Halide Abstraction from $[(\eta^5\text{-}C_5H_5)NbCl_4]$ leading to Novel Cationic Niobium(v) Species: Crystal Structure of the 'Double' Hexachloroantimonate(v) Salt $[(\eta^5\text{-}C_5H_5)NbCl(MeCN)_4]^{3+}[(\eta^5\text{-}C_5H_5)Nb(MeCN)_6]^{4+}[SbCl_6]_7\cdot 7MeCN$

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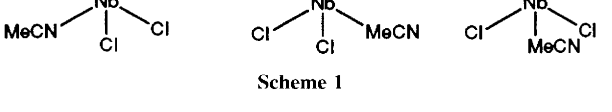
Sequential removal of chloride ions from $[(\eta^5\text{-}C_5H_5)NbCl_4]$ can be realised using antimony(v) chloride in acetonitrile under controlled stoichiometry; the formation and structural characterisation of the novel Nb(v) cations $[(\eta^5\text{-}C_5H_5)NbCl(MeCN)_4]^{3+}$ and $([\eta^5\text{-}C_5H_5)Nb(MeCN)_6]^{4+}$ are described.

Organometallic group 5 compounds involving both mono- and di-cyclopentadienyl $(\eta^5\text{-}C_5H_5)_nM$ units (n = 1,2; M = V, Nb, Ta) have attracted recent interest as possible catalyst precursors for the polymerisation of olefins.[1] For Ziegler–Natta group 4 metallocene systems with cocatalysts such as aluminium alkyls or methylaluminoxanes (MAO), it is the 14-electron cationic complexes $[(\eta^5\text{-}C_5H_5)_2M^*R]^+$ (M* = Ti, Zr, Hf; R = alkyl) that are held to be the active species.[2] The isoelectronic species for group 5 would be the dications $[(\eta^5\text{-}C_5H_5)_2MR]^{2+}$ based on M^V (d^0), but no such species have been reported. A search of the Cambridge Data Base files reveals that the structural chemistry of cationic group 5 complexes is sparse; specifically for niobium, crystal structure determinations are limited to the following compounds (all based on Nb^V except where stated otherwise): $[(\eta^5\text{-}C_5H_5)NbCl(CNBu^t)_4]^+$ (based on Nb^{III});[3] $[(\eta^5\text{-}C_5H_5)_2Nb\{(2\text{-}CH_2C_6H_4)_2\}]^+$;[4] $[(\eta^5\text{-}C_5H_5)_2NbCl(CH_2SiMe_3)]^+$;[5] $[(\eta^5\text{-}C_5H_5)_2NbCl_2]^+$;[6] $[(\eta^5\text{-}C_5H_5)_2Nb(SPh)_2]^+$;[7] $[(\eta^5\text{-}C_5H_5)_2Nb(\mu\text{-}SPh)_2Mo(CO)_4]^+$;[7] $[(\eta^5\text{-}C_5H_5)_2Nb(MeCN)_2]^{2+}$ (based on Nb^{IV});[8] $[(\eta^5\text{-}C_5H_5)_2NbCl_2]^+$;[9] $[(\eta^5\text{-}C_5H_5)_2Nb(bipy)]^{2+}$ (based on Nb^{IV});[10] $[\{\eta^5\text{-}C_5H_4(SiMe_3)\}_2Nb(\eta^2\text{-}Ph_2CCNPh\text{-}C,N)(MeCN)]^+$.[11]

Here we show that halide abstraction from $[(\eta^5\text{-}C_5H_5)NbCl_4]$ using antimony(v) chloride in acetonitrile solution is a viable approach to Nb^V cations. Direct treatment of $[(\eta^5\text{-}C_5H_5)NbCl_4]$ (1 mol) and $SbCl_5$ (1 mol) in acetonitrile results in single chloride abstraction and, following conventional work-up procedures, provides the bright red hexachloroantimonate(v) salt $[(\eta^5\text{-}C_5H_5)NbCl_3(MeCN)_2][SbCl_6]$ **1**. Satisfactory microanalytical data for $C_9H_{11}Cl_9N_2NbSb$ was obtained. The ^1H NMR spectrum of **1** shows three signals for cyclopentadienyl ring protons (δ 7.26, 7.29 and 7.33), indicative of the presence of the three possible isomers (Scheme 1) and a broad singlet at δ 2.39 arising from coordinated acetonitrile. The IR spectrum shows characteristic cyclopentadienyl bands (3122, 1130, 1025 and 857 cm^{-1}), a sharp doublet at 2315, 2288 cm^{-1} indicative of coordinated acetonitrile, and broad intense bands at 347 cm^{-1} [ν(Sb–Cl)] and 375, 295 cm^{-1} [ν(Nb–Cl)].

