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SYNTHESIS, STRUCTURE AND MAGNETIC PROPERTIES OF A TRINUCLEAR π-CYCLOPENTADIENYLNIOBIUM COMPLEX CONTAINING THE FORMATE, HYDROXYLIC AND OXYGEN BRIDGES

V.T. KALINNIKOV, A.A. PASYNSKII, G.M. LARIN, V.M. NOVOTORTSEV
Institute of General and Inorganic Chemistry, Academy of Sciences, Moscow (U.S.S.R.)
Yu. T. STRUCHKOV, A.I. GUSEV and N.I. KIRILLOVA
Institute of Organo-Element Compounds, Academy of Sciences, Moscow (U.S.S.R.)

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Summary

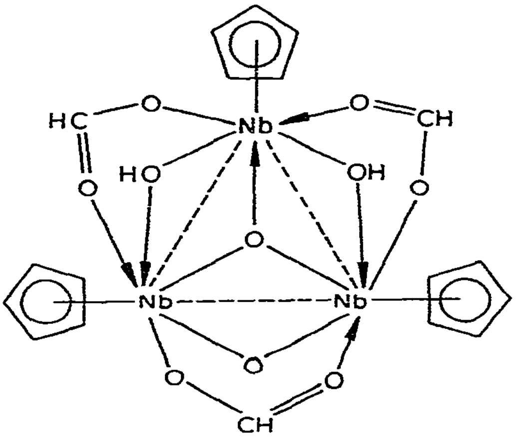
The trinuclear complex $[C_5H_5NbOOCH]_3(OH)_2(O)_2$ was prepared by heating $C_5H_5Nb(CO)_3PPh_3$ with anhydrous HCOOH in xylene. The niobium atoms are located at the vertices of an almost regular triangle with short Nb$\cdots$Nb distance equal to 3.14 Å. The electronic configuration of niobium is d^1. Analysis of the magnetic properties and location of the niobium atoms indicated that they bind only by the formate, hydroxylic and oxygen bridges instead of by direct Nb—Nb bonds.

Introduction

The study of specificities of chemical bonding and structure of the polynuclear transition element compounds containing the intermediately bound ions is interesting in many aspects. In particular it may shed light on the nature of collective magnetic interactions taking place in the crystal lattices of magnetic semiconductors. Since the problem is rather complicated it may only be solved in terms of some simplified models such as paramagnetic clusters of the metal atoms which are magnetically shielded from each other by diamagnetic ligands. Usually such clusters contain bridging ligands. Thus besides direct interaction of the neighbouring paramagnetic ions a "superexchange" via the bridges may take place in the molecule. The most interesting case is when these two types of exchange can be separated. Thus we have studied the dimeric cyclopentadienylvanadium dicarboxylates, $[C_5H_5V(OOCR)_2]_2$ (I) where R = CF_3 [1] or furanyl [2, 3]. Exchange was observed only over the π-systems of four carboxylate bridges because of the absence of direct V—V bonding (the V$\cdots$V separation is ca. 3.7 Å). It was found to be due to a repulsion of cyclopentadienyl and bridged carboxylate ligands. A weaker repulsion might be expected in the similar niobium complexes because of its larger radius (1.60 Å compared to 1.49 Å) [4] and the direct Nb—Nb bonding along with formation of carboxylate bridges.

Results and discussion

An attempt to obtain the niobium analogue of I with the less bulky formate bridges by treating $C_5H_5Nb(CO)_3PPh_3$ with anhydrous HCOOH in boiling xylene led to the trinuclear complex $[C_5H_5NbCOOH]_3(OH)_2(O)_2$ (II) in the form of black lustrous prisms:



(II)

Such a structure is in agreement with elemental analysis. The IR spectrum of II shows bands ascribable to the modes of π-cyclopentadienyl ligands (815, 1020, 1440 and 3100 cm^{-1}) [5], symmetric (1360, 1388 cm^{-1}) and antisymmetric (1565 cm^{-1}) stretching OCO vibrations and the stretching C—H vibrations of the formate groups (2850, 2890 and 2920 cm^{-1}) and O—H groups (3400 cm^{-1}). Unfortunately involatility of II and its insolubility in the common organic solvents prevented its molecular weight being determined by mass-spectrometry or cryoscopy. We note, however, that the nickel and cobalt complexes $(\pi\text{-}C_5H_5M)_3XY$ where X and Y are tridentate bridged oxygen or sulfur groups [6, 7], and the trinuclear arene complexes of niobium, tantalum, titanium and zirconium $(C_6Me_6MCl_2)_3^+Cl^-$[8] have been described.

