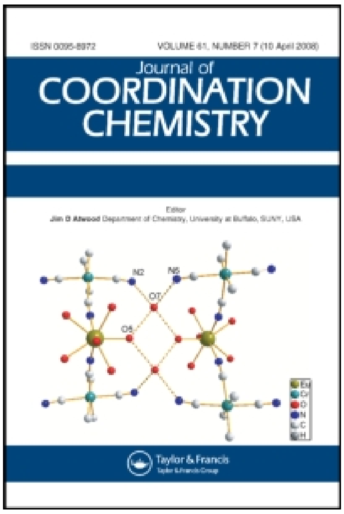

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NEW MACROCYCLIC LIGANDS [28]ane-N_6O_2 and [26]ane-N_6O_2 AND THEIR MONONUCLEAR AND DINUCLEAR COMPLEXES

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Two new macrocycles,[28]ane-N_6O_2 and [26]ane-N_6O_2, have been synthesized, purified and characterized. The protonation constants of the ligands and the formation constants of their mononuclear and dinuclear metal complexes with Cu(II), Ni(II), Zn(II) and Co(II) were measured potentiometrically at 25.0°C and ionic strength 0.10 M (KCl). Compared with the other transition metal dinuclear chelates, the dicopper complexes are relatively stable in aqueous solution. The hydroxo-bridged monohydroxo dinuclear copper(II) complex forms through a dissociation of a proton from coordinated water. Potentiometric p[H] measurements on the dicobalt(II) complex of [26]ane-N_6O_2 demonstrate formation of a hydroxo-bridged μ-peroxo type dioxygen complex with a water molecule coordinated to each cobalt center.

KEYWORDS: hexaaza macrocyclic ligands; transition metal complexes; dinuclear macrocyclic complexes; potentiometric pH measurements; mononuclear macrocyclic complexes; dicobalt dioxygen complexes

INTRODUCTION

Polyaza macrocyclic ligands and their reactions have been described in many reviews.[1–5] Their host-guest chemistry involves the reactions of protonated forms of these ligands, or their mononuclear or dinuclear complexes, with secondary coordinated organic or inorganic anions or molecules as coordinated guests. The ability of macrocyclic ligands to function as hosts in binding to metal ions and anions as guests depends on their structures, in particular on their degree of preorganization,[6] and on the nature of the donor atoms, as well as on the functional groups and size of the guests. It has been found that the well known macrocyclic ligand [24]ane-N_6O_2, (**1**), (1,4,7,13,16,19-hexaaza-10,22-dioxacyclotetracosane), OBISDIEN, forms mononuclear complexes of Cu(II), Co(II), Ni(II) and Zn(II), dinuclear complexes of Cu(II) and Co(II).[7] The dinuclear complexes are stabilized by secondary ligands that form bridges between the metal ions. Formation of the

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bridged dinuclear complexes has been verified by crystal structures of copper complexes of OBISDIEN with hydroxide[8] imidazolate[9] and azide[10]. The oxygenation reactions of dinuclear cobalt(II) complexes of [24]ane-N_6O_2 have also been investigated by potentiometric and spectrophotometric methods,[11,12] Recently, protonated forms of [24]ane-N_6O_2 (**1**) and its mononuclear and dinuclear cobalt(II) complexes have been of interest as hosts for inorganic anions, and its dicobalt dioxygen complex has been employed for oxidation of anionic guests.[13,14,15]

Two new dinucleating macrocyclic ligands [28]ane-N_6O_2, **2**, 1,15-dioxa-4,8,12,18,22,26-hexaazacyclooctacosane, OBISDIPN, and [26]ane-N_6O_2, **3**, 1,13-dioxa-4,7,10,16,20,24-hexaazacyclohexacosane, OBISDIPEN, which are homologs of [24]ane-N_6O_2, OBISDIEN, have been synthesized and studied in this laboratory. Each of these ligands contains two chelating subunits separated by two five-atom bridges at the center of which is located an ether oxygen. There are two ditrimethylenetriamine moieties in [28]ane-N_6O_2. The analogous macrocycle [26]ane-N_6O_2, **3**, is unsymmetrical and contains diethylenetriamine and ditrimethylenetriamine (1,5,9-triazanonane) moieties. The two new ligands [28]ane-N_6O_2, **2**, and [26]ane-N_6O_2, **3**, together with the known ligand [24]ane-N_6O_2, **1**, make up a series of macrocyclic ligands having six amino nitrogen donor atoms and two ether oxygens in the macrocyclic ring. This series of ligands provides an opportunity to study the effect of the size of the macrocyclic ring, the basicity and the steric effects, on the stabilities of their metal complexes.

This paper reports the synthesis, purification, characterization, basicity and metal binding properties of the new ligands [28]ane-N_6O_2 and [26]ane-N_6O_2. These properties are compared with those of the analogous macrocyclic ligand [24]ane-N_6O_2.

