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SYNTHESIS AND PROPERTIES OF CYCLOPENTADIENYLNIOBIUM TRIMETHYLACETATES

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Summary

Reaction of Cp_2NbBH_4 with Me_3CCOOH gives the diamagnetic monomerical $Cp_2NbOOCCMe_3$, which contains a terminal carboxyl and reacts readily with an equimolar amount of CMe_3COOH to give the paramagnetic monomerical $Cp_2Nb(OOCCMe_3)_2$ containing terminal carboxyls and, probably, non-equivalent cyclopentadienyl ligands. The latter compound easily loses two C_5H_5 ligands under the action of two moles of Me_3CCOOH, giving the paramagnetic monomerical $Nb(OOCCMe_3)_4$ in which the carboxylate groups are chelated and the niobium coordination number is eight. Refluxing a 1 : 5 Cp_2NbBH_4/Me_3CCOOH mixture in xylene leads to the diamagnetic pentacarboxylate $(Nb(OOCCMe_3)_5)_n$ (probably a dimer).

Introduction

Unusual magnetic properties of the antiferromagnetic binuclear complexes $CpM(OOCR)_4MCp$ (Cp is π-C_5H_5; M is Ti(III) [1], V(III) [2,3]), which have a "bay structure" containing four OOCR bridges and no direct M—M bonds (the distances are: Ti...Ti, 3.63—3.74 Å (R = Ph, [4]); V...V, 3.62 Å ($R = C_4H_3O$ [5]), 3.70 Å ($R = CF_3$, [6])), stimulated the search for analogous complexes of other metals. It turned out, however, that with Cr(III) a cyclopentadienyl ligand might be fixed only in the monomerical $CpCr(OOCCF_3)_2 \cdot THF$ obtained from Cp_2Cr and CF_3COOH whereas weaker acids RCOOH ($R = CMe_3$) led only to the carboxylates of the known type, $RCOOH \cdot Cr(OOCR)_4Cr \cdot HOOCR$ [7]. A similar loss of cyclopentadienyl was observed in the reactions of RCOOH with $CpMn(CO)_3$ or $(CpFe(CO)_2)_2$, leading to nothing but the respective carboxylates $(M(OOCR)_2)_n$ [8]. The fact that Mn or Fe carboxylates cannot hold a cyclopentadienyl ligand may be explained by the sterical strain due to relatively small covalent radii of the complexes; indeed, even in complexes of titanium or vanadium there is a strong repulsion between the cyclopentadienyl and the carboxylate ligands [4—6].

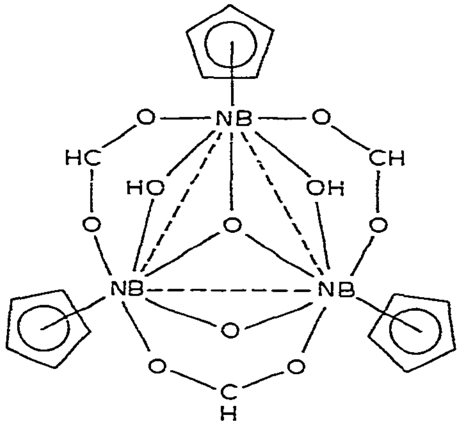
Of the second-row transition metals, we believe niobium, an electron analogue of vanadium and a coordination analogue of titanium [9], to be the most attractive. Earlier [2,6] we used a modified King technique [10] for the synthesis of vanadium(III) dimerical complexes.

$$2CpV(CO)_4 + 4RCOOH \xrightarrow[MeC_6H_5]{110^\circ C} CpV(OOCR)_4VCp$$

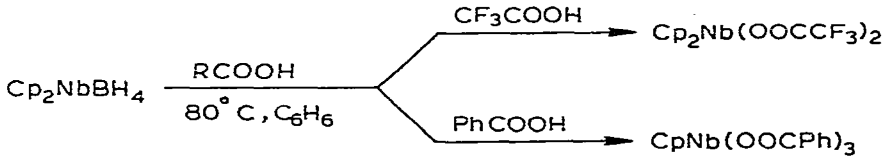
R = H, CH_3, CF_3, Ph...

