
$(Ni_2L3)^{4+}$	940 (15.7)	577 (11.8)	366 (18.1)
$(Ni_2L4)^{4+}$	927 (15.0)	573 (9.9)	362 (15.6)

[a] λ_{max} given in nm, ϵ in $dm^3\ mol^{-1}\ cm^{-1}$. Molar extinction coefficients are given for a single nickel(II) ion.

coordinated nitrogen atom of the hexaaza ligand occurring upon protonation of $NiL1^{2+}$. On the other hand, protonation of the complex $NiL2^{2+}$, in which at least one donor atom of the heptaaza ligand L2 is not coordinated, does not affect the spectral properties of the complex, thus indicating that protonation does not cause significant modification in the ligand field of the Ni^{2+} ion.

As far as the relative stability of the complexes of each one of the L1–L4 ligands is considered, we observe that despite the different number of nitrogen atoms involved in the coordination to the metal ions (5 for Cu^{2+} and Zn^{2+}, 6 for Cd^{2+}, Ni^{2+} and Co^{2+}), an Irving–Williams stability order is followed.

As already observed the longest ligands of the present series are able to bind a second metal ion forming stable binuclear species (Tables 1 and 2). The stability of the species Ni_2L^{4+} increases with the number of nitrogen atoms in the ligands (L3, L4) in accord with the increasing number of nitrogens involved in the binding to the two Ni^{2+} ions. In the same way the spectral bands for the dinickel(II) complexes experience a high-energy shift (Table 3) in accord with the stronger overall ligand field interaction of L4 with respect to L3.

Also the stability constants of the M_2L^{4+} ($M = Co^{2+}$, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}) binuclear complexes studied so far follow the Irving–Williams order.

The dinickel(II) complexes of L3 and L4 bear monoprotonation (Table 1); the resulting monoprotonated binuclear species are still characterized by high thermodynamic stability. On the other hand no protonated species of the binuclear Co_2L4^{4+} complex have been observed.

It is worth noting that Co_2L4^{4+} gives rise, in alkaline solutions, to the formation of very stable mono- and bishydroxo species. The values of the equilibrium constants (Table 1) for the addition of the first and the second OH^- anion to Co_2L4^{4+} (log $K = 5.35$ and 4.22 respectively) compare well with those already found for the addition of OH^- to the corresponding macrocyclic complex $Co_2([27]aneN_9)^{4+}$ (log $K =$ 4.76[3i]).

As far as the macrocyclic effect is considered the metathetical reaction $[M_nL_{cyclic}] + L_{open\ chain} = [M_nL_{open\ chain}] + L_{cyclic}$ ($M = Co^{2+}$, Ni^{2+}; $n = 1,2$) has to be analyzed. When the macrocyclic effect is operating this reaction presents negative log K values. The stability constants for the Co^{2+} and Ni^{2+} complexes of $[3k]aneN_k$ ($k = 6–9$) are reported in Table 4. By comparison with the corresponding stability constants (Tables 1 and 2) found for the analogous complexes with the open-chain L1–L4 ligands we find that the macrocyclic effect is present only for the cobalt(II) mononuclear complexes of the hexa- and heptaaza ligands and for the nickel(II) mononuclear complexes of the hexaaza ligands.

TABLE 4. Logarithms of the stability constants for the formation of some Ni^{2+} and Co^{2+} complexes of the large polyazacycloalkanes $[3k]aneN_k$ ($k = 6–9$) in 0.15 mol dm^{-3} $NaClO_4$ aqueous solution at 298.15 K

Reaction	log K			
	$[18]aneN_6$	$[21]aneN_7$	$[24]aneN_8$	$[27]aneN_9$
$Co^{a} + L = CoL$	18.9^{b}	14.69^{c}	13.20^{c}	11.84^{c}
$Ni + L = NiL$	19.6^{b}	16.56^{d}	13.94^{d}	
$2Co + L = Co_2L$				18.85^{c}
$2Ni + L = Ni_2L$			23.30^{d}	26.24^{d}

[a] Charges have been omitted. [b] Taken from ref. 10. [c] Taken from ref. 3i. [d] Taken from ref. 3l.

In conclusion only the smallest macrocyclic ligand $[18]aneN_6$ forms, with all the studied metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+}), mononuclear complexes presenting an enhanced stability with respect to those of the open-chain counterparts. Two further cases in which the macrocyclic effect is observed are presented by the Co^{2+} and Cd^{2+} mononuclear complexes of $[21]aneN_7$. On the other hand this effect has not been observed for binuclear species.

Acknowledgements

Financial support by the Italian Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST) and by the Spanish Comisión de Ciencia y Tecnologia (Proyecto PB90-0567) is gratefully acknowledged. We are also indebted to Dr S. Seniori Costantini, Dr P. Mariani and Mr M. Fontanelli for technical assistance.

References

1 J. Aragó, A. Bencini, A. Bianchi, E. Garcia-España, M. Micheloni, P. Paoletti, J. A. Ramirez and P. Paoli, *Inorg. Chem., 30* (1991) 1843.

2 J. Aragó, A. Bencini, A. Bianchi, E. Garcia-España, M. Micheloni, P. Paoletti, J. A. Ramirez and A. Rodriguez, *J. Chem. Soc., Dalton Trans.,* (1991) 3077.

3 (a) M. Micheloni, P. Paoletti and A. Bianchi, *Inorg. Chem., 24* (1985) 3702; (b) A. Bianchi, S. Mangani, M. Micheloni, V. Nanini, P. Orioli, P. Paoletti and B. Seghi, *Inorg. Chem., 23* (1984) 1182; (c) A. Bencini, A. Bianchi, E. Garcia-España, M. Giusti, M. Micheloni and P. Paoletti, *Inorg. Chem., 26* (1987) 681; (d) A. Bencini, A. Bianchi, E. Garcia-España, M. Giusti, S. Mangani, M. Micheloni, P. Orioli and P. Paoletti, *Inorg. Chem., 26* (1987) 1243; (e) A. Bencini, A. Bianchi, E. Garcia-España, M. Micheloni and P. Paoletti, *Inorg. Chem., 27* (1988) 176; (f) A. Bencini, A. Bianchi, E. Garcia-España, S. Mangani, M. Micheloni, P. Orioli and P. Paoletti, *Inorg. Chem., 27* (1988) 1104; (g) A. Bencini, A. Bianchi, P. Dapporto, E. Garcia-España, M. Micheloni and P. Paoletti, *Inorg. Chem., 28* (1989) 1188; (h) A. Bencini, A. Bianchi, M. Castelló, M. Di Vaira, J. Faus, E. Garcia-España, M. Micheloni and P. Paoletti, *Inorg. Chem., 28* (1989) 347; (i) A. Bencini, A. Bianchi, E. Garcia-España, M. Micheloni and P. Paoletti, *Inorg. Chem., 28* (1989) 2480; (1) 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.

4 D. K. Cabbines and D. W. Margerum, *J. Am. Chem. Soc., 91* (1969) 6540; F. P. Hinz and D. W. Margeum, *J. Chem. Soc., Dalton Trans., 13* (1976) 2941.

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

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

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

8 G. Gran, *Analyst (London), 77* (1952) 661; F. J. Rossotti and H. Rossotti, *J. Chem. Educ., 42* (1965) 375.

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

10 M. Kodama, E. Kimura and S. Yamaguchi, *J. Chem. Soc., Dalton Trans.,* (1980) 2536.