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Note

THERMAL DECOMPOSITION OF METAL COMPLEXES. XII. URANYL CHLORIDE COMPLEXES WITH SEVERAL O-DONOR LIGANDS

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In our previous work on the thermal decomposition of uranyl nitrate and acetate adducts with oxygen or nitrogen donor atoms, using thermal, IR and calorimetric analyses, the composition of the products and the intermediate and final products was established. The influence of the ligands in the equatorial plane on the decomposition mechanism and on the kinetic and thermodynamic parameters was evaluated in comparison with the spectroscopic characteristics.

In the present note we report the thermal behaviour of some uranyl chloride complexes with the following O-donor ligands: pyridine-*N*-oxide (PyNO), *p*-nitroso-*N*,*N*-dimethylaniline (*p*-NODMA), *N*,*N*-dimethylformamide (DMF), semicarbazide (SCA), and urea (L). The complexes are $UO_2Cl_2(PyNO)_2$, $UO_2Cl_2(p\text{-NODMA})_2$, $UO_2Cl_2(SCA)_3$, $UO_2Cl_2(DMF)_2 \cdot 2\ H_2O$, and UO_2Cl_2L. It is important to note that the adducts have different general formulae and, consequently, different structures and coordination numbers.

RESULTS AND DISCUSSION

In all the complexes examined, steps corresponding to the loss of neutral ligands were not observed individually. The thermogravimetric curves are reported in Fig. 1 and the thermal behaviour is briefly discussed below.

$UO_2Cl_2(PyNO)_2$ was obtained by adding alcoholic $UO_2Cl_2 \cdot 3\ H_2O$ solution to alcoholic PyNO solution dropwise, with stirring, at 0°C. (Anal.: U%

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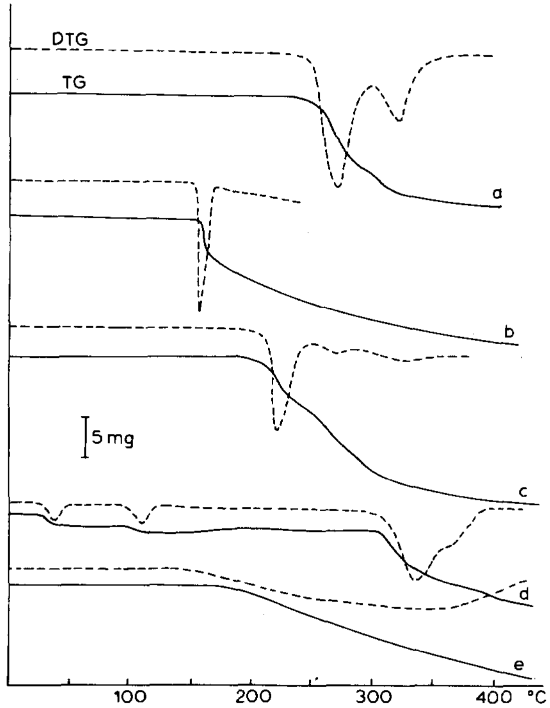

Fig. 1. Thermal behaviour of: (a) $UO_2Cl_2(PyNO)_2$ (44.2 mg); (b) $UO_2Cl_2(p\text{-NODMA})_2$ (61.7 mg); (c) $UO_2Cl_2(SCA)_3$ (21.9 mg); (d) $UO_2Cl_2(DMF)_2 \cdot 2\ H_2O$ (32.9 mg); (e) UO_2Cl_2L (56.3 mg).

44.82 calcd., 44.75 found; Cl% 13.35 calcd., 13.43 found; N% 5.27 calcd., 5.31 found.) This compound is thermally stable up to 260°C and then decomposes. Loss of the PyNO molecule occurs in two non-stoichiometric steps; the DTA curve simultaneously exhibits only a broad exothermic effect (Fig. 1a).

$UO_2Cl_2(p\text{-NODMA})_2$ was prepared as reported in ref. 1. (Anal.: U% 37.12 calcd., 37.21 found; Cl% 11.06 calcd., 10.99 found; N% 8.74 calcd., 8.81 found.) The complex decomposes quickly at 150°C, losing ca. 16% of the weighed compound. The residual product slowly decomposes. No evidence of stable intermediate products was observed (Fig. 1b).

$UO_2Cl_2(SCA)_3$ was prepared as described for the analogous nitrato complexes [2]. (Anal.: U% 42.06 calcd., 41.98 found; Cl% 12.52 calcd., 12.62 found; N% 22.26 calcd., 22.33 found.) Thermally stable up to 215°C, it melts and loses a SCA molecule endothermically. Subsequently the $UO_2Cl_2(SCA)_2$ decomposes non-stoichiometrically (Fig. 1c).

$UO_2Cl_2(DMF)_2 \cdot 2\ H_2O$ was obtained using the method described by

Frigerio and Coley [2]. (Anal.: U% 45.51 calcd., 45.57 found; Cl% 13.55 calcd., 13.63 found; N% 5.35 calcd., 5.28 found.) The first water molecule is lost at 40°C, whereas the last is released at 105°C; both processes are endothermic. The anhydrous compound is thermally stable up to 300°C and then decomposes exothermically with the formation of several gaseous products (Fig. 1d).

UO_2Cl_2L was obtained as described in the literature for the nitrato complex [3], by refluxing an ethanolic solution of $UO_2Cl_2 \cdot 3\ H_2O$ and urea. (Anal.: U% 59.36 calcd., 59.42 found; Cl% 17.68 calcd., 17.73 found; N% 6.98 calcd., 7.05 found.) The loss of the neutral ligand begins exothermically, with decomposition, at 160°C and slowly continues up to 400°C (Fig. 1e).

The $E_a^{\neq}$ values related to the loss of the neutral ligands, calculated using methods described in the literature, could be diagnostic for a series of compounds having similar structures and the same rate determining steps, as recently observed for the series of $UO_2(NO_3)_2L_2$ adducts ($L =$ neutral N-donor ligands) [4] and $UO_2(NO_3)_2L_2$ adducts ($L =$ O-donor ligands) [5] in which the $E_a^{\neq}$ values increase in the same order of the ν_{as} of O–U–O frequency. However, in this case, owing to simultaneous redox reactions between the neutral ligands and the uranyl salt, which are very evident during the thermal decomposition (exothermic DTA peak), the formation of coordinated unsaturated species cannot be excluded. Therefore the interpretation of the $E_a^{\neq}$ values in terms of UO_2 ligand-bond breakage appears doubtful. The order of decreasing temperature at which the adducts begin to decompose, chosen as the basis of comparison of the thermal stability of the ligands, can be applied, in our opinion, as criterium to evaluate the coordinating ability of the ligands. Thus no significant correlation between thermoanalytical parameters and chemical properties of these complexes can be made.

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