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Thermodynamic and structural aspects of transition metal compounds. Polynuclear complexes of aza-macrocycles

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CONTENTS

A. INTRODUCTION

Polynuclear macrocyclic complexes of transition metal ions represent a helpful tool in the study of the mechanisms governing metal–metal interactions and substrate activation by metal centres [1–7]. The recognition that the accomplishment of several biological functions needs polynuclear metal centres [8–18] has given a strong impulse to the study of multi-site macrocyclic complexes as model systems [8–13,18,19].

This review collects significant examples of equilibria in aqueous solution in which polynuclear transition metal complexes of macrocyclic ligands are formed and analyses the formation of these complexes from the thermodynamic and structural points of view. When possible, data for successive complexation steps will be examined and discussed. The ligands considered here will be aza-macrocycles, and also some macrocycles which behave as aza-ligands, but contain some different donor atoms in addition to nitrogen. In the last case, the non-nitrogen donor atoms, due to their nature and/or position in the ligand molecule, coordinate poorly to transition metal ions. The first time that a ligand is encountered in the text, we shall use the IUPAC designation together with a numbered structural formula and, when available, the usual simplified notation.

Three main synthetic strategies to obtain polynuclear macrocyclic complexes have been followed: (i) synthesis of macrocycles or macrobicycles able to incorporate

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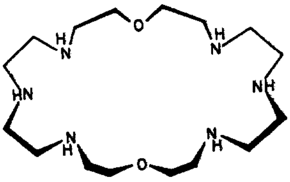
several metal ions, (ii) synthesis of bis(macrocycles), and (iii) use of chelating agents bridging two complexed macrocyclic units. This review will be organised according to this subdivision.

B. MACROCYCLES AND MACROBICYCLES ABLE TO INCORPORATE SEVERAL METAL IONS

Both aza-ligands in which the donor atoms form separate subunits within the same macrocyclic ring and macrocycles with homogeneous distribution of nitrogen donor atoms have been considered to study the coordination equilibria involving more than one transition metal ion. A typical example of the former kind of ligand is the hexamine (**1**) bisdien (1,4,7,13,16,19-hexaaza-10,22-dioxacyclotetracosane),



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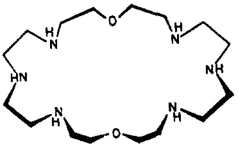
synthesized by Lehn et al. [20,21], in which two diethylentriamine units are separated by two five-atom bridges. The ether oxygen atoms of these bridges have a weak tendency to coordinate to first-row transition metal ions and, as a matter of fact, bisdien behaves as a hexaaza-ligand toward Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} [22]. In the case of Co^{2+}, Cu^{2+} and Zn^{2+}, binuclear complexed species have been observed. The equilibrium constants for the formation of these species were determined by potentiometric measurements [22] and are reported in Table 1. The binuclear complex $Cu_2(\mathbf{1})^{4+}$ is sufficiently stable to form extensively in solution, while in the case of Co^{2+} and Zn^{2+}, the ability of the ligand to bind a second metal ion is small and for Ni^{2+} only mononuclear complexes have been observed. The formation of bridged mono- and dihydroxo species of $Cu_2(\mathbf{1})^{4+}$ and monohydroxo species of $Zn_2(\mathbf{1})^{4+}$ contributes to further stabilize these binuclear complexes. The ligand is flexible enough [22] to allow four to six nitrogen donor atoms to coordinate to a single metal ion and then form stable mononuclear complexes. On the other hand, bisdien has an insufficient number of nitrogen atoms to fulfil the coordination spheres of two metal ions. As a consequence, the ligand presents a small ability to form binuclear complexes and a high tendency to use auxiliary ligands to stabilize the binuclear species. This situation, in which a primary ligand binds one or more metal ions inducing coordination of secondary species (molecules or ions) has been termed "cascade" coordination [6].

The OH^- anion can act as a secondary ligand both in solution [22], as noted above, and in the solid state [23]. The crystal structure of the $[Cu_2(\mathbf{1})(OH)ClO_4]^{2+}$ cation [23] is reported in Fig. 1. The Cu^{2+} ions present a distorted square-pyramidal geometry with the basal plane positions occupied by the amine nitrogen atoms and the oxygen atom of the μ-hydroxo ion and the apical position by a weakly bound oxygen atom of the bridging ClO_4^- [23]. Other ligands such as ethylendiamine [22], acetate [23], imidazole [24], and N_3^- [21] have been used as auxiliary ligands in the formation of dicopper(II) complexes of bisdien. The crystal structure of an imidazole derivative of $Cu_2(\mathbf{1})^{4+}$ has been reported [24]. In this structure (Fig. 2), both imidazole and imidazolate ligands are present. The geometry around the copper atoms is best described as distorted trigonal bipyramidal with the apical positions occupied by N11 of the bridging imidazolate and N4 of the macrocycle. The crystal structure of the binuclear complex $Cu_2(\mathbf{1})(N_3)_4$ (Fig. 3) has also been reported [21]. The copper atoms are pentacoordinated by N atoms in a distorted square-pyramidal geometry, the apical position being occupied by a N_3^- ion. None of the N_3^- anions acts as a bridging ligand. The macrocycle adopts a "chair" conformation.

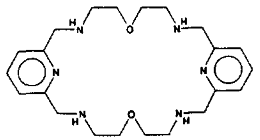
TABLE 1

log K, ΔH^0, and $T\Delta S^0$ values for the formation of polynuclear complexes of macrocyclic azaligands in aqueous solution[a]



1,4,7,10,13,16,19-hexaaza-10,22-dioxacyclotetracosane
bisdien

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
Co(II)	L + 2Co	12.4	pot			25	0.1 KNO_3	22
	CoL + Co	2.7	pot			25	0.1 KNO_3	22
Cu(II)	L + 2Cu	27.30	pot			25	0.1 KNO_3	22
	CuL + Cu	10.84	pot			25	0.1 KNO_3	22
	$Cu_2L + H_2O$	-6.51	pot			25	0.1 KNO_3	22
	$Cu_2LOH + H_2O$	-10.40	pot			25	0.1 KNO_3	22
Zn(II)	L + 2Zn	14.86	pot			25	0.1 KNO_3	22
	ZnL + Zn	4.20	pot			25	0.1 KNO_3	22
	$Zn_2L + H_2O$	>-7	pot			25	0.1 KNO_3	22

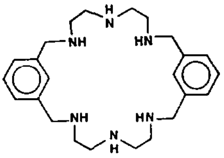


3,9,17,23,29,30-hexaaza-6,20-dioxatricyclo[23.3.1.$1^{11,15}$]triaconta-1(28),11,13,15(30),25,26-hexaene
bisbamp

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
Co(II)	L + 2Co	12.05	pot			25	0.1 KNO_3	28
	CoL + Co	3.00	pot			25	0.1 KNO_3	28
	$Co_2L + H_2O$	-7.90	pot			25	0.1 KNO_3	28

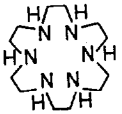
TABLE 1 (*continued*)

Ni(II)	L + 2Ni	14.98	pot			25	0.1 KNO$_3$	28
	NiL + Ni	3.73	pot			25	0.1 KNO$_3$	28
	Ni$_2$L + H$_2$O	-5.11	pot			25	0.1 KNO$_3$	28
Cu(II)	L + 2Cu	24.01	pot			25	0.1 KNO$_3$	28
	CuL + Cu	8.82	pot			25	0.1 KNO$_3$	28
	Cu$_2$L + H$_2$O	-6.51	pot			25	0.1 KNO$_3$	28
	Cu$_2$LOH + H$_2$O	-9.12	pot			25	0.1 KNO$_3$	28
Zn(II)	L + 2Zn	12.69	pot			25	0.1 KNO$_3$	28
	ZnL + Zn	3.80	pot			25	0.1 KNO$_3$	28
	Zn$_2$L + H$_2$O	-7.07	pot			25	0.1 KNO$_3$	28



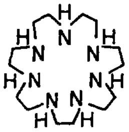
3,6,9,17,20,23-hexaazatricyclo[23.3.1.1^{11,15}]triaconta-1(29),11(30),12,14,25(26),27-hexaene

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
Cu(II)	L + 2Cu	23.47	pot			25	0.1 KNO$_3$	29
	CuL + Cu	9.68	pot			25	0.1 KNO$_3$	29
	Cu$_2$L + H$_2$O	-7.26	pot			25	0.1 KNO$_3$	29
	Cu$_2$LOH + H$_2$O	-8.40	pot			25	0.1 KNO$_3$	29



1,4,7,10,13,16,-hexaazacyclooctadecane
[18]aneN$_6$

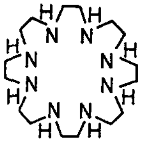
cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
Pd(II)	L + 2Pd + 2Cl	51.8	pot			25	0.5 NaCl	40,42



1,4,7,10,13,16,19-heptaazacycloheneicosane
[21]aneN$_7$

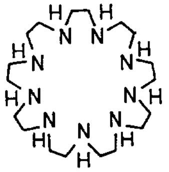
cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
Cu(II)	L + 2Cu	30.49	pot			25	0.15 NaClO$_4$	41
	CuL + Cu	11.01	pot			25	0.15 NaClO$_4$	41
	L + 2Cu + H$_2$O	23.75	pot			25	0.15 NaClO$_4$	41
	Cu$_2$L + OH	7.00	pot			25	0.15 NaClO$_4$	41
Pd(II)	L + 2Pd + Cl	>52	pot			25	0.5 NaCl	40,42

TABLE 1 (*continued*)



1,4,7,10,13,16,19,22-octaazacyclotetracosane
[24]aneN_8

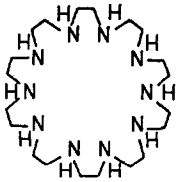
cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
Ni(II)	L + 2Ni	23.30	pot			25	0.15 $NaClO_4$	39
	NiL + Ni	9.36	pot			25	0.15 $NaClO_4$	39
	L + 2Ni + H_2O	13.19	pot			25	0.15 $NaClO_4$	39
	Ni_2L + OH	3.62	pot			25	0.15 $NaClO_4$	39
Cu(II)	L + 2Cu	35.25	pot	163.2 cal		25	0.15 $NaClO_4$	41
	L + 2Cu + H	38.15	pot			25	0.15 $NaClO_4$	41
	L + 2Cu + H_2O	26.25	pot			25	0.15 $NaClO_4$	41
	Cu_2L + OH	4.74	pot			25	0.15 $NaClO_4$	41
Zn(II)	L + 2Zn + H_2O	12.60	pot			25	0.15 $NaClO_4$	36
	L + 2Zn + $2H_2O$	3.0	pot			25	0.15 $NaClO_4$	36
	Zn_2LOH + OH	4.1	pot			25	0.15 $NaClO_4$	36
Cd(II)	L + 2Cd	18.21	pot			25	0.15 $NaClO_4$	37
	CdL + Cd	3.69	pot			25	0.15 $NaClO_4$	37