EXPERIMENTAL

Materials

All inorganic substances were of reagent grade quality and were used without further purification. The carbonate-free potassium hydroxide solution was obtained from Baker Dilut-it carbonate-free sealed ampoules and diluted according to directions. A CO_2-free atmosphere for the base was maintained at all times. Argon was used to protect the experimental solutions from CO_2 contamination, while the O_2 employed was first purged through a dilute KOH trap. All solutions were prepared with distilled water that was deionized by means of an ion-exchange column from which oxygen and carbon dioxide were removed by boiling and subsequent cooling under argon. The metal salts were standardized complexometrically by ethylenediaminetetraacetic acid (EDTA) titration.[16,17]

Purification and Characterization of the Ligands

The products obtained above were contaminated mainly by the small macrocycle [14]ane-N_3O, 1-oxo-4,8,12-triazacycloheptadecane, which is another new ligand that is described elsewhere.[18] The impure mixtures containing [28]ane-N_6O_2 and [26]ane-N_6O_2 were purified with the same procedure by use of chromatography on silica gel. In both cases the hexabromide salt was obtained by adding ethanol to an acidic solution containing the amine and hydrobromic acid. The white solid formed was filtered off and recrystallized from an ethanol/H_2O mixed solvent. *Anal.* Calcd. for $C_{20}H_{46}N_6O_2 \cdot 6HBr$: C, 27.03; H, 5.96; N, 9.45. Found: C, 26.85; H, 6.04; N, 9.30. *Anal.* Calcd. for $C_{18}H_{42}N_6O_2 \cdot 6HBr$: C, 25.14; H, 5.62; N, 9.77. Found: C, 25.10, H, 5.95; N, 9.54. Mass spectrum (FAB^+) for [28]ane-$N_6O_2 \cdot 6HBr$: m/z 403 $(M + H)^+$, 483 $(M + HBr)^+$, 565 $(M + 2HBr)^+$, and 645 $(M + 3HBr)^+$. Mass spectrum (FAB^+) for [26]ane-$N_6O_2 \cdot 6HBr$: m/z 375 $(M + H)^+$, 455 $(HBr)^+$, 537 $(M + 2HBr)^+$ and 617 $(M + 3HBr)^+$. ^1H NMR for [28]ane-N_6O_2 (in D_2O/DCl): 2.25 (m, 8H, 4(C-CH_2-C)), 3.35 (m, 16H, 8(CH_2-N)), 3.48 (triplet, 8H, 4(N-CH_2-C-O)) and 3.92 (triplet, 8H, 4(-CH_2-O))ppm. ^1H NMR for [26]ane-N_6O_2 (in D_2O/DCl): 2.29 (m, 4H, 2(C-CH_2-C)), 3.3-3.8 (m, 24H, 12(CH_2-N)) ppm.

General Techniques

Positive-ion fast atom bombardment (FAB) mass spectra were determined with a GV Analytical 70S high resolution, double focusing, sectored (EB) mass spectrometer equipped with a VG Analytical 11/250J data system. ^1H NMR spectra in D_2O solution were measured on a Varian XL-200 spectrometer. Sodium 3-(trimethylsilyl)propane-1 sulfonate (DSS) was used as an internal standard. Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Potentiometric determinations

The potentiometric apparatus consisted of a Corning Research pH meter Model 150 fitted with glass and calomel reference electrodes (Fisher), a water-jacketed titration cell, a 10 mL capacity Metrohm piston buret which delivers standard KOH titration solution directly to the air-sealed cell through a buret tip which is secured to the cell cap with a clamp and O-rings, and a thermostated constant temperature bath. All systems were studied under anaerobic conditions established by a stream of purified argon.

The pH meter was calibrated to read p[H] directly prior to each potentiometric equilibrium experiment with a freshly prepared solution of standard dilute acid (HCl) at an ionic strength adjusted to 0.10 M with KCl. The day-to-day changes observed were of the order of < 0.002 pH units at about p[H] 2.5. The term p[H] in this work is defined as -log $[H^+]$, and the direct pH meter readings were used in the calculations of the equilibrium constants. The value of Kw($[H^+][OH^-]$) used in the computations was found to be $10^{-13.78}$.[19] The ionic strength was adjusted to 0.10 M by the addition of KCl as supporting electrolyte, and the concentrations of the experimental solutions of ligand and metal were on the order of 2×10^{-3} M, with a slight excess of the macrocycle ligands. Experimental runs were carried out by adding increments of standard base to a solution containing the acid form of a macrocycle plus other components, as appropriate, so that 60 or more equilibrium data points were obtained per run.

