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DIAMAGNETIC AND PARAMAGNETIC BINUCLEAR CYCLOPENTADIENYL-FULVALENE-NITRENE COMPLEXES OF NIOBIUM: SYNTHESIS, SPECTRA AND STRUCTURE

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Summary

Oxidation of the diamagnetic binuclear niobium complexes $(\eta^5:\eta^5\text{-}C_5H_4C_5H_4)(C_5H_5)_2Nb_2(\mu\text{-}NC_6H_4R)_2$ (R = H and OCH_3) (I) yields stable paramagnetic cations $[(\eta^5:\eta^5\text{-}C_5H_4C_5H_4)(C_5H_5)_2Nb_2(\mu\text{-}NC_6H_4R)_2]^{+\cdot}$ (II). IR, EPR, and UV spectra of I and II have been studied. The crystal and molecular structures of I and II with R = OCH_3 have been determined and compared.

Introduction

Metallocenes are among the most widespread types of organo-transition metal complexes. The stereochemistry of the bis(cyclopentadienyl)metal fragment of metallocene molecules depends strongly on the position of a given metal atom in the transition series. Thus the formation of stable homoligand metallocenes, Cp_2M, with parallel cyclopentadienyl rings is not characteristic for the Group IV to VI elements, especially for heavy ones. In fact, they are known to form mostly wedge-like derivatives, Cp_2MX_n (n = 1, 2, 3), and binuclear metallocene compounds with various bridging ligands: π-σ-cyclopentadienyl, $\eta^5:\eta^1\text{-}C_5H_4$; π-fulvalene, $\eta^5:\eta^5\text{-}C_5H_4C_5H_4$; and several heteronuclear σ-ligands, X (including hydride ligands). Recent X-ray structural investigations of several bismetallocene complexes have revealed a variety of their structures. Stable structural and geometrical isomers are even possible for some of them. It has also been established that the ligands in these binuclear complexes are stereochemically mobile and that the structure of a binuclear molecule depends strongly on specific size and electronic characteristics of the metal atoms. Many chemical transformations result in deep changes of the ligand environment of metal atoms, but curiously, do not lead to splitting of these binuclear structures into monometal complex species. So the great "vitality" of the binuclear structures is a general feature (not the only one of course) of these complexes. On

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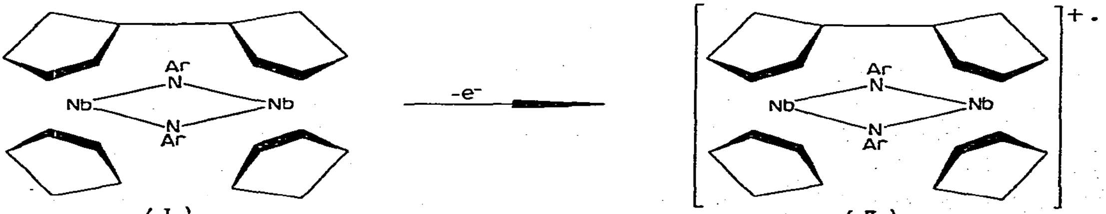
the whole, it may be accounted for the polyelectronic and polycentric nature of interactions in the central fragment of these binuclear molecules. This fragment resembles a heteronuclear cluster in its nature and its framework comprises many atoms bridging the two metal ones.

Redox processes which do not result in addition or/and elimination of the ligands are the simplest reactions of these molecules. Nevertheless, they are of principal importance. The structural changes and corresponding changes in the spectra of the compounds concerned as a rule involve rearrangement of electrons only in the central fragments of the metal complex species. Meanwhile these simple redox processes have been studied for various bismetallocene derivatives only insufficiently.

In our previous works we have investigated the redox reactions of bisniobocene, $(C_5H_5)_2(C_5H_4)_2Nb_2H_2$ and its derivatives, which do not lead to splitting of their binuclear structures [1]. Transformations of bisniobocenes resulting in formation of either paramagnetic fulvalene-type bimetal complexes with a halo bridge [2,3] or diamagnetic ones with two nitrene bridges [4] also have been studied. Fulvalene π-complexes of early transition metals structurally related to those dealt with in this work have been synthesized in recent years for titanium [5,6], molybdenum [7] and vanadium [8]. In this paper we present our investigation of the oxidizing properties of diamagnetic binuclear fulvalene-nitrene complexes of niobium.

Results and discussion

Binuclear fulvalene Nb complexes with bridging arylnitrene ligands, $(C_{10}H_8)(C_5H_5)_2Nb_2(\mu\text{-}NAr)$ (I), are the most stable derivatives of niobocene. Their thermal stability is surprising. These complexes withstand heating to 300—350°C for a significant period of time; they resist the action of atmospheric oxygen and moisture. At elevated temperatures under comparatively low vacuum (0.1 mmHg), these compounds easily sublime without decomposition. They resemble ferrocene to some extent in their behaviour in solutions and thermal stability. This is rather surprising if one takes into consideration the presence of strong steric strain in the molecule of I as revealed by our X-ray study. This strain is displayed in the extraordinary distortion of the fulvalene ligand. On the grounds of our previous investigations of redox reactions of bisniobocenes [1], and because of the resemblance of fulvalene-nitrene complexes I to ferrocene, the binuclear structure of I was expected to remain intact in redox transformations. In particular, we supposed I to give stable ionic mono- or dication compounds in the oxidation.



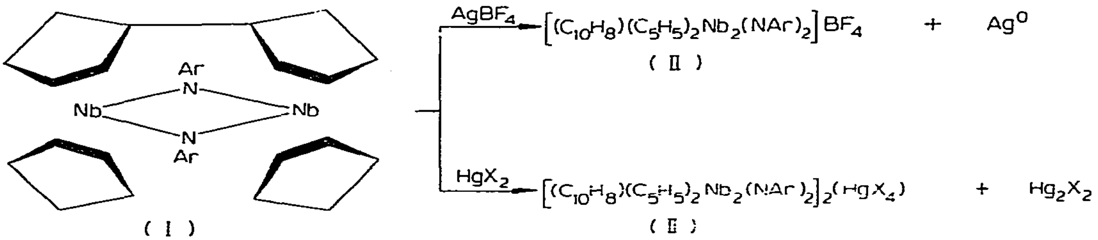
(I)

(II)

Ar = $C_6H_4\text{-}p\text{-}OCH_3$ (a); C_6H_5 (b)

We have found that compounds I are oxidized very easily, in fact. There are many agents which may be used for this purpose. We used $AgBF_4$, HNO_3, O_2 in acidic medium (HBF_4) and HgX_2 (X = Cl, Br). In all the cases I loses one electron and gives a singly-charged paramagnetic ion in solution.

The cationic complexes obtained may be isolated as salts with anions of suitable size. The salts are quite stable in the air. $AgBF_4$ and HgX_2 have been found to be the most suitable oxidizing agents. The reaction with $AgBF_4$ is very fast, the equivalent amount of silver being released. The reaction with mercury salts requires prolonged heating (80 h at 80—110°C) to be completed. This is probably due to the heterogeneity of the reaction mixture.



The solid salts II synthesized are rather soluble in CH_3NO_2. They are slightly soluble in alcohol, dichloromethane and chloroform and are insoluble in other common organic solvents. They resist heating in the air to ~190°C.

IR (solid salts) and EPR (diluted solutions) spectra of II have been studied. The spectral data led us to the firm conclusion that the initial ligand environment of the metal atoms in I does not change much on oxidation, i.e. the resulting cationic complexes II retain the initial binuclear fulvalene and nitrene-bridges structure of the same symmetry. IR spectra of salts II in the range 4000—400 cm^{-1} are very close to the superpositions of the spectra of I and the frequencies of the corresponding anions: tetrafluoroborate or tetrahalomercurate. The differences in frequencies and intensities of most of the bands in the spectra of I and niobium part of II are insignificant and do not exceed 10—15 cm^{-1}.