1,4,7,10,13,16,19,22,25-nonaazacycloheptacosane
[27]aneN_9

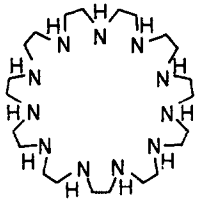
cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
Co(II)	L + 2Co	18.85	pot			25	0.15 $NaClO_4$	38
	CoL + Co	7.0	pot			25	0.15 $NaClO_4$	38
	L + 2Co + 2H	31.32	pot			25	0.15 $NaClO_4$	38
	L + 2Co + H_2O	9.88	pot			25	0.15 $NaClO_4$	38
	Co_2L + OH	4.76	pot			25	0.15 $NaClO_4$	38
Ni(II)	L + 2Ni	26.24	pot			25	0.15 $NaClO_4$	39
	L + 2Ni + H	31.46	pot			25	0.15 $NaClO_4$	39
	L + 2Ni + 2H	36.73	pot			25	0.15 $NaClO_4$	39
Cu(II)	L + 2Cu	36.03	pot	179.0 cal	26.0	25	0.15 $NaClO_4$	32
	L + 2Cu + H	40.66	pot			25	0.15 $NaClO_4$	32
	L + 2Cu + 2H	43.83	pot			25	0.15 $NaClO_4$	32
	L + 2Cu + 3H	47.10	pot			25	0.15 $NaClO_4$	32
	L + 2Cu + H_2O	26.24	pot			25	0.15 $NaClO_4$	32
	Cu_2L + OH	3.94	pot			25	0.15 $NaClO_4$	32
Zn(II)	L + 2Zn	20.55	pot			25	0.15 $NaClO_4$	35
	L + 2Zn + H	26.98	pot			25	0.15 $NaClO_4$	35
	L + 2Zn + 2H	32.79	pot			25	0.15 $NaClO_4$	35
	L + 2Zn + H_2O	13.56	pot			25	0.15 $NaClO_4$	35
	L + 2Zn + $2H_2O$	4.71	pot			25	0.15 $NaClO_4$	35
	Zn_2L + OH	6.7	pot			25	0.15 $NaClO_4$	35
	Zn_2LOH + OH	4.9	pot			25	0.15 $NaClO_4$	35
Cd(II)	L + 2Cd	20.75	pot			25	0.15 $NaClO_4$	37
	L + 2Cd + H	26.38	pot			25	0.15 $NaClO_4$	37
	L + 2Cd + 2H	32.21	pot			25	0.15 $NaClO_4$	37

TABLE 1 (*continued*)



1,4,7,10,13,16,19,22,25,28-decaazacyclotriacontane
[30]aneN_{10}

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
Co(II)	L + 2Co	21.85	pot			25	0.15 $NaClO_4$	38
	L + 2Co + 2H	34.67	pot			25	0.15 $NaClO_4$	38
	L + 2Co + 3H	39.79	pot			25	0.15 $NaClO_4$	38
	L + 2Co + H_2O	11.94	pot			25	0.15 $NaClO_4$	38
	Co_2L + OH	3.82	pot			25	0.15 $NaClO_4$	38
Ni(II)	L + 2Ni	30.02	pot			25	0.15 $NaClO_4$	39
	L + 2Ni + 2H	40.17	pot			25	0.15 $NaClO_4$	39
Cu(II)	L + 2Cu	37.77	pot	190.4 cal	25.1	25	0.15 $NaClO_4$	33
	L + 2Cu + H	43.36	pot			25	0.15 $NaClO_4$	33
	L + 2Cu + 2H	47.21	pot			25	0.15 $NaClO_4$	33
	L + 2Cu + 3H	50.52	pot			25	0.15 $NaClO_4$	33
	L + 2Cu + H_2O	26.43	pot			25	0.15 $NaClO_4$	33
	Cu_2L + OH	2.39	pot			25	0.15 $NaClO_4$	33
Zn(II)	L + 2Zn	22.51	pot			25	0.15 $NaClO_4$	35
	L + 2Zn + 2H	35.22	pot			25	0.15 $NaClO_4$	35
	L + 2Zn + 3H	40.41	pot			25	0.15 $NaClO_4$	35
	L + 2Zn + H_2O	14.16	pot			25	0.15 $NaClO_4$	35
	L + 2Zn + $2H_2O$	3.19	pot			25	0.15 $NaClO_4$	35
	Zn_2L + OH	5.4	pot			25	0.15 $NaClO_4$	35
	Zn_2LOH + OH	2.7	pot			25	0.15 $NaClO_4$	35
Cd(II)	L + 2Cd	23.21	pot			25	0.15 $NaClO_4$	37
	L + 2Cd + 2H	35.07	pot			25	0.15 $NaClO_4$	37
	L + 2Cd + 3H	39.94	pot			25	0.15 $NaClO_4$	37

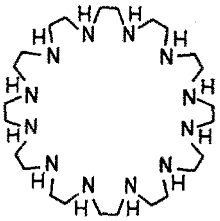


1,4,7,10,13,16,19,22,25,28,31-undecaazacyclotritriacontane
[33]aneN_{11}

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
	L + 2Co	22.90	pot			25	0.15 $NaClO_4$	38
	L + 2Co + 2H	35.83	pot			25	0.15 $NaClO_4$	38
	L + 2Co + 3H	40.91	pot			25	0.15 $NaClO_4$	38
	L + 2Co + H_2O	12.72	pot			25	0.15 $NaClO_4$	38
	Co_2L + OH	3.55	pot			25	0.15 $NaClO_4$	38
Ni(II)	L + 2Ni	31.07	pot			25	0.15 $NaClO_4$	39
	L + 2Ni + H	36.98	pot			25	0.15 $NaClO_4$	39
	L + 2Ni + 2H	40.98	pot			25	0.15 $NaClO_4$	39
	L + 2Ni + 3H	46.44	pot			25	0.15 $NaClO_4$	39
Cu(II)	L + 2Cu	38.77	pot			25	0.15 $NaClO_4$	34
	L + 2Cu + H	45.28	pot			25	0.15 $NaClO_4$	34
	L + 2Cu + 2H	51.18	pot			25	0.15 $NaClO_4$	34
	L + 2Cu + 3H	53.86	pot			25	0.15 $NaClO_4$	34

TABLE 1 (*continued*)

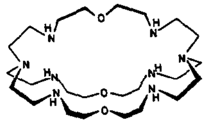
	L + 2Cu + H_2O	27.29	pot			25	0.15 $NaClO_4$	34
	Cu_2L + OH	2.25	pot			25	0.15 $NaClO_4$	34
	L + 3Cu	48.03	pot			25	0.15 $NaClO_4$	34
	Cu_2L + Cu	9.3	pot			25	0.15 $NaClO_4$	34
	L + 3Cu + H_2O	40.62	pot			25	0.15 $NaClO_4$	34
	L + 3Cu + $2H_2O$	30.2	pot			25	0.15 $NaClO_4$	34
	Cu_3L + OH	6.32	pot			25	0.15 $NaClO_4$	34
	Cu_3LOH + OH	3.31	pot			25	0.15 $NaClO_4$	34
Zn(II)	L + 2Zn	23.91	pot			25	0.15 $NaClO_4$	35
	L + 2Zn + 2H	36.66	pot			25	0.15 $NaClO_4$	35
	L + 2Zn + 3H	42.17	pot			25	0.15 $NaClO_4$	35
	L + 2Zn + H_2O	15.40	pot			25	0.15 $NaClO_4$	35
	L + 2Zn + $2H_2O$	4.87	pot			25	0.15 $NaClO_4$	35
	Zn_2L + OH	5.2	pot			25	0.15 $NaClO_4$	35
	Zn_2LOH + OH	3.2	pot			25	0.15 $NaClO_4$	35
Cd(II)	L + 2Cd	23.63	pot			25	0.15 $NaClO_4$	37
	L + 2Cd + 2H	36.06	pot			25	0.15 $NaClO_4$	37
	L + 2Cd + 3H	41.39	pot			25	0.15 $NaClO_4$	37



1,4,7,10,13,16,19,22,25,28,31,34-dodecaazacyclohexatriacontane
[36]aneN_{12}

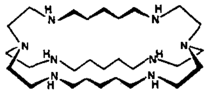
cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
Co(II)	L + 2Co + H	31.29	pot			25	0.15 $NaClO_4$	38
	L + 2Co + 2H	37.62	pot			25	0.15 $NaClO_4$	38
	L + 2Co + 3H	43.45	pot			25	0.15 $NaClO_4$	38
	L + 2Co + 4H	48.76	pot			25	0.15 $NaClO_4$	38
	L + 2Co + H_2O	13.87	pot			25	0.15 $NaClO_4$	38
	Co_2L + OH	3.05	pot			25	0.15 $NaClO_4$	38
Ni(II)	L + 2Ni	32.09	pot			25	0.15 $NaClO_4$	39
	L + 2Ni + H	38.62	pot			25	0.15 $NaClO_4$	39
	L + 2Ni + 2H	44.46	pot			25	0.15 $NaClO_4$	39
	L + 2Ni + 3H	48.95	pot			25	0.15 $NaClO_4$	39
	L + 2Ni + 4H	53.42	pot			25	0.15 $NaClO_4$	39
Cu(II)	L + 2Cu	39.25	pot			25	0.15 $NaClO_4$	34
	L + 2Cu + H	47.09	pot			25	0.15 $NaClO_4$	34
	L + 2Cu + 2H	53.96	pot			25	0.15 $NaClO_4$	34
	L + 2Cu + 3H	58.07	pot			25	0.15 $NaClO_4$	34
	L + 2Cu + 4H	61.42	pot			25	0.15 $NaClO_4$	34
	L + 3Cu	51.43	pot			25	0.15 $NaClO_4$	34
	Cu_2L + Cu	12.2	pot			25	0.15 $NaClO_4$	34
	L + 3Cu + H	55.38	pot			25	0.15 $NaClO_4$	34
	L + 3Cu + H_2O	42.53	pot			25	0.15 $NaClO_4$	34
	L + 3Cu + $2H_2O$	31.62	pot			25	0.15 $NaClO_4$	34
	Cu_3L + OH	4.83	pot			25	0.15 $NaClO_4$	34
	Cu_3LOH + OH	2.82	pot			25	0.15 $NaClO_4$	34
Zn(II)	L + 2Zn	26.27	pot			25	0.15 $NaClO_4$	36
	L + 2Zn + H	32.83	pot			25	0.15 $NaClO_4$	36
	L + 2Zn + 2H	39.16	pot			25	0.15 $NaClO_4$	36
	L + 2Zn + 3H	44.81	pot			25	0.15 $NaClO_4$	36
	L + 2Zn + 4H	49.99	pot			25	0.15 $NaClO_4$	36
	L + 2Zn + H_2O	16.09	pot			25	0.15 $NaClO_4$	36
	Zn_2L + OH	3.5	pot			25	0.15 $NaClO_4$	36

TABLE 1 (*continued*)



7,19,30-trioxa-1,4,10,13,16,22,27,33-octaazabicyclo[11.11.11]pentatriacontane
bistren

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
Co(II)	L + 2Co	16.80	pot			25	0.1 KNO_3	44
	CoL + Co	5.60	pot			25	0.1 KNO_3	44
	$Co_2L + H_2O$	-7.20	pot			25	0.1 KNO_3	44
Cu(II)	L + 2Cu	29.21	pot			25	0.1 KNO_3	44
	L + 2Cu	27.32	pot			25	0.1 KCl	45
	L + 2Cu	29.05	pot			25	0.1 $NaClO_4$	45
	L + 2Cu	32.9	pot			25	0.025 NaF	46
	L + 2Cu	30.2	pot			25	1.0 $NaClO_4$	46
	L + 2Cu	31.0	pot			25	0.5 $NaClO_4$+0.5 NaCl	46
	L + 2Cu	30.2	pot			25	1.0 NaCl	46
	L + 2Cu	29.4	pot			25	1.0 NaBr	46
	L + 2Cu	28.32	pot			25	0.1 $NaClO_4$	47
	CuL + Cu	12.67	pot			25	0.1 KNO_3	44
	CuL + Cu	9.96	pot			25	0.1 KCl	45
	CuL + Cu	12.51	pot			25	0.1 $NaClO_4$	45
	CuL + Cu	14.6	pot			25	0.025 NaF	46
	CuL + Cu	11.5	pot			25	1.0 $NaClO_4$	46
	CuL + Cu	13.2	pot			25	0.5 $NaClO_4$+0.5 NaCl	46
	CuL + Cu	12.8	pot			25	1.0 NaCl	46
	CuL + Cu	11.2	pot			25	1.0 NaBr	46
	CuL + Cu	10.73	pot			25	0.1 $NaClO_4$	47
	$Cu_2L + H_2O$	-4.26	pot			25	0.1 KNO_3	44
	$L + 2Cu + H_2O$	25.07	pot			25	0.1 KCl	45
	$L + 2Cu + H_2O$	23.63	pot			25	0.1 $NaClO_4$	45
	$Cu_2L + H_2O$	-5.3	pot			25	0.025 NaF	46
	$Cu_2L + H_2O$	-3.1	pot			25	1.0 $NaClO_4$	46
	$Cu_2L + H_2O$	-4.4	pot			25	0.5 $NaClO_4$+0.5 NaCl	46
	$Cu_2L + H_2O$	-4.5	pot			25	1.0 NaCl	46
	$Cu_2L + H_2O$	-2.6	pot			25	1.0 NaBr	46
	$Cu_2L + H_2O$	-3.89	pot			25	0.1 $NaClO_4$	47
Ni(II)	L + 2Ni	~18.5	pot			25	0.1 KNO_3	44
	NiL + Ni	~6.8	pot			25	0.1 KNO_3	44
	$Ni_2L + H_2O$	~-6.0	pot			25	0.1 KNO_3	44
Zn(II)	L + 2Zn	18.22	pot			25	0.1 KNO_3	44
	ZnL + Zn	6.36	pot			25	0.1 KNO_3	44
	$Zn_2L + H_2O$	-6.00	pot			25	0.1 KNO_3	44



