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Charge Transfer Complexes of Hexamethylmelamine With Uranium, Thorium and Chromium

by

N. GÜNDÜZ

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Adres: Fen Fakültesi Tebliğler Dergisi, Fen Fakültesi, Ankara, Turquie.

Charge Transfer Complexes of Hexamethylmelamine With Uranium, Thorium and Chromium

N. GÜNDÜZ

Department of Chemistry, Faculty of Science,
University of Ankara
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ABSTRACT

Hexamethylmelamine gives 1:1 charge transfer complexes with uranyl-chloride, chromyl-chloride and thorium nitrate in dry ethylacetate at room temperature. Experimental data have shown that the oxidation state of the cations in these complexes are six, five and four respectively and in all these complexes the cations have unusual coordination numbers.

INTRODUCTION

Although hexamethylmelamine has six donor sites, it behaves like a unidante ligand (1.2). So if a cation combines with one molecule hexamethylmelamine, it is presented one pair of electrons. Donor properties of hexamethylmelamine is not known in detail. For that reason it is difficult to say about its strength as a donor but it can be impressed that it is rather strong one.

Some charge transfer complexes of hexamethylmelamine with a few of transition metal elements such as uranium, thorium and chromium were obtained and their properties were examined. In these complexes the ratio of donor to acceptor is 1:1 and all these complexes are fairly stable in air.

Uranyl chloride reacts with hexamethylmelamine in dry ethyl acetate to give yellow cyrstalline, UO_2Cl_2. IHMM (HMM stands for hexamethylmelamine, $C_9H_{12}N_6$) This complex also obtained from the reaction of uranyl chloride with an excess of hexamethylmelamine in order to obtaine two and three coordinated complex. In this complex the coordination number of uranium seems to be

five and this is an unusual coordination number for the metal. Since the energies of the d and f levels are much closer together in the actinides, the prediction of the electronic configüration of uranium is very difficult (3, 4, 5). Magnetic susceptibility measurements (6) have shown that complex is diamagnetic. This supports the other analytical results.

Tetra aqua thorium-IV-nitrate gives a white crystalline compound with hexamethylmelamine in dry ethylacetate and much better in dry ether. Analytical data have shown that in this complex the ratio of thorium nitrate to hexamethylmelamine is 1:1 and magnetic susceptibility measurements (6) have indicated that the complex is diamagnetic. Although it was also tried to obtain the ratio of donor to acceptor 2:1 and 3:1 in all cases the ratio 1:1 was found. Thus this complex has also an odd number like in uranium complex. The electronic configuration of the complex is very difficult to predict (3. 4. 5)

Hexamethylmelamine also reacts with chromyl chloride to give light pink crystalline compound in dry ethylacetate. Analytical results have shown that in this complex, there is one molecule of hexamethylmelamine to one group of CrO_2Cl. This indicates that a redox reaction takes place in the formation of the complex. This also shows that chromium ion should contain one unpaired electron. Magnetic susceptibility measurements (6) on a Gouy type magnetic balance have shown 1.74 B. M. which means one free electron in the 3 d subshell. This coordination number for chromium is very rare (7). Attempts were made to prepare 2:1 and 3:1 complexes but in all cases 1:1 was obtained.

The electronic configuration of chromium in the complex might be (4)

It indicates that a set of sp^3 hybrid orbitals has been formed and that these are occupied by electron pairs (xx) donated by the four ligands which are, one hexamethylmelamine, two oxygens and one chlorine. It also shows that one of the d orbitals remains to be occupied by the one of the 3 d electrons. It thus pre-

dicts that there will be paramagnetism due to one unpaired electron. The colour of complex changes slowly from yellow to green.

The solubilities of these complexes are too low for molecular weight determinations.

EXPERIMENTAL

Hexamethylmelamine was prepared from cyanuric chloride and dimethylamine in dry acetone (8)

Ethylacetate was dried over calcium chloride.