EPR spectra of complex cations II consist of 19 equidistant lines. Two equivalent Nb atoms (s_{Nb} = 9/2) result the splitting of the signal of the unpaired electron. The corresponding Nb-nuclear-electron spin-spin coupling constants, A_{Nb}, are 49.0 gauss for IIa and 49.5 gauss for IIb. g-Factors of the complexes are close to 2.0; the single line width is about 10 gauss, due to the presence of nitrogen atoms. The doubled values of A_{Nb} for the cations II fall in the range 65—117 gauss, characteristic of A_{Nb} in mononuclear niobocene derivatives, Cp_2NbY_2 [9]. So the delocalization of the unpaired electron in these mono- and binuclear fulvalene complexes synthesized in this work is governed by the same law.

We have investigated the electronic spectra of Ia and IIa (Fig. 1, Table 1). The general picture is presented in Fig. 1, the spectrum of azoanisole is also given for comparison. The spectra of Nb derivatives lack absorption bands in the region of about 360 nm characteristic of azo groups in azo-aromatic compounds. This is in good agreement with the absence of an N—N bond between two NAr fragments in niobium complexes I and II. On the other hand, in the

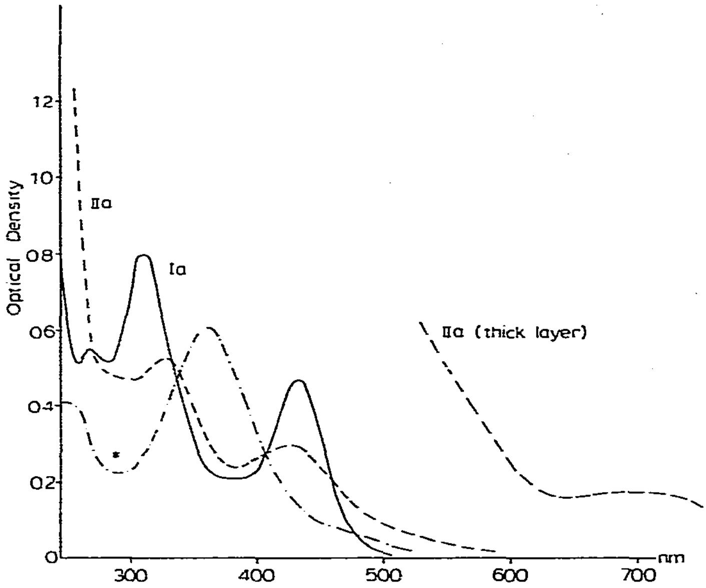


Fig. 1. Electronic spectra of neutral Ia (in THF), cation-radical IIa (in THF/MeNO$_2$) and azoanisole (*) (in THF) at 298 K. Concentrations are equal: C_M(Ia) = C_M(IIa) = C_M(azoanisole).

spectra of Ia and IIa there is an intense absorption at longer wavelength. Neutral complex Ia is characterised by the intense narrow absorption maximum at 440 nm. The latter may be attributed to the allowed $\sigma(M{-}M) \rightarrow \sigma^*(M{-}M)$ transition, as in the series of other binuclear metal complexes with direct M—M bonds, including Nb—Nb ones [1,10]. The similar band in the cationic IIa shifts gipsochromically, lowers in intensity and widens. All the effects are in agreement with the suggested presence of direct Nb—Nb interaction in I and II and correlate with the observed geometrical difference in Nb_2N_2 fragments of both molecules and the loss of an electron from this central fragment in II. It is also worth noting that the more intense brown coloration of IIa compared with Ia is due to a tail of the 425 nm absorption band in a considerable part of visible range. The investigation of very thick layers of IIa makes it possible to see a broad and not intense band at about ~700 nm ($\epsilon < 100$).

We have investigated the structures of Ia and IIa (with BF_4^- anions). The molecule Ia and the cation IIa have similar total configuration (Fig. 2, the indices of

TABLE 1

ELECTRONIC SPECTRA OF Ia AND IIa (298 K)

Ia		IIa	
ν (cm^{-1} (nm))	ϵ (cm^{-1}/mol)	ν (cm^{-1} (nm))	ϵ (cm^{-1}/mol)
37 310(268)	25 410		
32 260(310)	40 180	30 670(326)	22 830
22 730(440)	20 320	23 530(425)	14 020

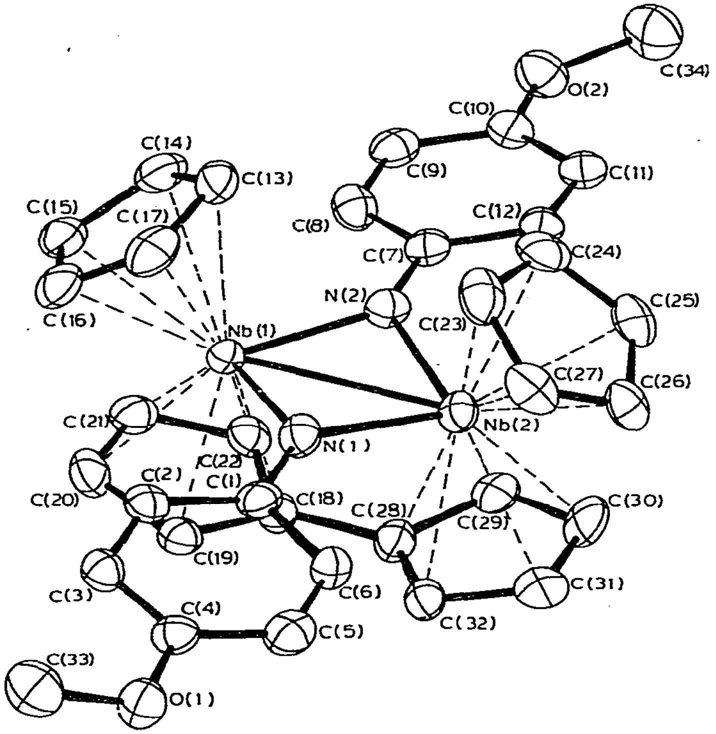


Fig. 2. Configuration of molecule Ia and cation IIa (the indices of the atoms are the same in both species).

the atoms in Ia and IIa are the same). Bond lengths of Ia are given in Table 2, bond angles values in Table 3. In Tables 4 and 5 the bond lengths and the bond angles values of IIa are presented.

The non-crystallographic symmetry of both Ia and IIa is close to C_2, the two-fold axis being perpendicular to the Nb(1)—Nb(2) line and the exocyclic C(18)—C(28) bond of the fulvalene ligand (see Fig. 2). Some important geometric parameters of Ia and IIa given in Table 6 may be compared with those of the binuclear paramagnetic fulvalene π-complex of Nb with one bridging Cl atom studied earlier [3].