1,4,10,13,16,22,27,33-octaazabicyclo[11.11.11]pentatriacontane

C-bistren

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
Cu(II)	L + 2Cu	28.76	pot			25	0.1 $NaClO_4$	47

TABLE 1 (*continued*)

CuL + Cu	13.37	pot	25	0.1 NaClO4	47
Cu2L + H	5.40	pot	25	0.1 NaClO4	47
Cu2L + H2O	-7.59	pot	25	0.1 NaClO4	47
Cu2LOH + H2O	-10.81	pot	25	0.1 NaClO4	47

[a] Only the left side (reactants) of the equilibrium reactions is indicated. Reactions including water molecules refer to: $m\mathrm{M}+l\mathrm{L}+n\mathrm{H_2O}=\mathrm{M}_m\mathrm{L}_l(\mathrm{OH})_n+n\mathrm{H}$. Charges have been omitted. Experimental methods for the determination of the equilibrium constants are abbreviated as follows: potentiometric (pot). Only direct calorimetric methods (cal) for the determination of ΔH^0 are indicated.

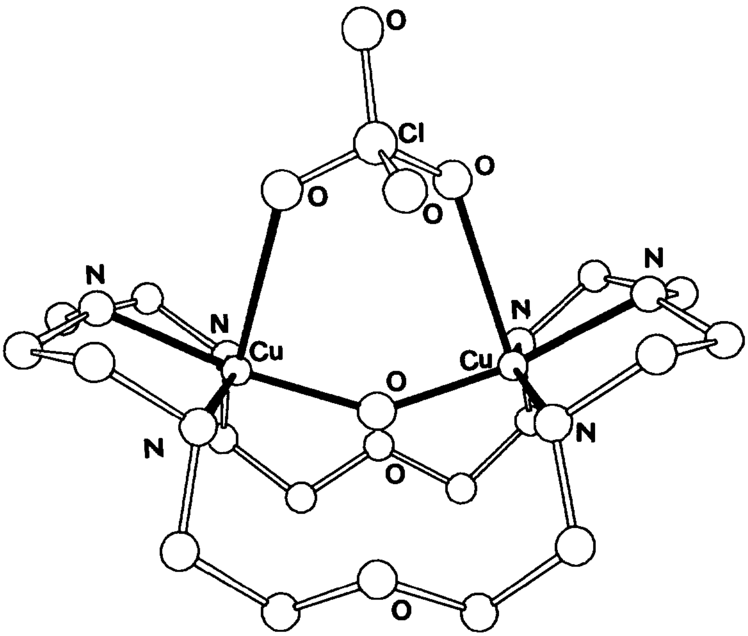


Fig. 1. Crystal structure of the $[\mathrm{Cu_2(1)(OH)ClO_4}]^{2+}$ complexed cation.

In spite of its weak tendency to bind two $\mathrm{Co^{2+}}$ ions in solution, bisdien in the presence of molecular oxygen forms a very stable dibridged (μ-peroxo)(μ-hydroxo) dicobalt complex [22] whose proposed structure is shown in Fig. 4. Other bidentate ligands such as oxalate [25], mesoxalate [26], catecholate, hydroquinone and TIRON (1,2-dihydroxy-3,5-disulphobenzene) [27] have been employed to bind in turn to the dioxygen dicobalt complexes of bisdien.

More recently, the two polynucleating ligands related to bisdien (**2**) bisbamp

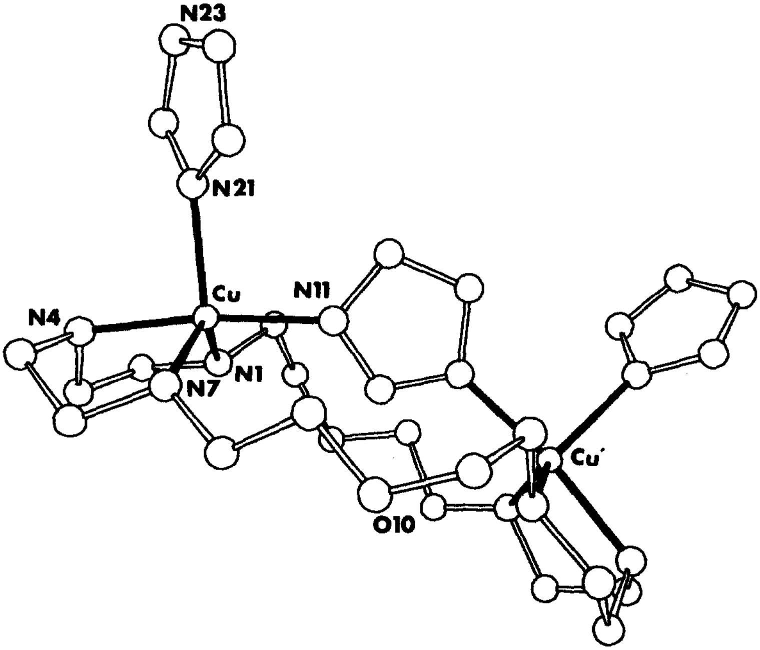


Fig. 2. Crystal structure of the $[Cu_2(1)(im)(imH)_2]^{3+}$ (imH = imidazole) centrosymmetric complexed cation.

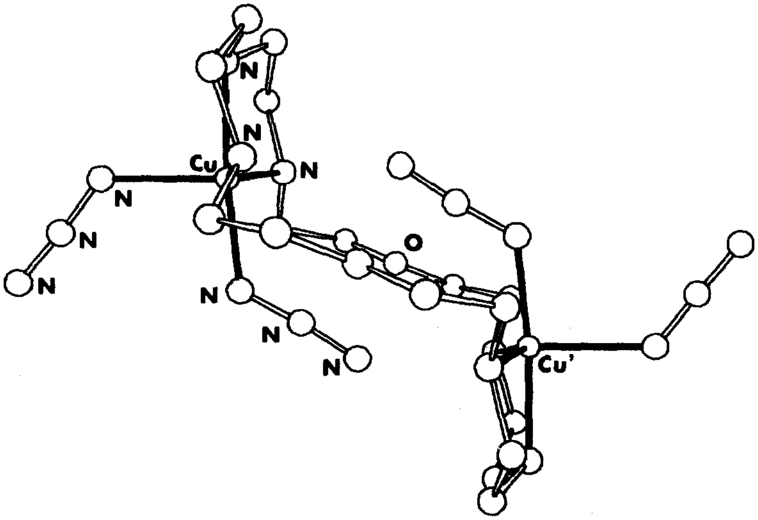


Fig. 3. Crystal structure of the centrosymmetric $Cu_2(1)(N_3)_4$ complex.

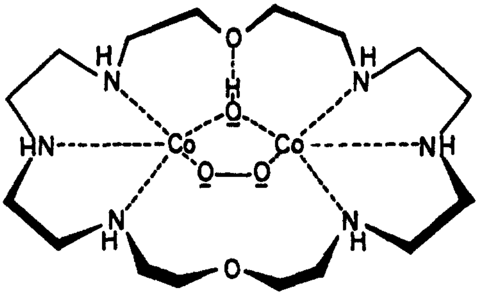
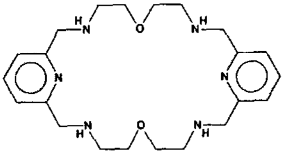


Fig. 4. Proposed structure [22] for the (μ-peroxo)(μ-hydroxo) dibridged dicobalt complex of bisdien (**1**).

(3,9,17,23,29,30-hexaaza-6,20-dioxatricyclo[23.3.1$1^{11,15}$]triaconta-1(28),11,13,15(30), 25,26-hexaene [28] and (**3**) (3,6,9,17,20,23-hexeazatricyclo[23.3.1$1^{11,15}$]triaconta-1(29),11(30),12,14,25-(26),27-hexaene [29] have been synthesized. Compounds (**2**) and



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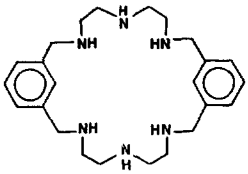

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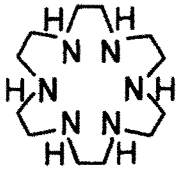
(**3**) can be considered to contain two 2,6-bis(aminomethyl)pyridine (bamp) units and two diethylentriamine units, respectively, linked together by two five-atom bridges. In (**2**), these bridges are equal to those of bisdien, while in (**3**) they include a phenyl group.

The complexation equilibria of (**2**) toward Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} [28] and of (**3**) toward Cu^{2+} [29] have been studied by potentiometric measurements. Both ligands form binuclear species with the reported metal ions [28,29]. The equilibrium constants for the formation of these species are shown in Table 1. With the exception of Ni^{2+}, whose binuclear complex with bisdien was not observed [22], bisbamp form binuclear complexes of lower stability than bisdien. This decrease of stability has been ascribed to lower basicity of bisbamp with respect to bisdien [28]. A further decrease of stability is observed for the dicopper(II) complex of the ligand (**3**).

The binuclear complexes of bisbamp and (**3**) are characterized by strong hydrolytic tendencies to form mono- and dihydroxo species. Monohydroxo species are also formed by the binuclear complexes of bisbamp with Co^{2+}, Ni^{2+} and Zn^{2+} [28]. In accordance with the analogous complexes of bisdien [22], it has been suggested [28,29] that hydroxide ions are bridging groups coordinated simultaneously to both metal ions.

As observed for $Co_2(\mathbf{1})^{4+}$, the dicobalt(II) complex of bisbamp also binds molecular oxygen. O_2 binding by $Co_2(\mathbf{3})^{4+}$ gives the formation of a dibridged (μ-peroxo)(μ-hydroxo) complex which forms several hydroxo species [28].