Computations

The experimental p[H] values were plotted as a function of *a* values to obtain p[H] profiles for each system. An *a* value is the ratio of moles of base added per mole of ligand present, and *a* = 0 corresponds to the hexaprotonated form (H_6L) of the ligand. Calculations with potentiometic equilibrium data were performed with the program BEST.[19] The species considered present in the experimental solutions were those that one would expect to form according to established principles of coordination chemistry, and care was exercised to avoid the assumption of unnecessary species to improve the fit of the data. The program refines stability constants by iterative nonlinear least-squares fits of potentiometric equilibrium curves through a set of simultaneous mass balance equations for all the components expressed in terms of known and unknown equilibrium constants. Species distribution curves were calculated with the program SPE.[19]

RESULTS AND DISCUSSION

Protonation Constants

The protonation constants were determined by means of potentiometric titration. The potentiometric equilibrium curve for [26]ane-N_6O_2 (Figure 1) possesses an inflection at *a* = 1 followed by an extensive (five equivalent) buffer region (from *a* = 1 to 6). Accordingly there are one low and four relatively high protonation constants. The logarithmic values listed in Table 1 are 10.21, 9.33, 8.54, 7.77, 6.94 and 3.67.

A potentiometric titration curve (not shown) was obtained for [28]ane-N_6O_2. This ligand, also behaves as a hexaprotic base with the following six protonation constants: 10.35, 9.79, 8.92, 8.12, 7.41 and 6.81.

Of interest is the decrease between the fifth and sixth stepwise protonation constants. The difference is around 3 log units for [26]ane-N_6O_2 and <1 for [28]ane-N_6O_2, which is much larger than other decreases (around 1 log unit or less). This behaviour can be explained as due to the minimization of electrostatic

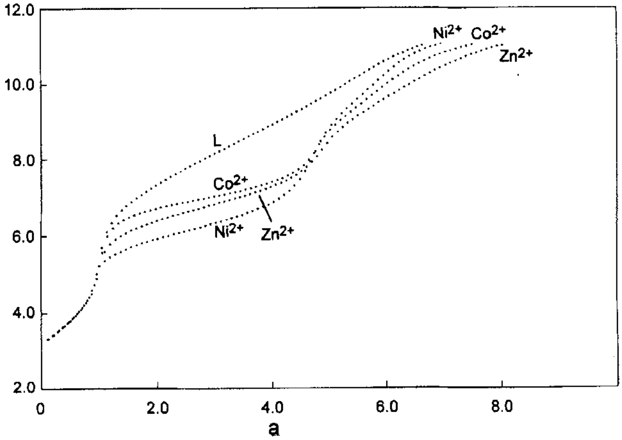


Figure 1 Potentiometric p[H] profiles of [26]ane-N_6O_2 and its 1:1 systems with Co(II), Zn(II) and Ni(II) at 2.20 × 10^{-3} M; t = 25 °C and μ = 0.10 M (KCl); *a* = mole of base added per mole of ligand.

Table 1 Protonation constants at 25.0 °C and μ = 0.10M in aqueous solution

Equilibrium Quotient	LogK				
	[28]ane-N_6O_2[a] (OBISDIPN)	[26]ane-N_6O_2[a] (OBISDIPEN)	[24]ane-N_6O_2[b] (OBISDIEN)	DIPN[c]	DIEN[c]
[HL]/[L][H]	10.35	10.21	9.61	10.65	9.84
$[H_2L]/[HL][H]$	9.79	9.33	8.92	9.57	9.02
$[H_3L]/[H_2L][H]$	8.92	8.54	8.28	7.69	4.23
$[H_4L]/[H_3L][H]$	8.12	7.77	7.62		
$[H_5L]/[H_4L][H]$	7.41	6.94	3.75		
$[H_6L]/[H_5L][H]$	6.81	3.67	2.95		

[a] Estimated errors for the protonation constants are ±0.5 of the last significant number.[b] Ref. 7, 11. [c] Ref. 20.