Each Nb atom in Ia and IIa is coordinated to two Cp ligands to form a wedge-shaped sandwich. The parameters of the sandwich environment d(Nb—C) and ω (Table 6) fall within the range common for biscyclopentadienyl-Nb compounds [11]. The small number of observed reflections and pseudosymmetry in Ia lowered the accuracy of the determination of its crystal structure. As a result, the range of the bond length and the valence angle values obtained for Ph groups, and especially for Cp ligands, in Ia is unrealistically wide (Tables 2 and 3). But in both Ia and IIa the average distances Nb—C(π) 2.481(8) (Ia) and 2.452(3) (IIa), C(Cp)—C(Cp) 1.43(3) (Ia) and 1.411(3) (IIa), C(Ph)—C(Ph)

TABLE 2

BOND LENGTHS d (Å) IN Ia

Bond	d	Bond	d
Nb(1)—Nb(2)	2.834(5)	C(6)—C(1)	1.35(4)
Nb(1)—N(1)	2.01(3)	C(7)—C(8)	1.49(4)
Nb(1)—N(2)	2.10(3)	C(8)—C(9)	1.34(4)
Nb(2)—N(1)	1.96(3)	C(9)—C(10)	1.32(5)
Nb(2)—N(2)	2.08(3)	C(10)—C(11)	1.46(5)
Nb(1)—C(13)	2.50(3)	C(11)—C(12)	1.47(5)
Nb(1)—C(14)	2.46(3)	C(12)—C(7)	1.44(4)
Nb(1)—C(15)	2.45(3)	C(4)—O(1)	1.42(3)
Nb(1)—C(16)	2.47(2)	C(10)—O(2)	1.42(4)
Nb(1)—C(17)	2.46(3)	C(13)—C(14)	1.21(4)
Nb(1)—C(18)	2.47(2)	C(14)—C(14)	1.36(4)
Nb(1)—C(19)	2.47(2)	C(15)—C(16)	1.28(4)
Nb(1)—C(20)	2.52(2)	C(16)—C(17)	1.35(4)
Nb(1)—C(21)	2.47(3)	C(17)—C(13)	1.45(4)
Nb(1)—C(22)	2.47(2)	C(18)—C(19)	1.46(3)
Nb(2)—C(23)	2.44(2)	C(19)—C(20)	1.59(3)
Nb(2)—C(24)	2.47(3)	C(20)—C(21)	1.68(4)
Nb(2)—C(25)	2.48(3)	C(21)—C(22)	1.46(4)
Nb(2)—C(26)	2.54(2)	C(22)—C(18)	1.45(3)
Nb(2)—C(27)	2.59(3)	C(23)—C(24)	1.04(4)
Nb(2)—C(28)	2.45(2)	C(24)—C(25)	1.34(4)
Nb(2)—C(29)	2.48(2)	C(25)—C(26)	1.34(3)
Nb(2)—C(30)	2.50(3)	C(26)—C(27)	1.34(3)
Nb(2)—C(31)	2.52(3)	C(27)—C(23)	1.55(4)
Nb(2)—C(32)	2.46(2)	C(28)—C(29)	1.39(3)
N(1)—C(1)	1.37(4)	C(29)—C(30)	1.46(4)
N(2)—C(7)	1.41(4)	C(30)—C(31)	1.61(4)
C(1)—C(2)	1.43(4)	C(31)—C(32)	1.47(4)
C(2)—C(3)	1.31(5)	C(32)—C(28)	1.58(3)
C(3)—C(4)	1.37(5)	C(18)—C(28)	1.53(3)
C(4)—C(5)	1.44(4)	C(33)—O(1)	1.44(3)
C(5)—C(6)	1.52(4)	C(34)—O(2)	1.41(3)

1.42(2) (Ia) and 1.390(3) (IIa) Å are equal within accuracy limits.

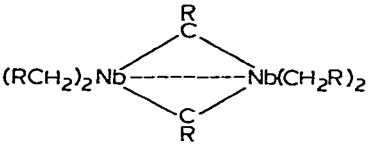
The molecule Ia is a binuclear fulvalene π-complex of Nb with two bridging nitrene ligands. The structure of the binuclear compounds of Ti [5,6] and Mo [7] with similar composition has also been investigated. However, the structure of Ia differs greatly in some aspects from them. The essential structural feature of Ia, which determines most of its geometrical features, is the existence of a stable tetranuclear Nb_2N_2 fragment. In Ia this fragment is close to the square plane (average Nb—N distance 2.04(3) Å, the maximum deviation of atoms from the mean plane 0.04 Å). The coordination of N atoms is trigonal planar. The distance between Nb(1) and Nb(2) 2.834(5) Å is practically equal to the shortest interatomic distance in the niobium metal 2.86 Å, and is substantially shorter compared with the length of Nb—Nb ordinary bond in dimeric niobocene 3.105(6) Å [12]. The distance between N(1) and N(2), 2.92(4) Å, is close to the doubied Van der Waals's radius of the N atom (3.10 Å [13]). Earlier

TABLE 3

BOND ANGLES ω(°) IN Ia

Angle		Angle	
N(1)Nb(1)N(2)	95(1)	C(11)C(12)C(7)	118(3)
N(1)Nb(2)N(2)	88(1)	C(4)O(1)C(33)	120(2)
Nb(1)N(1)Nb(2)	87(1)	C(10)O(2)C(34)	113(2)
Nb(1)N(2)Nb(2)	89(1)	C(13)C(14)C(15)	90(2)
Nb(1)N(1)C(1)	141(2)	C(14)C(15)C(16)	116(3)
Nb(2)N(1)C(1)	132(2)	C(15)C(16)C(17)	113(2)
Nb(1)N(2)C(7)	142(2)	C(16)C(17)C(13)	88(2)
Nb(2)N(2)C(7)	129(2)	C(17)C(13)C(14)	128(3)
N(1)C(1)C(2)	123(2)	C(18)C(19)C(20)	121(2)
N(1)C(1)C(6)	118(3)	C(19)C(20)C(21)	88(2)
C(6)C(1)C(2)	113(3)	C(20)C(21)C(22)	117(2)
C(1)C(2)C(3)	123(3)	C(21)C(22)C(18)	108(2)
C(2)C(3)C(4)	124(4)	C(22)C(18)C(19)	105(2)
C(3)C(4)C(5)	118(3)	C(22)C(18)C(28)	124(2)
C(3)C(4)O(1)	121(3)	C(19)C(18)C(28)	129(2)
C(5)C(4)O(1)	119(2)	C(23)C(24)C(25)	96(3)
C(4)C(5)C(6)	114(3)	C(24)C(25)C(26)	115(2)
C(5)C(6)C(1)	121(3)	C(25)C(26)C(27)	110(2)
N(2)C(7)C(8)	125(2)	C(26)C(27)C(23)	89(2)
N(2)C(7)C(12)	115(2)	C(27)C(23)C(24)	130(3)
C(12)C(7)C(8)	113(2)	C(28)C(29)C(30)	106(2)
C(7)C(8)C(9)	120(3)	C(29)C(30)C(31)	119(2)
C(8)C(9)C(10)	124(3)	C(30)C(31)C(32)	91(2)
C(9)C(10)C(11)	119(3)	C(31)C(32)C(28)	118(2)
C(9)C(10)O(2)	132(3)	C(32)C(28)C(29)	105(2)
C(11)C(10)O(2)	108(3)	C(32)C(28)C(18)	125(2)
C(10)C(11)C(12)	118(3)	C(29)C(28)C(18)	127(2)

Wilkinson and collaborators found [14] in the structure of



(IV, R = SiMe$_3$)

with bridging carbyne ligands a similar tetratomic fragment Nb_2C_2 (the Nb—Nb distance 2.897(2) Å, the Nb—C distance 1.995(9) and 1.954(9) Å). It seems that the formation of a planar four-membered cycle consisting of two Nb atoms and two bridging *sp*^{2}-hybridized atoms is energetically advantageous. For example, this cycle is present in the molecule Ia in spite of the significant distortion of regular wedge-shaped environment of the Nb atoms and the corresponding steric strain of the whole molecule. However, Ia is very stable. Inclusion of the bridging N(1) and N(2) atoms in the planar Nb_2N_2 fragment results in a significant deviation of the bridging N atoms from the bisector plane of the wedge-shaped sandwiches towards the fulvalene ligand, in contrast to the structures of common biscyclopentadienyl derivatives of transition metals, as well as binuclear fulvalene complexes [3,5—7]. The dihedral angles between the least squares plane Nb(1)N(1)Nb(2)N(2) and the planes of five-membered rings of

