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Effect of the spin-orbit interaction of ligands on the parameters of EFK spectra for a series of niobium(IV) complexes of trans-[NbX4(OPPh3)2] (X = Cl, Br, I)

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Keywords: Niobium(IV) complex, d1 configuration, spin-orbital interaction, X-ray crystal structure, EPR, magnetic susceptibility, DFT calculations

Abstract: Two crystal modifications of new molecular niobium(IV) complex *trans*-NbI₄(OPPh₃)₂ were obtained by ampoule synthesis, and their X-ray crystal structures were solved (*P*-1, *a*=9.5795 Å, *b*=9.7287 Å, *c*=11.2337 Å, *a*=107.984°, *β*=104.061°, *γ*=95.500°, V= 949.24Å³; *P*2₁, *a*=10.204 Å, *b*=16.039 Å, *c*=11.857 Å, *β*=102.663°, V= 1893.3Å³). For the series of molecular complexes *trans*-NbX₄(OPPh₃)₂ (X=Cl, Br, I) magnetic properties were studied and systematized using EPR, magnetic susceptibility measurements, and theory calculations with DFT approximation. Theory calculations of EPR parameters have shown good accordance with experimental data and allowed to establish a negative sign of the principal hyperfine tensor values.

1. Introduction

The study of the magnetic properties of coordination compounds has a rich history, which includes the development of methods for measuring, synthetic methods of new complexes of metals of interest, and of course, the discussion related to this, including theoretical modelling and quantum calculations [1,2].

Nb(IV) molecular complexes are one of group d^1 complexes interesting from the point of studying magnetic properties. Among the works presenting EPR data of niobium(IV) compounds, products of interaction of NbCl₄ with substituted pyridines [3], and products of electrochemical reduction of NbCl₅ in HCl saturated ethanol solution [4] are mentioned. Niobium(IV)

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pntnaiocyanine oxocomplexes [5], as well as N_1N -dietnylcaroamato and nexafluoroacetylacetonato derivatives of niobium(IV) (Nb(O₂CNEt₂)₄ and Nb(hfacac)₄) [6] were isolated as crystalline samples, and charge state of niobium(IV) was confirmed by EPR. A series of works are devoted to halogenide niobium(IV) complexes with different phosphines [7-9], at that synthesis and their crystal structures are discussed. In the case of phosphines without voluminous substituents, formation of niobium dimers with Nb–Nb bond are observed (for example, Nb₂Cl₈(PMe₃)₄).

Mononuclear niobium(IV) complexes are usually synthesized from tetra- or pentahalogenides by solution chemistry methods. Recently [10] we proposed procedure for preparation of niobium(IV) complexes *trans*-NbX₄(OPPh₃)₂ (X = Cl (1), Br (2)) using one step synthesis in an evacuated ampoule. To complement the present data on magnetic properties of niobium(IV) compounds, we synthesized new complex *trans*-NbI₄(OPPh₃)₂ (**3a**, **3b**), and systematically studied magnetic properties of *trans*-NbX₄(OPPh₃)₂ (X = Cl, Br, I) series. For the complexes of the same structure and symmetry, we investigated the effect of halogens on the EPR spectra.

2. Experimental section

2.1. Materials

Niobium powder, and iodine (99%, "Iodobrom" Russia), triphenylphosphine (Acros, 99%), triphenylphosphine oxide (Sigma Aldrich, 98%), and acetonitrile (Reakhim, analytical grade) were used without pre-purification.

2.2. Synthetic procedures

2.2.1. Synthesis of NbI₅. NbI₅ was obtained by the reaction of the elements with a 10% excess of iodine in evacuated two-zone quartz ampoule. Nb powder (0.639g, 6.88 mmol) and iodine (4.8g, 19 mmol) were put into a quartz ampoule with 50 ml total volume. The end of the ampoule containing iodine was maintained at room temperature. The other end containing niobium was heated (400°C, 2h) until most of the iodine is reacted. During this time the ampoule was carefully pushed into the furnace in order to accelerate the evaporation of iodine. Then ampoule was heated in a muffle furnace (400°C, 40h) to complete the reaction. Excess of iodine was condensed in the one end by heating the other end to 120°C, and then the ampoule part with the product was soldered apart.

2.2.2. Synthesis of Nb₃I₈. Nb₃I₈ was obtained by the reaction of niobium metal with stoichiometric amount of iodine in evacuated two zone quartz ampoule. Nb powder (0.645 g, 6.94 mmol) and iodine (2.4 g 9.5 mmol) put into a quartz ampoule of volume 50 ml. The one end of the ampoule containing iodine was maintained at room temperature. The other end containing

Journal Pre-proofs niobium was neated (400°C, 2n) until most of the logine is reacted. During this time the ampoule was carefully pushed into the furnace in order to accelerate the evaporation of iodine. Then ampoule was heated in muffle furnace (700°C, 80h) in order to achieve completion of the reaction. The purity of NbI₅ and Nb₃I₈ was confirmed by XRPD (Fig. S1 and S2, respectively).

