

# Notes

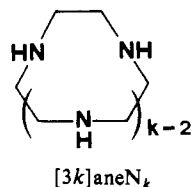
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## Anaerobic Complexation of Cobalt(II) by $[3k]aneN_k$ ( $k = 7-12$ ) Polyazacycloalkanes

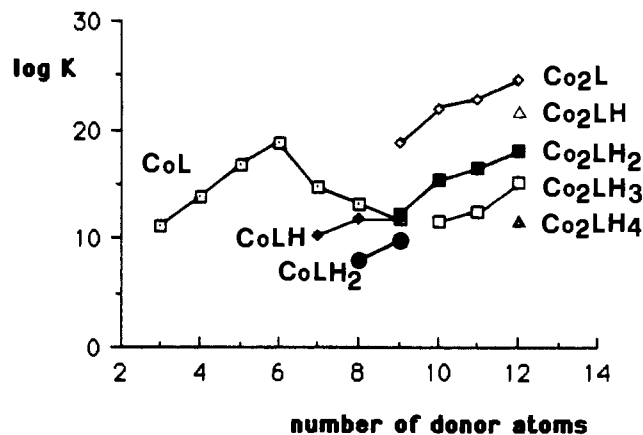
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In consideration of the chemical results obtained in the study of the ligating ability of  $[3k]aneN_k$  polyazacycloalkanes ( $k =$



$7-12$ ) toward metal ions such as cadmium(II),<sup>2</sup> zinc(II),<sup>3,4</sup> copper(II),<sup>5-9</sup> and nickel(II),<sup>10</sup> an extension to cobalt(II) seems of natural interest. Also, the formation of cobalt(II)-polyaza complexes is interesting because of their implication in transport and storage of molecular oxygen.<sup>11</sup> For this purpose, tetraaza-,<sup>12</sup> pentaaza-,<sup>13</sup> and hexaazamacrocyclic<sup>14</sup> ligands have been studied. The kinetics and thermodynamics of the formation of their O<sub>2</sub> adducts are strongly affected by the structure of the macrocyclic ligand. Tetraazacycloalkanes form oxygenated complexes  $[(CoL)_2O_2OH]^{3+}$  and  $[(CoL)_2O_2]^{4+}$ , in which two complexed subunits are bridged by molecular oxygen.<sup>12</sup> In pentaazacycloalkanes, the additional nitrogen donor atom in the macrocyclic framework appreciably promotes the uptake of molecular oxygen.<sup>13</sup> On the other hand, the coordination of hexaazacycloalkanes to the cobalt(II) ion produces only a very slow and difficult oxygenation of the resulting complex.<sup>14</sup> Owing to their ability to form dinuclear complexes,<sup>2-10</sup> large  $[3k]aneN_k$  polyazacycloalkanes, containing up to 12 nitrogen donors, could represent a good field



**Figure 1.** Logarithms of the equilibrium constants related to the reaction of cobalt(II) with  $[3k]aneN_k$  ( $k = 3-12$ ) ligands and with their protonated forms,  $nCo + LH_m = Co_nLH_m$  ( $n = 1, 2; m = 0-4$ ). Charges have been omitted for clarity.

in which to study O<sub>2</sub> uptake, as inside the macrocyclic cavity they can potentially produce two binding sites in which the two cobalt(II) ions could possess variable surroundings in geometry and number of coordinated donor atoms. However, the first step in these types of studies is undoubtedly the determination of the equilibria between cobalt(II) and the macrocyclic ligands under anaerobic conditions. Therefore, in this paper we present the results of a study of the complexation between  $[3k]aneN_k$  macrocycles ( $k = 7-12$ ) and cobalt(II) in aqueous solution under an Ar atmosphere.