TABLE 4

BOND LENGTHS *d* (Å) IN THE CATION IIa

Bond	*d*	Bond	*d*
Nb(1)—Nb(2)	2.921(1)	C(6)—C(1)	1.409(10)
Nb(1)—N(1)	2.048(6)	C(7)—C(8)	1.376(9)
Nb(1)—N(2)	2.031(5)	C(8)—C(9)	1.392(10)
Nb(2)—N(1)	2.035(5)	C(9)—C(10)	1.381(11)
Nb(2)—N(2)	2.055(6)	C(10)—C(11)	1.383(10)
Nb(1)—C(13)	2.453(7)	C(11)—C(12)	1.397(11)
Nb(1)—C(14)	2.469(7)	C(12)—C(7)	1.408(10)
Nb(1)—C(15)	2.469(8)	C(4)—O(1)	1.377(9)
Nb(1)—C(16)	2.451(7)	C(10)—O(2)	1.378(9)
Nb(1)—C(17)	2.448(7)	C(33)—O(1)	1.420(9)
Nb(1)—C(18)	2.445(7)	C(34)—O(2)	1.419(10)
Nb(1)—C(19)	2.432(7)	C(13)—C(14)	1.408(11)
Nb(1)—C(20)	2.438(7)	C(14)—C(15)	1.417(11)
Nb(1)—C(21)	2.460(7)	C(15)—C(16)	1.396(11)
Nb(1)—C(22)	2.471(7)	C(16)—C(17)	1.406(11)
Nb(2)—C(23)	2448(7)	C(17)—C(13)	1.416(11)
Nb(2)—C(24)	2.449(7)	C(18)—C(19)	1.418(9)
Nb(2)—C(25)	2.465(8)	C(19)—C(20)	1.418(10)
Nb(2)—C(26)	2.468(8)	C(20)—C(21)	1.410(11)
Nb(2)—C(27)	2.454(7)	C(21)—C(22)	1.393(9)
Nb(2)—C(28)	2.454(6)	C(22)—C(18)	1.434(11)
Nb(2)—C(29)	2.430(6)	C(23)—C(24)	1.399(10)
Nb(2)—C(30)	2.437(6)	C(24)—C(25)	1.421(11)
Nb(2)—C(31)	2.460(7)	C(25)—C(26)	1.407(11)
Nb(2)—C(32)	2.470(7)	C(26)—C(27)	1.409(11)
N(1)—C(1)	1.404(9)	C(27)—C(23)	1.401(11)
N(2)—C(7)	1.408(9)	C(28)—C(29)	1.420(9)
C(1)—C(2)	1.385(9)	C(29)—C(30)	1.426(11)
C(2)—C(3)	1.391(10)	C(30)—C(31)	1.399(11)
C(3)—C(4)	1.379(10)	C(31)—C(32)	1.394(10)
C(4)—C(5)	1.383(10)	C(32)—C(28)	1.432(10)
C(5)—C(6)	1.406(11)	C(18)—C(28)	1.464(10)

the fulvalene ligand are equal to 15° and 17°, whereas the dihedral angles between the former plane and the planes of Cp ligands are equal to 35° and 36°. Distortion of this type leads to close non-valent contacts between N(1) and N(2) atoms with carbon atoms of the fulvalene ligand, the distances being equal to 2.57—2.90 Å. This is considerably shorter than the sum of the corresponding Van der Waals's radii, 3.25 Å [13] (Table 7). As a result of the shortened Nb(1)—Nb(2) distance and, more likely, the aforementioned close C···N contacts, the planarity of the fulvalene ligand is highly distorted (the dihedral angle value α being 32°). This exceeds all hitherto known values for binuclear fulvalene π-complexes [3,5] (see also Table 6). Each Nb atom is surrounded by two bridging N atoms and two centres of Cp cycles to form a distorted tetrahedron, the torsional angle values being 1° for Cp(1)Nb(1)Nb(2)Cp(3) and 0° for Cp(2)Nb(1)Nb(2)Cp(4) *, so the idealized symmetry of the coordination of two Nb atoms in the binuclear complex Ia is approximately C_{2v}.

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* Cp(1) is the centre of the five-membered cycle C(13)—C(17), Cp(2) of C(18)—C(22), Cp(3) of C(23)—C(27), and Cp(4) of C(28)—C(32).

TABLE 5

BOND ANGLES ω(°) IN THE CATION IIa

Angle	ω(°)	Angle	ω(°)
N(1)Nb(1)N(2)	87.7(2)	C(14)(C15)C(16)	108.1(7)
N(1)Nb(2)N(2)	87.4(2)	C(15)C(16)C(17)	108.7(7)
Nb(1)N(1)Nb(2)	91.3(2)	C(16)C(17)C(13)	107.4(7)
Nb(1)N(2)Nb(2)	91.3(2)	C(17)C(13)C(14)	108.2(6)
Nb(1)N(1)C(1)	134.9(4)	C(18)C(19)C(20)	107.7(6)
Nb(2)N(1)C(1)	132.4(4)	C(19)C(20)C(21)	108.3(6)
Nb(1)N(2)C(7)	133.0(5)	C(20)C(21)C(22)	108.5(6)
Nb(2)N(2)C(7)	134.5(5)	C(21)C(22)C(18)	108.2(6)
C(1)C(2)C(3)	123.4(6)	C(22)C(18)C(19)	107.4(6)
C(2)C(3)C(4)	119.3(6)	C(22)C(18)C(28)	124.4(6)
C(3)C(4)C(5)	120.2(7)	C(19)C(18)C(28)	126.6(6)
C(3)C(4)O(1)	124.6(6)	C(23)C(24)C(25)	107.7(7)
C(5)C(4)O(1)	115.2(6)	C(24)C(25)C(26)	107.9(7)
C(4)C(5)C(6)	119.5(7)	C(25)C(26)C(27)	107.7(7)
C(5)C(6)C(1)	121.7(7)	C(26)C(27)C(23)	108.2(7)
C(6)C(1)C(2)	116.0(6)	C(27)C(23)C(24)	108.5(7)
C(7)C(8)C(9)	122.9(6)	C(28)C(29)C(30)	107.3(6)
C(8)C(9)C(10)	119.4(6)	C(29)C(30)C(31)	108.1(6)
C(9)C(10)C(11)	120.7(7)	C(30)C(31)C(32)	109.1(6)
C(9)C(10)C(2)	124.6(6)	C(31)C(32)C(28)	107.9(6)
C(9)C(10)O(2)	115.4(6)	C(32)C(28)C(29)	107.5(6)
C(10)C(11)C(12)	119.7(7)	C(32)C(28)C(18)	124.2(6)
C(11)C(12)C(7)	121.4(7)	C(29)C(28)C(18)	126.2(6)
C(12)C(7)C(8)	116.7(6)	N(1)C(1)C(2)	122.4(6)
C(4)O(1)C(33)	116.7(6)	N(1)C(1)C(6)	121.6(6)
C(10)O(2)C(34)	116.6(6)	N(2)C(7)C(8)	122.4(6)
C(13)C(14)C(15)	107.5(7)	N(2)C(7)C(12)	120.9(6)

TABLE 6

SOME GEOMETRIC PARAMETERS OF BINUCLEAR FULVALENE π-COMPLEXES OF Nb [a]

Parameter	Ia	IIa	$(C_{10}H_8)Cp_2Nb_2Cl$ (III) [3]
$d_{(Nb—Nb)}$ (Å)	2.834(5)	2.921(1)	3.270(2)
$d_{(Nb—C)}$ (Å)	2.481(8)	2.452(3)	2.37(1)
$d_{(C_5H_4—C_5H_4)}$ (Å)	1.53(3)	1.46(1)	1.46(2)
ω(°)	51	48.3	44
α(°)	32	24.5	15.1

[a] $d_{(Nb—C)}$ = an average distance between Nb and C atoms of π-bonded Cp ligands. $d_{(C_5H_4—C_5H_4)}$ = length of C—C exocyclic bond in fulvalene ligands ω = diherdal angle between least-squares planes of Cp ligands at each Nb atom (average value for both Nb atoms). α = dihedral angle between least-squares planes of five-membered cycles in fulvalene ligands.