The compound $CpNb(CO)_4$ or its phosphine-containing analogues only reacted, however, under more drastic conditions (refluxing in xylene) and, with HCOOH, a complicated process involving a trinuclear antiferromagnetic oxo-cluster of Nb(IV) [11] was observed.

$$3\,CpNb(CO)_3PPh_3 \xrightarrow[150^\circ C]{HCOOH} 3\left\{CpNb(OOCH)_3\right\} \xrightarrow[-6CO,\,-2\,H_2O]{}$$



Under milder conditions (even at room temperature), dimer vanadium(III) complexes may be obtained from Cp_2V and $(RCOO)_2$ [12] or from an RCOOH containing a sufficiently electron-donating R (R = CH_3, C_6H_5 [13], CMe_3 [14]; with an electron withdrawing R (R = CCl_3), the cyclopentadienylic structure was retained and the compound $Cp_2V(OOCCCl_3)$ [13] was formed. A similar difference as a function of R was observed by us in the reactions of Cp_2NbBH_4 [15].

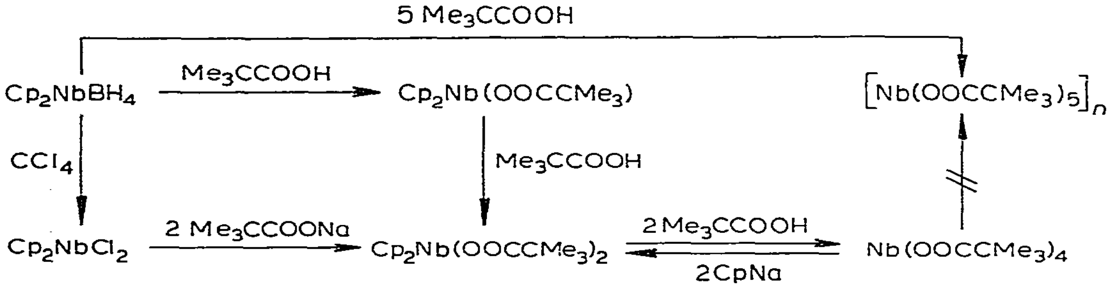


These processes lead to oxidation of Nb(III) to Nb(IV) under the action of RCOOH, therefore there was some hope that using a very weak acid, Me_3CCOOH, would replace BH_4 and C_5H_5 by the RCOO groups without affecting the Nb(III) oxidation and would, consequently, result in the desired dimer $(CpNb(OOCCMe_3)_2)_2$.

Results and discussion

The reaction mixture composition resulting from the reaction of Cp_2NbBH_4 with Me_3CCOOH depends, first of all, on the reactants' ratio and the reaction conditions (Scheme 1).

SCHEME 1



At the first step, two moles of trimethylacetic acid were added and the mixture was refluxed in toluene for 2 h, giving the monocarboxylate $Cp_2Nb(OOCCMe_3)$ (1). This is a greenish brown diamagnetic crystalline solid (m.p. 224—225°C dec.), air-sensitive, especially when in solution (the compound is soluble in benzene, THF, poorly in heptane, and reacts with CS_2 or CCl_4). The NMR spectrum in benzene contains two singlets (δ 0.805 ppm (CH_3) and δ 5.29 ppm (C_5H_5)) with the intensities ratio being, as expected, 9 : 10. The IR spectrum contains characteristic cyclopentadienyl ligand bands (820, 1020, 1445 and 3125 cm^{-1}) [16] while the OCO stretching vibrations are observed at 1305 and 1652 cm^{-1}. It corresponds to a terminal coordination of the carboxylate group [17], a surprising fact since in the analogous complexes $Cp_2Ti(OOCR)$ [18], the carboxylate group is chelated (ν(OCO) 1540, 1430 cm^{-1}). This is so for R = CMe_3 as well [7]. The non-bridging coordination of $OOCCMe_3$ agrees also with monomerism of the vapours (the mass spectrum contains the M^+ 324) and the solutions (cryoscopy in benzene, $M = 342$). The difference between the OOCR coordination in the complexes of Ti(III) and Nb(III) may be due to the difference between the electron configurations, d^1 and d^2, respectively, but this is so far only a plausible assumption.

