

Synthesis and Molecular Structures of the Sandwich Anion [K(18-crown-6)][Nb(η -C₇H₇)(η -C₅H₅)] and Cation [Nb(η -C₇H₇)(η -C₅H₄Me)(thf)]PF₆⁺

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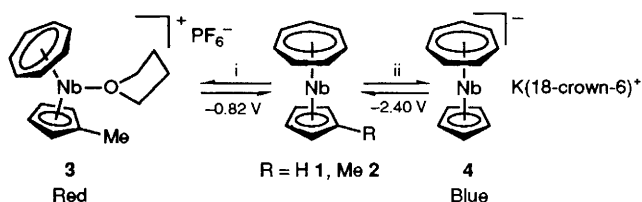
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The 17-electron compounds Nb(η -C₇H₇)(η -C₅H₄R) undergo reversible one-electron oxidation and reduction giving the structurally characterised compounds [Nb(η -C₇H₇)(η -C₅H₄Me)(thf)]PF₆⁺ and [K(18-crown-6)][Nb(η -C₇H₇)(η -C₅H₅)]⁻ respectively; the latter has an unusual distorted chain structure.

We have recently reported an improved synthesis of Nb(η -C₇H₇)(η -C₅H₅) **1**.¹ Here we report the products of chemical oxidation and reduction of this compound and the analogous Nb(η -C₇H₇)(η -C₅H₄Me).

Compounds **1** and **2** in thf undergo quasi-reversible one-electron oxidation at -0.82 V and quasi-reversible one-electron reduction at -2.40 V.[‡] Treatment of **2** in thf with 1 equivalent of ferrocenium hexafluorophosphate gives red crystals of [Nb(η -C₇H₇)(η -C₅H₄Me)(thf)]PF₆⁺ **3** in high yield (see Scheme 1).§

A single-crystal X-ray diffraction study¶ of **3** shows a bent sandwich structure with a coordinated thf ligand (Fig. 1). In



Scheme 1 Reagents: i, [Fe(η -C₅H₅)₂]PF₆, thf, 80%; ii, K film, thf, then 18-crown-6, 84%

† Abbreviations used; 18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane, thf = tetrahydrofuran, dme = 1,2-dimethoxyethane, cot = η -cyclooctatetraene, tmeda = 1,2-bis(dimethylamino)ethane.

‡ Cyclic voltammetry experiments were performed in thf saturated with tetrabutylammonium hexafluorophosphate. Potentials at a Pt disk working electrode were referenced to a saturated calomel electrode (SCE) via the ferrocenium/ferrocene couple and a silver wire pseudo-reference electrode.

§ Satisfactory microanalysis has been obtained for all new compounds.

¶ *Crystallographic details:* Compound **3**: C₁₇H₁₈F₆NbOP, *M* = 476.19, orthorhombic, *P*₂₁2₁2₁, *a* = 8.207(8), *b* = 11.594(1), *c* = 19.111(3) Å, *F*(000) = 952, scan mode ω -2 θ , θ_{\max} = 27°, *V* = 1818.6 Å³, *Z* = 4, *D*_c = 1.739 g cm⁻³, μ (Mo-K α) = 7.798 cm⁻¹, crystal size *ca.* 0.20 × 0.30 × 0.35 mm, *R* = 0.0296, *R*_w = 0.0325 from 2029 reflections [*I* > 3 σ (*I*)] and 236 independent parameters. Compound **4**: C₂₄H₃₆KNbO₆, *M* = 552.5, monoclinic, *P*₂₁/*m*, *a* = 9.329(3), *b* = 13.360(4), *c* = 10.680(3) Å, β = 106.00(2)°, *F*(000) = 576, scan mode θ -2 θ , θ_{\max} = 30°, *V* = 1279.5(6) Å³, *Z* = 2, *D*_c = 1.434 g cm⁻³, μ (Mo-K α) = 6.46 cm⁻¹, crystal size *ca.* 0.55 × 0.35 × 0.30 mm, *R* = 0.0425, *R*_w = 0.0464 from 3437 reflections [*I* > 2 σ (*I*)] and 154 independent parameters.