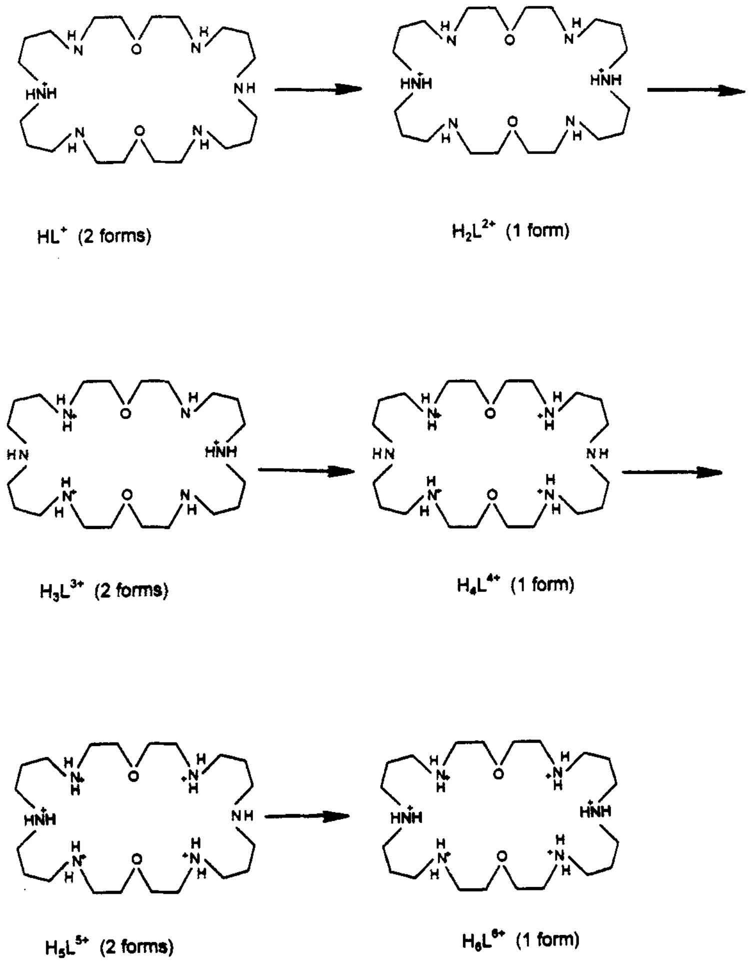
repulsion between positive charges in protonated species of the polyaza macrocycles. The first five protons can occupy positions on basic amino groups separated by an unprotonated amino group. That is, the ligand follows a protonation pattern with positive nitrogens as far apart as possible, which minimizes electrostatic repulsions. In the penta and hexa protonated species, the electrostatic repulsion between the positive charges are obviously higher. The buildup of positive charge destabilizes the protonated forms, leading to lower protonation constants. Six protonation steps are proposed as shown in Scheme 1.

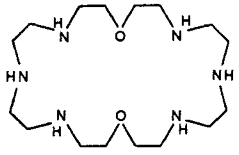
It is seen from Table 1 that [28]ane-N_6O_2 is more basic than [26]ane-N_6O_2 and the previously known ligand [24]ane-N_6O_2 because of the fact that the amino groups of [28]ane-N_6O_2 are farther apart. That is, the protons in the equally polyprotonated forms of [28]ane-N_6O_2 with respect to polycharged species of [26]ane-N_6O_2 and [24]ane-N_6O_2 are localized farther from each other achieving a better minimization of the electrostatic repulsion between positive charges. Another reason is the inductive effect due to the greater number of methylene groups of [28]ane-N_6O_2 in the chain. This is especially true for the first protonation constant. The protonation constants of analogous DPN, **4**, 1,5,9-triazanonane (or ditrimethylenetriamine), and DIEN, diethylenetriamine, which are listed in Table 1 for comparison, provide a good example of the inductive effect. All the pKs of DPN are considerably higher than the corresponding values of DIEN.

Metal Binding Constants

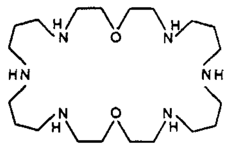
The potentiometric equilibrium titration curves for Co(II), Zn(II) and Ni(II) are shown in Figure 1. The related stability constants are listed in Tables 2 and 3. The dinuclear complexes of these metal ions are weakly stable. For Ni(II), Co(II) and Zn(II) 2:1 ratios of metal ion to ligand resulted in precipitation of metal hydroxide from neutral to alkaline solution. It is interesting to observe the dinuclear cobalt(II) complex, which can form, but is, as in the cases of Ni(II) and Zn(II), not stable in alkaline solution. It was found that the Co(II) dinuclear complex can be stabilized by the presence of dioxygen. The titration curves for the Co(II) system are illustrated in Figure 2. In comparison with the titration curve of the free ligand, the pH values of the metal-containing solutions after $a = 1$ are shifted to lower pH through hydrogen ion displacement. The depression of the buffer region provides a qualitative measure of the affinity of the metal ion for the ligand. It is seen that the

Scheme 1 Suggested protonation steps for [28]ane-N_6O_2

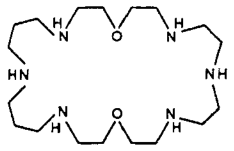




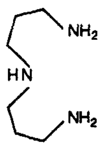
1. [24]-aneN$_6$O$_2$



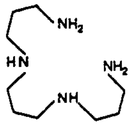
2. [28]-aneN$_6$O$_2$



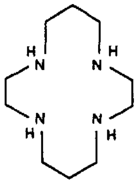
3. [26]-aneN$_6$O$_2$



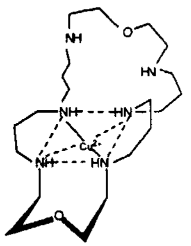
4. Dipn



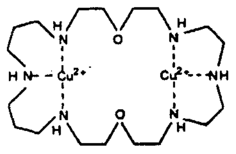
5. Tripn



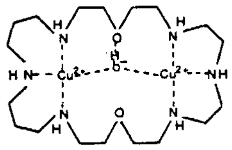
6. [14]-aneN$_4$



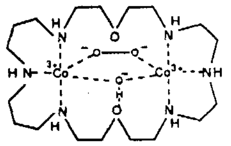
7. Mononuclear Cu(II) complex of [28]-aneN$_6$O$_2$