The polyazacycloalkanes (**4**) [18]aneN_6 (1,4,7,10,13,16-hexaazacyclooctadecane), (**5**) [21]aneN_7 (1,4,7,10,13,16,19-heptaazacyclohenicosane), (**6**) [24]aneN_8 (1,4,7,10,13,16,19,22-octaazacyclotetracosane), (**7**) [27]aneN_9 (1,4,7,10,13,16,19,22,25-nonaazacycloheptacosane), (**8**) [30]aneN_{10} (1,4,7,10,13,16,19,22,25,28-decaazacyclotriacontane), (**9**) [33]aneN_{11} (1,4,7,10,13,16,19,22,25,28,31-undecaazacyclotritriacontane) and (**10**) [36]aneN_{12} (1,4,7,10,13,16,19,22,25,28,31,34-dodecaazacyclohexatriacontane), belonging to the series [3k]aneN_k, have been employed to study the equilibria of formation of transition metal complexes in which more than one metal ion is coordinated by the same macrocyclic ring [30–42]. Among these ligands, which present a homogeneous distribution of donor atoms, the large macrocycles (**5**)–(**10**) were purposely synthesized for polynuclear complex formation [30–34]. The equilibrium constants obtained by potentiometric titrations [30–42] for the polynuclear complexes of [3k]aneN_k ($k = 6$–12) macrocycles are presented in Table 1.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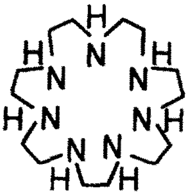
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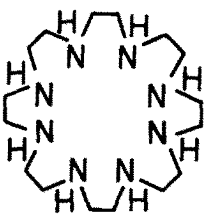
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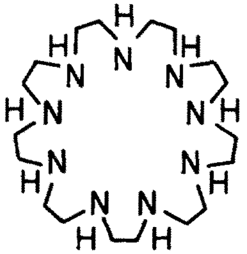
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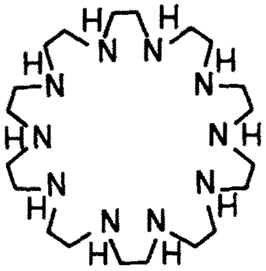
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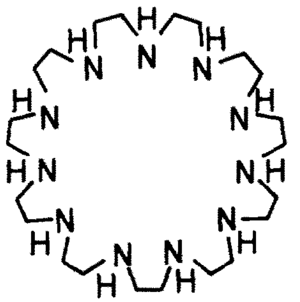
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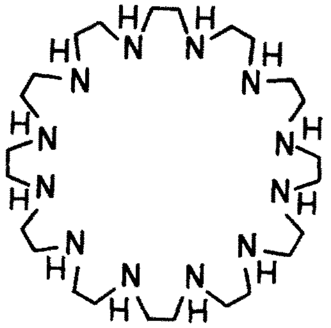
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The first characteristic to be noted in this series of ligands is the existence for each metal ion of only one ligand able to form both mono- and binuclear complexes, while the smaller and the larger ligands form only either mononuclear or binuclear complexes. These intermediate ligands are [21]aneN_7 in the case of Cu^{2+} [30–34,42],

[24]aneN$_8$ for Zn^{2+} [35,36], Cd^{2+} [37] and Ni^{2+} [39] and [27]aneN$_9$ for Co^{2+} [38]. In the case of Cu^{2+}, the two ligands [33]aneN$_{11}$ and [36]aneN$_{12}$ are also able to form tricopper(II) complexes [34].

With respect to stepwise complexation, we observe that the tendency to bind a second metal ion, presented by the intermediate ligands, is high in the case of Cu^{2+} [31,41], Ni^{2+} [39] and Zn^{2+} [36], somewhat lower for Co^{2+} [38] and low for Cd^{2+} [37]. With the exception of Cd^{2+}, the formation of hydroxo species contributes to further stabilization of the binuclear complexes of these ligands. In the case of Zn^{2+}, the species $Zn_2(\mathbf{6})OH^{3+}$ is so stable that the unhydrolyzed complex $Zn_2(\mathbf{6})^{4+}$ is not formed in solution. However, this species has been isolated in the solid state as $[Zn_2(\mathbf{6})Cl_2](ClO_4\cdot H_2O$ whose crystal structure has been determined [36] (Fig. 5). The tendency of the binuclear complexes of the ligands (**5**)–(**10**) to form hydroxo species generally decrease with the increasing number of donor atoms in the macrocycle (Table 1). Only in the case of Cd^{2+} has no hydroxo species been observed [37]. In the case of Ni^{2+}, hydroxo binuclear species have also been observed for the ligands (**7**)–(**10**) but, due to the slowness of their formation, the equilibrium constants have not been determined [39]. Bihydroxo complexes $Zn_2L(OH)_2^{2+}$ (L=(**5**)–(**9**)) are also formed [35,35]. The formation of mono- and bihydroxo species also contributes to the stabilization of the tricopper complexes of [33]aneN$_{11}$ and [36]aneN$_{12}$. The abundance of nitrogen atoms in large [3*k*]aneN$_k$ ligands allows the formation of polynuclear protonated species. Binuclear protonated complexes are formed in which the number of nitrogen atoms available for coordination to the two metal ions is lower than that of the smaller ligands able to form the corresponding binuclear species. In fact, [21]aneN$_7$ is the smallest [3*k*]aneN$_k$ ligand which forms a Cu_2L^{4+} complex, but a smaller number of nitrogen donor atoms (six) coordinated to two Cu^{2+} ions is observed in $[Cu_2(\mathbf{7})H_3]^{7+}$. Similarly, [24]aneN$_8$ is the smallest ligand forming dinuclear complexes with Ni^{2+}, Zn^{2+} and Cd^{2+}, but only seven donor

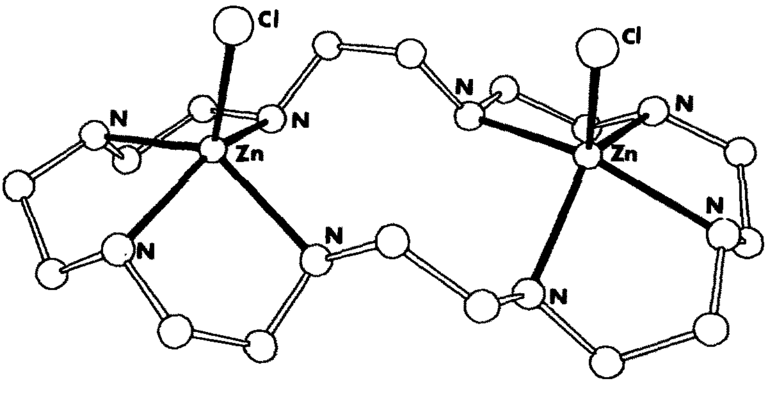


Fig. 5. Crystal structure of the $[Zn_2(\mathbf{6})Cl_2]^{2+}$ complexed cation.

atoms are coordinated in the diprotonated dinuclear complexes of (**7**) with these metal ions. Further, [27]aneN_9 is the smallest ligand which forms dicobalt(II) complexes, but a smaller number of nitrogen atoms (seven) coordinated to two Co^{2+} ions is presented by $[Co_2(\mathbf{8})H_3]^{7+}$. This happens at the expense of severe electrostatic repulsion between positive charges.

As observed, not only the total number of donor atoms, but also the dimensions of the ligand and the disposition of the available donor atoms in the ligand play an important role in determining the ability of a macrocycle to form polynuclear complexes. Furthermore, due to the cyclic nature and the closed assembly of nitrogen atoms in these ligands, the coordinating ability of a single donor is strongly influenced by the state of the others. For example, the breaking of two metal–nitrogen donor bonds, induced by protonation of only one nitrogen atom in the binuclear complexes of [3*k*]aneN_k ligands, has been proposed for some equilibria involving Cd^{2+} [37] and Ni^{2+} ions and observed in the solid state in the compound $[Cu_2(\mathbf{8})HCl_2](ClO_4)_3 \cdot 4H_2O$ [33]. The crystal structure of this complex (Fig. 6) shows the copper atoms coordinated by four nitrogen atoms of the macrocycle and one Cl^- ion in a slightly distorted square-pyramidal geometry, Cl^- being in the apical position. The site of protonation must be on the N(1) or N(1)′ atoms of the macrocycle, but owing to the presence of a twofold axis, these nitrogen atoms are crystallographically equivalent and therefore the proton is statistically distributed between them [33].

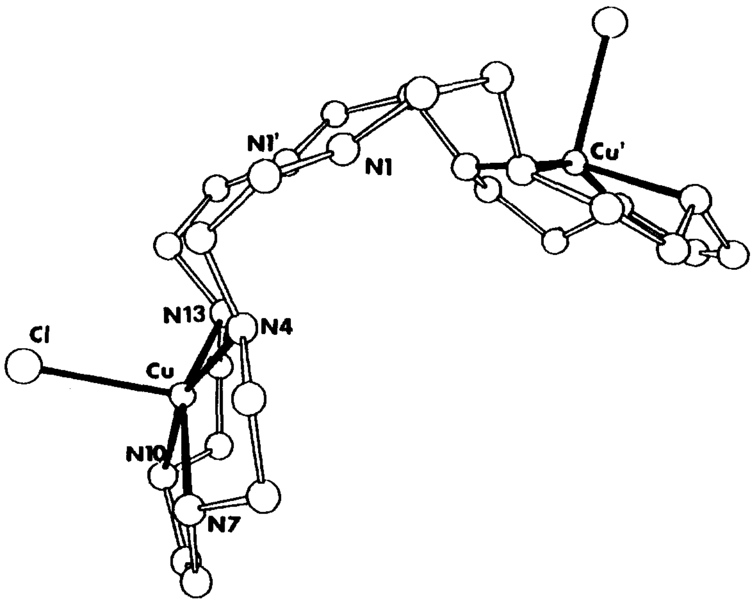


Fig. 6. Crystal structure of the $[Cu_2(\mathbf{8})HCl_2]^{3+}$ complexed cation. The proton is statistically distributed between the two crystallographically equivalent N1 and N1′ atoms.

An uncoordinated nitrogen atom is also present in the structure of the dizinc(II) complex $[Zn_2(\mathbf{8})NCS](ClO_4)_3$ (Fig. 7). In this compound, the two zinc ions show essentially the same five-coordinate geometry, which can be best described as distorted trigonal pyramidal. Zn(1) is coordinated by five nitrogen atoms of the macrocycle, whereas Zn(2) is coordinated by four nitrogen atoms of the macrocycle and the nitrogen atom of a thiocyanate anion. Another interesting crystal structure in which two metal ions present quite different coordination spheres is presented by the dicadmium(II) complex of the same ligand (**8**) [37]. As shown in Fig. 8, in the $[Cd_2(\mathbf{8})Cl_2]^{2+}$ complexed cation, both Cd^{2+} ions are hexacoordinated. However,

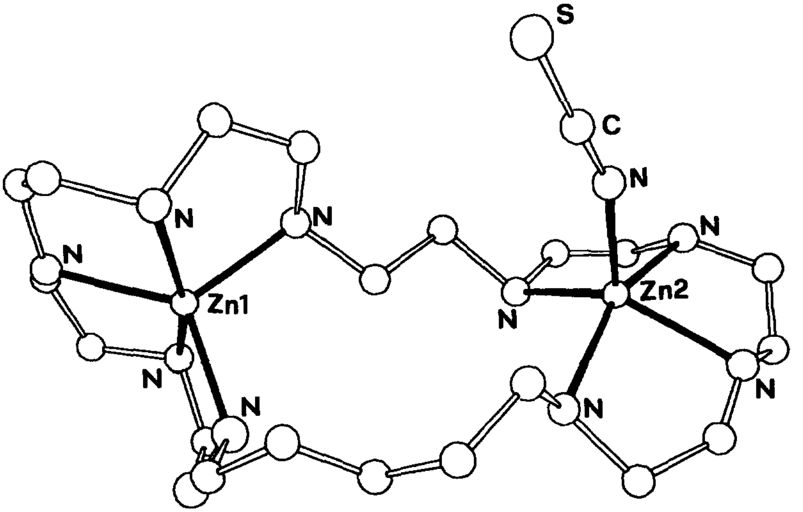


Fig. 7. Crystal structure of the $[Zn_2(\mathbf{8})NCS]^{3+}$ complexed cation.