### Experimental Section

**Emf Measurements.** All potentiometric measurements were carried out in 0.15 mol dm<sup>-3</sup> NaClO<sub>4</sub> (C. Erba ACS grade) purified according to a previously reported procedure.<sup>15</sup> The stock solution of cobalt(II) chloride was prepared in doubly distilled water and the concentration of the metal ion determined by standard gravimetric methods. CO<sub>2</sub>-free NaOH and HCl solutions used in the titrations were prepared as described in ref 16. Hydrochloride salts of the  $[3k]aneN_k$  ( $k = 7-12$ ) ligands employed here were obtained as described in ref 5-9. The potentiometric titrations were carried out by using equipment that has been fully described.<sup>17</sup> All solutions used were exhaustively deaerated by an argon flow and kept under the same atmosphere during the measurements. At least two titration curves were used for each system investigated. In order to reach the equilibrium in these complex formation reactions, several minutes were allowed to elapse between each emf reading. Moreover, several measurements were made both in formation and in dissociation (from acid to alkaline solutions and vice versa) in order to test for reversibility of the reactions. The computer program SUPERQUAD<sup>18</sup> was used to process emf data and to calculate the stability constants by following the procedure reported in ref 9.

### Results and Discussion

The coordination ability of  $[3k]aneN_k$  ligands ( $k = 3-12$ ) toward the cobalt(II) ion is shown in Figure 1, where the logarithms of the stability constants of the cobalt(II) complexes have been plotted versus the number of nitrogen donor atoms of each macrocyclic ligand. This figure was obtained by using stability constants experimentally determined in this work ( $k = 7-12$ , Table I) and taken from previous reports ( $k = 3-6$ ).<sup>12-14,19</sup> Under the

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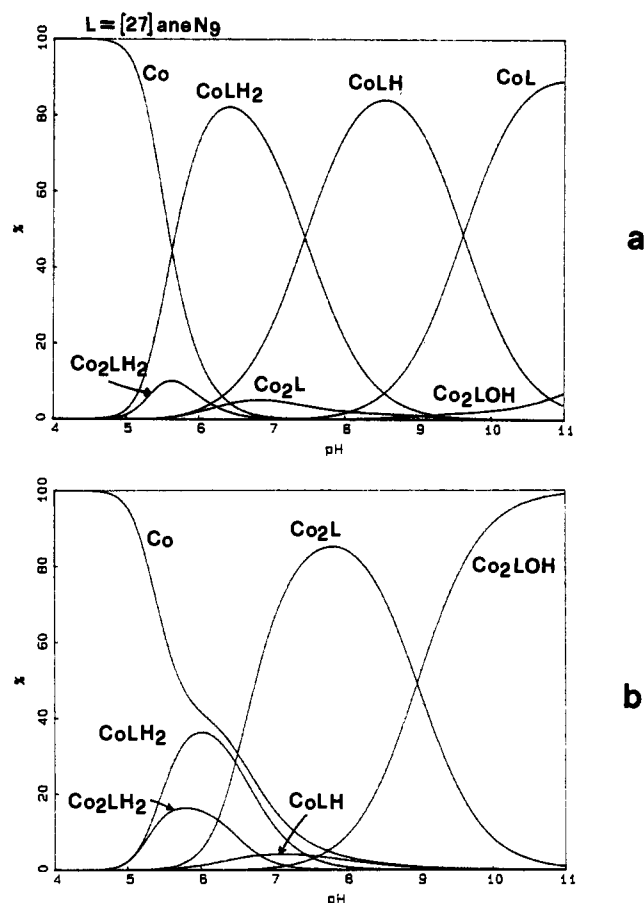
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**Table I.** Formation Constants of Cobalt(II) Complexes of Macrocycles [3*k*]aneN<sub>*k*</sub> (*k* = 7–12) in 0.15 mol dm<sup>-3</sup> NaClO<sub>4</sub> Aqueous Solution at 25 °C

