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Preparation of Trihaloderivatives of Niobiumtetraphenylporphyrin

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Following our interest in the chemistry of electron-rich complexes of the early transition metals, we wished to find out whether such complexes were available in organo-metalloporphyrin systems.

The synthesis of the oxo-niobium(V) porphyrin complex $[Nb_2(TPP)_2O_3]$, **1**, (TPP = meso-tetraphenylporphyrin) in high yield has been reported [1, 2]. However halides or acetylacetonato-complexes are more commonly used as starting material for syntheses of organometallic complexes. Therefore we set out to prepare chloro- and acetylacetonato derivatives of the niobiumtetraphenylporphyrin system.

The direct preparation of a chloride complex from the reaction between $NbCl_5$ and $H_2(TPP)$ gave no tractable product. The treatment of $Nb_2(TPP)_2O_3$, **1**, with aqueous HCl resulted in a partial demetallation of the porphyrin complex. However we found that a toluene solution of the oxo-complex **1**, when treated with dry gaseous HCl, deposits purple crystals of $[Nb(TPP)Cl_3]$, **2**, in 81% yield. The compound **2** was recrystallised as purple needles in a HCl- saturated toluene: chlorobenzene mixture. It was identified by a total elemental analysis and mass spectrometry. Using chemical ionisation technique, the parent ion appeared at $M^+/e = 775$ corresponding to $[Nb(TPP)Cl_2]^+$. The molecular ion $[Nb(TPP)Cl_3]^+$ did not appear. The compound **2** easily hydrolysed quantitatively to the parent oxo-complex **1**.

The bromide complex $[Nb(TPP)Br_3]$, **3**, was prepared in the same way using dry HBr. The infrared spectrum of **3** is similar to that of the chloride complex **2**. The elemental analysis is consistent with the formula $[Nb(TPP)Br_3 \cdot 3HBr]$.

The acetylacetonato-complex [Nb(TPP)(acac)O], **4**, was readily prepared in 78% yield by reacting the oxo-complex **1** with an excess of acetylactone. The complex **4** crystallises as purple crystals from a mixture of toluene and petroleum ether. The infrared spectrum shows bands characteristic of the acetylacetone ligand at 1594 and 1525 cm^{-1} and a band at 898 cm^{-1} which can be assigned to Nb=O similarly to the observed absorption in Nb(TPP)(Ac)O [1]. The mass spectrum of compound **4** showed a peak at $M^+/e = 820$ corresponding to the molecular ion $[Nb(TPP)(acac)O]^+$ and an intense peak at $M^+/e = 721$, corresponding to the fragment $[Nb(TPP)O]^+$.

We tried to react the complexes **2**, **3**, **4** with various alkylating or hydride exchange reagents such as Grignard reagents, alkyllithium, alkylaluminium, sodium borohydride or aluminium hydrides. In all cases reactions occurred, but we were unable to isolate any tractable complex containing a metal–carbon or a metal–hydrogen bond. It thus appears that the porphyrin ligand does not readily provide stable organoniobium derivatives, compared to cyclopentadienyl–niobium systems.

Experimental

All preparations and manipulations were carried out under nitrogen or *in vacuo*. Solvents were dried by reflux over and distillation from sodium or calcium hydride. The compound $[Nb_2(TPP)_2O_3]$ was prepared as previously described [1].

[Nb(TPP)Cl₃]

Dry HCl gas was passed through $[Nb_2(TPP)_2O_3]$ (3.0 g, 2.05×10^{-3} mol) in dry degassed toluene (500 cm^3) at r.t. for 1 h giving purple crystals. The reaction mixture was then cooled at –20 °C for 3 h and filtered. The resulting purple crystals were washed twice with petroleum ether (40–60 °C, 50 cm^3) and dried *in vacuo*. Recrystallization from hot HCl saturated 1:1 chlorobenzene:toluene gave 2.7 g (81%) of $[Nb(TPP)Cl_3]$ as purple needles. Found: C, 64.65; H, 3.5; N, 6.7; Cl, 12.9; Nb, 11.7%; $C_{44}H_{28}Cl_3N_4Nb$ requires C, 65.1; H, 3.5; N, 6.9; Cl, 13.1; Nb, 11.4%. I.r. spectrum (mull), cm^{-1}: 3050w, 1598w, 1487w, 1442w, 1365w, 1345m, 1075m, 1003s, 990s, 810s, 755s, 725s, 700s, Mass spectrum $M^+/e = 775$ $[Nb(TPP)Cl_2]^+$.

[Nb(TPP)Br₃]

This compound was obtained as for the chloride complex in 72% yield. Found: C, 43.8; H, 2.5; N, 4.7; Br, 42.2%; $[Nb(TPP)Br_3] \cdot 3HBr$ requires C, 44.5; H, 2.6; N, 4.7; Br, 40.35%. I.r. spectrum (mull), cm^{-1}: 3050w, 1598w, 1487w, 1440w, 1355m, 1345m, 1072m, 1000s, 985m, 808s, 753s, 738s, 718s, 696s.

[Nb(TPP)(acac)O]

A mixture containing $[Nb_2(TPP)_2O_3]$ (0.89 g, 0.61×10^{-3} mol) and acetylacetone (10 g) in toluene (50 cm^3) was refluxed for 4 h. The volume of the solution was then reduced *in vacuo* to *ca.* 10 cm^3 and toluene : petroleum ether, 1 : 3 (60 cm^3) was added. After cooling at −20 °C for 24 h, 0.95 g (78%) of purple crystals were collected, washed with petroleum ether (40–60 °C) and dried *in vacuo*. Found: C, 72.1; H, 4.4; N, 6.8%; $C_{49}H_{35}N_4O_3Nb$ requires C, 71.7; H, 4.3; N, 6.8%. I.r. spectrum (mull), cm^{-1}: 1594s, 1525s, 1345m, 1070m, 1003m, 982s, 898s, 803s, 750m, 720s, 698s. Mass spectrum: M^+/e = 820, Nb(TTP)(acac)O$^+$, 721, Nb(TPP)O$^+$.

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References

1 C. Lecomte, J. Protas, R. Guilard, B. Fliniaux and P. Foumari, *Chem. Commun.*, 434 (1976).

2 J. F. Johnson and W. R. Scheidt, *J. Am. Chem. Soc., 99,* 294 (1977).