TABLE 7

NON-BONDED INTRAMOLECULAR DISTANCES (Å) IN Ia AND IIa

Atoms	Ia	IIa
N(1) ··· C(18)	2.77(3)	2.99(1)
N(1) ··· C(28)	2.90(3)	3.01(1)
N(1) ··· C(19)	2.58(3)	2.83(1)
N(1) ··· C(32)	2.76(3)	2.87(1)
N(2) ··· C(18)	2.77(3)	3.00(1)
N(2) ··· C(28)	2.86(4)	3.00(1)
N(2) ··· C(22)	2.57(4)	2.87(1)
N(2) ··· C(29)	2.75(4)	2.82(1)
N(1) ··· N(2)	2.92(4)	2.83(1)

In the cation IIa the geometrical parameters of the wedge-shaped sandwich environment at each Nb atom are changed only insignificantly. The η^5-Cp ligands in IIa are planar within 0.004 Å, their conformation is intermediate between eclipsed and staggered, the torsional angle values being the same for both Cp_2Nb fragments. Both Nb atoms are situated somewhat closer to the least-squares planes of the η^5-cycles of the fulvalene ligand (the distance Nb(1)—Cp(2) is 2.133(1) Å and the distance Nb(2)—Cp(4) is 2.134(1) Å) than to best planes of the corresponding unsubstituted Cp ligands (the distances Nb(1)—Cp(1) and Nb(2)—Cp(3) are 2.146(1) Å). The same difference has also been established for Ia and III, whereas in the determined structure of $(C_5H_5)_2(C_{10}H_8)Ti_2Cl_2$ the distance Ti—C_5H_5 (2.054 Å) is somewhat shorter than the distance between Ti and the least-squares plane of the C_5H_4 cycle of the fulvalene ligand (2.059 Å) [5]. The C—C bond lengths (1.39—1.43 Å) and C—C—C bond angle values (107.3—109.1°) for all the five-membered cycles of the cation IIa are usual for η^5-Cp ligand. These parameters in the fulvalene cyles reveal no significant deviations from regular pentagonal geometry. The length of the C(18)—C(28) exocyclic bond, 1.464(10) Å, is common for binuclear fulvalene complexes [5]. The region of short contacts of Cp ligands at each Nb atom is situated on the extension of the Nb(1)—Nb(2) line. The idealized coordination symmetry C_{2v} remains unchanged in IIa.

Most interesting from structural point of view are the changes in the Nb_2N_2 fragment caused by the transition from Ia to IIa. In the cation IIa this fragment is substantially non-planar, the deviation of each atom from the least-squares plane being 0.10 Å. The atoms N(1) and N(2) are drawn to the opposite side from the fulvalene ligand while in Ia they are situated more closely. The displacement of the N atoms causes bending of the cycle Nb(1)N(1)N(2)Nb(2) along the line Nb(1)—Nb(2) (the dihedral angle value being 16.4°), the bridging nitrene ligands being drawn closer to the bisector planes of the wedge-shaped sandwiches when compared with Ia. Thus the values of dihedral angles between the Nb(1)N(1)N(2) plane and the best planes C(13)—C(17) and C(18)—C(22) are 28.1° and 20.2°, and the values of dihedral angles between the Nb(2)N(1)N(2) plane and best planes C(23)—C(27) and C(28)—C(32) are 28.3° and 20.1°, respectively. All the Nb—N bond lengths (2.031(5)—2.055(6) Å) are the same within the accuracy limits, the average value being 2.041(6) Å (for Ia 2.04(3) Å). The coordination of nitrene ligands N(1) and N(2) in IIa, as in the case of carbyne ligands in IV [14], is slightly non-planar. The deviation of the *ipso* atoms C(1) and C(7) of the Ph-rings from the plane of the corresponding Nb_2N fragment in the direction towards the fulvalene ligand is 0.23 and 0.21 Å, respectively, the sum of the valence angles values at N(1) and N(2) being 358.6° and 358.8°, respectively. Values of the angles Nb(1)—N(1)—Nb(2) and Nb(1)—N(2)—Nb(2) are 91.3(2)°. Values of the angles N(1)—Nb(1)—N(2) and N(1)—Nb(2)—N(2) are 87.7(2)° and 87.4(2)°, respectively. The distance between N(1) and N(2) in IIa (2.83(1) Å) is slightly shorter than in Ia (2.92(4) Å), and the distance between Nb(1) and Nb(2) is slightly longer (2.921(1) Å in IIa and 2.834(5) Å in Ia). The latter difference may seem to be unimportant (only 0.087 Å), nevertheless it is 14 times more than the sum of the standard deviations and is accompanied with a decrease of the dihedral angle α value in the fulvalene ligand from 32° in Ia to 24.5° in IIa. The fact that the interatomic

Nb—Nb distance is sensitive to a change of the total number of electrons in the molecule makes it obvious that close location of Nb atoms in Ia is caused not only by the small covalent radii of the bridging N atoms, but also by Nb—Nb bonding. It is likely that the scheme of the "quasiaromatic" four-membered ring with delocalized bonds with order more than 1 suggested in [14] for the close structure of IV, should include direct metal—metal bonding.

The significant change in the configuration of the Nb_2N_2 fragment when passing from Ia to IIa is caused by the joint action of two opposite factors in their structures: first, the stability of the planar Nb_2N_2 fragment (strong "electronic" factor) and second, the distortion of the structure of the wedge-shaped sandwiches at Nb(1) and Nb(2) atoms due to formation of the planar Nb_2N_2 fragment (combination of "electronic" contribution of the wedge-shaped sandwich Cp_2ML_n, with equatorial orbitals being placed in the bisector plane of corresponding Cp_2M group [15] and "steric" repulsion of bridging N atoms drawn closer to the fulvalene ligand). The planar stability of the Nb_2N_2 fragment in the cation IIa is lowered in comparison with Ia, so the tendency to reduce distortions of the wedge-shaped sandwich fragments due to removal of N atoms from the fulvalene ligand is observed. The equilibrium of these opposite factors in both Ia and IIa is achieved at different configurations of the Nb_2N_2 fragment. The distances N···C(fulvalene) in IIa are lengthened when compared with Ia by approximately 0.2 Å (Table 7). In order to evaluate steric strain caused by short non-valent contacts of N atoms with one another and with 6 C atoms of the fulvalene ligand in Ia and IIa (the distances are given in Table 7), their contribution to the general energy of the molecule was calculated. The potential function $V = -a/r^6 + b\exp[-cr]$ was used; parameters a, b and c are given in the literature [16]. The steric strain energy for Ia and IIa was found to be equal to 6.2 kcal/mol and 1.6 kcal/mol, respectively. So the steric strain in Ia due to short N···C contacts is releaved significantly in IIa through the distortion of the planar structure of the Nb_2N_2 fragment. It is noteworthy that the extent of satisfaction of "steric requirements" in the structures Ia and IIa is ruled by the extent of their correspondence with strong "electronic" factors.

One may suppose that removal of one more electron from the cation IIa should lead to more important distortions of the Nb_2N_2 fragment and should result in formation of a N(1)—N(2) bond in the hypothetical dication $[(C_{10}H_8)(C_5H_5)_2Nb_2(NC_6H_4OCH_3)_2]^{2+}$. The Nb_2N_2 fragment should have tetrahedral configuration in this case due to the presence of 12 bonding electrons. This amount of bonding electrons is typical for tetrahedral cluster framework [17].

