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Synthesis and Metal Complexing Properties of the Mixed-Donor (Nitrogen-Oxygen) Macrocycle, 1-Oxa-4,7,11-Triaza-Cyclotridecane

VIVIENNE J. THÖM and ROBERT D. HANCOCK*

Department of Chemistry, University of the Witwatersrand, Johannesburg, South Africa

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The synthesis of the ligand 1-oxa-4,7,11-triazacyclotridecane is described. The ligand reacts rapidly with transition metal ions to form complexes. A glass electrode study gives pK_{a1} as 10.34, pK_{a2} as 8.64, and pK_{a3} as 2.79, in 0.1 *M* $NaNO_3$ at 25 °C, as well as log K_1 for Cu(II) as 16.92, and for Zn(II) as 9.94. The formation constants determined are compared with log K_1 values for non-cyclic triamines such as 1,4,8-triazaoctane, and it is concluded that the macrocyclic effect for ligands with an oxygen donor in the ring is smaller than when all the donor atoms are nitrogen.

An interesting feature of macrocyclic chemistry is that the ionically bound alkali and alkali-earth metal ions bind most strongly to oxygen-donor macrocycles, whilst the more covalently bound transition metal ions prefer the nitrogen-donor macrocycles. An area of macrocyclic chemistry which is still largely unexplored is that of mixed nitrogen-oxygen donor macrocycles of a size suitable for complexing transition metal ions. The work of Lindoy *et al.* [1] on ligands such as I shown in Fig. 1 has been of great interest, but, because of low solubility and the lack of any open-chain analogues for comparison, this has not provided us with any quantitative measure of the macrocyclic effect in such mixed-donor ligands. We have recently [2] investigated the complexing properties of the ligand 9-aneN_2O shown in Fig. 1, and found that a smaller macrocyclic effect exists than is found for the ligand 9-aneN_3, *i.e.* log K_1 (9-aneN_3) – log K_1 (dien) is 5.74, while log K_1 (9-aneN_2O) – log K_1 (ODEN) is only 2.97 log units for the Ni(II) complexes. This is possibly an indication that the suggestion of Margerum *et al.* [3] that steric hindrance to solvation of the macrocycle contributes to the macrocylic effect may be correct. Solvation of oxygen by hydrogen bonding to water is weaker than for nitrogen, so that the gain in stability of the complex by removing this water is less than if we sterically desolvate a nitrogen. This conclusion must be regarded as tentative until more complexes of mixed nitrogen-oxygen donor macrocycles have been investigated. We have therefore prepared the title compound, abbreviated 13-aneN_3O, and studied its complexes with Cu(II) and Zn(II).

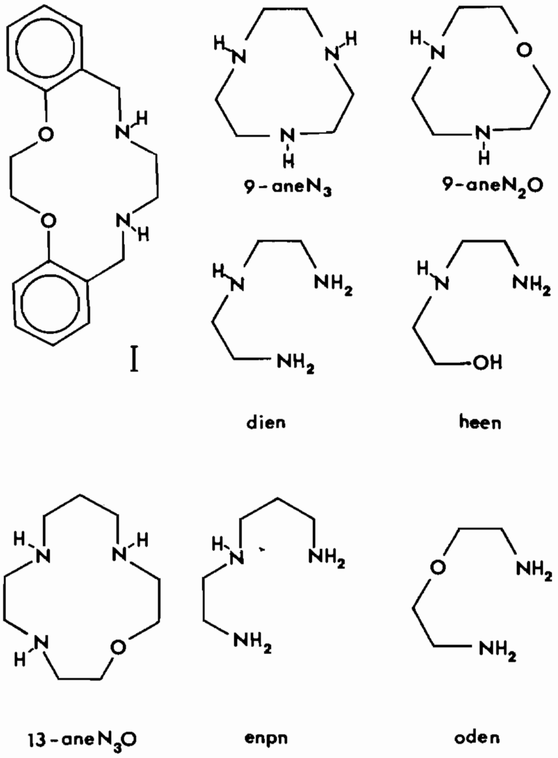

Fig. 1. Ligands discussed in this paper.

Experimental

Synthesis of the macrocycle: the general synthetic procedure followed was that outlined in Fig. 2. The ditosylate (tosyl = *p*-toluenesulphonyl chloride derivative) of 1,4,7-trioxaheptane was prepared as described by Dale and Kristiansen [4]. The tritosylate of 1,4,8-triazaoctane was prepared as described by Koyama and Yoshino [5]. These two tosylates were condensed by heating in DMF at 110 °C, to give the N,N′,N″-tritosylate of 13-aneN_3O, M.Pt 175 °C. This was detosylated by refluxing in an HBr/Acetic acid mixture [5] to give the tri-hydrobromide of 13-aneN_3O, M.Pt 285 °C (d). CHN analyses were satisfactory.

Formation constant studies: equilibration of the system was fairly rapid, as was found for the complex-formation reactions of 9-aneN_2O, in contrast to the all nitrogen donor analogues, which

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*Author to whom correspondence should be addressed.

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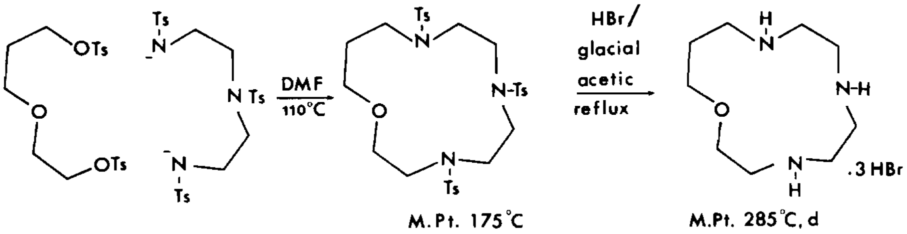

Fig. 2. Synthetic route followed for synthesis of 13-aneN_3O.