Data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer (for **3**) or a Nicolet R3m/V (for **4**) using graphite-monochromated Mo-K α radiation. Empirical absorptions were applied and the structures solved using direct methods (**3**) or Patterson (**4**) and difference Fourier syntheses and refined using full-matrix least-squares, with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were placed in calculated positions (C-H = 0.96 Å) with fixed isotropic thermal parameters. Crystallographic calculations were carried out using CRYSTALS⁶ on a Micro VAX 3800 (for **3**) or using SHELXTL PLUS on a Micro VAX II (for **4**). Atomic coordinates, thermal parameters and bond lengths and angles for both structures have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

contrast, the 16-electron vanadium complex [V(η -C₇H₇)(η -C₅H₅)]⁺ shows no tendency to form stable 18-electron adducts,² presumably because of the smaller atomic radius of vanadium. Surprisingly, the η -cycloheptatrienyl ligand in **3** is not planar as has always been observed previously, but displays a significant dishing of the ring as defined by the Nb-C bond lengths. Attempts to restrain this ring to within the usual limits of planarity led to a significant lowering of the goodness of fit of the X-ray data to the model.

The cyclic voltammogram of **3** is indistinguishable from the neutral 17-electron parent **2**. This indicates that the couple observed in oxidation is that shown in Scheme 1, and is not simply a [16e]⁺-[17e] process. Presumably the addition of a thf ligand to the presumed 16-electron cationic intermediate [Nb(η -C₇H₇)(η -C₅H₅)]⁺ is fast and does not effect the reversibility of the couple.

Treatment of a red-brown solution of **1** in thf with a freshly-prepared potassium film gives an extremely air- and water-sensitive blue solution containing the [Nb(η -C₇H₇)(η -C₅H₅)]⁻ anion. Addition of 18-crown-6 gives blue crystals of [K(18-crown-6)][Nb(η -C₇H₇)(η -C₅H₅)] **4**.

The crystal structure of **4** has been determined, and views of the molecular structure of the anionic and cationic units are shown in Fig. 2. The parallel-ring, sandwich structure of the anion is in accordance with a bonding description which locates the HOMO as an essentially non-bonding Nb 4d_{z²} orbital pointing towards the centroids of the two rings. The ring conformation of the anion is eclipsed, as required by a crystallographic mirror plane which passes through C(1), the midpoint of C(4) and C(4A), and the niobium atom. The [K(18-crown-6)]⁺ ion displays no unexpected structural features.

Fig. 3 shows the crystal structure of **4** whereby the cations and anions are joined alternately in an infinite distorted chain. The mode of cation-anion coordination in **4** is most unusual in comparison with the structures of other sandwich anions in that the alkali-metal ion is not equidistant from each of the carbons of a particular ring. This contrasts markedly with the

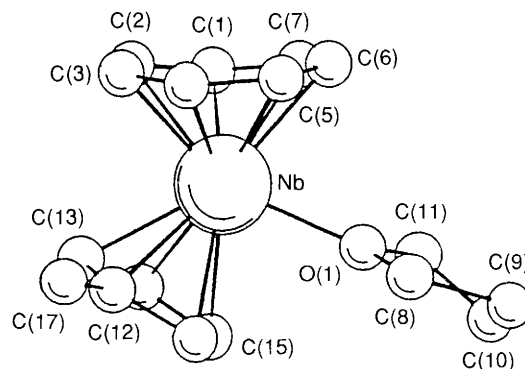


Fig. 1 Molecular structure of **3** (PF₆ ion and H atoms omitted). Selected bond lengths (Å): C-C(C₇-ring, mean), 1.408(2); C-C(C₅-ring, mean), 1.40(1); Nb-C(C₅-ring, mean), 2.409(2); Nb(1)-C(1), 2.281(5); Nb(1)-C(2), 2.331(5); Nb(1)-C(3), 2.323(6); Nb(1)-C(4), 2.273(5); Nb(1)-C(5), 2.340(6); Nb(1)-C(6), 2.398(6); Nb(1)-C(7), 2.357(6); Nb(1)-O(1), 2.308(4).