An alternative explanation of the change in geometry of the Nb_2N_2 fragment on removing electrons from Ia seems to be possible, however. The removal of electrons from normal two-centre two-electron σ-Nb—Nb bond is accompanied by lengthening of the bond and general loosing of bonding in the planar fragment. So bending of the fragment due to steric factors becomes possible. This interpretation suggests another configuration for the hypothetical dication, viz. the absence of both Nb—Nb and N—N bonds in it. Elucidation of the structure of this dication would help to make a choice between the alternative interpretations.

The benzene rings of the *p*-methoxyphenyl groups at N(1) and N(2) are planar within a 0.006 Å limit; values of dihedral angles between them and the planes of $Nb_2N(1)$ and $Nb_2N(2)$ fragments being 14.1° and 13.8°, respectively. The value of the dihedral angle between the benzene rings themselves is 18.1°. The distances N(1)—C(1) (1.404(3) Å) and N(2)—C(7) (1.408(9) Å) are equal to the N—C(phenyl) bond length in aromatic amines. The *p*-methoxyphenyl groups in IIa are exactly planar, with torsional angle values of 169(5)° for C(5)—C(4)—O(1)—C(33) and 168(5)° for C(11)—C(10)—O(2)—C(34). Values of C(Ph)—C(Ph)—O bond angles in trans positions to the methyl groups are significantly decreased when compared with 120° (115.2(6)° for C(5)—C(4)—O(1) and 115.4(6)° for C(11)—C(10)—O(2)). The same conformation established for the majority of structurally investigated oxyphenyl derivatives and proved by non-empirical conformational calculations [18] was explained through the suggestion of conjugation of the p_π unshared electron pair of oxygen with the π-system of the benzene ring. The presence of steric repulsion, Me···H(*ortho*) is also suggested. Conjugation effects tend to stabilize the planar configuration and the steric effect reduces the value of the C—C—O angle trans to the O—C(Ph) bond.

The BF_4^- anions in the crystal of IIa are located in infinite rows on the axes $\bar{3}$, with isolated cations and irregularly situated solvate CH_3NO_2 molecules in general positions. Intermolecular contacts in IIa are realized within limits of usual Van der Waals's distances.

Experimental

Spectra

IR spectra of Nujol mulls were measured with a UR-20 spectrometer. EPR spectra of IIa and IIb were studied with an E-3 instrument, in $MeNO_2$ or in the mixture THF/$MeNO_2$. UV spectra were recorded on a Specord-UV instrument; I in THF; II in a mixture of THF/$MeNO_2$.

X-ray study

The X-ray study was carried out on a four-circle automatic diffractometer, Syntex $P2_1$, at 20°C for Ia and —120°C for IIa′.

Crystals of Ia are monoclinic, $a = 7.996(1)$, $b = 17.558(3)$, $c = 9.666(1)$ Å, $\beta = 96.21(1)°$, $V = 1349.1(4)$ Å^3, $M = 686$ ($C_{34}H_{32}N_2O_2Nb_2$), $d_{calc.} = 1.698$ g/cm^3, $Z = 2$. 1329 Unique reflections with $I > 2\sigma$ were measured (λ(Mo-K_α), graphite monochromator, $\theta/2\theta$ scan, $2\theta \leqslant 48°$), no absorption correction was applied (μ(Mo-K_α) = 8.70 cm^{-1}). The structure of Ia was solved by a standard heavy atom method and refined by full matrix least-squares with an anisotropic (Nb)-isotropic approximation to $R = 0.055$, $R_G = 0.038$. Hydrogen atoms were included in the refinement with fixed positional and isotropic thermal parameters ($B_{iso} = 6.0$ Å^2). The pseudo-centrosymmetric arrangement of Nb atoms in the structure of Ia resulted in the absence of measurable reflections $h0l$ with $h = 2n + 1$. Together with the observed extinction of $0k0$ reflections (k odd), this corresponds to the $P2_1/a$ space group, where the molecule Ia must be centrosymmetric, while the E statistics are characteristic for a non-centrosymmetric space group. Successfull solution and refinement of the crystal structure of Ia

(continued on p. 168)

TABLE 8

ATOMIC COORDINATES (X10^4) AND ISOTROPIC THERMAL PARAMETERS (X10) OF Ia

Atom	x	y	z	B_{iso}(Å^2)
Nb(1)	−2335(6)	576(0)	4005(5)	—
Nb(2)	−2694(6)	−576(1)	6005(5)	—
O(1)	3602(18)	1786(9)	9790(16)	27(4)
O(2)	−9004(19)	−1638(9)	388(16)	31(4)
N(1)	−1091(34)	363(14)	5882(27)	23(7)
N(2)	−3736(38)	−335(17)	3982(31)	39(8)
C(1)	194(29)	646(17)	6790(25)	22(6)
C(2)	362(33)	494(18)	8252(28)	17(6)
C(3)	1549(50)	798(23)	9123(49)	34(12)
C(4)	2608(39)	1357(16)	8764(32)	20(7)
C(5)	2399(35)	1636(17)	7352(31)	27(7)
C(6)	858(38)	1326(19)	6479(36)	31(9)
C(7)	−4903(29)	−760(14)	3100(25)	18(6)
C(8)	−6106(38)	−1329(18)	3568(34)	19(8)
C(9)	−7126(36)	−1714(17)	2620(32)	26(7)
C(10)	−7600(43)	−1463(18)	1356(36)	32(9)
C(11)	−6780(42)	−792(19)	853(37)	25(8)
C(12)	−5542(43)	−387(20)	1821(38)	41(9)
C(13)	−4510(35)	1555(16)	3247(30)	38(6)
C(14)	−4945(30)	1271(14)	4296(28)	37(6)
C(15)	−3690(36)	1648(18)	5068(34)	59(8)
C(16)	−2570(30)	1959(13)	4398(24)	31(5)
C(17)	−2874(33)	1854(15)	3016(28)	63(6)
C(18)	−367(20)	−457(12)	3574(18)	28(4)
C(19)	619(20)	242(10)	3773(19)	22(4)
C(20)	188(28)	965(13)	2819(25)	27(6)
C(21)	−1122(32)	415(17)	1779(28)	46(7)
C(22)	−1458(22)	−341(11)	2296(20)	26(4)
C(23)	−5266(28)	−657(18)	7145(25)	38(5)
C(24)	−5118(31)	−70(17)	7100(29)	54(6)
C(25)	−3808(30)	−26(15)	8085(26)	34(5)
C(26)	−3191(25)	−698(13)	8549(21)	37(5)
C(27)	−4120(30)	−1263(14)	7937(26)	50(6)
C(28)	−584(24)	−1099(12)	4604(22)	31(4)
C(29)	−1861(28)	−1636(13)	4527(23)	29(5)
C(30)	−1857(35)	−1946(16)	5923(32)	47(7)
C(31)	−698(39)	−1545(17)	7175(31)	53(8)
C(32)	164(29)	−1099(13)	6181(25)	34(6)
C(33)	4565(29)	2425(14)	9383(25)	40(6)
C(34)	−10 016(25)	−2217(12)	861(22)	25(5)

TABLE 9

ANISOTROPIC THERMAL PARAMETERS FOR Nb ATOMS OF Ia IN THE FORM $T = \exp[-1/4(B_{11}a^{*2}h^2 + ... + 2B_{23}b^*c^*kl)]$ (X10)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Nb(1)	21(2)	20(2)	21(2)	−1(2)	−1(2)	−2(2)
Nb(2)	27(2)	32(2)	17(2)	2(2)	3(2)	1(2)

TABLE 10

ATOMIC COORDINATES ($\times 10^4$) AND ANISOTROPIC THERMAL PARAMETERS ($\times 10$) IN THE FORM $T = \exp[-1/2(B_{11}h^2a^{*2} + ... + 2B_{23}klb^*c^*)]$ FOR THE CATION OF IIa