The yield of I is rather low, about 25%, and there is one more product, a green oil containing niobium, $OOCMe_3$ and no C_5H_5 (according to data from alkaline hydrolysis followed by distilling the volatile products off into a TIOH solution). On the other hand, the Cp_2NbBH_4 : Me_3CCOOH ratio of 1 : 1 leads to a steep decrease in the yield of I, with an unreacted Cp_2NbBH_4 remaining in the reaction mixture. It is clear that I readily reacts with Me_3CCOOH and the resulting products easily lose their C_5H_5 ligands.

Accordingly, slow addition of Me_3CCOOH to a solution of the equimolar amount of I in benzene followed by refluxing the mixture gives $Cp_2Nb(OOCCMe_3)_2$ (II) in a 42% yield. The compound II is a blue crystalline solid (m.p. 219—223°C dec.) extremely sensitive to moisture and atmospheric oxygen, and easily soluble in all usual organic solvents except cold heptane. The compound II is monomeric in the vapour (parent ion M^+ 425 in the mass spectrum), and paramagnetic (μ_{eff} 1.62 Bohr magneton, temperature-invariable at 295—79 K and close to the pure spin value of 1.73 Bohr magneton). The ESR spectrum contains a well-resolved decuplet (g = 1.971) due to the unpaired electron coupling with ^{93}Nb (I = 9/2; A = 125 Gauss). The IR spectrum contains characteristic terminal carboxylate bands (ν(OCO) 1315 and 1630 cm^{-1}) [17]. The cyclopentadienyl bands at 1000—3200 cm^{-1} are doublets (1020 and 1035 cm^{-1}; 1435 and 1465 cm^{-1}; 3100 and 3115 cm^{-1}), inferring non-equivalence of cyclopentadienyl ligands in the compound. Fragmentation of II under electron impact leads mainly to I, although there is also the ion $CpNb(OOCCMe_3)_2$ (m/e 360), a product due to loss of a cyclopentadienyl. The structure of II was verified by an independent synthesis from sodium trimethyl acetate in THF and Cp_2NbCl_2 readily obtainable from Cp_2NbBH_4 and carbon tetrachloride. The easy transformation of I to II in the presence of the equimolar amount of Me_3CCOOH is one difference between I and $Cp_2TiOOCCMe_3$ which is not affected even by an excess of the acid [7]. The difference may be due to a vacant coordination site in I, whose $OOCCMe_3$ is terminal unlike the titanium complex where the group is chelated [7].

The complex II loses, in turn, both its cyclopentadienyls in the presence of two moles of Me_3CCOOH extremely readily, yielding the tetracarboxylate $Nb(OOCCMe_3)_4$ (III). The cyclopentadienyl complexes $CpNb(OOCCMe_3)_2$ or $CpNb(OOCCMe_3)_3$ failed to be isolated, regardless of the reactants ratio. We have already mentioned that the reaction of Cp_2NbBH_4 with an excess of RCOOH leads to retention of both C_5H_5 ligands (R = CF_3) or one of them (R = Ph), yielding $Cp_2Nb(OOCCF_3)_2$ or $CpNb(OOCPh)_3$, respectively [15]. This displays the role of the RCOO anion nucleophilicity the growth of which favours the M—Cp bond decomposition. The fact that the monocyclopentadienyl complexes cannot be isolated may be explained by assuming that the complexes are victims to a nucleophilic attack made by the excess Me_3CCOOH on their vacant coordination sites *. On the other hand, in dimerisation of monocyclopentadienyl compounds such as, e.g. $(CpNb(OOCCMe_3)_2)_2$, an increase in the RCOO nucleophilicity should facilitate the disproportionation of the dimer to I and III, similarly to the formation of $Cp_2TiOOCR$ from $CpTi(OOCR)_4TiCp$ with R being H, CH_3, Et, but not CF_3 [17].

