Inorganica Chimica Acta, 53 (1981) L17–L18

The Chemistry of Quadrivalent Lanthanoids.
Part I. New Preparative Methods for Cerium(IV) Chloride Complexes

J. BARRY, J. G. H. DU PREEZ*, E. ELS, H. E. ROHWER and P. J. WRIGHT

Uranium Chemistry Research Unit, University of Port Elizabeth, P.O. Box 1600, Port Elizabeth, South Africa

Received September 20, 1980

In a recent report the interest in the chemistry of $CeCl_4$ complexes was indicated by us [1] especially with reference to comparison with quadrivalent actinoids, in particular uranium(IV). The preparation of $CeCl_4$ has not been reported in the literature and few of its complexes with neutral ligands are known, *viz.* $CeCl_4(dmso)_3$ [2], $CeCl_4(tppo)_2$ [2], $CeCl_4(bipyO_2)_2$ [3] and $CeCl_4(tdpo)_2$ [1] (dmso = dimethylsulphoxide, tppo = triphenylphosphine oxide, $bipyO_2$ = bipyridyl N,N′-dioxide and tdpo = tris(dimethylamido)phosphine oxide).

Present problems associated with the preparation of $CeCl_4$ complexes are various. The unavailability of $CeCl_4$ as a result of its instability, the slow rate of formation of $CeCl_6^{2-}$ using the common preparative methods, *viz.* the reaction of HCl gas on $CeO_2(H_2O)_2$ either in aqueous [4] or non-aqueous [5] solution at 0 °C and gradual decomposition of the $CeCl_6^{2-}$ solution, are some major ones. A number of the weaker neutral ligands cannot replace the chloride ion from the $CeCl_6^{2-}$ species to form neutral complexes and even in cases where it can, impure products are readily obtained. The other starting materials, used in the past for the preparation of chloro complexes, *viz.* $Ce(ClO_4)_4$ [6] and $(NH_4)_2Ce(NO_3)_6$ [1] are less attractive, since the preparation of pure chloro complexes are even more difficult using these. Efforts were, therefore, made to obtain more stable and suitable starting materials and derive convenient methods for the preparation of $CeCl_4$ complexes.

Results and Discussions

In view of the fact that the Cs_5MCl_6 (M = U, Np, Pu) analogues could be used [7] to prepare neutral ligand complexes of the actinoid tetrachlorides, efforts were made to obtain a rapid method for the preparation of pure Cs_2CeCl_6. Since it was previously found that the reaction between $CeO_2(H_2O)_2$ and HCl gas occurs relatively rapidly in 2-methoxy ethanol it was used instead of methanol (see preparation (a) under experimental).

Solid neutral $CeCl_4$ complexes of relatively weaker ligands like N,N′-dimethyl acetamide or N,N′-dimethyl formamide could not be prepared from Cs_2CeCl_6, like *e.g.* in the case of Cs_2UCl_6 [7], those of stronger ones could, however, be prepared under the correct conditions, *e.g.* $CeCl_4(tdpo)_2$ (see preparation (b) under experimental).

It was previously indicated [5] that onium formation plays an important role in the dissolution of $CeO_2(H_2O)_2$ by HCl gas, *e.g.* through the formation of the unstable $H_2CeCl_6(dioxane)_4$. It was, therefore, decided to use a tri-ether *viz.* diethylene glycol dimethyl ether (dmdg) as solvent and $SOCl_2$ as chlorinating agent instead of HCl. The initial reaction of thionyl chloride with the dried cerium(IV) hydroxide suspended in dmdg was performed at −22 °C. The orange solid obtained ultimately (preparation (c)) varied in analysis and agreed approximately with $H_2CeCl_6(dmdg)_3$. Thermogravimetric analysis indicated that mass losses occur at ~60 °C, 160 °C and 320 °C, respectively. Upon heating it at 45 °C under vacuum for half an hour, the mass loss at 60 °C disappeared. The mass loss at ~160 °C was ~13% and the orange Ce(IV) product became a cream coloured Ce(III) product. A loss of two mol of HCl and one chlorine atom per mol compound amounts to 14%, if the product is assumed to be $H_2CeCl_6(dmdg)_3$.

This compound is indefinitely stable at room temperature, soluble in methanol, ethyl acetate and nitromethane. It could be used, very conveniently, as a starting material for the preparation of both M_2CeCl_6 (M = quaternary ammonium or phosphonium) and neutral $CeCl_4$ complexes, *e.g.* $CeCl_4(tdpo)_2$ (see preparation (d) under experimental).

Since it is known that boiling thionyl chloride provides an anhydrous oxidative chlorinating medium, the reaction of hydrated $CeCl_3$ with a soluble chloride salt of which the cation does not form a very insoluble $CeCl_6^{2-}$ complex, *e.g.* tetrabutyl ammonium chloride, was studied in thionyl chloride. At room temperature apparently little reaction other than slowly dehydrating the $CeCl_3$, occurred. Upon boiling the yellow thionyl chloride gradually changed through orange to red simultaneously dissolving the $CeCl_3$. Even bubbling chlorine gas through a thionyl chloride solution at room temperature containing tetrabutylammonium chloride and anhydrous $CeCl_3$, did not lead to oxidation over a considerable length of time, whereas refluxing for 80 minutes lead to a quantitative oxidation to $CeCl_6^{2-}$, independent of whether free chlorine gas was lead through or not. The red solution could be used to precipitate $CeCl_6^{2-}$ complexes of a number of cations in thionyl chloride, *e.g.* NEt_4^+, PPh_4^+, *etc.* (see preparation (e) under experimental). This method is without doubt the most

---

*Author to whom correspondence should be addressed.

rapid and convenient method for the preparation of $CeCl_6^{2-}$ species if the starting material of method (c) is not available.