The main bulk of information on the electronic and molecular structure of II was obtained from magnetochemical and X-ray investigations.

Complex II is paramagnetic and exhibits a wide singlet in the ESR spectrum. Its static magnetic susceptibility measured by the Faraday method between 77 and 295 K showed that it disobeyed the Curie law. The effective magnetic moment (μ_{eff}) per niobium atom decreases with decreasing temperature from 1.17 B.M. (295 K) to 1.00 B.M. (77 K) (Fig. 1) which is far below the purely spin value for an unpaired electron (1.73 B.M.). Since the local symmetry of the niobium ions is known to be below cubic the influence of spin-orbital effects should be negligible. Thus the abnormal temperature dependence of μ_{eff} may be due to only spin-spin interaction between the paramagnetic ions within the polynuclear molecules [9]. From the structure of II the oxidation state of niobium in the complex is no less than +4. However the elemental

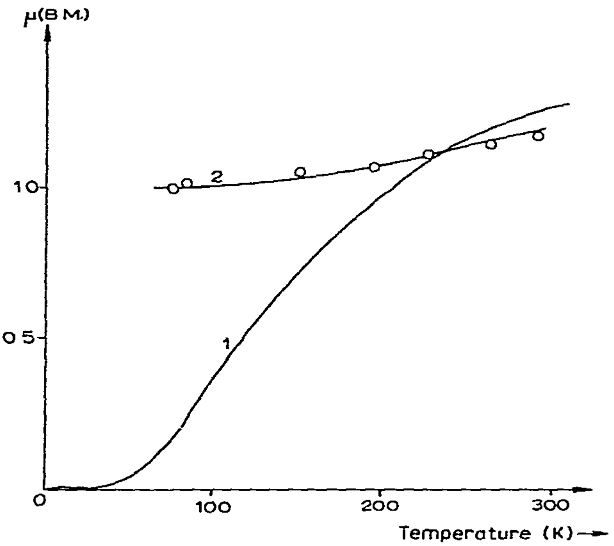


Fig. 1. Temperature dependence of magnetic susceptibility.

analysis and IR spectral data alone do not serve as evidence for excluding the formula $(\pi\text{-}C_5H_5NbOOCH)_3(OH)(O)_3$ (IIa) with one niobium in +5 oxidation state. A choice between two sets of niobium electronic configurations in the triangle (d^1, d^1, d^1 in II or d^0, d^1, d^1 in IIa) may be made by analysing the temperature dependence of the effective magnetic moment:

$$\mu_{eff} = (3KT\chi_M/N\beta^2)^{1/2} \tag{1}$$

1. Configuration d^0, d^1, d^1 has two paramagnetic ions with spin $S\ \frac{1}{2}$ coupled by an exchange. In such a case the temperature dependence of magnetic susceptibility follows Bleaney–Bouwers law and the effective magnetic moment is given by [10]:

$$\mu^2_{eff} = g^2\,[1 + \tfrac{1}{3}\exp(-J/KT)^{-1}] \tag{2}$$

where J is the exchange parameter and g is the Lande factor. Thus for this configuration $\mu(T) \to 0$ as $T \to 0$ (curve 1, Fig. 1).

2. For configuration d^1, d^1, d^1 in a regular triangle the effective magnetic moment per paramagnetic ion is defined by the formula [11]:

$$\mu^2_{eff} = \frac{g^2}{4}\left[\frac{1 + 5\exp(3J/KT)}{1 + \exp(3J/KT)}\right] \tag{3}$$

and $\mu_{eff} \to 1$ B.M. as $T \to 0$ which corresponds to one unpaired electron for three niobium atoms (curve 2, Fig. 1.).

A comparison of the experimental and theoretical data shows that in this case configuration d^1, d^1, d^1 is realized, i.e. three paramagnetic Nb^{IV} ions located at the vertices of regular triangle are interacting via the antiferromagnetic mechanism with exchange energy $(-J) \sim 225$ K $(-156\ cm^{-1})$.