The complex III is a violet crystalline solid (m.p. 198—202°C dec.), very sensitive to moisture and oxygen of the air, easily soluble in benzene, THF, CH_2Cl_2, and moderately soluble in heptane. The compound is a monomer in benzene (found 439, calculated 497); it is paramagnetic, and the effective magnetic moment (1.4 Bohr magneton) is temperature-invariable although it is somewhat lower than the purely spin value of 1.73 Bohr magneton. The ESR spectrum contains a well-resolved decuplet (g = 1.948) due to the coupling with ^{93}Nb (I = 9/2; A = 162 Gauss). An IR spectrum of III displays only chelated

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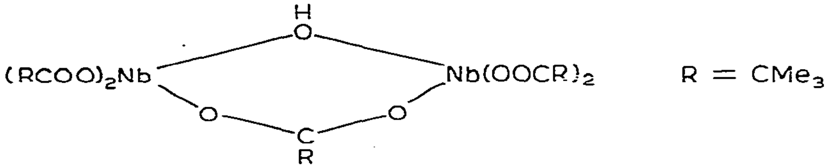
* The usual presentation of cyclopentadienyl as tridentate ligand gives us the coordination numbers of 5 or 6 for $CpNb(OOCCMe_3)_2$ or $CpNb(OOCCMe_3)_3$, respectively; recently, however, eight-coordinate complexes such as $NbCl_4L_2$ (L is $R_2PCH_2CH_2PR_2$, R is Me or Et, ref. 19) have been found to form easily.

$OOCCMe_3$ groups (ν(OCO) 1490 and 1550 cm^{-1}), so the Nb atom in III may be assumed to be eight-coordinate. The compound III is a rare example of an Nb(IV) compound containing no π-cyclopentadienyl stabilizers, monomeric, and soluble in unpolar hydrocarbons. Of Nb(IV) halides, these properties are only possessed by the adducts $NbCl_4 \cdot (PEt_3)_2$ and $NbCl_4 \cdot 2L$ [19]. Noteworthy also is the high reactivity of III, which readily reacts with two moles of CpNa giving II in high yield (about 70%) due to the fact that there is no CMe_3COOH that could have decomposed II in the reaction mixture. Thus, III may be an interesting starting compound for the synthesis of Nb(IV) compounds. The study of reactions of III is under way. The compound may also be obtained directly from Cp_2NbBH_4 and Me_3CCOOH (1/4) refluxed in benzene, but in this case the yield goes down to 28%. The action of five moles of Me_3CCOOH on Cp_2NbBH_4 under drastic conditions (refluxing in xylene) gives orange diamgnetic crystals of $Nb(OOCCMe_3)_5$ (IV), m.p. 235—236°C dec. An IR spectrum of IV taken at the stretching vibrations region (ν(OCO) 1300 to 1700 cm^{-1}) is very complicated; it contains bands corresponding to terminal chelated and bridging carboxylate groups (see Experimental section). The NMR CH_3 signal taken in CS_2 is an unsymmetrical triplet (δ 1.09, 1.13, 1.23 ppm), also indicative of the non-equivalence of Me groups. The molecular weight is 870 (cryoscopy in benzene); this is higher than the value assignable to the monomer ($Nb(OOCCMe_3)_5$, M = 598) and lower than the dimeric value (M = 1196 for $(Nb(OOCCMe_3)_5)_2$). Probably, the dimer IV dissociates in solution. The structure and the Nb coordination in IV are so far not known. By analogy with dimerisation of $NbCl_5$ [20], we may say that two of the carboxylate groups are bridging while the other ones are chelated or terminal. A mass spectrum of IV contains no parent ions assignable to the monomer or the dimer. An intense peak at m/e 652 (the maximal m/e value observed) may be due to the following ion:



Ions produced by abstraction of CO_2 and H from the m/e 652 are also observed. Heating the tetracarboxylate III with RCOOH fails to give any IV.