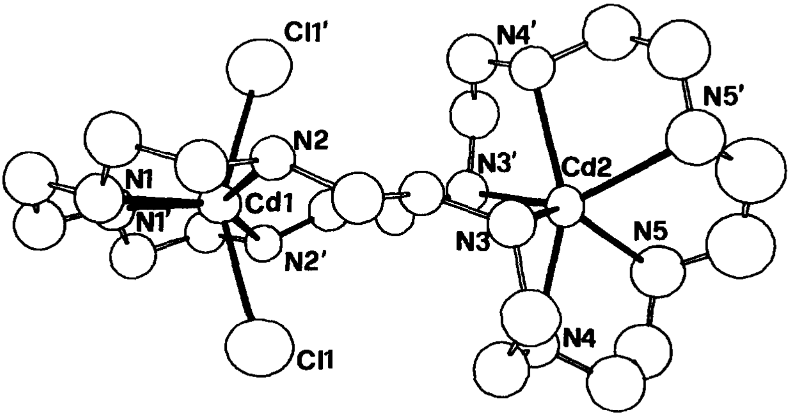


Fig. 8. Crystal structure of the $[Cd_2(\mathbf{8})Cl_2]^{2+}$ complexed cation.

Cd(1) is surrounded by four nitrogen atoms of (**8**) and two Cl^- anions in a quite distorted 4+2 pseudo-octahedral geometry, whereas the environment of Cd(2) is even more unusual and could be described as a distorted trigonal prism whose basal faces are defined by N(3), N(4)′, N(5)′ and N(4), N(3)′, N(5)′ (Fig. 8). The crystal structure of the binuclear complex of [30]aneN_{10} with Ni^{2+} has also been obtained [39]. The compound $[Ni_2(\mathbf{8})(H_2O)_2](NO_3)_4$ contains the centrosymmetric cation $[Ni_2(\mathbf{8})(H_2O)_2]^{4+}$ (Fig. 9) in which the nickel atoms are hexacoordinated by five nitrogen atoms of the macrocycle and one water molecule in an octahedral distorted environment.

The stability profile of the binuclear complexes M_2L^{4+} ($M = Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}$) of the ligands (L) (**5**)–(**10**) is shown in Fig. 10 [43]. As can be seen, for each metal ion the stability of the M_2L^{4+} species increases with the number of donor atoms of the macrocycle according to the increasing number of nitrogen atoms involved in the coordination to the metal ions. Furthermore, the enthalpy changes for the formation of the dicopper(II) complexes $Cu_2(\mathbf{6})^{4+}$, $Cu_2(\mathbf{7})^{4+}$ and $Cu_2(\mathbf{8})^{4+}$, obtained by means of direct microcalorimetric techniques [30,32,33] (Table 1), proved that the increasing stability of these complexes with increasing number of nitrogen donor atoms is due to a stronger overall metal to ligand donor atom interaction. Considering that all the nitrogen donor atoms of [24]aneN_8 are coordinated in $Cu_2(\mathbf{6})^{4+}$, as observed in the crystal structure of the compound $[Cu_2(\mathbf{6})Cl_2](ClO_4)_2$ [30] (Fig. 11), it is likely that all the nitrogen atoms of (**7**) and (**8**) are involved in the coordination of the two Cu^{2+} ions.

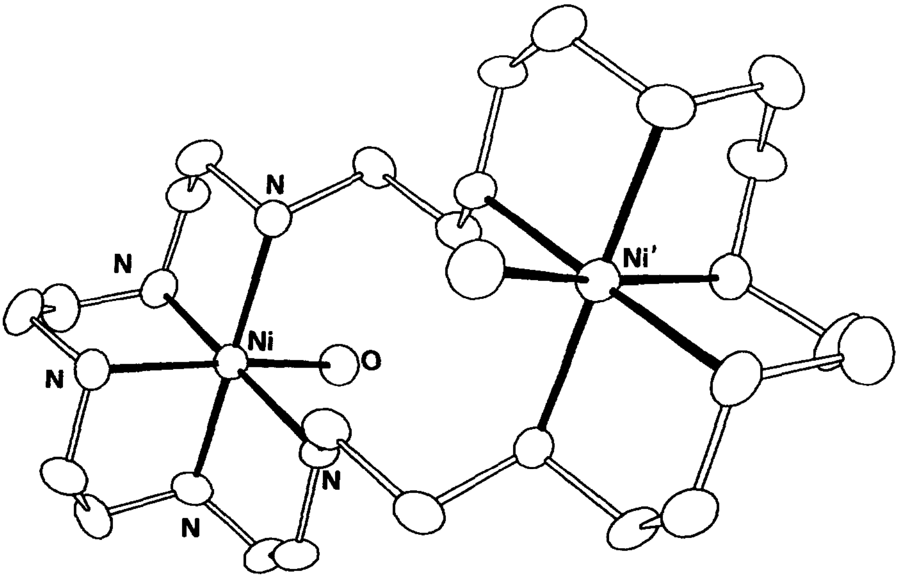


Fig. 9. Crystal structure of the $[Ni_2(\mathbf{8})(H_2O)_2]^{4+}$ centrosymmetric complexed cation.

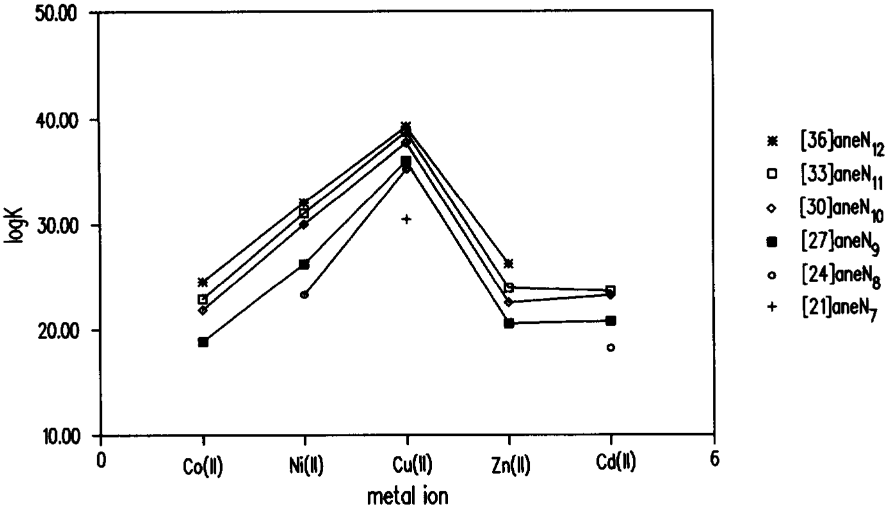


Fig. 10. Stability profile of the binuclear complexes of $[3k]aneN_k$ ($k=7$–12) ligands with Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} cations.

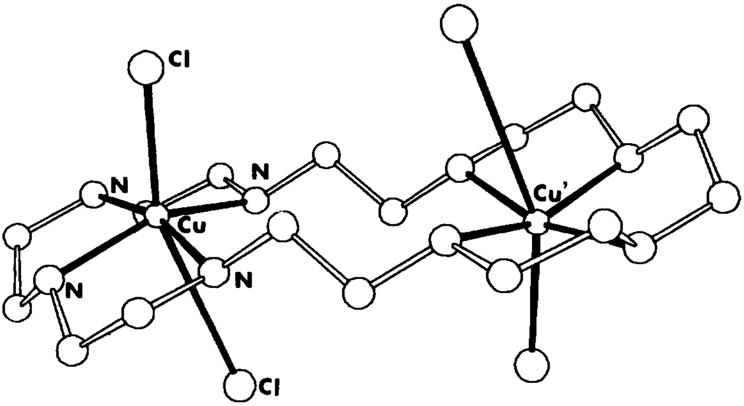


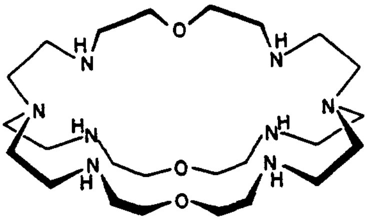
Fig. 11. View of the centrosymmetric $Cu_2(\mathbf{6})Cl_4$ unit observed in the crystal structure of the complex $[Cu_2(\mathbf{6})Cl_2](ClO_4)_2$.

For each ligand, the stability of the binuclear species follows the usual order $Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+} \sim Cd^{2+}$ [Fig. 10].

A case of particular interest has been offered by the palladium(II) complexes of $[18]aneN_6$ and $[21]aneN_7$ [40,41]. Both ligands are able to form very stable binuclear complexes (Table 1). The equilibrium constant for the formation of the species $[Pd_2(\mathbf{4})Cl_2]^{2+}$ is very high ($\log K = 51.8$) and its determination by potentiometric methods was achieved via competition between the azamacrocycle and the chloride ion. In the case of [21]aneN_7, this method allowed only an estimation of the stability constant ($\log K > 52$) of the binuclear complex [40]. The crystal structure of the binuclear cation $[Pd_2(\mathbf{4})Cl_2]^{2+}$ is reported in Fig. 12. As shown, the hexaazamacrocycle adopts an S-like conformation in order to allow each Pd^{2+} ion to bind to three nitrogen atoms and complete the required square-planar geometry by a chloride anion.

$[Pd_2(\mathbf{4})Br_2]Br_2 \cdot 4H_2O$, in which the $[Pd_2(\mathbf{4})Br_2]^{2+}$ cation presents essentially the same coordination features of $[Pd_2(\mathbf{4})Cl_2]^{2+}$, has been reported [41]. The $[Pd_2(\mathbf{4})Cl_2]^{2+}$ complex, whose structure is likely maintained in solution [40], is quite inert toward acid dissociation; some months are required for its complete dissociation in 2 mol dm^{-3} HCl solution. The binuclear complex of [21]aneN_7 is able to coordinate to a further Pd^{2+} ion. On formation of the tripalladium(II) compound, an amine group of [21]aneN_7 deprotonates to bridge two Pd^{2+} ions. This complex has been isolated in the solid state and its crystal structure determined [40,41]. The geometry around the three Pd^{2+} ions is square-planar (Fig. 13), each Pd^{2+} ions being bound by three nitrogen atoms of the macrocycle and one chloride ion. The deprotonated amine group and a chloride ion bridge two Pd^{2+} cations.

Macrobicyclic ligands containing two binding subunits able to form cryptate binuclear complexes are widely known [6]. Among these ligands, few azamacropolycycles have been employed in the study of the thermodynamic properties of transition metal complexes. A significant example of this class of ligand is the macrobicycle (**11**) bistren (7,19,30-trioxa-1,4,10,13,16,22,27,33-octaazabicyclo[11.11.11]pentatriacontane) synthesized by Lehn et al. [20]. The coordinating ability of this ligand toward Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} has been studied and the stability constants for formation of the relevant binuclear species have been potentiometrically determined [44] (Table 1). While the ligand forms stable 1 : 1 complexes with these cations, the inclusion of a second metal ion within the macrobicyclic ligand occurs with much lower binding affinity. The formation of bridged hydroxo species contributes to stabilize the binuclear $M_2(\mathbf{11})^{4+}$ ($M = Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}$) complexes. In particular, the unusually high binding constant for hydroxide bridging in the binuclear



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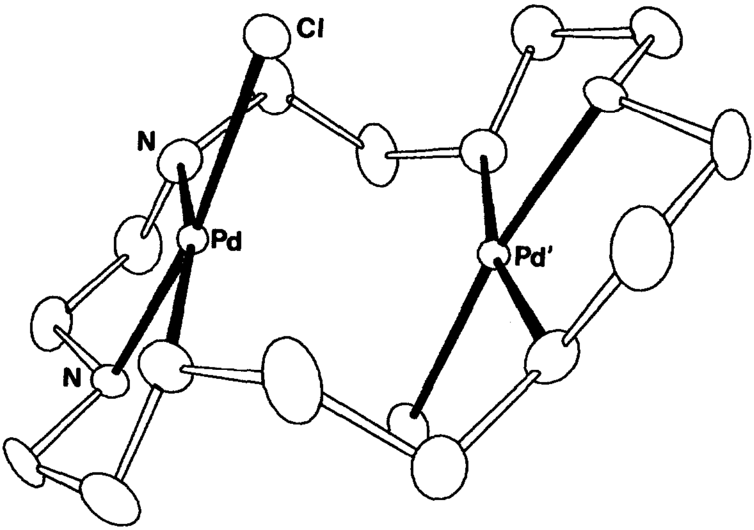


Fig. 12. Crystal structure of $[Pd_2(4)Cl_2]^{2+}$. The complexed cation possesses a 2/m symmetry.