X-ray analysis of II supported the conclusion that the three niobium atoms

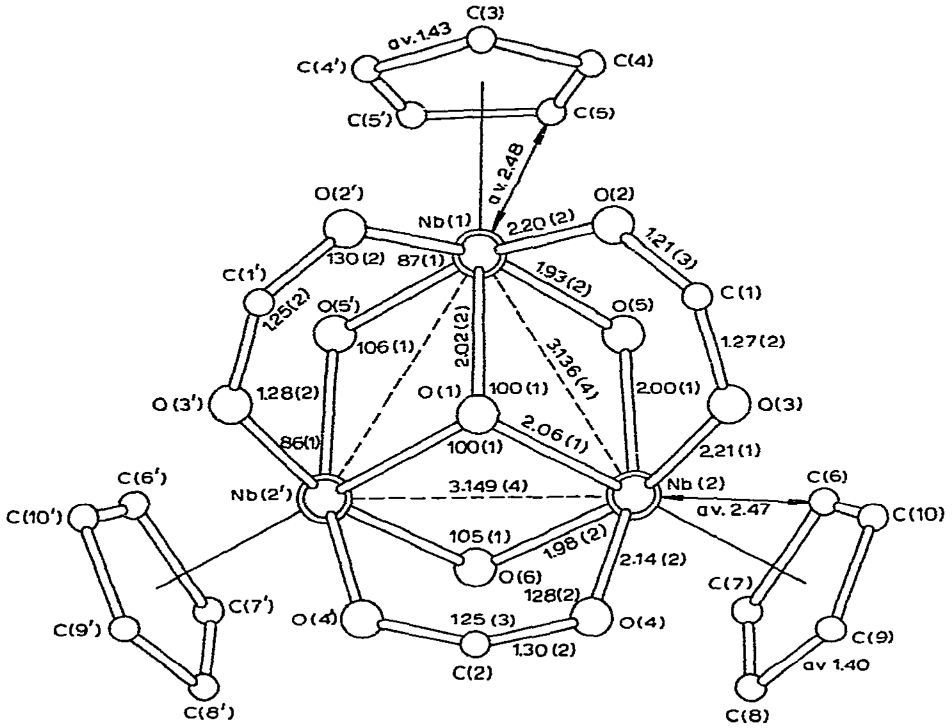


Fig. 2. Molecular geometry of II.

were equivalent (Fig. 2). The niobium atoms (each of them is bound to a π-cyclopentadienyl ligand) form an almost regular triangle with each pair of metal atoms linked by two bridging ligands, formate and hydroxyl (or bidentate oxygen)*. Moreover an oxygen atom O(1) is bound to three niobium atoms.

The Nb—O distance from bridged O(5) and O(6) (1.93—2.00 Å) is considerably shorter than that from the formate ligand oxygens (2.14—2.21 Å), while the central tridentate-bridged O(1) separation is intermediate (2.02, 2.06, 2.06 Å).

The planar metal—formate groups NbOCONb′ and the triangle of niobium atoms have a mean dihedral angle equal to 52°. A mean C—O bond length (1.26 Å) is close to the 1.26 and 1.23 Å observed in I [2]. The OCO bond angles in these bridges (mean 125°) are also close to those in I, which manifests their rigidity. Earlier we found for vanadium complexes I that a constant OCO angle as the metal atoms approach forces the carboxylate bridged oxygens and cyclopentadienyl carbons together, giving a large repulsion between these ligands. In I where the V—C and V—O bond lengths are 2.34 and 2.04 Å respectively the least contacts O···C (2.8—2.9 Å) are attained even at V···V equal to 3.7 Å and ∠VOC 137°. In II the bonds Nb—C and Nb—O are elongated (2.47 and 2.14—2.21 Å respectively) due to the larger niobium radius com-

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* Unfortunately there is no unequivocal evidence for such a structure because the hydrogen atoms have not been located.

pared to vanadium, thus the same shortest contacts O···C (2.8—2.9 Å) arise only at an Nb—Nb distance of 3.24 Å and an NbOC angle of 129°. We note that in this case the niobium atoms are essentially drawn together by oxygen and hydroxylic bridges and an interligand repulsion causes an elongation of Nb—C(C_5H_5) bonds to 2.47 Å, which is beyond the upper limit of 2.37—2.45 range characteristic of the monocyclopentadienylniobium π-complexes [12, 13].

