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Synthesis and Characterization of Tetranuclear Nb^{III} Clusters, using Cycloaddition of Double-Bonded Dimers by $MeN(PF_2)_2$

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The chemistry of niobium and tantalum halogenide complexes in oxidation state +3 is currently dominated by the formation of dinuclear species, including $M_2X_6L_3$ (M = Nb or Ta; X = Cl or Br; L = SC_4H_8 [1], SMe_2 [2]), $M_2Cl_6(PhPMe_2)_4$ [3] and $Ta_2Cl_6L_4$ (L = PMe_3 [4], C_5H_5N [5], C_6H_7N (γ-picoline) [6] for which a metal–metal double bond has been assumed or established by X-rays. Derivatives with multidentate donors are limited to niobium compounds of formula Nb_2Cl_6 (L–L)$_2$, which are obtained by an exchange reaction from $Nb_2Cl_6(SMe_2)_3$ and where L–L is $(Ph_2PCH_2)_2$ or $MeC(CH_2AsMe_2)_3$ or o-$C_6H_4(AsMe_2)_2$ [2]. Chelating π-acceptor phosphanes such as $MeN(PF_2)_2$ should also be able to stabilize lower oxidation states of niobium or tantalum, as observed for other early transition metals [7].

We now report the unexpected formation of the first niobium(III) tetranuclear clusters $Nb_4Cl_{12}(PhPMe_2)_6$ and $Nb_4Cl_{12}(PhPMe_2)_6[MeN(PF_2)_2$ during ligand exchange reactions between $Nb_2Cl_6(PhPMe_2)_4$ and $MeN(PF_2)_2$. The (methylamino)bis(difluorophosphane) ligand thus appears to induce the condensation of the double-bonded Nb(III) dimers.

Results and Discussion

Various attempts to obtain low-valent niobium-(methylamino)bis(difluorophosphane) complexes starting directly from Nb(V) or Nb(IV) chloride have all failed. Reduction of $NbCl_5$ by magnesium turnings or sodium naphthalenide in the presence of the phosphorus bidentate was accompanied by side reactions which prevented the isolation of pure compounds. The low affinity of $MeN(PF_2)_2$ towards Nb(IV) chloride (for instance, no exchange between $NbCl_4(THF)_2$ and $MeN(PF_2)_2$ was observed at room temperature in CH_2Cl_2, even after one month) precluded the production of niobium(IV)–(methylamino)bis(difluorophosphane) complexes by a more selective route.

Ligand exchange reactions starting from Nb(III) complexes appear to us to be an attractive alternative for providing more interesting routes to (methylamino)bis(difluorophosphane) complexes. Thus, the room temperature reaction between the dark green $Nb_2Cl_6(PhPMe_2)_4$ complex and excess of $MeN(PF_2)_2$ in methylene chloride led, after about 5 hours, to a light-salmon precipitate whose empirical formula corresponds to $Nb_2Cl_6(PhPMe_2)_3$ (55%) (compound *1*), and to a solution from which $Nb_4Cl_{12}(PhPMe_2)_6[MeN(PF_2)_2]$ (30%) (compound *2*) could be isolated. These new products were characterised by the usual methods: microanalytical data, molecular weight measurements, IR, ^1H and ^{19}F NMR.

Compounds *1* and *2* were found to be diamagnetic in the solid as in solution. In view of their poor solubility even in polar media such as MeCN or $MeNO_2$, a monomeric dinuclear structure seems less probable for $Nb_2Cl_6(PhPMe_2)_3$, although such monomeric complexes are now known with strongly basic and crowded phosphanes [8]. Molecular weight data on benzene solutions established its dimeric character (M_{found} = 1380 ± 140, M_{cal} = 706.5), and thus excluded the obtention of a more extended polynuclear species. Furthermore, the air-sensitivity of $Nb_4Cl_{12}(PhPMe_2)_6$ (although less than that of $Nb_2Cl_6(PhPMe_2)_4$) is also in favour of an oligomeric species, rather than a polymeric one.