Experimental

(a) The Preparation of Cs_2CeCl_6

Dry HCl gas was lead through a suspension of $CeO_2(H_2O)_2$ (5.2 g) in 2-methoxy ethanol (20 cm^3) at −17 °C for 60 minutes. To the resulting red centrifuged cerium(IV) solution was then added a solution of CsCl (1.5 equivalents) dissolved in a minimum of 1:1 mixture of conc. HCl and ethanol. The orange yellow precipitate was centrifuged, the supernatent decanted, the solid suspended in ether, filtered, vacuum dried and analysed. Found: Ce: 22.54; Cl: 34.3%. Calculated for Cs_2CeCl_2: Ce: 22.69; Cl: 34.38%.

(b) Preparation of $CeCl_4(tdpo)_2$ from Cs_2CeCl_6

A mixture of N,N′-dimethyl formamide (10 cm^3) and nitromethane (20 cm^3) was added to Cs_2CeCl_6 (1 g), stirred and centrifuged. The resulting red solution was decanted from the yellow white precipitate and 1.8 equivalents of tdpo dissolved in nitromethane (5 cm^3) added and kept at 0 °C for 12 hours. The red crystals of $CeCl_4(tdpo)_2$ which formed slowly were filtered, washed with ethyl acetate, ether, vacuum dried and analysed. Found: Ce: 21.8; Cl: 22.0%. Calculated for $CeCl_4(tdpo)_2$: Ce: 21.88; Cl: 22.15%.

(c) Preparation of '$H_2CeCl_6(dmdg)_3$' Starting Material

A mixture of dmdg (100 cm^3) and thionyl chloride (50 cm^3) was cooled to −22 °C using a carbon tetrachloride slush in a thermosflask. $CeO_2(H_2O)_2$ (10 g) was slowly added to the above solution while stirring continually. After the $CeO_2(H_2O)_2$ was added the reaction mixture was left in the thermosflask and allowed to gradually reach room temperature (~12 hours). It was left for a further 24 hours with occasional stirring, the supernatent decanted washed twice with petroleum ether and vacuum dried for two hours. The cerium(IV) and chloride analysis for a number of preparations varied from 17 to 19% (Ce(IV)) and 27 to 29% (Cl^-). (Calculated for $H_2CeCl_6(dmdg)_3$: Ce(IV): 18.50%; Cl^-: 28.08%).

(d) Application of Product under (c) to Prepare Neutral Complexes

'$H_2CeCl_6(dmdg)_3$' (1 g) was dissolved in a mixture of ethyl acetate (35 cm^3) and methanol (8 cm^3) by stirring for five minutes. The red solution was centrifuged and decanted. To this was added two equivalents of the ligand dissolved in a minimum of ether, ethyl acetate, methylene dichloride or nitro methane. Ether was then added dropwise until the solution became turbid. Red crystals formed upon standing when cooled in an ice/water slush. The product was filtered washed with ether, vacuum dried and analysed. Found: Ce: 21.8; Cl: 22.1%. Calculated for $CeCl_4(tdpo)_2$: Ce: 21.88; Cl: 22.15%.

(e) Preparation of $(Net_4)_2CeCl_6$ from $CeCl_3(H_2O)_7$

$CeCl_3(H_2O)_7$ (2.5 g) was placed in a roundbottom flask. To this was added a thionyl chloride solution (40 cm^3) containing tetrabutyl ammonium chloride (4.6 g, 2.4 equivalents) and refluxed for 80 minutes. The red solution was pressure filtered through a sintered glass disc using dried nitrogen gas. A concentrated solution of tetraethylammonium chloride (2.1 equivalents) was added when a yellow orange precipitate formed immediately. The solution was filtered, the precipitate washed twice with petroleum ether containing 5% thionyl chloride, vacuum dried and analysed. Found: Ce: 22.7; Cl: 34.5%. Calculated for $(Net_4)_2CeCl_6$: Ce: 22.85; Cl: 34.69%.

Analysis

Ce(IV) was analysed by reacting with excess ferrous ammonium sulphate in H_2SO_4 medium and back titrating potentiometrically with dichromate. Chloride was determined by dissolving the cerium(IV) complex in methanol and titrating potentiometrically by silver nitrate. Cerium(IV) hydroxide ($CeO_2(H_2O)_2$) was prepared as described previously [5].

Acknowledgements

The authors wish to acknowledge the financial assistance received from the South African Council for Scientific and Industrial Research, the South African Atomic Energy Borad and the University of Port Elizabeth.

References

1 J. G. H. du Preez, H. E. Rohwer, J. F. de Wet and M. R. Caira, *Inorg. Chim. Acta, 26,* L59 (1978).

2 F. Brezina, *Collection of Czechoslovak Chem. Commun., 36,* 2889 (1971).

3 F. Brezina, *Collection of Czechoslov. Chem. Commun., 39,* 2162 (1973).

4 J. L. Ryan, C. K. Jørgensen, *J. Phys. Chem., 70,* 2845 (1969).

5 S. S. Moosath, M. R. A. Rao, *Indian Academy of Sciences Proc., 43A,* 213 (1956).

6 D. T. Cramer, R. J. Kline, *J. Am. Chem. Soc., 76,* 5282 (1954).

7 K. W. Bagnall, A. M. Deane, T. L. Martin, P. S. Robinson and M. A. A. Stewart, *J. Chem. Soc.,* 611 (1961).

8 S. S. Moosath, *Indian Academy of Sciences Proc., 43A,* 220 (1956).