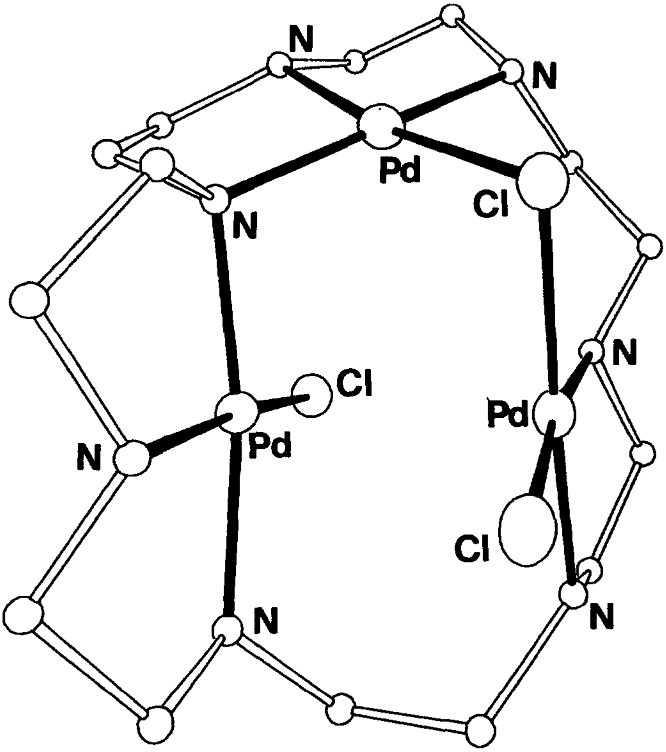


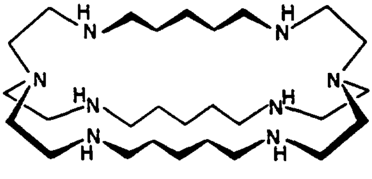
Fig. 13. Crystal structure of the complexed cation $\{Pd_3[(4)\text{-}H)Cl_3]\}^{2+}$. The deprotonated nitrogen atom of (4) bridges two Pd^{2+} ions.

Cu^{2+} cryptate was noted and it was suggested that the hydroxo bridge could be stabilized by hydrogen bonding to one or more oxygen atoms of bistren [45,46] (Fig. 14).

The ability of the $Cu_2(\mathbf{11})^{4+}$ species to form cascade complexes with halogenide ions has been investigated by studying the equilibria of complexation between Cu^{2+} and bistren in various ionic media [45–47]. The binding constants of F^-, Cl^- and I^- to $Cu_2(\mathbf{11})^{4+}$ have been determined [45–47].

The dicobalt(II) complex of bistren binds molecular oxygen forming a (μ-peroxo)(μ-hydroxo) dibridged species [25,44]. The tendency of $Co_2(\mathbf{11})^{4+}$ to undergo oxygenation is markedly lower than that presented by the related ligand bisdien [22].

The macrobicycle (**12**), C-bistren (1,4,10,13,16,22,27,33-octaazabicyclo[11.11.11] pentatriacontane, having a structure similar to that of bistren but without the bridging ether oxygens, was synthesized [48] as a reference ligand to investigate the importance of the oxygen atoms of bistren in stabilizing its hydroxo dicopper(II) complex [47]. C-bistren presents a higher tendency to form dicopper(II) complexes with respect to bistren and, as expected, the resulting binuclear complex shows a largely lower ability in hydroxide binding (Table 1). Further differences between the two parent ligands are the formation of bihydroxo and monoprotonated dicopper(II) complexes by C-bistren.



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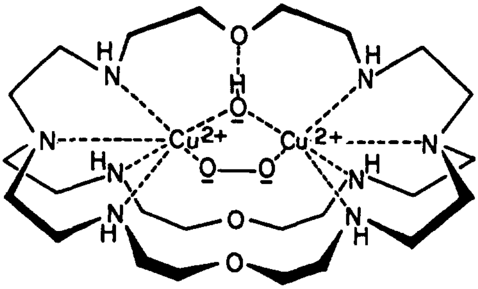
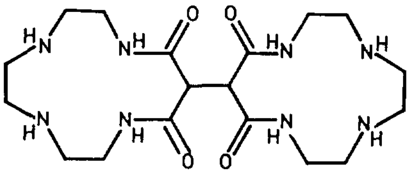


Fig. 14. Proposed structure [45,46] for the (μ-peroxo)(μ-hydroxo) dibridged dicopper(II) complex of bistren (**11**).

C. BIS(MACROCYCLES)

Several bis(tetraazamacrocycles) in which two macrocyclic subunits are linked together either through an aliphatic chain joining two nitrogen atoms or by a carbon–carbon bond have been synthesized and used to study the formation of binuclear complexes with transition metal ions [49–60]. In the case of the ligands (**13**) [13-13]bisdioxocyclam (bis(11,13-dioxo-1,4,7,10-tetraazacyclotridecan-12-yl)) and (**14**) [14-14]bisdioxocyclam (bis(5,7-dioxo-1,4,8,11-tetraazacyclotetradecan-6-yl)),



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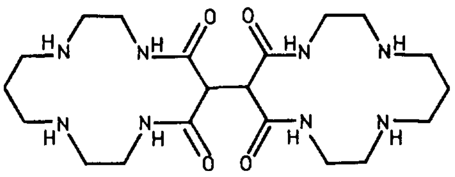

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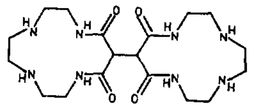
equilibrium constants for the formation of dicopper(II) species have been reported [54,55] (Table 2). [14-14]Bisdioxocyclam binds the two Cu^{2+} ions in two successive steps [54], while for [13-13]bisdioxocyclam, only simultaneous coordination has been observed [55]. The equilibrium constants (Table 2) for the formation of these dicopper(II) complexes are very low when compared with those of other complexes with ligands containing an equal or even smaller number of nitrogen atoms (see, for example, [24]aneN_8 and [21]aneN_7 in Table 1). This behaviour has been justified by assuming that only the amino groups contribute significantly to coordination [54,55].

An important feature of complexes of these ligands is the release of protons from the amido groups. The hypothesized coordination scheme for the binding of two Cu^{2+} by (**13**) and (**14**) and successive release of protons is represented in Fig. 15 [54,55]. The stepwise, two by two, deprotonation of the amido groups of each macrocyclic subunit is suggested by the absence of "odd" stoichiometry such as $[Cu_2(L-H)]^{3+}$ or $[Cu_2(L-3H)]^{+}$ and comparison with related single-ring systems [54,55]. Furthermore, deprotonation of both amido groups of a macrocyclic subunit should allow the Cu^{2+} ion to be coordinated better by all four nitrogen atoms of this subunit.

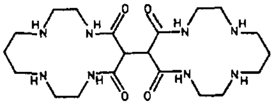
TABLE 2

log *K* values for the formation of binuclear complexes of aza-bis(macrocycles) in aqueous solution[a]



bis(11,13-dioxo-1,4,7,10-tetraazacyclotridecan-12-yl)
[13-13]bisdioxocyclam

cation	reaction	logK	method	T °C	medium	ref
Cu(II)	$L + 2Cu = Cu_2L$	14.00	pot	25	0.1 $NaClO_4$	55
	$L + 2Cu = Cu_2(L\text{-}2H) + 2H$	3.66	pot	25	0.1 $NaClO_4$	55
	$L + 2Cu = Cu_2(L\text{-}4H) + 4H$	-7.09	pot	25	0.1 $NaClO_4$	55
	$Cu_2L = Cu_2(L\text{-}2H) + 2H$	-10.34	pot	25	0.1 $NaClO_4$	55
	$Cu_2(L\text{-}2H) = Cu_2(L\text{-}4H) + 2H$	-10.75	pot	25	0.1 $NaClO_4$	55



bis(5,7-dioxo-1,4,8,11-tetraazacyclotetradecan-6-yl)
[14-14]bisdioxocyclam

cation	reaction	logK	method	T °C	medium	ref
Cu(II)	$L + 2Cu = Cu_2L$	17.79	pot	25	0.1 $NaClO_4$	54
	$CuL + Cu + Cu_2L$	3.25	pot	25	0.1 $NaClO_4$	54
	$L + 2Cu = Cu_2(L\text{-}2H) + 2H$	8.59	pot	25	0.1 $NaClO_4$	54
	$L + 2Cu = Cu_2(L\text{-}4H) + 4H$	-1.34	pot	25	0.1 $NaClO_4$	54
	$Cu_2L = Cu_2(L\text{-}2H) + 2H$	-9.20	pot	25	0.1 $NaClO_4$	54
	$Cu_2(L\text{-}2H) = Cu_2(L\text{-}4H) + 2H$	-9.93	pot	25	0.1 $NaClO_4$	54

[a] Charges have been omitted. Experimental methods for the determination of the equilibrium constants are abbreviated as follows: potentiometric (pot).

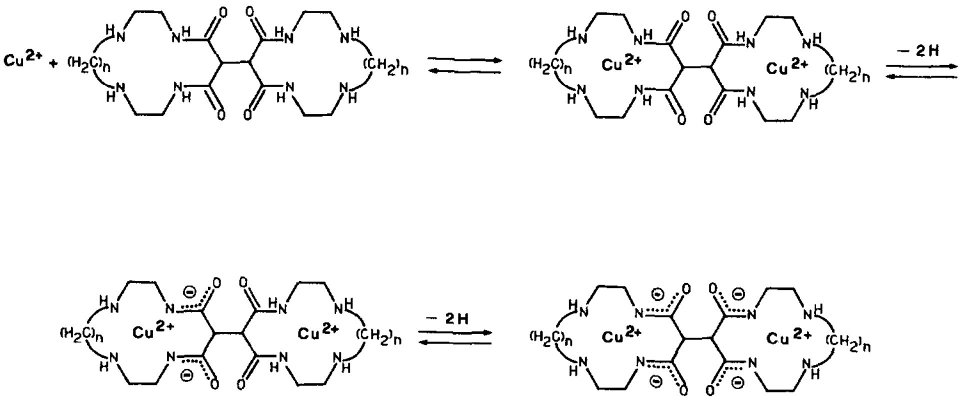
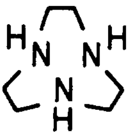


Fig. 15. Hypothesized [54,55] coordination scheme for the binding of two Cu^{2+} ions by (**13**) ($n = 2$) and (**14**) ($n = 3$) and successive release of protons.

D. BRIDGED MACROCYCLIC METAL COMPLEXES

We have previously discussed (Sect. B) the ability of hydroxide ions in solution to bind metal ions in polynuclear macrocyclic complexes to form stable μ-hydroxo species. In these complexes, the metal ions are coordinated within the same macrocyclic cavity and the formation of hydroxo bridges contributes to the further stabilization of the polynuclear species.