8. Dinuclear Cu(II) complex of [26]-aneN$_6$O$_2$



9. Hydroxo-bridged dicopper(II)-[26]aneN$_6$O$_2$



10. Suggested arrangement of coordinate bonds in dibridged dioxygen dicobalt complex of [26]-aneN$_6$O$_2$

Table 2 Stability Constants[a] of Metal Complexes of [26]ane-N_6O_2, OBISDIPEN, and [28]ane-N_6O_2, OBISDIPN, (μ = 0.10 M KCl; t = 25.0 °C)

Quotient (K)	Cu(II)	Ni(II)	Zn(II)	Co(II)
[26]ane-N_6O_2[b]				
[ML]/[M][L]	14.91	10.84	8.03	8.04
[MHL]/[ML][H]	9.40	9.51	9.02	9.50
[MH_2L]/[MHL][H]	7.89	7.09	7.34	7.41
[MH_3L]/[MH_2L][H]	7.27	6.15	7.01	5.9
[ML]/[M(OH)L][H]	10.50	11.6	10.23	10.77
[28]ane-N_6O_2[c]				
[ML]/[M][L]	12.58	7.35	8.21	5.98
[MHL]/[ML][H]	9.59	9.58	8.85	8.26
[MH_2L]/[MHL][H]	8.16	8.45	8.45	8.68
[MH_3L]/[MH_2L][H]	7.14	7.13	6.65	8.35
[ML]/[M(OH)L][H]	-	11.3	9.49	10.00

[a] Estimated errors are ±0.02, or about 3 times the σ_{fit}. [b] log K([Co_2L]/[Co][CoL]) = 3.1; log K ([Zn_2L]/[ZnL][Zn]) = 6.16; log K ([Zn_2OHL][H]/[Zn_2L]) = −7.05; log K ([$Zn_2(OH)_2L$][H]/[$Zn_2(OH)L$]) = −10.21. [c] log K ([Ni_2L]/[NiL][Ni]) = 5.54; log K ([Co_2L]/[CoL][Co]) = 3.40; log K ([Zn_2L]/[nL][Zn]) = 4.85; log K) [Zn_2OHL][H]/[Zn_2L]) = −7.95; log K ([$Zn_2(OH)_2L$][H]/[$Zn_2(OH)L$]) = −10.3.

buffer region above pH 7 is further depressed in the presence of 1 atm of oxygen, indicating the formation of dioxygen complex, and the involvement of two hydrolytic species. For 2:1 system under argon, precipitation occurred at around pH 8. Under O_2 the buffer region was extended.

The curves for the Cu(II) system (Figure 3) indicate that Cu(II) reacts much more strongly with the ligand compared to Ni(II), Zn(II) and Co(II). The curve for 1:1 Cu(II) system shows a sharp inflection at a = 3, followed by a two proton neutralization step, which suggests that both diethylenetriamine and ditrimethylenetriamine moieties of [26]ane-N_6O_2 and [28]ane-N_6O_2 may form coordinate bonds to Cu(II). Formation of dinuclear Cu(II) complexes is obvious from the equilibrium curves of Cu(II) systems. For the 2:1 system of [26]ane-N_6O_2, all six protons are displaced by Cu(II) above pH 7. It is apparent from visual inspection of the equilibrium curves that the dinuclear Cu(II) complex forms a monohydroxo chelate, involving neutralization of an additional proton from the dinuclear complex in the pH range of both [26]ane-N_6O_2 and 8 to 10 for [28]ane-N_6O_2. Table 3 lists the stability constants for the mononuclear and dinuclear copper(II) complexes of [28]ane-N_6O_2 and [26]ane-N_6O_2, along with the literature values of

Table 3 Stability Constants of Cu(II) complexes

Quotient(K)	[28]ane-N_6O_2	[26]ane-N_6O_2	[24]ane-N_6O_2[a]
[ML]/[M][L]	12.58	14.91	16.46
[MHL]/[ML][H]	9.59	9.40	8.01
[MH_2L]/[MHL][H]	8.16	7.89	7.46
[MH_3L]/[MH_2L][H]	7.14	7.27	3.45
[M(OH)L][H]/[ML]	-	-10.50	-10.63
[M_2L]/[ML][M]	9.99	10.24	10.84
[M_2L]/[M]^2[L]	27.79	25.15	27.30
[$M_2(OH)L$][H]/[M_2L]	-9.20	-8.50	-6.51
[$M_2(OH)_2L$][H]/[$M_2(OH)L$]	-9.95	-10.67	-10.4

[a] Ref. 17,11.