Preparation of uranium compound : UO_2Cl_2 (0, 340 g = 10^{-3} m) was dissolved in warm ethyl acetate and added drop by drop into the hexamethylmelamine solution which prepared by dissolving (0, 212 g = 10^{-3} m) hexamethylmelamine in Et Ac too. Light yellow crystalls were formed in each drop of addition of uranyl chloride solution. Crystalls so formed were filtered from a buchner funnel, three hours later. As the crystalls are not soluble in common organic solvents, recyrstallization could not be made, instead crystalls were formed in dilute media and washed with fresh Et Ac for several times and then dried in a vacuum dessicator, yield, m. p and analytical results for the product are given Table I.

TABLE I

Compound	Found (%)			
	C	H	N	Cl
UO_2Cl_2.IH.M.M.	18.96	3.34	15.50	11.80
$C_9H_{18}N_6O_2Cl_2$ U	Required (%)			
	19.59	3.29	15.23	12.69
Yield	: % 91			
M. P	: 238°C (decomp.)			

Preparation of thorium compound; Th $(NO_3)_4$. $4H_2O$ (0,562 g = 10^{-3} m) was dissolved in Et Ac. H. M. M (0.210 g = 10^{-3} m) was dissolved in Et Ac too. Thorium nitrate solution was added dropwise into the hexamethylmelamine solution. White crystalls formed immediately. After addition was completed the precipi-

tate was allowed to stand for three hours. The crystalls were filtrred by a buchner funnel and washed with Et Ac. As the appropriate solvent could not be found recyrstallization could not be made instead the precipitation was slowly carried out in dilute solutions and the crystalls washed with the fresh solvent for several times. Compound was dried in a vacuum dessicator. Yield, m, p and analytical results for the product are given Table 2.

TABLE II

Compound	Found (%) C	H	N
$Th(NO_3)_4$ H.M.M	16.10	3.04	20.27
Formula	Required (%)		
	C	H	N
$C_9H_{18}N_{10}O_2Th$	15.65	2.61	20.29
Yield : % 72 M.P : 190 – 191°C			

Preparation of Chromium compound: Chromyl chloride was prepared from $K_2Cr_2O_7$, Na Cl and H_2SO_4 in the usual way. The dark red liquid was collected in Et Ac. The increase of weight was taken as the amount of chromyl chloride. From the solution appropriate volume was taken and added dropwise into equimolar H. M. M solution. Light Pink crystalls formed. Crystalls left an hour to stand. Filtered, washed and dried as described in the previous work.

Yield, m. p and analytical results for the product are given in Table 3.

TABLE III

Compound	Found (%) C	H	N	Cl
CrO_2Cl. IH. M.M	31.44	5.53	25.91	10.50
Formula	Required (%)			
$C_9H_{18}N_6O_2ClCr$	32.75	5.46	25.49	10.77
Yield : % 81 M.P : 265°C (decomp)				

REFERENCES

[1] S. K. Das. T. Gündüz R. A. Shaw and B. C. Smith. J. Chem. Soc. (1969) 1403–1404

[2] S. K. Das, T. Gündüz, R. A. Shaw and B. C. SmithJ. Chem. Soc. (1969) 524–525–526

[3] E. S. Makarov. "Crystal chemistry of simple compounds of Uranium, Thorium. plutonium, Neptunuim" Consultants Bureau Newyork, 1959 P. 126.

[4] F. A. Cotton and G. Wilkinson "Advanced Inorganic Chemistry" Interscience, London, second edition 1966 P. 627. 631. 682

[5] Nyholm. R. S. Proc. Chem. Soc. London, 1961, 273, "Electron configuration transition metal elements".

[6] Selwood P. M. Magneto Chemistry 2 nd ed., Interscience, 1956.

[7] P. T. Durrant and B. Durrant" Introduction to Advanced Inorganic Chemistry" First published. London. 1962 P. 989

ÖZET

Uranil klorür, kromil klorür ve toryum nitrat, heksametilmelaminle susuz etil asetatlı ortamda yük aktarma kompleksleri verirler. Deneyler, bu komplekslerdeki katyonların yükseltgenme basamaklarının sırasıyle 6, 5 ve 4, koordinasyon sayılarının da 5, 4 ve 5 olduğunu göstermektedir. Bu koordinasyon sayıları adı geçen element katyonları için beklenmedik sayılardır.

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