In a repeat experiment aimed at the removal of all four chlorine atoms, $[(\eta^5\text{-}C_5H_5)NbCl_4]$ (1 mol) was treated with a large excess of $SbCl_5$ (10 mol) in acetonitrile. The red solid obtained following slow concentration of the solution was recrystallised from $MeCN\text{–}CH_2Cl_2$ as ruby red needle crystals and identified as $[(\eta^5\text{-}C_5H_5)NbCl(MeCN)_4]^{3+}[(\eta^5\text{-}C_5H_5)Nb(MeCN)_6]^{4+}[SbCl_6]_7\cdot 7MeCN$ **2** by X-ray diffraction studies. Satisfactory microanalytical data for $C_{44}H_{61}Cl_{43}N_{17}Nb_2Sb_7$ was obtained.



Scheme 1

The structure of **2** consists of discrete $[(\eta^5\text{-}C_5H_5)NbCl(MeCN)_4]^{3+}$ and $[(\eta^5\text{-}C_5H_5)Nb(MeCN)_6]^{4+}$ cations, seven $SbCl_6^-$ anions and seven MeCN solvent molecules.† The 3+ cation is disordered over a centre of symmetry with the metal and chlorine atoms in equivalent positions. An ordered molecule is depicted in Fig. 1 with the atomic numbering system. The geometry of the niobium atom environment can be viewed as six-coordinate distorted octahedral with a unidentate cyclopentadienyl ligand; the alternative view accords the metal a formal coordination number of eight with the cyclopentadienyl anion taking up three coordination positions. The chlorine atom lies *trans* to the cyclopentadienyl ring with the four acetonitrile molecules lying in an equatorial plane [Nb–N 2.10(2)–2.17(2) Å]. The four nitrogen atoms are coplanar to within 0.01 Å and the niobium atom is situated 0.49 Å from this plane in the direction of the ring; this metal displacement leaves the four Cl–Nb–N angles compressed to significantly less than 90° (mean 76.9°). The niobium(III) isocyanide complex $[(\eta^5\text{-}C_5H_5)NbCl(CNBu^t)_4]^+$ (ref. 3) adopts a similar structure, but whereas the $Nb\text{–}C_{ring}$ distances [2.37(1)–2.40(1) Å] are comparable, the Nb–Cl bond distance of 2.505(4) Å is appreciably longer than the 2.13(1) Å in the present structure, thus reflecting the change in metal oxidation state from +5 to +3. However, this latter distance is seriously affected by the disorder.

The structure of the 4+ cation, which has crystallographic *m* symmetry, is shown in Fig. 2 with atom labelling. In this case the niobium coordination sphere includes the cyclopentadienyl group and six *N*-bonded acetonitrile ligands approximating to a pentagonal-bipyramidal geometry with axial positions occupied by the cyclopentadienyl group and one acetonitrile molecule. The equatorial girdle of coordinated solvent molecules is planar within experimental error (maximum deviation of a contributing atom 0.02 Å) and the metal

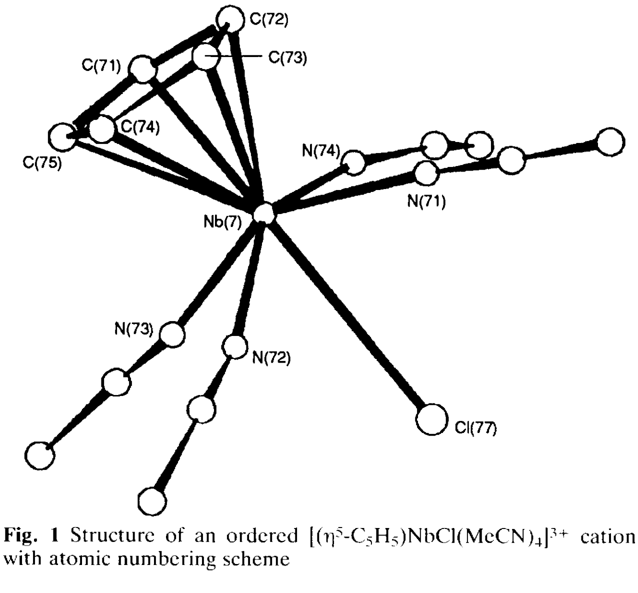


Fig. 1 Structure of an ordered $[(\eta^5\text{-}C_5H_5)NbCl(MeCN)_4]^{3+}$ cation with atomic numbering scheme