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Nb(1)	8227.6(3)	2539.0(3)	1578.4(3)	20.5(2)	18.4(2)	18.1(2)	−4.4(2)	−1.9(2)	−4.3(2)
Nb(2)	6772.5(3)	3421.7(3)	2460.6(3)	20.6(2)	18.2(2)	18.4(2)	−1.8(2)	−4.3(2)	−4.3(2)
O(1)	5039(3)	1417(3)	529(3)	29(2)	39(3)	29(2)	−12(2)	−8(2)	−10(2)
O(2)	9962(3)	4472(3)	3580(3)	27(2)	31(2)	36(2)	−9(2)	−8(2)	−12(2)
N(1)	7022(3)	2758(3)	1604(3)	25(3)	18(2)	20(2)	−2(2)	−6(2)	−3(2)
N(2)	7982(3)	3391(3)	2244(3)	25(3)	20(2)	21(3)	−4(2)	−4(2)	−4(2)
C(1)	6534(4)	2439(4)	1305(4)	24(3)	19(3)	21(3)	−5(2)	−8(2)	1(2)
C(2)	6844(4)	1977(4)	725(4)	22(3)	21(3)	17(3)	−3(2)	−4(2)	−3(2)
C(3)	6376(4)	1630(4)	442(4)	25(3)	21(3)	24(3)	−5(3)	−8(3)	0(2)
C(4)	5560(4)	1744(4)	748(4)	24(3)	25(3)	25(3)	−10(3)	−8(3)	−5(3)
C(5)	5215(4)	2193(4)	1335(4)	25(3)	24(3)	27(3)	−3(3)	−5(3)	0(3)
C(6)	5701(4)	2535(4)	1613(4)	25(3)	26(3)	25(3)	−7(3)	−5(3)	−8(3)
C(7)	8468(4)	3696(4)	2564(4)	23(3)	17(3)	22(3)	−3(2)	−6(2)	0(2)
C(8)	8154(4)	4274(4)	3021(4)	26(3)	19(3)	20(3)	−4(2)	−4(2)	−3(2)
C(9)	8623(4)	4557(4)	3367(4)	28(3)	22(3)	20(3)	−8(3)	−4(3)	−4(2)
C(10)	9440(4)	4249(4)	3256(4)	26(3)	21(3)	26(3)	−6(2)	−9(3)	−4(2)
C(11)	9783(4)	3663(4)	2806(4)	24(3)	25(3)	28(3)	−4(3)	−3(3)	−3(3)

C(12)	9301(4)	3390(4)	2462(4)	27(3)	22(3)	25(3)	−2(3)	−5(3)	−8(2)
C(13)	8775(4)	2394(4)	182(4)	31(3)	31(4)	15(3)	−12(3)	7(3)	−5(3)
C(14)	9430(4)	2418(4)	488(4)	22(3)	38(4)	20(3)	−10(3)	3(2)	−6(3)
C(15)	9298(4)	3192(5)	654(4)	31(4)	41(4)	25(3)	−18(3)	−2(3)	−8(3)
C(16)	8570(5)	3633(4)	455(4)	37(4)	24(3)	22(3)	−7(3)	4(3)	−4(3)
C(17)	8240(4)	3150(4)	160(4)	32(4)	37(4)	15(3)	−7(3)	−2(3)	0(3)
C(18)	7859(4)	1666(4)	2882(4)	23(3)	19(3)	20(3)	−1(2)	−3(2)	−2(2)
C(19)	7884(4)	1251(4)	2883(4)	24(3)	16(3)	24(3)	−6(2)	−4(2)	−2(2)
C(20)	8692(4)	1085(4)	1862(4)	33(3)	16(3)	28(3)	0(3)	−7(3)	−4(2)
C(21)	9162(4)	1393(4)	2200(4)	26(3)	20(3)	25(3)	−7(2)	−6(3)	0(2)
C(22)	8663(4)	1744(4)	2826(4)	27(3)	16(3)	21(3)	−4(2)	−3(2)	−2(2)
C(23)	6755(4)	4841(4)	1852(4)	30(3)	16(3)	37(4)	−3(3)	−5(3)	0(3)
C(24)	6234(4)	4818(4)	2602(4)	30(3)	17(3)	33(4)	3(3)	−9(3)	−6(3)
C(25)	5572(4)	4511(4)	2577(5)	27(3)	23(3)	36(4)	2(3)	−10(3)	−7(3)
C(26)	5700(4)	4343(4)	1809(5)	28(3)	27(3)	36(4)	3(3)	−16(3)	−9(3)
C(27)	6434(5)	4547(4)	1364(4)	42(4)	23(3)	24(3)	7(3)	−5(3)	−5(3)
C(28)	7142(4)	2112(4)	3336(4)	23(3)	18(3)	17(3)	−4(3)	−2(2)	−3(2)
C(29)	7120(4)	2716(4)	3745(4)	21(3)	25(3)	15(3)	−1(2)	−4(2)	−2(2)
C(30)	6307(4)	3137(4)	3913(4)	37(4)	26(3)	15(3)	−5(3)	0(3)	5(2)
C(31)	5843(4)	2797(4)	3609(4)	22(3)	25(3)	21(3)	−4(3)	−4(2)	0(2)
C(32)	6339(4)	2173(4)	3253(4)	26(3)	22(3)	15(3)	−5(2)	−2(2)	−2(2)
C(33)	5317(5)	1130(5)	−198(5)	36(4)	39(4)	41(4)	−11(3)	−14(3)	−16(3)
C(34)	9682(5)	5199(5)	3865(5)	36(4)	40(4)	41(4)	−14(3)	−11(3)	−14(3)

proved $P2_1$ to be the correct space group *.

Crystals of IIa′ are trigonal in the rhombohedral system $a = 17.618(5)$ Å, $\alpha = 74.98(2)°$, $V = 4992(2)$ Å^3, $M = 832$ ($C_{34}H_{32}N_2O_2Nb_2BF_4 \cdot CH_3NO_2$, (vide infra)), $d_{calc.} = 1.674$ g/cm^3, $Z = 6$. 3246 Unique reflections with $I > 2\sigma$ were measured (λ(Cu-K_α), graphite monochromator, $\theta/2\theta$ scan, $2\theta \leqslant 110°$). An absorption correction was made as described previously [19] taking into account the real shape of the crystal. The positions of Nb atoms were established by the direct method. Successive Fourier syntheses in the $R3$ group revealed two independent cations in general position and 6 disordered BF_4^- anions. Two of six boron atoms are situated in 0, 0, 0 and 1/2, 1/2, 1/2 special positions. The other four atoms are situated in unique positions x, x, x, each BF_4^- anion has in the crystal two orientations differing in inversion with regard to B atom. Analysis of the coordinates of the two cations (independent in the $R3$ space group) made it possible to determine true space group $R3$ in which previously suggested independent cations were related by the centre of inversion. Both positions of four symmetrically independent in $R\bar{3}$ and disordered BF_4^- anions were refined with half weights. B(1) and B(2) atoms are located in unique positions in the inversion centres 0, 0, 0 and 1/2, 1/2, 1/2 respectively. B(3) and B(4) atoms (F(1), F(3), F(5), F(5′), F(7) and F(7′) also) are situated in unique positions x, x, x on the axis $\bar{3}$ **. Refinement by full matrix anisotropic (isotropic for anions) least-squares technique gave a value of 0.072 for R factor. At this stage the difference electron density map revealed all hydrogen atoms and solvate CH_3NO_2 molecule disordered in two positions. Further refinement was carried out using block-diagonal anisotropic(nonhydrogen atoms of the cation)-isotropic approximation with 3084 reflections ($F^2 > 3\sigma$). Only the coordinates of H atoms were refined with fixed isotropic temperature parameters ($B_{iso} = 4.0$ Å^2). Finally $R = 0.037$, $R_G = 0.049$. Because of the disorder of BF_4^- anions the B—F bonds lying on the $\bar{3}$ axis turned out to be unreally long (1.57—1.86 Å) whereas B—F distances for other F atoms situated in general position are of usual values (1.31—1.35 Å). No attempts to carry out the further refinement of BF_4^- anion positions and geometry were made because the geometry of the cation IIa, which was of main interest, had been determined with a rather satisfactory accuracy. The planar solvate CH_3NO_2 molecule fragment is disordered in two positions with one common non-disordered O(3) atom; N(3)—C(35), 1.50(3) Å, and N(3′)—C(35′), 1.49(3), bonds lengths are usual within the accuracy limits.

