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Synthesis and Stability of the Complexes of the Mixed-Donor Macrocycle 13-ANE-N_2O_2

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We have previously reported [1, 2] the synthesis of mixed-donor macrocycles containing oxygen and nitrogen donor atoms and the structures of some of their complexes with metal ions [3, 4]. We report here the synthesis of the novel macrocyclic ligand 13-aneN_2O_2 (1,4-dioxa-7,11-diazacyclotridecane) and the stability of its complexes with Cu(II) and Zn(II). This data can then be combined with that obtained previously for 13-aneN_3O (see Fig. 1 for structure of ligands), and the literature [5] data on 13-aneN_4, to gain a more complete picture of the effect of replacing nitrogen by oxygen donors on the complexing ability of the ligands.

Experimental

The ditosylated (tosyl = p-toluenesulphonyl) cyclic precursor was prepared as described by Rasshofer, Wehner, and Vogtle [6]. It was found that the usual method of detosylation using HBr and glacial acetic acid [7] gave no product. An alternative procedure due to Klamann and Bertsch [8] was found to be satisfactory. This method involves sodium in isoamyl alcohol as a detosylating agent. The impure product obtained was purified by forming the hydrochloride salt by precipitation with HCl gas from an ethereal solution. The hydrochloride salt was recrystallized from water-ethanol mixture. M.pt. 266 °C. Elemental analyses were satisfactory.

It was found that the reactions of Cu(II) and Zn(II) with 13-aneN_2O_2 were rapid, and stability constant studies could be carried out with no special problems caused by slow rates of equilibration. The pK_a values and formation constants were determined using glass electrodes as described previously [9].

Results and Discussion

The formation constants for 13-aneN_2O_2, together with those for 13-aneN_3O and 13-aneN_4 are seen in Table I. It is seen that both the pK_a values and formation constants fall off rapidly as nitrogens are replaced by oxygens. The fall-off in pK_a values must relate [1] to the poorer hydrogen-bonding ability of the oxygens than nitrogens, leading to a weakening of the cooperative solvation of the bound protons by the donor atoms. A further factor lowering the pK_a values of 13-aneN_2O_2 is the fact that the two nitrogen donors are adjacent to each other, leading to greater electrostatic repulsion between bound protons than is found for polyamines where the first and second protons bound are not forced to be on adjacent nitrogens.

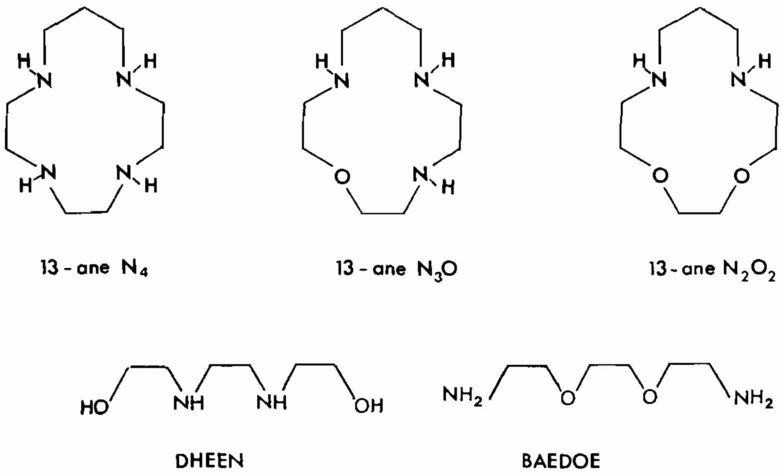

Fig. 1. Ligands discussed in this paper. Abbreviatons are: 13-aneN_4 = 1,4,7,11-tetraaacyclotridecane; 13-aneN_3O = 1-oxa-4,7,11-triaza-cyclotridecane; 13-aneN_2O_2 = 1,4-dioxa-7,11-diazacyclotridecane; DHEEN = N,N′-bis(2-hydroxyethyl)ethylenediamine, BAEDOE = O,O′-bis(2-aminoethyl)-1,2-dioxyethane.

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TABLE I. Stability of Some Complexes of, and pK_a Values for, Some Thirteen-membered Ring Macrocycles, and Their Open-chain Analogues.[a]

ligand:[b]	13-aneN$_4$[c]	13-aneN$_3$O[d]	13-aneN$_2$O$_2$[e]
log K_1 (Cu^{2+})	24.4[f]	16.92	8.39 ± 0.04
log K_1 (Zn^{2+})	15.6	9.90	4.89 ± 0.04
pK_{a1}	11.0	10.34	10.36 ± 0.02
pK_{a2}	10.0	8.64	6.62 ± 0.02
ligand:	trien[g]	DHEEN[h]	BAEDOE[i]
log K_1 (Cu^{2+})	20.1	9.77	7.89
log K_1 (Zn^{2+})	12.0	4.79	
pK_{a_1}	9.7	9.32	9.73
pK_{a_2}	9.1	6.52	8.75

[a] At 25 °C and ionic strength 0.1, unless otherwise indicated. [b] For key to abbreviations, see Fig. 1. [c] From ref. 5. [d] From ref. 2. [e] This work, 25 °C, 0.1 M NaNO$_3$. [f] Unpublished work, V. J. Thöm and R. D. Hancock, determined spectroscopically. [g] Ref. 11. [h] Ref. 13. [i] Ref. 14.