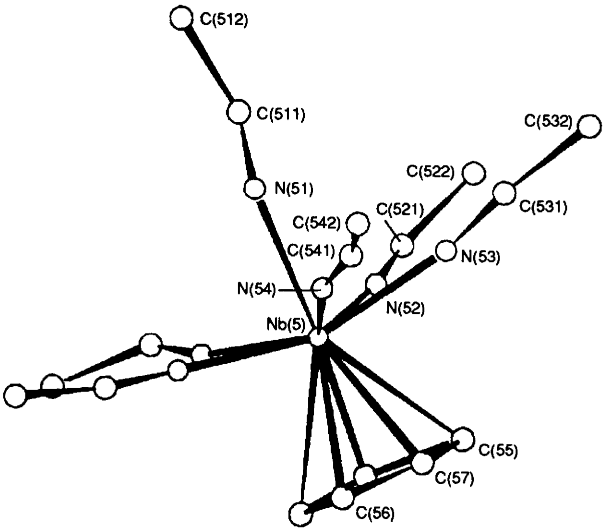


Fig. 2 Structure of the $[(\eta^5\text{-}C_5H_5)Nb(MeCN)_6]^{4+}$ cation with atomic numbering scheme

atom lies 0.38 Å from the plane in the direction of the cyclopentadienyl ring, thereby compressing the N_{ax}–Nb–N_{eq} angles to *ca.* 80°. There is no significant difference in the Nb–N_{ax} and Nb–N_{eq} bond lengths [2.17(2) and 2.10(2), 2.16(2), 2.17(2) Å respectively].

It is interesting that the metal coordination number increases from six to seven on going from the 3+ cation to the 4+ cation. Evidently the $[(\eta^5\text{-}C_5H_5)Nb]^{4+}$ unit can accommodate six MeCN molecules once all the bulky chlorine atoms have been removed. Presumably the 'extra' solvent molecule more than compensates for the loss of electron density associated with the 'electron-rich' ($\sigma + \pi$) halogen atoms; the effective atomic numbers (EAN) for the two cations are $[(\eta^5\text{-}C_5H_5)NbCl(MeCN)_4]^{3+}$ (16e) and $[(\eta^5\text{-}C_5H_5)\text{-}Nb(MeCN)_6]^{4+}$ (18e). The corresponding monocyclopentadienyl titanium(IV) cation $[(\eta^5\text{-}C_5H_5)Ti(MeCN)_5]^{3+}$ (16e) shows a pseudo-octahedral metal coordination sphere.[12]

Further investigations of the structural and coordination chemistry of cationic Nb^V and related group 5 metal species are now in progress.

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Footnote

† *Crystal data* for $[(\eta^5\text{-}C_5H_5)Nb(MeCN)_6]^{4+}[(\eta^5\text{-}C_5H_5)NbCl(MeCN)_4]^{3+}\cdot 7SbCl_6^{-}\cdot 7MeCN$: Monoclinic, space group $P2_1/m$, $a = 15.606(6)$, $b = 22.431(6)$, $c = 17.359(6)$ Å, $\beta = 104.6(1)°$, $U = 5880.4$ Å^3, $Z = 2$. 34751 reflections were measured on a Marresearch Image Plate system, 95 frames at 2° intervals were measured for 2 min each. 34751 reflections were measured of which 10497 were independent in a monoclinic unit cell ($R_{int} = 0.060$). Cell dimensions were determined from analysis of 2345 independent reflections. The structure was solved by direct methods. Of the two possible space groups $P2_1$ and $P2_1/m$, refinement of the latter led to the most likely structure although two ions *i.e.* $[(\eta^5\text{-}C_5H_5)NbCl(MeCN)_4]^{3+}$ and one of the $SbCl_6^-$ were disordered. The structure was refined on F^2 using SHELXL (G. M. Sheldrick, SHELXL, program for crystal structure refinement, University of Gottingen). The conventional R factor for the 4590 reflections with $I > 3\sigma(I)$ was 0.085. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No 1.

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