The preparation of tetranuclear niobium clusters from the doubly bonded dimer $Nb_2Cl_6(PhPMe_2)_4$ requires the loss of the initial coordinated ligand (confirmed by ^{31}P NMR monitoring: appearing of the resonance of free $PhPMe_2$ at −45 ppm), which seems initiated by the $MeN(PF_2)_2$ ligand. The $Nb_2Cl_6(PhPMe_2)_3$ species which could result is probably unstable, rapidly condensing to form a tetranuclear unit. On the other hand, this condensation reaction might compete with the formation of an adduct such as $Nb_2Cl_6(PhPMe_2)_3[MeN(PF_2)_2]$ where $MeN(PF_2)_2$ behaves as a monodentate or as a bidentate. However, a chelating behaviour of (methylamino)bis(difluorophosphane) is generally not favoured, as its 'bite' is small for functioning as a biligate monometallic ligand [9], and metal-metal bonding is therefore preferred. Thus $MeN(PF_2)_2$ provokes Lewis-base associations reactions to compound *2*; this probably proceeds *via* an intermediate in which $MeN(PF_2)_2$ is monodentate, but which could not be detected. The formation of compound *2* is always less favoured with respect to the formation of compound *1* (55%).

Similar coupling reactions to tetranuclear clusters, either spontaneous [10] or induced by various reactants [11], have already been reported for molybdenum quadruply [10, 11] or triply [12] bonded dimers. However, to our knowledge, our results are the first example reported for group V metals.

The IR spectra of compounds *1* or *2* are less informative, as they show mainly the absorptions of the

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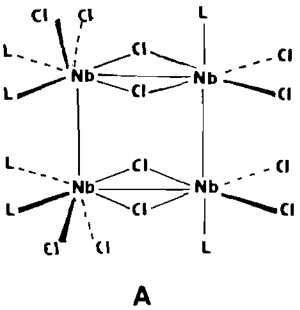
phenyldimethylphosphane ligand. The presence of $MeN(PF_2)_2$ for compound *2* is confirmed by the observation of a ν P–F stretching band at 798 cm^{-1} [9]. The metal–chlorine vibrational modes are located as usual below 400 cm^{-1} [13].

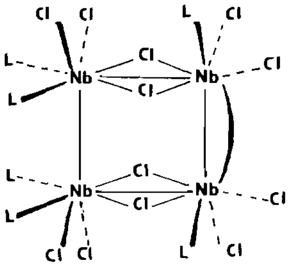
The poor solubility of $Nb_4Cl_{12}(PhPMe_2)_6$ and of $Nb_4Cl_{12}(PhPMe_2)_6[MeN(PF_2)_2]$ prevented their characterisation by ^{31}P NMR, and only ^1H and ^{19}F data could be obtained. The spectra obtained on CD_2Cl_2 solutions for each compound are in agreement with the presence of a single molecular species. The ^1H room temperature spectra of $Nb_4Cl_{12}(PhPMe_2)_6$ and $Nb_4Cl_{12}(PhPMe_2)_6[MeN(PF_2)_2]$ each show two types of phenyldimethylphosphane ligands, as evidenced by the presence for the methyl region of two doublets in a 2:1 intensity ratio [δ_{Me} = 1.83, 2.00 (J = 14 Hz); and 1.89, 2.11 ppm (J = 13.2 Hz) respectively]. The presence of an additional molecule of $MeN(PF_2)_2$ in the coordination sphere of compound *2* is confirmed by the observation for ^1H NMR of a broad singlet at 2.65 ppm, shifted to lower field with respect to the free ligand (δ_{Me} = 2.4 ppm, $^3J_{P-H}$ = 3.2 Hz, $^4J_{F-H}$ = 1.6 Hz) which was never observed. Furthermore, the ^{19}F NMR spectra established a bidentate — chelating or bridging — coordination mode for $MeN(PF_2)_2$ as only one doublet at –34.2 ppm ($^1J_{P-F}$ = 1400 Hz) is observed for the PF_2 groups.

Unfortunately, compounds *1* and *2* were obtained as microcrystalline powders; their poor solubility and/or their low stability prevented us from obtaining suitable X ray crystals. Therefore no precise indications concerning the relationships of the metallic centers are available. Moreover, niobium tetranuclear species are limited to MNb_4X_{11} (X = Cl, Br; M = Cs, Rh) having planar Nb_4 groups with an octahedral environment of the metal [14].