reaction	L					
	[21]aneN <sub>7</sub>	[24]aneN <sub>8</sub>	[27]aneN <sub>9</sub>	[30]aneN <sub>10</sub>	[33]aneN <sub>11</sub>	[36]aneN <sub>12</sub>
Co + L = Co(L) <sup>a</sup>	14.69 (1) <sup>b</sup>	13.20 (2)	11.84 (6)			
Co + L + H = Co(L)H	19.96 (2)	21.53 (1)	21.46 (5)			
Co + L + 2H = Co(L)H <sub>2</sub>		28.93 (2)	28.91 (1)			
2Co + L = Co <sub>2</sub> (L)			18.85 (1)	21.85 (2)	22.90 (2)	24.55 (2)
2Co + L + 4H = Co <sub>2</sub> (L)H <sub>4</sub>						48.76 (2)
2Co + L + 3H = Co <sub>2</sub> (L)H <sub>3</sub>				39.79 (4)	40.91 (4)	43.45 (4)
2Co + L + 2H = Co <sub>2</sub> (L)H <sub>2</sub>			31.32 (4)	34.67 (1)	35.83 (1)	37.62 (4)
2Co + L + H = Co <sub>2</sub> (L)H						31.29 (3)
2Co + L + H <sub>2</sub> O = Co <sub>2</sub> (L)OH + H			9.88 (2)	11.94 (6)	12.72 (4)	13.87 (3)
Co(L) + H = Co(L)H	5.27	8.33	9.62			
Co(L)H + H = Co(L)H <sub>2</sub>		5.40	7.45			
Co <sub>2</sub> (L) + H = Co <sub>2</sub> (L)H						6.73
Co <sub>2</sub> (L)H + H = Co <sub>2</sub> (L)H <sub>2</sub>						6.34
Co <sub>2</sub> (L)H <sub>2</sub> + H = Co <sub>2</sub> (L)H <sub>3</sub>				5.12	5.08	5.83
Co <sub>2</sub> (L)H <sub>3</sub> + H = Co <sub>2</sub> (L)H <sub>4</sub>						5.31
Co <sub>2</sub> (L) + OH = Co <sub>2</sub> (L)OH			4.76	3.82	3.55	3.05

<sup>a</sup>Charges omitted for clarity. <sup>b</sup>Values in parentheses are the standard deviations in the last significant figure.