Experimental

General

All operations were carried out in a pure argon atmosphere. Tetrahydrofuran was distilled over benzophenoneketyl sodium; benzene, toluene, xylene and heptane were distilled over dispersed sodium metal, CH_2Cl_2 was distilled over P_2O_5 in an argon atmosphere. Cp_2NbCl_2 and Cp_2NbBH_4 were synthesized by literature methods [21] and [22]. Commercial CMe_3COOH was purified by fractional distillation. Infrared spectra were run as KBr tablets on a UR-20 machine at 400—3500 cm^{-1}. Magnetic measurements were made by the Faraday method in evacuated sealed ampoules. Melting and decomposition temperatures were taken in sealed capillaries. Nuclear magnetic resonance spectra were recorded on a Perkin—Elmer instrument (60 MHz) against a $(Me_3Si)_2O$ internal reference. Mass spectra were obtained on an ARJ MS spectrometer fitted with a DS data processing system. The direct inlet temperature was 100°C, the ionising electrons energy was 70 eV. Electron spin resonances were taken at 1,000 to 5,000 Oersted on a JES-3BX instrument.

$Cp_2NbOOCCMe_3$

A solution of CMe_3COOH (1.43 ml, 12.6 mmol) in 5 ml toluene was added to a dark green solution of Cp_2NbBH_4 (1.50 g, 6.3 mmol) in 35 ml toluene. After gas evolution ceased the mixture was refluxed for two hours, its colour becoming greenish-brown towards the end of the refluxing period. The solvent was removed in vacuo, the dry greenish brown residue was recrystallized from a 1/1 benzene/heptane mixture, to give 0.52 g (25.6%) of brown-green crystals, m.p. 224—225°C. Found: C, 57.44; H, 6.10; Nb, 27.75. $C_{15}H_{19}O_2Nb \cdot 0.2\ C_6H_6$ calcd.: C, 57.24; H, 6.00; Nb, 27.33%. IR spectrum (cm^{-1}): 435w, 525w, 545m, 563w, 605m, 782w, 820vs, 870m, 915w, 990vw, 1020w, 1075vw, 1105vw, 1210vs, 1305vs, 1362w, 1395m, 1445m, 1485m, 1652vs, 2880w, 2915w, 2940w, 2975m, 3125m.

$Cp_2Nb(OOCCMe_3)_2$

(a) From $Cp_2NbOOCCMe_3$ and CMe_3COOH. A solution of CMe_3COOH (0.148 g, 1.45 mmol) in 5 ml benzene was slowly added dropwise to a brown-green solution of $Cp_2NbOOCCMe_3$ (0.47 g, 1.45 mmol) in 20 ml benzene and stirred at room temperature. After this, heptane (10 ml) was added, the mixture was evaporated to 15 ml of the residue, and refluxing for 1 h. The homogeneous reaction mixture was cooled down, to give a green crystalline precipitate, which was separated by decanting, washed with pentane, and dried in vacuo. The yield was 0.26 g (42.4%), m.p. 218°C dec. (the capillary was immersed in the block heated up to 180°C beforehand). Found: C, 56.51; H, 6.75; Nb, 22.38. Calcd.: C, 56.47; H, 6.64; Nb, 21.84%. IR spectrum (cm^{-1}): 425w, 440w, 530vw, 567m, 600m, 610m, 625sh, 705w, 750w, 790m, 825vs, 870m, 890w, 942vw, 1020w, 1035w, 1180(sh), 1210vs, 1315vs, 1370m, 1398m, 1435m, 1465w, 1485s, 1570m, 1630vs, 1720m, 2880w, 2940(sh), 2920(sh), 2980m, 3100m, 3115w.

(b) From Cp_2NbCl_2 and $NaOOCCMe_3$. $NaOOCCMe_3$ (1.5 g, 12.2 mmol) was added to a suspension of Cp_2NbCl_2 (1.8 g, 6.1 mmol) in 50 ml THF. The reaction mixture was stirred for 4 h at room temperature, its colour changing from brown to blue. It was evaporated in vacuo, and the dry blue solid was extracted with boiling pentane (70 ml). The extract was evaporated to 20 ml of the residue, the resulting blue crystals were separated, washed with pentane, and dried in vacuo. The yield was 1.18 g (45.6%), m.p. 223—224°C dec.

