Inorganica Chimica Acta, 90 (1984) L83–L84

Macrocyclic Complexes of Copper(II) as Lewis Acids

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Received July 23, 1984

Macrocyclic complexes of saturated amines such as cyclam, or its analogues 15-aneN$_4$ and tetramethyl cyclam (see Fig. 1 for structures of ligands) are of interest in that we have here the possibility of steric control of binding of unidentate ligands such as ammonia, hydroxide, cyanide, and so on, to the axial sites of the complexes. We report here the formation constants of the copper(II) complexes of the above macrocycles with a variety of unidentate ligands.

Experimental

Materials

The macrocycles were obtained from Strem Chemicals. Solutions of these were standardized with acid, and then used to make up 0.01 stock solutions of the metal complexes. NaCN, NaN$_3$, and NaSCN were obtained as high purity salts from MERCK. UV-visible spectra were run on a CARY 2300 spectrophotometer. The cells were thermostatted to 25 °C, and the equilibria were determined by varying the ratio of unidentate ligand to macrocyclic complex concentration, the latter being kept constant.

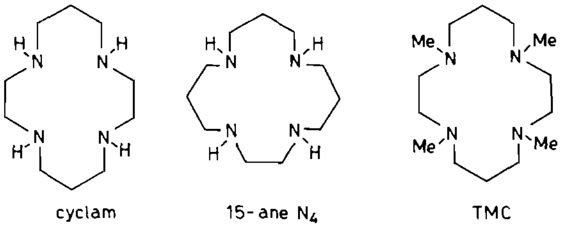

Fig. 1. Ligands discussed in this paper.

Results and Discussion

It was found that only the ligands cyanide, azide, and thiocyanate were bonded with any strength to the complexes. Experiments with hydroxide, ammonia, thiourea, fluoride, chloride, thiosulphate, and sulphite indicated at best very weak interaction. With ammonia, for example, a colour change was obtained in up to 16 M NH$_3$ which indicated a log K_1 value in the vicinity of -1.8 with the Cu(II) complex of cyclam. In contrast, as seen in Table I, the binding constants with cyanide, azide, and thiocyanate are large, not very different from the Cu(II) aquo ion. This parallels the findings of Kaden *et al.* [1] with the Co(II) complex of TMC, where it was found that the binding constants of the azide and thiocyanate were unusually high in comparison with the other ligands studied. It was suggested [1] that this arose from the steric hindrance of the four N-methyl groups, which was less severe for long thin ligands such as azideor thiocyanate. Our study here is in agreement with this interpretation, except that we see that other small ligands such as fluoride and hydroxide are excluded from complex-formation. This suggests an additional factor to be considered, which is the hydration of the ligand itself when complexed. Thus, we would expect the hydration of fluoride and hydroxide when complexed to be high in comparison with cyanide and azide, and that in all of these complexes

TABLE I. Formation Constants for the Binding of some Unidentate Ligands to Copper(II) Complexes of Macrocycles.[a]

Complex[b]	log K_1 (azide)	log K_1 (cyanide)	log K_1 (thiocyanate)
$[\mathrm{Cu(cyclam)}]^{2+}$	2.1	4.5[c]	1.8
$[\mathrm{Cu(15\text{-}aneN_4)}]^{2+}$	1.39	4.60	1.88
$[\mathrm{Cu(TMD)}]^{2+}$	1.79	5.2	2.2
Cu^{2+}	2.86[d]	6.2[e]	2.33

[a] At 25 °C. Ionic strength = 0.1, except for cyclam, where solubility difficulties lead to work being carried out at about 0.02 M. Accuracy of the constants is about 0.05 where reported to 2 decimal places, and 0.1 for those reported to one. [b] For abbreviations, see Fig. 1. [c] Log K_2 measured to be 2.65. [d] From reference [7]. [e] This is the value predicted for Cu^{2+} in reference [7].

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0020-1693/84/$3.00

steric hindrance to the solvation of the ligand is of importance. Steric hindrance to ligands on the axial sites of cyclam complexes is surprisingly severe [2]. If we examine the crystal structure of [Ni(cyclam)-$(NO_3)_2$], for example [2], we find unusually long Ni–O bonds to the axial nitrates of 2.17 Å instead of the more normal 2.09 Å, while a similar lengthening of the Ni–Cl bond length in the dichloro analogue is observed [3].

Cyanide does not reduce the cyclam complex of Cu(II). At 1:1 ratios a highly insoluble blue precipitate is formed, which hindered our complex-formation studies, but at higher ratios crystals of a stable dicyanide are obtained, which are purple. The Cu(II) complexes of the more sterically strained 15-aneN_4 and TMC appear to be able to coordinate only a single cyanide, giving blue complexes in solution. We are at present studying the complexes of 13-aneN_4 and 12-aneN_4. Crystallographic studies [2, 4–6] show that here the copper is some 0.5 Å up out of the plane of the macrocycle. This should limit considerably the amount of steric hindrance between the axially held unidentate ligand, and the macrocycle. In accord with our above steric interpretation, one finds that all ligands, whether of the highly hydrated fluoride, hydroxide, and ammonia type, or with bulky donor atoms such as chloride, bromide, or iodide, bind strongly, with no increase in the strength with which cyanide, azide, or thiocyanate are bound to the Cu(II) complexes of 12-aneN_4 and 13-aneN_4.

Acknowledgements

We thank the Senate Research Grant Committee of the University of the Witwatersrand, and the Council for Scientific and Industrial Research, for generous financial support.

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