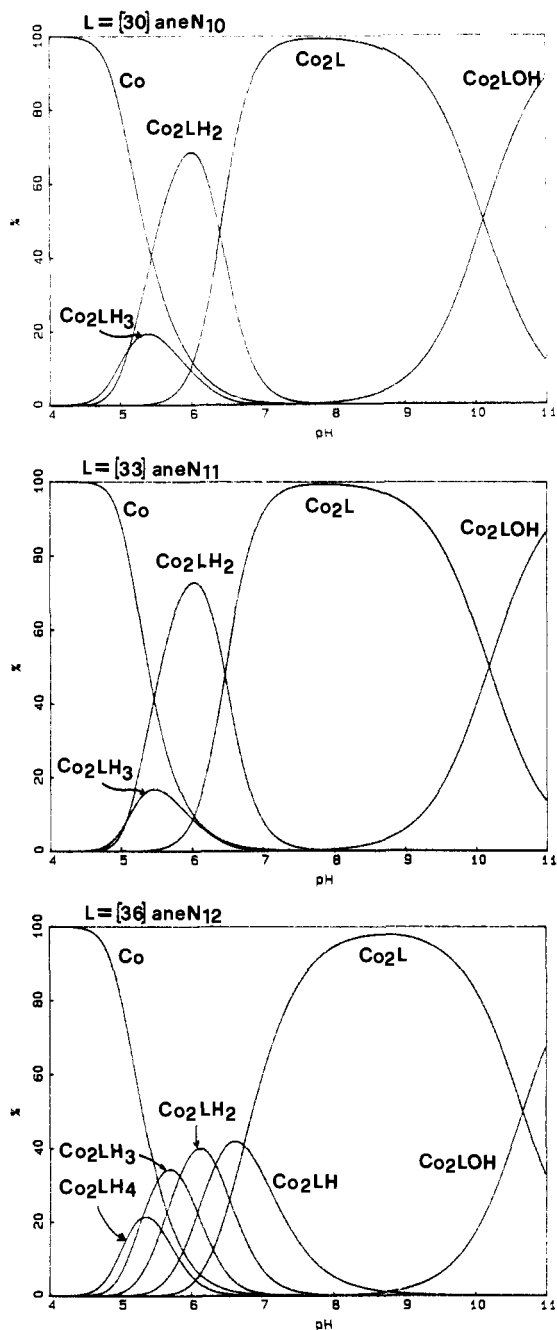
experimental conditions employed, mononuclear cobalt(II) complexes are formed by the ligands containing three to nine nitrogen donor atoms and dinuclear cobalt(II) complexes by those containing nine to twelve nitrogen donor atoms. Only nonadentate [27]aneN<sub>9</sub> is able to form both mononuclear and dinuclear complexes. The stability of the mononuclear complexes increases in going from small tridentate [9]aneN<sub>3</sub> to hexadentate [18]aneN<sub>6</sub>, for which a maximum in stability is reached, and then drops progressively with the large macrocycles [21]aneN<sub>7</sub>, [24]aneN<sub>8</sub>, and [27]aneN<sub>9</sub> (Figure 1). A similar trend was also observed in the corresponding mononuclear nickel(II) complexes.<sup>10</sup> In the last case a progressive occupation of the nickel(II) coordination sites was proposed to explain the increasing complex stability found upon going from [9]aneN<sub>3</sub> to [18]aneN<sub>6</sub>, the following decrease being due to the formation of large chelate rings containing noncoordinated nitrogen donors (e.g. one eight-membered chelate ring for [21]aneN<sub>7</sub> and one eleven-membered chelate ring or two eight-membered chelate rings for [24]aneN<sub>8</sub>). Also for the cobalt(II) complexes similar arguments can be advanced. In a previous report<sup>13</sup> the six-coordination of [18]aneN<sub>6</sub> in the cobalt(II) complex has already been considered on the basis of the larger complexing ability shown by this ligand toward the metal ion with respect to pentadentate [15]aneN<sub>5</sub>. It was also observed that a protonated [Co(H[18]aneN<sub>6</sub>)]<sup>3+</sup> species was formed, and its stability constant was obtained. On the basis of the equilibrium data reported in ref 14, the protonation constant of [Co([18]aneN<sub>6</sub>)]<sup>2+</sup> to produce [Co(H[18]aneN<sub>6</sub>)]<sup>3+</sup> can be readily calculated (log *K* = 3.1). This value is significantly lower than that, attained in the present work, for the formation of the corresponding [Co(H[21]aneN<sub>7</sub>)]<sup>3+</sup> species, in which protonation involves an uncoordinated nitrogen atom (log *K* = 5.27). These results agree with the absence of uncoordinated nitrogen atoms available for protonation in the complex [Co([18]aneN<sub>6</sub>)]<sup>2+</sup> in solution, although a lowering of the protonation constants of these complexes could be expected as a consequence of the necessary proximity of the protonated nitrogen to the cobalt(II) ion in [Co([18]aneN<sub>6</sub>)]<sup>2+</sup>. As mentioned above, once six-coordination has been reached, an enlargement of the macrocyclic ligand causes the formation of large chelate rings which produces a decrease in the stability of the complexes. On the other hand, the protonation of the complexes becomes easier (Table I), since the protonation sites can be located far away from the bound cation. It is worthwhile to note that the stability constant related to the protonation of [Co([27]aneN<sub>9</sub>)]<sup>2+</sup> is equal, within experimental error, to the protonation constant of the free ligand [27]aneN<sub>9</sub>.<sup>7</sup> In other words, the equilibrium constants related to the reaction of cobalt(II) with [27]aneN<sub>9</sub> and (H[27]aneN<sub>9</sub>)<sup>+</sup>, respectively,