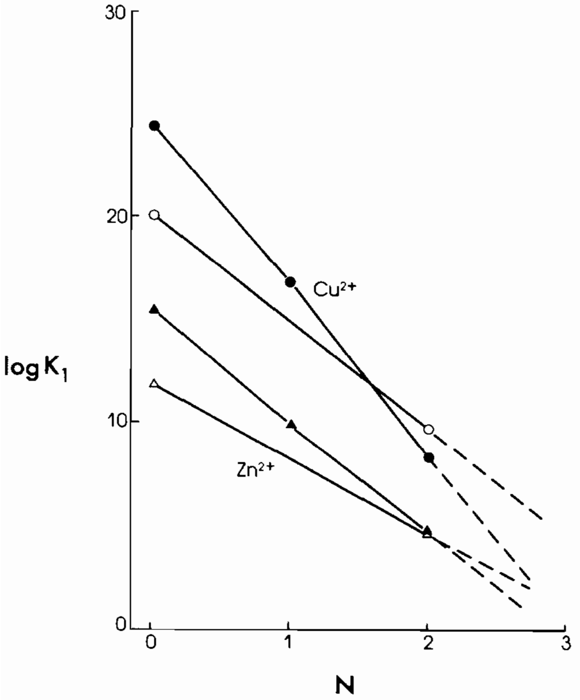

Fig. 2. Variation of the formation constant log K_1 of the thirteen membered ring macrocycles 13-aneN$_4$, 13-aneN$_3$O, 13-aneN$_2$O$_2$, . . . as a function of the number of nitrogens replaced by oxygens, N, as well as the variation of the open-chain analogues. The points are (●) Cu(II) with thirteen-membered ring macrocycles; (○) Cu(II) with the open-chain analogues trien and DHEEN. For Zn(II) the points (▲) are for the macrocyclic series, and (△) are the open-chain series.

In Fig. 2 is shown the variation in log K_1 for the Cu(II) and Zn(II) complexes of the 13-ane macrocycles as a function of the number of nitrogen donors replaced by oxygen. It is seen that the fall-off in stability is rapid, this fall-off being more rapid for Cu(II) than Zn(II). Extrapolation of Fig. 2 to 13-aneNO$_3$ and 13-aneO$_4$ (13-crown-4) suggests very low stability for the complexes of the latter two macrocycles with Cu(II) and Zn(II). Also included in Fig. 2 is the variation in stability of the open-chain analogues trien and DHEEN as a function of the number of replaced donor atoms. Of particular interest is the fact that the rate of fall-off in stability as nitrogens are replaced by oxygens is slower for the open-chain forms than the macrocycles. If we compare 13-aneN$_2$O$_2$ with DHEEN as its open-chain analogue, we see for Zn(II) there is still a small macrocyclic effect, but for Cu(II) there is an 'anti-macrocyclic' effect of some 1.4 log units, *i.e.* the complex of the open-chain ligand is the more stable.

We can choose as our open-chain analogue for 13-aneN$_2$O$_2$ either of the two available possibilities, namely DHEEN or BAEDOE, shown in Fig. I. That the stability of the complexes of BAEDOE is less than that of the DHEEN complexes, as seen in Table I, is attributed [1] to the presence of secondary nitrogens in DHEEN, whereas BAEDOE has primary nitrogens. A similar effect is found [1] in the complexes of the two ligands HEEN and ODEN (N(2-hydroxyethyl)ethylenediamine, and oxy-bis(2-ethylamine)). Thus, BAEDOE represents a more appropriate comparison with 13-aneN$_2$O$_2$ in that ring closure occurs across the two primary nitrogens of BAEDOE to give the macrocyclic 13-aneN$_2$O$_2$. This is then directly comparable with cyclisation of trien to give 13-aneN$_4$. We find that, even though cyclisation occurs across primary nitrogens to give secondary in both the 13-aneN$_2$O$_2$/BAEDOE and

13-aneN_4/trien sets, the magnitude of the macrocyclic effect (*i.e.* log K_1 (macrocycle) – log K_1 (open-chain analogue)) is only 0.5 log units for the Cu^{2+} complex of 13-aneN_2O_2, as compared with 4.3 log units for 13-aneN_4.

The most reasonable explanation for this is that of Margerum [10]. Cyclisation desolvates the nitrogen donor atoms, and thus contributes to the macrocyclic enthalpy because they do not have to be desolvated before complex-formation occurs. Thus, since solvation of nitrogens is stronger than neutral oxygen, there should be much less of an effect if cyclisation involves a ring containing oxygen rather than nitrogen donors.

Another possibility which might contribute to the decrease in the size of the macrocylic effect as nitrogens are replaced by oxygens is electronic. It is possible that the effect of the increased inductive effect as primary nitrogens are turned into secondary [12] on ring closure to form the macrocycle from the open-chain analogue is lessened as the attached groups are changed from nitrogen to oxygen donors. This type of effect may account for the difference in behaviour between HEEN and ODEN complexes [12] (HEEN is N(2-hydroxyethyl)ethylenediamine, and ODEN is oxybis(2-ethylamine)). We attribute [12] the greater log K_1 found for HEEN as compared to ODEN complexes to the presence of a secondary nitrogen in HEEN as against a primary in ODEN. Thus, log K_1 (HEEN) minus log K_1 (ODEN) is 1.14 for Ni(II), but log K_2 (HEEN) – log K_2 (ODEN) is 2.19. Thus, the effect of changing a primary into a secondary nitrogen increases as the number of nitrogens already attached to the metal ion increases.

Acknowledgements

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