Hydroxide ions can also link together two macrocyclic complexed units forming bridged or dibridged binuclear species [61–66]. Thermodynamic data for the formation of similar complexes (Table 3) have been obtained for the equilibria of Cu^{2+} with the triazamacrocycles (**15**) [9]aneN_3 (1,4,7-triazacyclononane), (**16**) [10]aneN_3 (1,4,7-triazacyclodecane), (**17**) [12]aneN_3 (1,5,9-triazacyclododecane),



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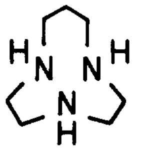

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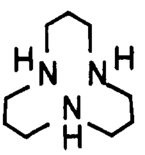

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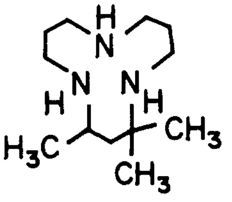

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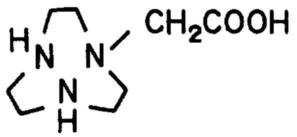

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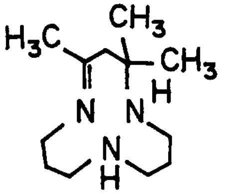

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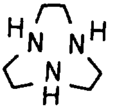
(**18**) (2,2,4-trimethyl-1,5,9-triazacyclododecane) and (**19**) (1-carboxymethyl-1,4,7-triazacyclononane), and for Ni^{2+} with (**18**) and (**20**) (2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene). Ligands (**15**)–(**20**) form dibridged dihydroxo complexes $[M_2L_2(OH)_2]^{2+}$. The stability (Table 3) of the species $[Cu_2L_2(OH)_2]^{2+}$ decreases from [9]aneN_3 to [12]aneN_3 as the size of the ligand increases. The presence of methyl groups on the carbon atoms of the macrocyclic framework (ligand (**18**)) produces a further decrease in stability. In the case of the ligand (**19**), only the monohydroxo complex $[Cu_2(\mathbf{19})_2OH]^+$ has been observed [64]. This is a consequence of the presence in (**19**) of the coordinating acetate arm which reduces the number of binding sites available on the metal ion for OH^- binding [64]. The complex cation $[Cu_2(\mathbf{19})_2OH]^+$ has been isolated in the solid state as a perchlorate salt and its crystal structure solved by X-ray analysis [64]. As shown by the structure (Fig. 16), each Cu^{2+} ion is coordinated by the three nitrogen atoms of the macrocycle, one oxygen atom of the carboxylate group and the oxygen atom of the bridging hydroxo group in a distorted square-pyramidal arrangement.

Due to the high number of free coordination sites remaining available in the metal complexes of triazamacrocyclic ligands, many bridged polynuclear species have been prepared. Their properties and structures have been extensively reviewed [65,66]. Because of the nature of the bridging agents, propagation of physico-chemical properties between the two metal centres is observed.

The efficiency of oxalate anion (ox^{2-}) as a bis-bidentate ligand between two complexed macrocyclic units, propagating electronic effects has been known for many years [67–74]. Only in the case of the Ni^{2+} complexes of ligand (**21**) cyclam (1,4,8,11-tetraazacyclotetradecane) has the formation in solution of the μ-oxalato

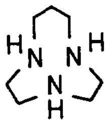
TABLE 3

log K, ΔH^0, and $T\Delta S^0$ values for the formation of bridged macrocyclic complexes of aza-ligands in aqueous solution[a]



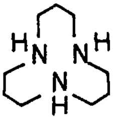
1,4,7-triazacyclononane
[9]aneN3

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
Cu(II)	2CuL + 2OH	15.04	pot			25	0.5 KNO3	61,62



1,4,7-triazacyclodecane
[10]aneN3

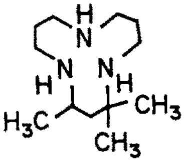
cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
Cu(II)	2CuL + 2OH	14.52	pot			25	0.5 KNO3	61,62



1,5,9-triazacyclododecane
[12]aneN3

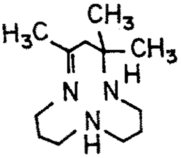
cation	reaction	logK	method	-ΔH(kJ/mol)	TΔS(kJ/mol)	T °C	medium	ref
Cu(II)	2CuL + 2OH	13.23	pot			25	0.5 KNO3	61,62

TABLE 3 *(continued)*



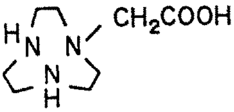
2,2',4-Trimethyl-1,5,9-triazacyclododecane
Me_3[12]aneN_3

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
Ni(II)	NiLOH + NiLOH	2.44	pot			25	0.1 $NaNO_3$	63
Cu(II)	2CuL + 2OH	12.6	pot			25	0.1 $NaNO_3$	63
	CuLOH + CuLOH	2.00	pot			25	0.1 $NaNO_3$	63



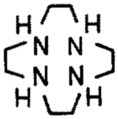
2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
Ni(II)	NiLOH + NiLOH	2.78	pot			25	0.1 $NaNO_3$	63



1-carboxymethyl-1,4,7-triazacyclononane

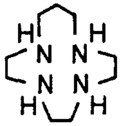
cation	reaction	logK	method	-ΔH(kJ/mol)	TΔS(kJ/mol)	T °C	medium	ref
Cu(II)	CuL + CuLOH	2.42	pot			25	0.5 KNO_3	64



1,4,7,10-tetraazacyclododecane
[12]aneN_4
cyclen

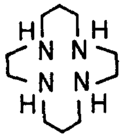
cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
Co(II)	2Co+2L+O_2+H_2O	28.4	pot			35	0.2 $NaClO_4$	78
	2CoL+O_2+H_2O	0.8	pot			35	0.2 $NaClO_4$	78
	2CoL+O_2+OH			159.0 cal				84

TABLE 3 (*continued*)



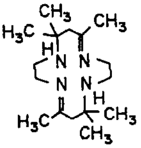
1,4,7,10-tetraazacyclotridecane
[13]aneN$_4$

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
Co(II)	$2Co+2L+O_2+H_2O$	29.8	pot			35	0.2 $NaClO_4$	78
	$2CoL+O_2+H_2O$	1.2	pot			35	0.2 $NaClO_4$	78



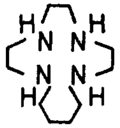
1,4,8,11-tetraazacyclotetradecane
[14]aneN$_4$
cyclam

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
Co(II)	$2CoL+O_2$	8.1	pol			25	0.1 KNO_3	76
	$2Co+2L+O_2$	27.1	pot			35	0.2 $NaClO_4$	78
	$2CoL+O_2$	1.7	pot			35	0.2 $NaClO_4$	78
	$2CoL+O_2$	9.8	kin			25	0.1 $HClO_4$	79
	$2CoL+O_2$	8.3	pot/spec/pol	86.1 cal	-38.7	25	0.1 KNO_3	82,85
	$2CoL+O_2+OH$	16.5	pot/spec/pol			25	0.1 KNO_3	82
	$2CoL+O_2+2OH$	23	pot/spec/pol	132.0 cal	~0	25	0.1 KNO_3	82,85
	$2CoLOH+O_2$			114.1		25	0.1 KNO_3	82



5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene

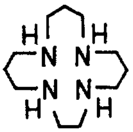
cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
Co(II)	$2CoL+O_2$	5.6	pol			25	0.1 KNO_3	76



1,4,7,10-tetraazacyclotetradecane

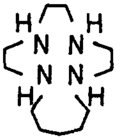
cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
Co(II)	$2Co+2L+O_2+H_2O$	27.6	pot			35	0.2 $NaClO_4$	81
	$2CoL+O_2+H_2O$	4.3	pot			35	0.2 $NaClO_4$	81

TABLE 3 (*continued*)



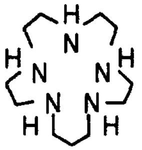
1,4,8,12-tetraazacyclopentadecane
[15]aneN$_4$

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
Co(II)	$2CoL+O_2$	5.2	spec			25	0.1 KNO_3	83
	$2CoL+O_2+H_2O$	19.3	spec	112.3 cal	~0	25	0.1 KNO_3	83,85
	$2CoL+O_2$	7/9	kin			25	0.1 KNO_3	79



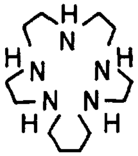
1,4,7,10-tetraazacyclopentadecane

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
Co(II)	$2Co+2L+O_2$	26.3	pot			35	0.2 $NaClO_4$	81
	$2CoL+O_2$	6.6	pot			35	0.2 $NaClO_4$	81



1,4,7,10,13-pentaazacyclohexadecane
[16]aneN$_5$

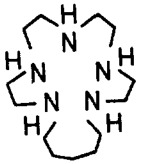
cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
Co(II)	$2Co+2L+O_2$	39.77	pot			35	0.2 $NaClO_4$	77
	$2CoL+O_2$	7.87	pot			35	0.2 $NaClO_4$	77



1,4,7,10,13-pentaazacycloheptadecane
[17]aneN$_5$

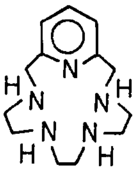
cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
Co(II)	$2Co+2L+O_2$	39.9	pot			35	0.2 $NaClO_4$	81
	$2CoL+O_2$	9.1	pot			35	0.2 $NaClO_4$	81

TABLE 3 (*continued*)



1,4,7,10,13-pentaazacyclooctadecane
[18]aneN5

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
Co(II)	$2Co+2L+O_2$	30.4	pot			35	0.2 $NaClO_4$	81
	$2CoL+O_2$	7.4	pot			35	0.2 $NaClO_4$	81

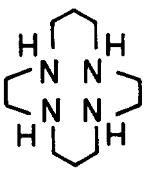


3,6,9,12,18-pentaazabicyclo[12.3.1]octadeca-1(18)14,16-triene

cation	reaction	logK	method	-ΔH°(kJ/mol)	TΔS°(kJ/mol)	T °C	medium	ref
Fe(II)	$2Fe+2L+O_2$	29.5	pot			35	0.2 $NaClO_4$	80
	$2FeL+O_2$	7.9	pot			35	0.2 $NaClO_4$	80
Co(II)	$2Co+2L+O_2$	37.5	pot			35	0.2 $NaClO_4$	80
	$2CoL+O_2$	9.6	pot			35	0.2 $NaClO_4$	80

[a] Only the left side (reactants) of the equilibrium reactions is indicated. Reactions including water molecules refer to: $m\mathrm{M}+l\mathrm{L}+n\mathrm{H_2O}=\mathrm{M}_m\mathrm{L}_l(\mathrm{OH})_n+n\mathrm{H}$; or to: $m\mathrm{M}+l\mathrm{L}+\mathrm{O_2}+n\mathrm{H_2O}=\mathrm{M}_m\mathrm{L}_l\mathrm{O_2}(\mathrm{OH})_n+n\mathrm{H}$. Charges have been omitted. Experimental methods for the determination of the equilibrium constants are abbreviated as follows: potentiometric (pot), spectrophotometric (spec), polarographic (pol), kinetic (kin). Only direct calorimetric methods (cal) for the determination of ΔH^0 are indicated.

bridged species $[\mathrm{Ni_2}(\mathbf{21})_2\mathrm{ox}]^{2+}$ been observed and the relevant stability constant determined [72] (Table 4). $[\mathrm{Ni}(\mathbf{21})]^{2+}$ is present in solution as a mixture of planar, *trans*-diaquo octahedral and *cis*-diaquo octahedral species, whose percentages vary with temperature and ionic strength. Among these forms, only the *cis*-diaquo



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complex is “well-disposed” to undergo chelation by the oxalate anion, while the other two species require a rearrangement of the ligand from planar to folded disposition. As a consequence, the binding constant (Table 4) for oxalate bridging

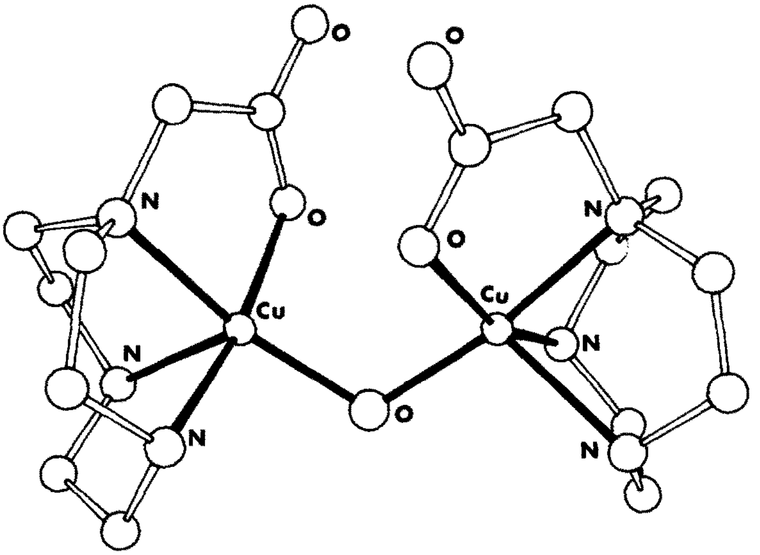
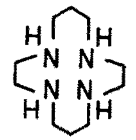


Fig. 16. Crystal structure of the μ-hydroxo complexed cation $[Cu_2(\mathbf{19})_2OH]^+$.

