Inorganica Chimica Acta, 110 (1985) L1–L2

Metal-templated Synthesis of Novel Macrocyclic Complexes of the Uranyl Ion

L. DE COLA, D. L. SMAILES and L. M. VALLARINO*

Department of Chemistry, Virginia Commonwealth University, Richmond, Va. 23284, U.S.A.

Received March 16, 1985

The ability of the transition metal ions to act as permanent or transient templates for the synthesis of macrocyclic ligands and their complexes has been extensively studied for over two decades and continues to attract considerable interest [1]. Macrocyclic template syntheses have also been achieved with the heavier alkaline earths [2], with several post-transition metals [3], and recently with the lanthanides [4]. For the actinides, in contrast, the only macrocyclic complex so far obtained by metal-templated condensation is the penta-aza-'superphthalocyanine' [5] that results from the reaction of 1,2-dicyanobenzene with anhydrous uranyl chloride in dimethylformamide solution.

Our interest in this area was stimulated by the consideration that the *trans*-dioxouranium(VI) ion, because of its intermediate size (100 pm for 8-coordination) and its preference for equatorially directed bonds, would be expected to promote the formation of flat macrocyclic systems with six-donor cavities. Indeed we found that the condensation of 1,2-diaminoethane with 2,6-diacetyl- and 2,6-diformyl-pyridine in the presence of uranyl acetate, in a 2:2:1 mole ratio, yielded the cations shown in Fig. 1, which were isolated in nearly quantitative yields as nitrate, perchlorate, and iodide salts. These are the first six-nitrogen macrocyclic complexes reported for any of the actinides.

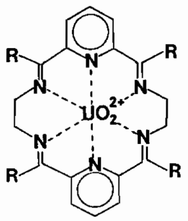

Fig. 1. Schematic structure of macrocyclic complexes of the uranyl ion. R = CH_3 for L^1 and H for L^2.

The $[UO_2L]X_2$ salts were obtained as crystalline solids of colors ranging from golden brown to almost black; they were stable to air and moisture fairly soluble in dimethylsulfoxide and dimethylformamide, sparingly soluble or insoluble in other common solvents. Their infrared spectra showed the following features: (1) The absence of OH, NH, and carbonyl absorptions; (2) The typical patterns of the cyclic ligands [6]; (3) A single sharp absorption for the uranyl ion (ν_{assym} (U–O): 930 cm^{-1}), and (4) The absorptions characteristic of the uncoordinated anions (NO_3^-: 1350s, 835m, 720w; ClO_4^-: 1100s, 620s). The carbon-13 nuclear magnetic resonance spectra in DMSO solution further showed the macrocyclic moieties to have a symmetrical structure, as only one resonance appeared for each type of carbon atom. (For the $[UO_2L^1]^{2+}$ complex, δ(ppm) at 32.8 KHz: 177.2 (C=N); 153.5 (α-C of pyridine); 143.8 (γ-C); 128.2 (β-C); 52.8 (CH_2); 18.1 (CH_3).) The proton spectra in the same solvent confirmed the symmetry of the organic ligands. (Again for $[UO_2L^1]^{2+}$, δ(ppm) at 44.8 KHz: 8.75 apparent singlet, 6H (pyridine); 4.62s, 12 H (CH_3); 2.84s, 8 H (CH_2).) Taken together, the infrared and nuclear magnetic resonance spectra of the $[UO_2L]^{2+}$ complexes conclusively showed the U(VI) to be coordinated to all six ring N-atoms and suggested an effective D_{6h} site symmetry for the central metal ion. This is in agreement with the preliminary results of a magnetic circular dichroism study [7] based on a recent crystal field analysis [8].

The remarkably facile preparation of these complexes show that the actinides can function as very effective templating agents for the synthesis of macrocycles with medium-size cavities. Furthermore, the exceptional inertness of the complexes toward release of UO_2^{2+} ion in solution, even in the presence of acids or strongly competing ligands, suggests that systems of this type may be used advantageously when effective sequestering of the actinide ions is an important requirement.

Acknowledgement

This work was supported in part by the U.S. National Institutes of Health, Grant No. R01-CA30148.

References

1 L.-Y. Chung, E. C. Constable, M. S. Khan, J. Lewis, P. R. Raithby and M. D. Vargas, *J. Chem. Soc., Chem. Commun.*, 1425 (1984);
C. W. G. Ansell, J. Lewis, P. R. Raithby and T. D. O'Donoghue, *J. Chem. Soc., Dalton Trans.*, 177 (1983);

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*Author to whom correspondence should be addressed.

0020-1693/85/$3.30

C. W. G. Ansell, J. Lewis and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 2557 (1982);
M. G. B. Drew, J. Nelson, F. S. Esho, V. McKee and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1837 (1982);
G. A. Melson (ed.), 'Coordination Chemistry of Macrocyclic Compounds', Plenum, New York, 1979.

2 M. G. B. Drew, F. S. Esho and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1653 (1983);
S. M. Nelson, F. S. Esho and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, 1857 (1983);
J. de O. Cabral, M. F. Cabral, W. J. Cummins, M. G. B. Drew, A. Rodgers and S. M. Nelson, *Inorg. Chim. Acta, 30,* L313 (1978).

3 M. G. B. Drew, C. Cairns, S. G. McFall and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 2020 (1980);
S. M. Nelson, S. G. McFall, M. G. B. Drew, A. H. bin Othman and N. B. Mason, *J. Chem. Soc., Chem. Commun.*, 167 (1977);
S. M. Nelson, S. G. McFall, M. G. B. Drew and A. H. bin Othman, *J. Chem. Soc., Chem. Commun.*, 370 (1977).

4 K. K. Abid and D. E. Fenton, *Inorg. Chim. Acta, 95,* 119 (1984);
K. K. Abid, D. E. Fenton, U. Casellato, P. A. Vigato and R. Graziani, *J. Chem. Soc., Dalton Trans.*, 351 (1984);
K. K. Abid and D. E. Fenton, *Inorg. Chim. Acta, 82,* 223 (1984);
W. Radecka-Paryzek, *Inorg. Chim. Acta, 52,* 261 (1981).

5 V. W. Day. T, J. Marks and W. A. Wachter, *J. Am. Chem. Soc., 97,* 4519 (1975).

6 D. L. Smailes and L. M. Vallarino, *Am. Chem. Soc. 18th Middle Atlantic Regional Meeting, 1984,* Abstr. No. 168.

7 L. De Cola, D. D. Shillady and L. M. Vallarino, *Am. Chem. Soc. 36th Southeastern Regional Meeting,* Abstr. No. 252.

8 C. Görller-Walrand and W. Colen, *Inorg. Chim. Acta, 84,* 183 (1984).