(c) From $Nb(OOCCMe_3)_4$ and CpNa. A solution of CpNa (6.2 mmol) in 7 ml THF (prepared from 0.15 g Na and 0.41 g C_5H_6) was added dropwise to a violet solution of $Nb(OOCCMe_3)_4$ (1.5 g, 3.1 mmol) in 25 ml THF. The reaction mixture turned brown and became a gel. The solvent was removed in vacuo, the residue was treated with 40 ml heptane, refluxed for 10 min, and the resulting hot blue solution was filtered and evaporated to 15 ml of the residue. The blue needles which precipitated were separated, washed with pentane, and dried in vacuo. The yield was 0.9 g (68.3%), m.p. 218—220°C dec. Found: C, 56.57; H, 6.63; Nb, 21.84. Calcd.: C, 56.47; H, 6.64; Nb, 21.84%.

$Nb(OOCCMe_3)_4$

(a) From $Cp_2Nb(OOCCMe_3)_2$ *and* CMe_3COOH. A solution of CMe_3COOH (0.163 g, 1.5 mmol) in 3 ml heptane was added to a hot dark blue solution of $Cp_2Nb(OOCCMe_3)_2$ (0.36 g, 0.8 mmol) in 20 ml heptane. After refluxing for 1 h, the mixture turned violet. It was evaporated, and a violet crystalline precipitate was formed, separated, washed with heptane, and dried in vacuo. The yield was 0.22 g (56.4%), m.p. 198—202°C dec. (the capillary was immersed in the block heated up to 170°C beforehand). Found: C, 48.14; H, 7.35; Nb, 19.39. $C_{20}H_{36}O_8Nb$ calcd.: C, 48.29; H, 7.31; Nb, 18.67%. IR spectrum (cm^{-1}): 445w, 610s,(br), 875w, 940(sh), 1037vw, 1210s, 1235m, 1312m, 1375m, 1435m, 1490s, 1550m, 1720vs, 2890(sh), 2945(sh), 2992m.

(b) From Cp_2NbBH_4 *and* Me_3COOH. Me_3CCOOH (2.6 ml, 22.7 mmol) was added to a darkblue solution of Cp_2NbBH_4 (1.55 g, 6.5 mmol) in 40 ml benzene. After gas evolution ceased the reaction mixture was refluxed for 1 h, its colour changing to brown-green. Heptane (20 ml) was added, and the mixture was evaporated in vacuo to give violet crystals which were separated, washed with heptane, and dried in vacuo. The yield was 0.91 g (28.2%), m.p. 195—197°C dec.

$(Nb(OOCCMe_3)_5)_n$

A solution of Me_3CCOOH (3.7 g, 36.5 mmol) in 5 ml xylene was added to a dark green solution of Cp_2NbBH_4 (1.76 g, 7.3 mmol) in 45 ml xylene. After gas evolution caesed the reaction mixture was refluxed for 5 h. It turned orange-brown at the end of this period. The solution was evaporated in vacuo, and the orange crystalline residue was recrystallised from heptane. The yield was 2.72 g (62.4%), m.p. 235—236°C dec. (the capillary was immersed in the block heated up to 205°C beforehand). Found: C, 50.62; H, 7.60; Nb, 15.05. $C_{25}H_{45}O_{10}Nb$ calcd.: C, 50.16; H, 7.59; Nb, 15.52%. IR spectrum (cm^{-1}): 405w, 425vw, 428w, 464m, 570m, 596m, 624s, 725m, 795m, 805m, 818w, 843s, 861m, 883s, 915s, 980s, 1020vs, 1030s, 1075s, 1200s, 1233vs, 1319m, 1370s, 1409s, 1440s, 1458s, 1500vs, 1520m, 1560m, 1600vs, 1640s, 1715vs, 2880w, 2940m, 2980m.

Cp_2NbCl_2

A solution of CCl_4 (2 ml, 20.7 mmol) in 5 ml THF was added dropwise to a stirred dark green solution of Cp_2NbBH_4 (0.85 g, 3.5 mmol) in 30 ml THF. Gas evolution was observed, the colour changed to brown. Brown needles precipitated and were separated from the solution, washed with a 1/1 pentane/THF mixture, then with pentane, and dried in vacuo. The yield was 0.8 g (82.3%). IR spectrum (cm^{-1}): 862vs, 880w, 1022m, 1440m, 3114m.

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