**Figure 2.** Calculated distribution of the equilibrium species formed in the system Co<sup>2+</sup>/[27]aneN<sub>9</sub> in 0.15 mol dm<sup>-3</sup> NaClO<sub>4</sub> solution at 25 °C: (a) Co<sup>2+</sup> and [27]aneN<sub>9</sub>, 10<sup>-3</sup> mol dm<sup>-3</sup>; (b) Co<sup>2+</sup>, 2 × 10<sup>-3</sup> mol dm<sup>-3</sup>, and [27]aneN<sub>9</sub>, 10<sup>-3</sup> mol dm<sup>-3</sup>. For a 2:1 molar ratio a very small amount of CoL, not reported in the figure, is also formed.

are equal within experimental error (Figure 1). In the case of [24]aneN<sub>8</sub> and [27]aneN<sub>9</sub>, a second protonation of the mononuclear cobalt(II) complexes takes place. It is interesting to note that the values of the second protonation constants of these complexes are still large, which suggests that the two protonated nitrogens belong to two chelate rings each located far from the other. Again, the equilibrium constant related to the addition of the second proton increases with the dimension of the cyclic ligand.

The smallest macrocycle of the series that forms dinuclear cobalt(II) complexes, under the experimental conditions employed,



**Figure 3.** Calculated distribution of the equilibrium species in the systems (a)  $\text{Co}^{2+}/[30]\text{aneN}_{10}$ , (b)  $\text{Co}^{2+}/[33]\text{aneN}_{11}$ , and (c)  $\text{Co}^{2+}/[36]\text{aneN}_{12}$  in  $0.15 \text{ mol dm}^{-3} \text{ NaClO}_4$  solution at  $25^\circ\text{C}$  for  $2 \times 10^{-3} \text{ mol dm}^{-3} \text{ Co}^{2+}$  and  $10^{-3} \text{ mol dm}^{-3}$  ligands.

is  $[27]\text{aneN}_9$ , while nickel(II),<sup>10</sup> zinc(II),<sup>4</sup> and cadmium(II)<sup>2</sup> also form dinuclear complexes with  $[24]\text{aneN}_8$ , and copper(II) forms dinuclear complexes even with  $[21]\text{aneN}_7$ .<sup>5</sup> The macrocycle  $[27]\text{aneN}_9$  is able to form in solution both mononuclear and dinuclear cobalt(II) complexes. From the equilibrium data obtained for the system  $\text{Co}^{2+}/[27]\text{aneN}_9$ , the distribution of the complexes formed as a function of pH has been calculated for the 1:1 and 2:1  $\text{Co}^{2+}:[27]\text{aneN}_9$  molar ratios, and the results have been plotted in Figure 2. For the 1:1 molar ratio, only mononuclear cobalt(II) complexes are formed as the main species (Figure 2a), while when the ratio is 2:1, dinuclear cobalt(II) complexes become of major importance (Figure 2b). Notwithstanding, the ability of  $[27]\text{aneN}_9$  to bind two cobalt(II) ions is not sufficiently large to prevent the presence of some free metal ion in alkaline solution (Figure 2b), and cobalt(II) hydroxide is formed as the pH is increased. For this reason the potentiometric measurements on this system were carried out without exceeding the 1.8:1 molar ratio. The dinucleating ability of large  $[3k]\text{aneN}_k$