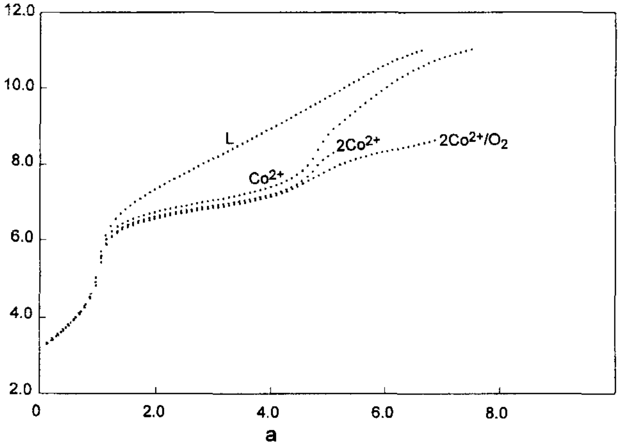


Figure 2 Potentiometric p[H] profiles of [26]ane-N_6O_2 and its 1:1 system with Co(II) and 2:1 systems in the presence and the absence of dioxygen at 2.20 × 10^{-3} M; t = 25°C and μ = 0.10 M (KCl); a = mole of base added per mole of ligand.

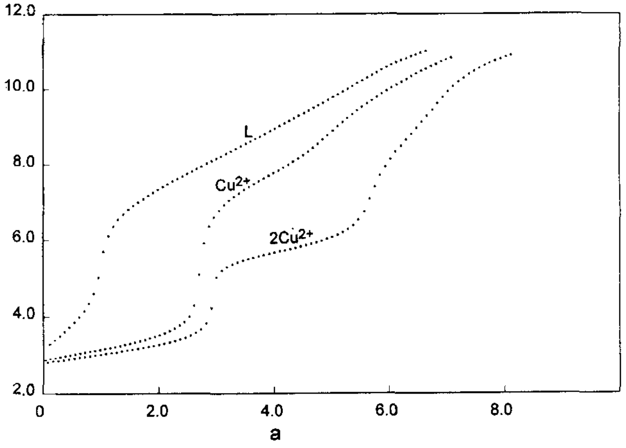


Figure 3 Potentiometric p[H] profiles of [26]ane-N_6O_2 and its 1:1 and 2:1 systems with Cu(II) at 2.20 × 10^{-3} M; t = 25°C and μ = 0.10 M (KCl); *a* = mole of base added per mole of ligand.

[24]ane-N_6O_2 for comparison. The 1:1 and 2:1 chelates as well as three protonated and one monohydroxo species were found for mononuclear complexes, two hydroxo species for dinuclear complexes were found for all three macrocycles.

Stability constants for Cu(II) complexes of some nitrogen-donor macrocycles and open-chain ligands are compared in Table 4. The stability of the [28]ane-N_6O_2 complex is somewhat lower than that of DIPN, **4**. The reason for this result is partly steric and partly reduced basicity of the four N's by the ethee oxygens. A tetradentate amine, TRIPN, **5**, 1,5,9,13-tetraazatridecane, is a more suitable ligand for comparison. As with [28]ane-N_6O_2, **2**, this open-chain ligand forms a Cu(II)

Table 4 Stability Constants of 1:1 Cu(II) Complexes of Nitrogen-donor Macrocycles and Open-chain Ligands

Ligand	Log K_1	Reference
1	16.46	7
2	12.58	this work
3	14.91	this work
4	14.2	22
5	17.05	22
6	26.5	20

complex with four Cu(II)-nitrogen coordinate bonds. But the stability of its Cu(II) complex is higher than that of **2**, because of its open structure.

When one compares the stability constant of the Cu(II) complex of the macrocyclic ligand [14]-aneN4, **6**, 1,4,8,11-tetraazacyclotetradecane, with four amino nitrogen donors, with that of the larger macrocyclic ligand [28]ane-N_6O_2, it is seen that the smaller macrocyclic ligand is 14 log units higher in stability because the latter is more preorganized for metal complex formation and does not have to undergo the extensive distortion illustrated by formula **7**.

When stabilities of the mononuclear Cu(II) complexes of **1**, **2** and **3** are compared, it is seen that the smaller macrocyclic ligands form the more stable complexes. It is also obvious that the larger macrocycles are more flexible, and may form metal complexes such as that illustrated by **7** readily. A possible structure similar to **7** has been suggested previously for [24]ane-N_6O_2 complexes.[7] Also the Cu(II) ion is the smallest of the metal ions investigated, and its complexes with ligands that form more six-membered chelate rings would be expected to be more stable than analogous complexes of ligands that form more five-membered chelate rings.[4,6,21] The other effects may account for the stability sequence of three mononuclear Cu(II) complexes, [28]ane-N_6O_2 < [26]ane-N_6O_2 < [24]ane-N_6O_2.