Coordinates of the atoms of the structure of Ia and their isotropic temperature parameters are listed in Table 8, and anisotropic temperature parameters of Nb atoms in Table 9. Coordinates of non-hydrogen atoms and corresponding parameters of the temperature factors of the structure IIa are listed in Tables 10 and 11.

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* Although in the course of the refinement a correction factor $\Delta f''$ for anomalous dispersion on Nb atoms was taken into account, R factors for an inverted structure were the same within accuracy limits. It is likely that determination of an absolute structure in this case is impossible without taking into consideration the absorption.

** Two more BF_4^- anions in the cell are related to anions $B(3)F_4^-$ and $B(4)F_4^-$ by the inversion centre 1/2, 1/2, 1/2.

TABLE 11

ATOMIC COORDINATES ($\times10^4$) AND ISOTROPIC THERMAL PARAMETERS ($\times10$) FOR TETRAFLUOROBORATE ANIONS AND NITROMETHANE MOLECULE IN THE STRUCTURE OF IIa.

Atom [a]	x	y	z	B_{iso}(Å^2)
O(3)	2499(4)	4603(4)	398(4)	64(2)
O(4)	3240(9)	5364(9)	689(9)	66(3)
O(4′)	1759(8)	4303(8)	—352(8)	61(3)
N(3)	2991(9)	4705(9)	827(9)	49(3)
N(3′)	2002(9)	4170(9)	292(9)	46(3)
C(35)	3236(13)	4022(13)	1484(13)	63(5)
C(35′)	1781(13)	3510(13)	976(13)	65(5)
B(1)	1/2	1/2	1/2	37(5)
B(2)	0	0	0	33(4)
B(3)	6470(6)	6470(6)	6470(6)	57(5)
B(4)	8534(6)	8534(6)	8534(6)	58(5)
F(1)[B(1)] [b]	4574(4)	4574(4)	4574(4)	38(3)
F(2)[B(1)]	4239(5)	5291(5)	5267(5)	40(2)
F(3)[B(2)]	—422(4)	—422(4)	—422(4)	38(3)
F(4)[B(2)]	264(5)	294(5)	—757(5)	39(2)
F(5)[B(3)]	6052(3)	6052(3)	6052(3)	30(3)
F(5)[B(3)]	6944(8)	6944(8)	6944(8)	113(8)
F(6)[B(3)]	6672(5)	7106(5)	5912(5)	41(2)
F(6)[B(3)]	6399(6)	7111(6)	5860(6)	47(2)
F(7)[B(4)]	8066(8)	8066(8)	8066(8)	112(8)
F(7)[B(4)]	8954(3)	8954(3)	8954(3)	28(2)
F(8)[B(4)]	8328(5)	9088(5)	7894(5)	40(2)
F(8)[B(4)]	9133(6)	7890(6)	8610(6)	47(2)

[a] Primed numbers correspond to the second halves of respective disordered atoms [b] The corresponding bonded B atoms are indicated in brackets.

All calculations were made with an Eclipse S/200 computer using EXTL programs modified by A.I. Yanovskii and R.G. Gerr in our laboratory.

Preparation of complexes

The complexes Ia and Ib were synthesized by the method elaborated in our previous work [4]. In this method, interaction of bisniobocene, $Cp_2(C_5H_4)_2$-Nb_2H_2, with azoaromatic compounds was used and Schlenk glassware-vacuum techniques were employed.

Synthesis of $[(C_{10}H_8)Cp_2Nb_2(NC_6H_4OMe)_2]BF_4 \cdot MeNO_2$ *(IIa′).* A suspension of 0.10 g (0.15 mmol) Ia in THF (20 ml) was vigorously stirred with 0.03 g (0.15 mmol) $AgBF_4$ for 15 min (it may be kept without stirring for several hours). A black precipitate was rapidly formed. It was filtered off and washed with hot THF (two times). A solid residue was extracted with 15 ml of CH_3NO_2. 0.12 g (quantitative yield) of crystalline IIa′ was obtained on slow evaporation of this solution; m.p. 208—210°C (with decomposition). Found: C, 50.47; H, 4.36; N, 4.92; $C_{35}H_{35}F_4O_4N_3Nb_2B$ calcd.: C, 50.39; H, 4.23; N, 5.04%. IR. IIa′ (cm^{-1}): 1603m, 1522m, 1309w, 1288w, 1254m, 1228s, 1079w, 1040s (broad), 925w, 832s, 800m, 785m, 734m. Ia (cm^{-1}): 1320w, 1286m, 1242s, 1194m, 1116w, 1051s, 1028m, 904m, 803s, 782s, 734m.

Synthesis of $[(C_{10}H_8)Cp_2Nb_2(NPh)_2]BF_4 \cdot MeNO_2$ *(IIb′).* Complex IIb′ was obtained in quantitative yield from Ib using the technique described above;

m.p. 206—212°C (with decomposition). Found: C, 50.92; H, 4.21; N, 5.02; $C_{33}H_{31}F_4N_3Nb_2O_2B$ calcd.: C, 51.18; H, 4.03; N, 5.43%.

Synthesis of $[(C_{10}H_8)Cp_2Nb_2(NC_6H_4OMe)_2]_2HgBr_4 \cdot MeNO_2 \cdot HgBr_2$ *(IIa″).* 0.36 g (1 mmol) of $HgBr_2$ was added to a suspension of 0.10 g (0.15 mmol) of Ia in THF (20 ml). The mixture was heated in a sealed tube to 100°C for 30 hours. A black precipitate was isolated and extracted with CH_3NO_2. 0.17 g (quantitative yield) of crystalline IIa″ was obtained from the solution in CH_3NO_2, m.p. 180—185°C (with decomposition). Found: C, 38.67; H, 2.79; Nb, 17.60; $C_{59}H_{67}Br_6O_6N_5Nb_4Hg_2$ calcd.: C, 38.46, H, 3.13; Nb, 17.25%. IR. IIa″ (cm^{-1}): 1600m, 1286m, 1250m, 1228s, 1180m, 1118w, 1045m, 898w, 868m, 852m, 826s, 797s, 736m.

The compound with a similar stoichiometric composition $[(C_{10}H_8)Cp_2Nb_2(NC_6H_4OMe)_2]_2HgCl_4 \cdot MeNO_2 \cdot HgCl_2$ was synthesized through the action of $HgCl_2$ on Ia. Appropriate analytic data were obtained.

Synthesis of $[(C_{10}H_8)Cp_2Nb_2(NPh)_2]_2HgBr_4 \cdot MeNO_2 \cdot HgBr_2$ *(IIb″).* The complex IIb″ was obtained from Ib using the technique described for preparing of IIa″. The yield of IIb″ was quantitative; m.p. 183—188°C (with decomposition). Found: C, 36.02; H, 2.89; Nb, 17.43; $C_{65}H_{59}Br_6N_5Nb_4Hg_2O_2$ calcd.: C, 35.57; H, 2.71; Nb, 16.95%.

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