ligands toward cobalt(II) ion increases from  $[27]\text{aneN}_9$  to  $[30]\text{aneN}_{10}$ ,  $[33]\text{aneN}_{11}$ , and  $[36]\text{aneN}_{12}$ , and only dinuclear cobalt(II) complexes are formed by the last three macrocycles (Figure 3). As shown in this figure, the species  $[\text{Co}_2(\text{L})]^{4+}$  ( $\text{L} = [30]\text{aneN}_{10}$ ,  $[33]\text{aneN}_{11}$ ,  $[36]\text{aneN}_{12}$ ), is largely predominant over a rather wide pH range. This is a favorable condition for the study of  $\text{O}_2$  uptake. From this point of view,  $[30]\text{aneN}_{10}$  seems to be the most promising ligand, yielding a dinuclear cobalt(II) complex in which two binding sites, one over each cobalt(II), could be available for coordination to molecular oxygen.  $[30]\text{aneN}_{10}$  and  $[33]\text{aneN}_{11}$  form triprotonated and diprotonated dinuclear cobalt(II) complexes in slightly acid solution (Figure 3a,b) while tetraprotonated to monoprotinated species are produced by the dinuclear complex of the largest macrocycle  $[36]\text{aneN}_{12}$  (Figure 3c). The  $[\text{Co}_2(\text{L})]^{4+}$  complexes are largely predominant from neutral to alkaline solution, and at higher pH values, hydroxydicobalt(II) species are formed (Figure 3). The stability constant related to the formation of the  $[\text{Co}_2(\text{L})]^{4+}$  species increases (Table I) from  $[27]\text{aneN}_9$  to  $[36]\text{aneN}_{12}$ , as the number of nitrogen atoms in the macrocycles increases, in accord with an increasing number of donor atoms involved in the coordination to the two cobalt(II) ions. The stability constants for the  $[\text{Co}_2(\text{L})]^{4+}$  species are somewhat lower than those of the corresponding complexes of zinc(II), and the general trend of stability  $\text{Co} < \text{Ni} < \text{Cu} > \text{Zn}$  can be outlined for each macrocycle, comparing the results obtained in this and in previous studies.<sup>2-10</sup>

**Registry No.**  $[21]\text{aneN}_7$ , 296-85-5;  $[24]\text{aneN}_8$ , 297-11-0;  $[27]\text{aneN}_9$ , 57970-53-3;  $[30]\text{aneN}_{10}$ , 862-28-2;  $[33]\text{aneN}_{11}$ , 60464-68-8;  $[36]\text{aneN}_{12}$ , 24904-24-3.

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### Molecular Structure of Hexakis(*N,N'*-diethylurea)manganese(II) Tetrabromomanganate(II)

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The absence of ligand field stabilization energy in high-spin manganese(II) complexes allows various coordination configurations. In previous report,<sup>1</sup> we described a pentacoordinated complex with monodentate ligands: dibromotris(*N,N'*-dimethylurea)manganese(II), with a distorted-bipyramidal structure having two bromine atoms in equatorial positions and the three dmu ligands (dmu = *N,N'*-dimethylurea) being oxygen bonded. Two axial dmu ligands are classically bonded with a Mn-O-C angle of  $129.5^\circ$ , whereas the equatorial dmu is unusually linearly bonded with a Mn-O-C angle of  $180^\circ$ . We report now the structure of a complex with the same stoichiometry, only with the dmu ligands replaced by *N,N'*-diethylurea (deu). From electronic spectra,<sup>2</sup> it was inferred that the compound was in fact an ionic mixed octahedral-tetrahedral complex:  $[\text{Mn}(\text{deu})_6][\text{MnBr}_4]$ . The X-ray structure has now been solved and is reported here as well as a comparison with the  $\text{Mn}(\text{dmu})_3\text{Br}_2$  structure.

### Experimental Section

**Preparation of  $\text{Mn}(\text{deu})_3\text{Br}_2$ .** The preparation of  $\text{Mn}(\text{deu})_3\text{Br}_2$  (white powder) has been described previously.<sup>2</sup> Monocrystals were obtained by slow evaporation at room temperature in a desiccator of a concentrated solution of the complex in dry 1-butanol and ethanol (50/50). Small moisture-sensitive transparent prisms or diamond-shaped crystals were obtained after 1 month. Anal. Calcd for  $\text{MnC}_{15}\text{H}_{36}\text{N}_6\text{O}_3\text{Br}_2$ : C, 31.99;

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