TABLE 4

log *K* values for the formation of oxalato-bridged complexes of $[Ni(cyclam)]^{2+}$[a]



1,4,8,11-tetraazacyclotetradecane
cyclam

reaction	logK	method	T °C	medium	ref
$2cis\text{-}[Ni(21)(H_2O)_2]^{2+} + ox^{2-}$	7.8	spec	25	$0.1\ KNO_3$	72
$2trans\text{-}[Ni(21)(H_2O)_2]^{2+} + ox^{2-}$	5.5	spec	25	$0.1\ KNO_3$	72
$2square\text{-}[Ni(21)]^{2+} + ox^{2-}$	4.7	spec	25	$0.1\ KNO_3$	72

[a] $[Ni(cyclam)]^{2+}$ in 0.1 mol dm^{-3} KNO_3 aqueous solution at 25°C is present as a mixture of *cis*-$[Ni(21)(H_2O)_2]^{2+}$ (69%), *trans*-$[Ni(21)(H_2O)_2]^{2+}$ (29%) and square-$[Ni(21)]^{2+}$ (2%).

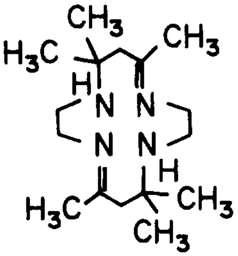
[b] Only the left side (reactants) of the equilibrium reactions is indicated. Experimental methods for the determination of the equilibrium constants are abbreviated as follows: spectrophotometric (spec).

two *cis*-$[Ni(\mathbf{21})(H_2O)_2]^{2+}$ is a full 2 log units higher than that for two *trans*-$[Ni(\mathbf{21})(H_2O)_2]^{2+}$ and 3 log units higher than that for two square-$[Ni(\mathbf{21})]^{2+}$.

The crystal structure of the $[Ni_2(\mathbf{21})_2ox]^{2+}$ complex, obtained by X-ray analysis [72], is presented in Fig. 17. Both Ni^{2+} are coordinated by the four nitrogen atoms of cyclam and two oxygen atoms of the bridging oxalate anion, in a distorted octahedral environment.

Another ligand able to link together two macrocyclic complexed units containing transition metal ions is molecular oxygen. Many transition metal complexes have attracted a great deal of interest for O_2-uptake due to their similarity to biological O_2 carriers and to their potential application in oxygen storage and activation [75]. Some thermodynamic data about dioxygen binding macrocyclic complexes are available [76–85]. Most deal with equilibrium constant determination, while a few also report the enthalpy contribution, obtained by direct microcalorimetry, for the formation the complexes [82–85]. Almost all of the complexes investigated contain Co^{2+} [76–86]; in one case [80] thermodynamic data for O_2 bridging two Fe^{2+} macrocyclic complexes have been reported.

In an earlier work [76], McLendon and Mason reported the equilibrium constant ($\log K = 8.1$; Table 3) for O_2 binding by the Co^{2+} complex of cyclam (**21**) to form the monobridged species μ-O_2-[Co(**21**)$H_2O]_2$, obtained at 25°C by polarographic methods. In the same paper, the stabilization of the oxygen adduct by trans axial ligands, such as pyridine, imidazole, NH_3, CN^-, as well as the reduction in oxygen affinity observed on modification of the equatorial ligand, substituting (**21**) by (**22**) (5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene), were analyzed. Later, Kodama and Kimura reported [78] a significantly smaller value ($\log K = 1.7$), obtained by potentiometry at 35°C, for oxygen binding by [Co(**21**)$H_2O]^{2+}$. Another value of the equilibrium constant ($\log K = 9.8$) for the same reaction at 25°C was presented by Wong et al. [79] as a result of kinetic studies. Finally, Cabani et al. [82,85] obtained $\log K = 8.3$ by potentiometric, spectrophotometric and polarographic methods at 25°C. In this accurate work, these authors also observed the formation of mono- and bihydroxo species of the μ-O_2 adduct and determined the relevant equilibrium constants (Table 3). Furthermore, they obtained calorimetrically the enthalpy changes (Table 3) for O_2 binding by [Co(**21**)]$^{2+}$ and [Co(**21**)OH]$^+$. The results clearly show that these processes are promoted by a great enthalpic contribution.



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Other tetraazamacrocycles, such as (**23**) cyclen (1,4,7,10-tetraazacyclododecane), (**24**) (1,4,7,10-tetraazacyclotridecane), (**25**) (1,4,7,10-tetraazacyclotetradecane), (**26**) (1,4,8,12-tetraazacyclopentadecane) and (**27**) (1,4,7,10-tetraazacyclopentadecane) have been employed for oxygen binding [78,79,81,83–85]. The Co^{2+} complex of cyclen, which does not maintain the obligatory trans geometry, binds molecular oxygen and

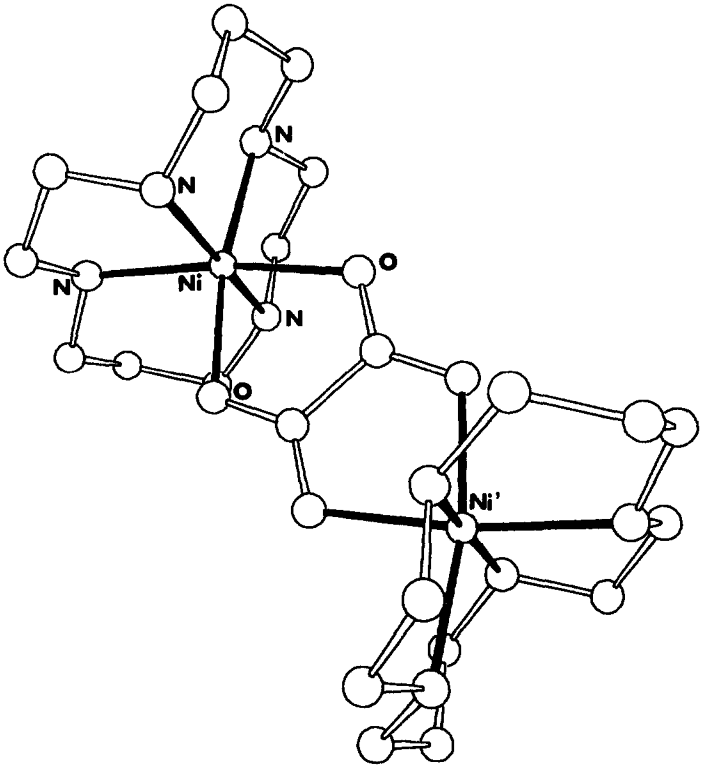
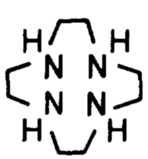


Fig. 17. Crystal structure of the centrosymmetric μ-oxalato complexed cation $[Ni_2(\mathbf{21})_2ox]^{2+}$.



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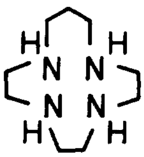

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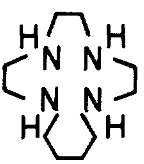

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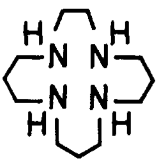

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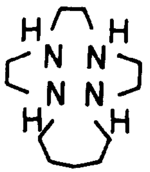

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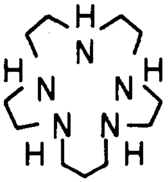
undergoes a simultaneous olation reaction forming (μ-peroxo)(μ-hydroxo) dibridged species [78,84]. Similar behaviour has also been reported for the Co^{2+} complex of (**25**) [81]. The synergy exercised by O_2 and OH^- in bridging two $[Co(\mathbf{23})]^{2+}$ complexed units is reflected by the large enthalpy change (159.0 kJ mol^{-1}) measured for this process [84]. This is 42 kJ mol^{-1} higher (Table 3) than that found for the reaction of $[Co(\mathbf{26})]^{2+}$ with O_2 and OH^- to form the μ-peroxo hydroxo monobridged complex [83,85], and 27 kJ mol^{-1} higher than that observed in the formation of the μ-peroxo bishydroxo monobridged $[Co_2(\mathbf{21})O_2(OH)_2]^{2+}$ complex [82,85].

The other tetraazacycloalkanes considered, (**24**), (**26**) and (**27**), form only monobridged μ-peroxo dicobalt complexes [78,81,83,85], which, in the case of (**24**) and (**26**), give rise to the formation of axially mono-olated species [78,83,85].

The pentaazamacrocycles (**28**) (1,4,7,10,13-pentaazacyclohexadecane), (**29**) (1,4,7,10,13-pentaazacycloheptadecane), (**30**) (1,4,7,10,13-pentaazacyclooctadecane) and (**31**) (3,6,9,12,18-pentaazabicyclo[12.3.1]octadeca-1(18),14,16-triene form



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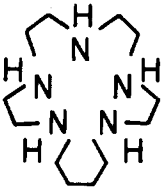

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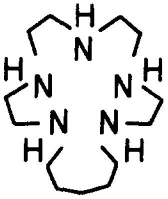

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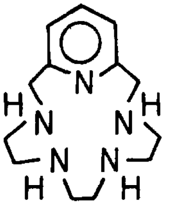

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cobalt(II) complexes which bind molecular oxygen giving rise to the formation of bridged μ-peroxo dinuclear complexes [77,80,81]. Given the number of nitrogen donor atoms in these macrocycles, no free binding sites are available for further coordination to the metal ions in the $LCo{-}O_2{-}CoL$ species and, indeed, only these species have been observed. With few exceptions, the stability constants for O_2 uptake by pentaazamacrocycles are generally higher (Table 3) than those found for the analogous tetraaza ligands. This has been ascribed [81] to the stabilizing effect of axial coordination of the fifth nitrogen atom, as already observed [76] for the binding of trans axial ligands to the oxygenated cobalt(II) complex of cyclam.

The ligand (**31**), which contains a pyridine group in its cyclic framework, offers a rare example of thermodynamically and kinetically resolved equilibria of O_2 binding by an Fe^{2+} complex of a non-porphyrin ligand in aqueous solution [80]. In this case, $LFe{-}O_2{-}FeL$ is the unique species being observed. $[Fe(\mathbf{31})]^{2+}$ shows a lower tendency to bind molecular oxygen than the related complex [Co(**31**)]$^{2+}$ (Table 3). Further equilibria involving O_2 uptake by some cyclam and oxo-cyclams derivatives were presented in ref. 81.

ACKNOWLEDGEMENTS

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