With increasing ring size of the macrocycle, the stability constants listed in Table 5 generally decrease for Ni(II), Zn(II) and Co(II). This applies to the behaviour of the Cu(II) complexes, as well despite the fact that these are larger metal ions, and it has been shown[21] that stabilities of larger metal ions are higher with five-membered chelate rings than are those with six-membered chelate rings. Also, it is possible that the larger macrocyclic rings incur more strain in conforming to the octahedral coordination sphere required by these metal ions than to the square or square-pyramidal arrangement of donors preferred by Cu(II).

The present experimental results indicate formation of dinuclear Cu(II) complexes of both [28]ane-N_6O_2 and [26]ane-N_6O_2. As expected, the inclusion of a second meal ion within the macrocycle occurs with much lower binding affinity

Table 5 Stability Constants of Metal Complexes

	$\log K_{ML}$		
	[28]ane-N_6O_2	[26]ane-N_6O_2	[24]ane-N_6O_2[a]
Cu^{2+}	12.58	14.91	16.46
Ni^{2+}	7.35	10.84	13.65
Zn^{2+}	8.21	8.03	10.66
Co^{2+}	5.98	8.04	9.73

[a] Ref. 7.

than does the first. Also the stability sequence [28]ane-N_6O_2 < [26]ane-N_6O_2 < [24]ane-N_6O_2, which is similar to the relative stabilities of the mononuclear complexes, is no doubt due to the fact that rearrangement of the ligand that must occur in going from the mononuclear to the dinuclear complex is larger for the larger macrocycles. Therefore this type of steric effect seems to account for the observed decrease in stability. It is noted that the overall log stability constant, $[M_2L]/[M]^2[L]$, of OBISDIEN is only a little larger than the corresponding constants of the complexes formed from the dinucleating macrocyclic ligands that form larger chelate rings, in spite of the greater flexibility and lower degree of preorganization of the latter. This characteristic, which tends to lower stability of the dinuclear complex, is compensated for by two factors: 1, the intrinsic basicities of the amino nitrogens are greater for the larger macrocycles, as shown above, so that the metal-nitrogen coordinate bonds are stronger; 2, the larger macrocyclic ligands tend to form more stable chelates with the small Cu(II) ion than do the smaller of (five-membered) chelate rings formed by OBISDIEN.

Of interest are the pKs for formation of the monohydroxo dinuclear complexes which are considerably lower than those for formation of corresponding mononuclear chelates. Strong binding of the hydroxide ion in dinuclear complexes is an indication that the hydroxide ion is bridged between the two Cu(II) centers, **9**. Formation of the hydroxo-bridged dinuclear Cu(II) complex of [24]ane-N_6O_2 has been confirmed by an X-ray crystal structure of the copper complex.[8] The higher basicities of the amino groups in [28]ane-N_6O_2, and to a lesser extent in [26]ane-N_6O_2, could be expected to produce stronger Cu-N coordinate bonds, and therefore weaker coordinate bonds to a secondary ligand such as the hydroxide anion. This expectation is verified by the fact that the affinity of the dinuclear Cu(II) complex of [24]ane-N_6O_2 for the OH^- ion is the highest among the three macrocycles listed in Table 3, and the affinity for OH^- becomes successively lower as the size of the macrocyclic ring increases, indicating that hydroxo bridging is successively weakened in the series [24]ane-N_6O_2 > [26]ane-N_6O_2 > [28]ane-N_6O_2.

Among the chelates of divalent metal ions used in this work (Table 5) the copper complexes have the highest stability. The pattern of stability constant variations illustrated in Figure 4 is typical of first row transition metal ions and Zn^{2+}. For Ni(II), Zn(II) and Co(II), a 2:1 ratio of metal ion to ligand results in precipitation of the second metal ion as the hydroxide in neutral and alkaline solution, indicating that the corresponding dinuclear complexes are very weak. The present results show that both macrocycles [28]ane-N_6O_2 and [26]ane-N_6O_2 have a tendency to form mononuclear rather than dinuclear complexes, probably because of the flexibility of the macrocycle ring and lack of sufficient preorganization needed to keep the two ditrimethylenetriamine moieties for [28]ane-N_6O_2, and the ditrimethylenetriamine and diethylenetriamine moieties for [26]ane-N_6O_2 separated from each other.

