Anomalous Behaviour of $[Nb(CO)_6]^-$ and $[Ta(CO)_6]^-$ towards Protons. Crystal and Molecular Structure of the Organometallic Acid $[C_4H_8OH]^+[Nb_2(CO)_8Cl_3]^-\cdot C_4H_8O$

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Treatment of $[M(CO)_6]^-$ with HX (X = Cl, AcO) under anhydrous conditions or in aqueous buffered solution yielded the diamagnetic $[M_2(CO)_8X_3]^-$ anions of d^4 niobium(I) and tantalum(I); the crystal and molecular structure of the title compound was solved by *X*-ray diffraction methods, showing that each niobium centre is heptaco-ordinated to four terminal carbonyl groups and to three bridging chlorides.

The reaction of binary mononuclear or polynuclear carbonyl metallates with protons is a matter of considerable interest in connection with the reduction of carbon monoxide to organic products.[1] Several patterns of reactivity are possible or have been detected such as (i) proton attack at the transition metal with formation of a covalently bonded hydride, *e.g.* for $MnH(CO)_5$, a weak acid in water,[2] (ii) proton transfer to water[3] or amines[4], as in the case of $[H_3O]^+[V(CO)_6]^-$ and $[NR_3H]^+[Co(CO)_4]^-$, respectively, (iii) one-electron transfer to proton, *e.g.* in the treatment of anhydrous and solvent-free $NaV(CO)_6$ with dry HCl in aprotic solvents, where H_2 and $V(CO)_6$ are the products,[3] (iv) protonation of the carbonyl oxygen, especially in the case of face-bridging[5] or edge-bridging[6] carbonyl groups, and (v) protonation of the carbonyl carbon with formation of metal-bonded formyl groups, which has not been observed as yet.

The type of behaviour of $[Nb(CO)_6]^-$ and $[Ta(CO)_6]^-$ towards acids is not yet known and acid treatment of these anions was recently reported[7] to yield unidentified products.

We have now found that the hexacarbonylniobate anion reacts with dry HCl under anhydrous conditions or in aqueous solution anomalously with respect to the corresponding vanadium(−I) derivative, leading to the formation of carbonyl complexes of d^4 niobium(I) with a two-electron transfer to protons. Tantalum was found to behave similarly.

Reaction of $[Na(thf)][Nb(CO)_6]$[8] (thf = tetrahydrofuran) with an excess of dry HCl in toluene or heptane, followed by filtration and cooling to solid CO_2 temperature gave the diamagnetic $[H(thf)_2]^+[Nb_2(CO)_8Cl_3]^-$ which was studied by *X*-ray diffraction methods.† *Crystal data: M* = 661.5, space group $P\bar{1}$, triclinic, a = 16.283(3), b = 9.293(2), c = 9.050(2) Å, α = 113.01(2), β = 96.56(2), γ = 98.39(2)°, U = 1224.7 Å^3, D_c = 1.792 g cm^{-3}, Z = 2, $\mu(Mo\text{-}K_\alpha)$ = 12.2 cm^{-1}.‡ Preliminary crystal examination and subsequent data collection were carried out with a Philips PW 1 100 four-cycle automatic diffractometer and graphite monochromated Mo-K_α radiation (λ = 0.71069 Å). A semi-empirical correction for absorption was applied.[9] A total of 2271 independent reflections was measured in the $2 \leqslant \theta \leqslant 20°$ range; 1765 of them having $I \geqslant 3\sigma$ were considered observed. The structure was solved by direct methods and by a full-matrix least-squares programme, SHELX-76,[10] to a conventional R value of 0.046. In the final stages of the refinement, when the R value was 0.05, a difference Fourier map revealed a residual electronic density maximum of 1.5 e/Å^3 located at *ca.* 1 Å from the oxygen atom of a thf molecule. This was assigned to the residual hydrogen atom of the chemical formula, which reduced the R to its final value.

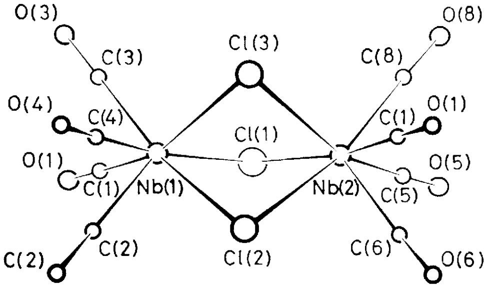

Figure 1. View of the $[Nb_2(CO)_8Cl_3]^-$ anion (**1**) with the labelling scheme. The ranges of some relevant bond distances and angles are: Nb–Cl, 2.592(3)—2.620(3); Nb–C, 2.021(12)—2.077(12) Å; Cl–Nb–Cl, 76.5(1)—77.2(1); Nb–Cl–Nb, 87.8(1)—88.8(1)°. The C–O distance was constrained to 1.16 Å.

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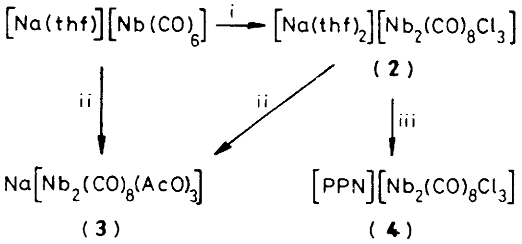
† All of the compounds reported in this paper gave satisfactory elemental analyses.

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



Scheme 1. i, 2HCl, thf; ii, aq. AcOH–AcONa; iii, PPNCl, CH_2Cl_2.

The molecular arrangement of $[Nb_2(CO)_8Cl_3]^-$ is shown in Figure 1. The two niobium atoms of the dimeric anion are bridged by three chlorides located at the vertices of an approximately equilateral triangle perpendicular to the ideal line connecting the two niobiums. The idealized molecular geometry of the anion is C_{2v}. The Nb . . . Nb nonbonding distance is 3.631(1) Å.

Compounds **(2)**—**(4)** also isolated in the course of this study, are shown in Scheme 1. By similar experimental procedures, the tantalum(I) acid, $[H(thf)_2][Ta_2(CO)_8Cl_3]$ and the bis(triphenylphosphine)iminium derivative $PPN[Ta_2(CO)_8Cl_3]$ were isolated. All of the compounds are yellow-to-orange solids sensitive to air and characterized by two i.r. carbonyl stretching vibrations at 2004—2022 m and 1885—1912 vs cm^{-1}, depending on solvent, countercation, and bridging unit, in agreement with the local C_{4v} symmetry of the $[M(CO)_4]$ moiety ($A_1 + E$).

During the preparations of these compounds, molecular hydrogen and carbon monoxide were detected in the gas phase; the formation of both the sodium derivative and the acid can therefore be represented by the general stoicheiometry shown in equation (1). The niobium and tantalum

$$2[M(CO)_6]^- + 4HCl \rightarrow 2H_2 + Cl^- + [M_2(CO)_8Cl_3]^- + 4\,CO \qquad (1)$$

anionic complexes react promptly in tetrahydrofuran with sodium under CO and with NaC_5H_5 to give $[M(CO)_6]^-$ and $M(C_5H_5)(CO)_4$, respectively, the latter in substantially quantitative yields.

The anionic trichloro-bridged complexes reported in this paper presumably originate from an exceedingly reactive complex $HM(CO)_6$ which we were unable to isolate. This is a feature that niobium and tantalum have in common with vanadium, for which no stable $HV(CO)_6$ has been detected.[3]

The compounds of this paper are the first halogenocarbonyl complexes of Group 5 metals to be reported.

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