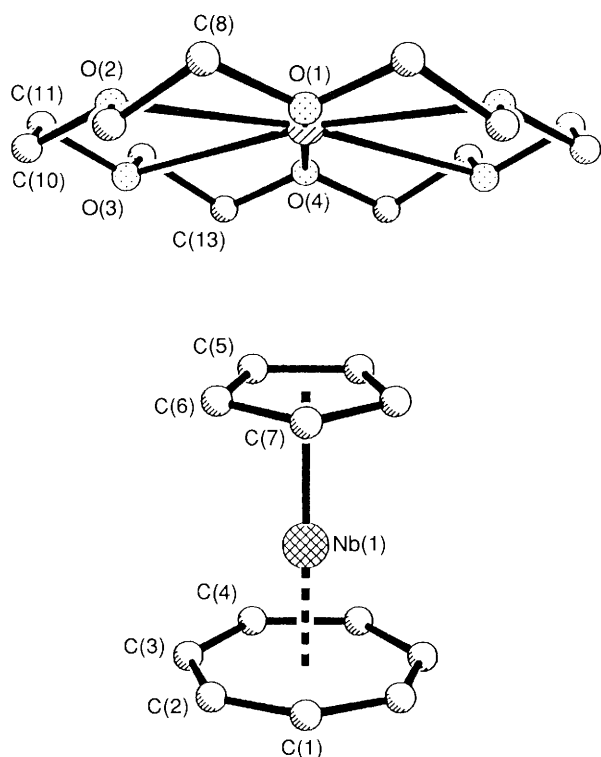


Fig. 2 Molecular structure of **4** (H atoms omitted). Selected bond lengths (Å) and angles (°): K–C(1), 3.006; K–C(2, 2A), 3.33(4); K–C(5, 5A), 3.34; Nb(1)–C(C₇-ring, mean), 2.31; Nb(1)–C(C₅-ring, mean), 2.43; Nb(1)–(C₇-ring centroid), 1.67; Nb(1)–(C₅-ring centroid), 2.15; C(1)–C(2), 1.333(5); C(2)–C(3), 1.361(6); C(3)–C(4), 1.417(6); C(4)–C(4A), 1.471(8); C(5)–C(5A), 1.393(6); C(5)–C(6), 1.373(5); C(6)–C(7), 1.382(5). (C₇-ring centroid)–Nb–(C₅-ring centroid), 176.8.

structures of, for example, [K(dme)]₂[Yb(cot)₂] which consists of symmetrically disposed quintuple ion pairs,³ and [K(thf)(dioxane)][V(η-mesitylene)₂] which has a zig-zag arrangement,⁴ analogous to that of [Na(tmeda)][C₅H₅].⁵ This asymmetric coordination of potassium in **4** is accompanied by a marked variation of C–C bond lengths within the η-C₇H₇ ring. The range found is between *ca.* 0.07 Å longer [C(4)–C(4A)] and 0.07 Å shorter [C(1)–C(2)] than that found (*ca.* 1.40 Å) for other (η-C₇H₇)Nb complexes.¹ In addition, a libration analysis has shown that the observed thermal parameters for carbon atoms are consistent with the presence of independent librational motion of both rings with the pivot centres displaced towards the carbon atoms closest to potas-

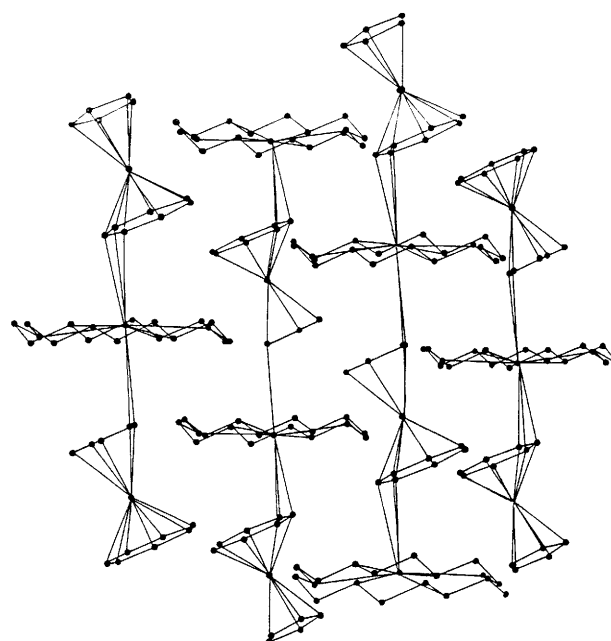


Fig. 3 Crystal structure of **4** viewed along *b*-axis

sium. We assume that the asymmetric coordination of the potassium ion is responsible for these effects.

Hence, both the oxidation and reduction products of the species Nb(η-C₇H₇)(η-C₅H₄R) (R = H **1**, Me **2**) have been characterised. In particular, the sandwich anion **4** displays a unusual and interesting crystal structure.

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