Of specific interest is the character of Nb···Nb bonding in II. Although the Nb···Nb distances (3.14 Å) are close to the length of the ordinary Nb—Nb bond in dimeric "niobocene" [14, 15] there are some facts which are against the presence of direct Nb—Nb bonds in II. Coordination of each niobium atom with the central oxygen atom increases the niobium coordination number by more than one compared to the ordinary seven coordination number in its monocyclopentadienyl compounds (e.g. in $\pi\text{-}C_5H_5Nb(CO)_4$ [16]). Thus the coordination capacity of the metal is perhaps exhausted and no Nb—Nb bond is formed in spite of the short metal separations. Thus II is essentially paramagnetic.

The opposite situation arises in the only known trinuclear niobium π-complex, $(\pi\text{-}C_6Me_6NbCl_2)_3^+Cl^-$[8] which has an electronic configuration d^3, d^3, d^2. In this complex each metal atom of the triangle is bound only via seven coordination sites with the arenic ligands and four bridged chlorines. Thus there is room for direct metal—metal interaction to provide diamagnetism of the complex.

The geometry of niobium-bridged oxygen bonds gives additional evidence for the absence of Nb—Nb bonding in II. The central O(1) atom lies out of the plane of the metallic triangle by 0.96 Å. The atoms O(5), O(5′) and O(6) lie on the other side of this triangle so that there are two strictly planar fragments Nb(1), Nb(2), O(1), O(5) and Nb(2), Nb(2′), O(1), O(6) having a dihedral angle with the Nb_3 plane equal to 48°. Each of these tetrahedra is a binuclear bridged system. Attention may be drawn to the angles at the bridged atoms O(1), O(5) and O(6) which are larger than 90° (99, 100 and 106°). Such increase in the angles of bridged atoms in binuclear complexes has been explained [17] by the absence of a metal—metal bond. Apparently this criterion is valid in the case of trinuclear complex II.

Complex II is the first example of a trinuclear π-cyclopentadienylniobium complex. Probably its formation from $C_5H_5Nb(CO)_3PPh_3$ and HCOOH follows the scheme:

$$C_5H_5Nb(CO)_3PPh_3 \xrightarrow[\substack{-3CO \\ -PPh_3}]{2HCOOH} \{C_5H_5Nb(OOCH)_2\} \xrightarrow[-CO]{} II$$

Decarbonylation of the formate group may be similar to dethiocarbonylation of dithioformate giving the $(C_5H_5)_2$ Nb(CO)SH complex [18]. It is interesting that the PPh_3 was eliminated did not add to II.

Experimental

All operations were performed under argon using absolute solvents saturated with argon. $C_5H_5Nb(CO)_3PPh_3$ was prepared as described previously [19].

HCOOH was dried by multiple distillation over P_2O_5. The IR spectra were taken on a UR-20 instrument in KBr pellets. The static magnetic susceptibility was studied by the Faraday method between 77 and 295 K. Lattice parameters and intensities of the reflections were measured on an automatic four circle diffractometer using Cu-K_α radiation [20]. The crystals are monoclinic: a 13.150, b 8.901, c 17.467 Å, γ 102.7°, Z 4. B $2/m$. The structure was decoded by a heavy atom method and improved by the least squares method ($R = 0.115$).

Synthesis of $[\pi\text{-}C_5H_5NbOOCH]_3(OH)_2(O)_2$

0.5 ml of anhydrous HCOOH was added to 0.25 g of $C_5H_5Nb(CO)_3PPh_3$ in 8 ml of p-xylene. The mixture homogenized on heating and the dark-red solution was refluxed for 7 h. The lustrous black prisms which gradually formed were separated after cooling from the light-red turbid mother solution, washed with ethanol and dried in vacuo. Yield 15 mg (16%). The product melted at 210° in a sealed capillary and decomposed with gas evolution at 220°. (Found: C, 31.70, 31.95; H, 2.65, 2.50; $C_{18}H_{20}O_{10}Nb_3$ calcd.: C, 32.0; H, 3.0%). IR spectrum: 525 m, 560 m, 590 w, 610 w, 705 s, 765 w, 815 s, 1020 w, 1360 s, 1388 m, 1440 w, 1567, vs, 1640 w(br), 2850 w, 2890 w, 2920 m, 3100, 3400 m(br).

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