In view of the metal electrons available and the various arrangements established for Mo_4 clusters, either rectangular or square units [10, 11] with simple metal–metal bonding, or a bisphenoid structure [15] — the two double-bonded metal–metal moieties being attached through bridging ligands —, are possible. However, although the factors which will favour dinuclear compounds containing M–M bonds of multiple order, (compared with cluster compounds of the same empirical formula in which metal–metal bonding is delocalized) are at present unknown; such a structural type is less compatible with the number of metallic substituents invoked and with the spectroscopic ^1H NMR data, either for compound *1* or compound *2*. Thus we favour a cluster structure in which the phenyldimethylphosphane ligands occupy magnetically inequivalent positions in a 2:1 intensity ratio. Structures A and B for compounds *1* and *2* respectively are compatible with the NMR information, as with the usual niobium coordination number in low valent derivatives.



A



B

L = $PhPMe_2$
⌒ = $MeN(PF_2)_2$

Experimental

All handling was performed under dry argon using Schlenk tube techniques. The solvents were purified and deoxygenated by the standard methods. (Methylamino)bis(difluorophosphine [9] and $Nb_2Cl_6(PhPMe_2)_4$ [3] were synthesized as reported in the literature. Infra-red spectra were taken in Nujol mulls and recorded on a Perkin-Elmer 577 spectrometer. ^1H, ^{19}F and ^{31}P NMR spectra were obtained on a WH-90 Bruker spectrometer operating in the Fourier transform mode. Fluorine-19 and phosphorus-31 chemical shifts are reported from external CCl_3F and 85% H_3PO_4 respectively and are given positively to low fields. Molecular weights were determined in benzine solutions with KNAUER vapour pressure osmometer. Microanalyses were performed by the Centre de Microanalyses du C.N.R.S..

Synthesis of $Nb_4Cl_{12}(PhPMe_2)_6$ and of $Nb_4Cl_{12}(PhPMe_2)_6[MeN(PF_2)_2]$

$MeN(PF_2)_2$ (0.4 ml, 3.14 mmol) was added to a solution of $Nb_2Cl_6(PhPMe_2)_4$ (980 mg, 1.03 mmol) in 15 ml CH_2Cl_2 at room temperature. After about 30 mn, a clear precipitate appeared and the solution turned to brown. Stirring was maintained for about 4 h, and the precipitate was then removed by filtration, washed with toluene, and vacuum dried. 406 mg (55%) of $Nb_4Cl_{12}(PhPMe_2)_6$ were obtained as a light salmon-coloured air-sensitive powder (becoming pasty blue in the air). *Anal.* Calcd for $C_{48}H_{66}Cl_2Nb_4P_6$: C, 35.42; H, 4.66; Cl, 26.19; P, 11.44. Found: C, 35.48; H, 4.72; Cl, 26.95; P, 11.15%. *IR*: (cm^{-1}): 1590 w (νC=C); 358m, 322sh, 300vs, 285m, 250w (νNb–Cl). *NMR*: ^1H (CD_2Cl_2): δMe_2: 1.83 (14 Hz), 2.00d (14 Hz) (2:1).

The brownish filtrate was concentrated to about 4 ml and a comparable volume of toluene or pentane was added. An oily product separated out. After about 12 h at room temperature, the mother liquor was eliminated with a syringe and the oil dried under high vacuum. 240 mg (30%) of $Nb_4Cl_{12}(PhPMe_2)_6[MeN(PF_2)_2]$ as a brown-orange air-sensitive product was obtained. *Anal.* Calcd for $C_{49}H_{69}Cl_{12}F_4NNb_4P_8$: C, 32.79; H, 3.88; Cl, 23.76; N, 0.78; P. 13.83. Found: C, 32.36; H, 4.02; Cl, 23.68; N, 0.91; P, 12.92%. *IR*: 798 (νP–F), 350m, 300sh, 290vs, 275vs (νNb–Cl). *NMR*: ^1H (CD_2Cl_2): δMe_2: 1.89d (13.2 Hz), 2.11d (13.2Hz) (2:1); δNMe = 2.65s.

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