TABLE I. Log K_1 Values for Cu(II) and Zn(II) Complexes with Macrocycles and their Open Chain Analogues, Contrasting the Macrocyclic Effect in All-Nitrogen Donor Macrocycles with that in Macrocycles which Have an Oxygen-Donor Atom in the Ring.

All-nitrogen donors			With one oxygen		
Ligand[a]	log K_1 Cu^{2+}	log K_1 Zn^{2+}	Ligand	log K_1 Cu^{2+}	log K_1 Zn^{2+}
13-aneN_4[b]	28.8	15.6	13-aneN_3O[c]	16.92	9.94
trien	20.1	12.1	dien	15.9	8.8
2,3,2-tet	23.9	12.8	enpn	16.6	8.8
9-aneN_3	15.5	11.6	9-aneN_2O	10.85	6.32
dien	15.9	8.8	HEEN	10.09	4.75
			ODEN	8.70	–

[a] Abbreviations: trien = 1,4,7,10-tetraazadecane, 2,3,2-tet = 1,4,8,11-tetraazaundecane, otherwise see Fig. 1. [b] Log K_1 values from reference 7, except 13-aneN_4 from reference 9, 9-aneN_3 from reference 10, and 9-aneN_2O from reference 2. [c] This work, 25 °C, 0.1 M $NaNO_3$.

have slow complex-formation reactions. The glass electrode potentiometric studies gave pK_a values for the ligand 13-aneN_3O of pK_1 = 10.34, pK_2 = 8.64, and pK_3 = 2.79, at 25 °C, and in 0.1 M $NaNO_3$. The cell used in the study was as described previously [6]. The log K_1 values obtained with Cu(II) and Zn(II) by potentiometric titration are shown in Table I, together with values for 1,4,8-triazaoctane (enpn) and dien for comparison. The spectral data reported here were recorded on a Cary 17 uv-visible spectrophotometer.

Results and Discussion

We do not have an open chain analogue of 13-aneN_3O for comparison. However, reported log K_1 values for hydroxy-ethylated polyamines do not show much change in stability as compared with their non-substituted analogues. Thus, log K_1 for HEEN (2-hydroxyethylethylenediamine) is [7] 10.02 with Cu(II), while for en (ethylenediamine) itself, it is 10.48. Thus enpn should make a reasonable open-chain analogue. Also included are results for dien, and for the analogous set of all-nitrogen donor ligands, 13-aneN_4, 2,3,2-tet, and trien. The results in the Table show that the increase in stability of the complexes of 13-aneN_3O over the non-cyclic ligands enpn and dien is small, being about one log unit. If we consider that adding an N-hydroxyethyl group to a polyamine, as for en above to give HEEN, normally drops the complex stability by about 0.5 log units, a reasonable value for the macrocyclic effect for 13-aneN_3O compared with the more appropriate analogue $HOCH_2CH_2NHCH_2CH_2NHCH_2CH_2CH_2NH_2$ would be about 1.5 log units. This is very close to the difference in log K_1 for 9-aneN_2O and HEEN of 1.6 log units found for Zn(II) and Ni(II). If instead of bridging across the hydroxyl and primary amine of HEEN to give us 9-aneN_2O, we bridge across the two primary nitrogens of ODEN, we obtain a macrocyclic effect of 3.0 log units, and by comparison we would expect for a ligand such as $NH_2CH_2CH_2CH_2NHCH_2CH_2OCH_2CH_2NH_2$ a macrocyclic effect for 13-aneN_3O of 2.9 log units. This is much less than the macrocyclic effect of 4.9 log units for 13-aneN_4 compared to 2,3,2-tet seen in the Table for Cu(II). For both 9-aneN_2O and 13-aneN_3O we appear to obtain smaller macrocyclic effects with transition metal ions than is found for the all-nitrogen analogues. For Zn(II) the difference in the macrocyclic effect for 13-aneN_3O and 9-aneN_2O on the one hand, and 13-aneN_4 and 9-aneN_3 on the other, is small. This suggests that Zn(II) is closer to the alkaline earth metal ions in its lack of discrimination between oxygen and nitrogen donors in macrocycles, than is the case for Cu(II).

The spectra of the mono-complexes of enpn, dien, and 13-aneN_3O with Ni(II) were recorded in aqueous solution, and band maxima were as follows: $[Ni(13\text{-}aneN_3O)(H_2O)_2]^{2+}$, 10810, 13140, 17153, and 27320 cm^{-1}; $[Ni(enpn)(H_2O)_3]^{2+}$ 11700, 13390, 17270, 27900 cm^{-1}; $[Ni(dien)(H_2O)_3]^{2+}$ 10470, 13440, 16800, and 27500 cm^{-1}. Assuming regular octahedral coordination geometry, these give rise to 10Dq and B values for the above complexes of 1081 and 873, 11100 and 879, and 10470 and 886 cm^{-1} respectively. The $^3A_{2g} \rightarrow {}^3T_{2g}$ band in the above enpn complex is clearly split, suggesting meridional coordination of the ligand. Thus, in calculating 10Dq we have ignored the band maximum, which clearly corresponds to one of the components of the splitting. Using only the energies of the remaining two bands, we still calculate a very high value of 10Dq. We suggest that what we are seeing here is the effect of a low-strain situation on 10Dq, which is allowing the inductive effect [8] of the secondary nitrogen donor to become apparent. This does not happen with 13-aneN_3O or dien because of steric strain [8]. 13-aneN_3O is too small to encircle a metal ion of the size of Ni^{II}, so that, coupled with the typical spectrum for octahedral Ni^{II}, we suggest that the complexes have the folded structure.

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