However, the stability of the dinuclear cobalt(II) complex of [26]ane-N_6O_2 is considerably increased by the presence of dioxygen, which is good evidence for increase in charge of the metal ion, as well as coordination of the dioxygen by formation of a peroxo bridge between the metal centers. The affinities of the metal ion for hydroxide ion in the dinuclear complexes are obviously much higher than that of the metal ion in the mononuclear complex, as shown by differences in equilibrium constants (Table 6). The low pK for formation of the monohydroxo dioxygen dinuclear complex indicates that the hydroxo group occupies a bridging position. Thus formula, **10**, is used to represent the dibridged (μ-peroxo-μ-hydroxo)

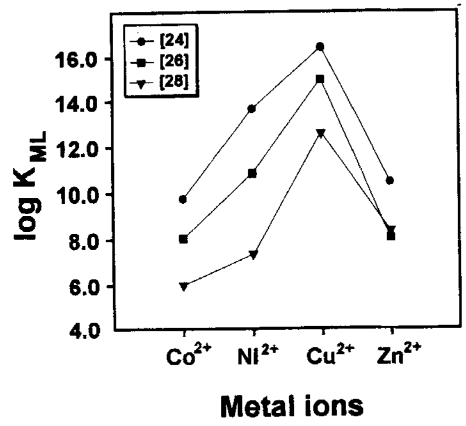


Figure 4 Plot of the stability constants (log K_{ML}) of the divalent metal complexes of the ligands [28]ane-N_6O_2, [26]ane-N_6O_2 and [24]ane-N_6O_2 *vs.* the atomic number of the metal ion.

Table 6 Equilibrium Constants of Cobalt(II) Complexes of [26]ane-N_6O_2 and [24]ane-N_6O_2.

Quotient(K)	[26]ane-N_6O_2	[24]ane-N_6O_2[a]
$CoL/Co \cdot L$	8.04	9.73
$CoHL/CoL \cdot H$	9.50	7.58
$CoH_2L/CoHL \cdot H$	7.41	5.97
$Co(OH)L \cdot H/Co \cdot L$	-10.77	-11.8
$Co_2L/CoL \cdot Co$	3.1	2.7
$[Co_2L(O_2)(OH)] \cdot [H]/[Co_2L]P_{O2}$	-7.97	-3.29
$[Co_2L(O_2)/(OH)_2] \cdot [H]/[Co_2L(O_2)(OH)]$	-8.19	-8.25
$[Co_2L(O_2)(OH)_3] \cdot [H]/[Co_2L(O_2)(OH)_2]$	-	-9.36

[a] Ref. 7.

dioxygen complex. Each metal ion in **10** has an additional coordination site which is not indicated in the formula, and may be occupied by a coordinated water molecule to complete six coordination of the metal ion, which is Co(III)-like in nature. It is noted that the complex, **10**, undergoes two additional successive hydrolysis steps to form a dihydroxo- and a trihydroxo-dioxygen complex as the p[H] of the solution is increased.

The distribution curves of the 2:1 molar ratio of Co(II):[26]-ane-N_6O_2 in the presence of excess oxygen illustrated in Figure 5 indicate that the hydroxo-bridged dinuclear dioxygen species begins to form around p[H] 6.7, and predominates over other solution species at p[H] 7.5. The monohydroxo-bridged dioxygen complex is converted to the dihydroxo and trihydroxo species at higher pH. The oxygenated species account for 95–100% of all complex species above p[H]9.

The oxygenation constants of the dinuclear Co(II) complex of [26]ane-N_6O_2, and the two subsequent hydrolysis steps are listed in Table 6, along with the corresponding values of OBISDIEN. The oxygen complex with one hydroxo bridge, $Co_2LO_2(OH)$, is about four orders of magnitude less table than the corresponding

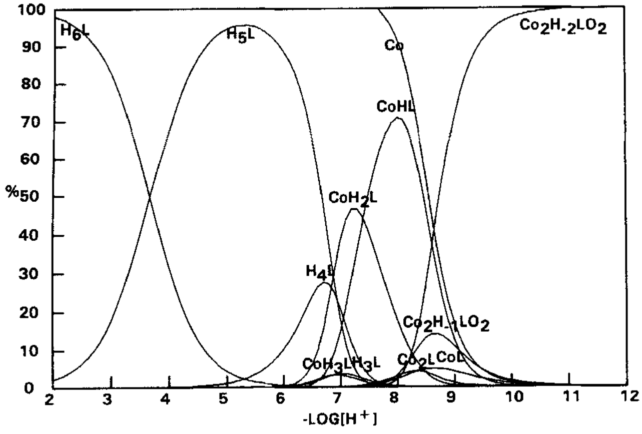


Figure 5 Species distribution curves of the 2:1 Co(II)-[26]ane-N_6O_2 system under dioxyen as a function of -log[H^+] for a solution initially containing 1.0×10^{-3} M [26]ane-N_6O_2 and 2.0×10^{-3} M Co(II) under oxygen (P_{O_2} = 1 atm), t = 25°C and μ = 0.10 M (KCl); *a* = mole of base added per mole of ligand.

dioxygen complex of OBISDIEN. Once formed, however, the two dioxygen complexes have similar tendencies to form dihydroxo and trihydroxo species at higher pH, as indicated by their hydrolysis constants.

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