2.2.3. Synthesis of *trans*-[NbCl₄(OPPh₃)₂] (1) and *trans*-[NbBr₄(OPPh₃)₂] (2). The crystalline powders 1 and 2 were synthesized according to the procedure in [10]. Generally, NbCl₅ (0.54g, 2.0 mmol) or NbBr₅ (0.98g, 2.0 mmol) were reacted with a mixture of PPh₃ (0.50g 1.9 mmol) and OPPh₃ (1.30g, 4.7 mmol). The samples were placed in sealed glass ampoules filled with argon; the ampoules were heated at 250°C. The ampoules were opened in air, and the product mixtures were washed with acetonitrile 3×20 ml. The yields were 80% (1) and 94% (2). The purity of 1 and 2 was confirmed by XRPD (Figs. S3 and S4, respectively).

2.2.4. Synthesis of crystals trans- $[NbI_4(OPPh_3)_2]$ (3a). Well-faceted brown-orange crystals of irregular habitus were obtained in the reaction of Nb₃I₈ (~50 mg, 0.04 mmol) and melt of PPh₃ (100 mg, 0.38 mmol) within an evacuated glass ampoule. The ampoule was heated 250°C during 35 h. The product of this reaction consisted of unreacted Nb₃I₈, 3a and 3b, according to XRPD (Fig. S5). The yield of crystals **3a** was not higher then 5-10%. EDX: Nb:P:I=1:1.9:3.9.

2.2.5. Synthesis of trans-[NbI4(OPPh3)2] (3b). NbI5 (1.45 g, 2.0 mmol), OPPh3 (1.30 g, 4.7 mmol) and PPh₃ (0.50 g, 1.9 mmol) were put into a glass ampoule; these manipulations were carried out in argon atmosphere using a dry box. The ampoule was sealed and heated up to 250°C, and kept at this temperature for 15 h. The ampoule was opened in air and the product mixture was washed with acetonitrile 3×20ml. The product **3b** was brown-orange fine crystalline powder, yield 2,31 g (98% referred to Nb). Crystal for X-ray diffraction was selected from the product manually. The product purity confirmed by X-ray powder diffractometry (Fig. S6). Analysis for light elements: C 37.3 % (clcd 37.4); H, 2.7 (clcd 2,6%). IR-spectrum of **3b**, as well as ones for **1** and **2**, is similar to the OPPh₃ spectrum (Fig.S7-10).

2.3. Methods

Diffraction patterns of powder samples were recorded using Philips PW 1830/1710 diffractometer (CuK_{α} radiation, graphite monochromator, silicon plate as the external standard). CHNS analyses were performed with Vario MICRO Cube CHNS analyser. The Nb:X:I element ratios were determined by a desktop scanning electron microscope with a Hitachi TM-3000 energy dispersive analyzer of the chemical composition. IR spectra were recorded on a SCIMITAR FTS 2000 instrument. EPR spectra were obtained on Varian E-109 and Bruker Elexsys E580 spectrometers in X and Q frequency ranges in the temperature range 50 - 300 K. The EPR spectra were modeled using the EasySpin toolbox in the MatLab software. Powdered samples of the

Journal Pre-proots syntnesized compounds were used as the objects of EPK study. The EPK spectrum of 2,2-dipnenyl-1-picrylhydrazyl (DPPH) with g = 2.0036 was used as the reference. The EPR spectra were recorded in the Q-band (35 GHz) at 20 mW microwave power, 100 kHz of modulation frequency, and 1 gauss of modulation amplitude. The EPR spectra of 1 and 2 samples were recorded at a temperature of 50 K because at temperatures above 77 K the lines of the EPR spectra broadened. For the sample 3b, no broadening of the EPR spectrum lines was observed in the temperature range 50 - 300 K.

The DFT calculations of g- and A-tensors were performed for 1, 2,3b, using the ADF 2019.3 program package [11,12] with a hybrid functional B3LYP [13]. Triple zeta basis sets and "no frozen core" approximations were used in all the calculations [14]. The relativistic effects were calculated at the Spin-Orbit ZORA level [15]. In such a calculation of g- and A-tensors a degenerate perturbation theory is used with the external magnetic field or nuclear magnetic field as perturbation [16,17]. The structures of complex molecules were taken from the structural data and were not optimized.

Magnetic susceptibilities of 1, 2, 3b complexes were measured by Faraday method. The data was obtained using quartz torque microbalance and recorded high precision digital voltmeter Keysight 34465A. The temperature stabilization was controlled using Delta DTB9696 temperature controller. The sample was placed in the open quartz ampoule and vacuumed to 0.01 Torr pressure. The measurements were carried out in the helium atmosphere with a pressure of 5 Torr. The magnetic field strength was 7.3 kOe. The measurements were carried out in two cycles (cooling 300-80K and heating 80-300K). The obtained values of magnetic susceptibilities were averaged.

X-ray single crystal diffraction of compound 3a was performed at 150 K on an automatic Bruker APEX Duo diffractometer (MoK_{α} radiation, $\lambda = 0.71073$ Å, graphite monochromator, twodimensional detector) by the standard procedure [18]. The crystal structure was solved by a direct method and refined by the full-matrix least squares technique using the SHELXTL program package [19] with an Olex2 graphical interface [20]. Atomic displacement parameters of nonhydrogen atoms were refined in the anisotropic approximation. Positions of all H atoms were found from the difference Fourier maps and included in the refinement in the riding model.

Diffraction data for single-crystal 3b were collected at 100 K on the 'Belok' beamline $(\lambda = 0.79272 \text{ Å}, \varphi$ -scans with a step of 1.0°) of the National Research Center 'Kurchatov Institute' (Moscow, Russian Federation) using a Rayonix SX165 CCD detector. The data were indexed, integrated and scaled, absorption correction was applied using the XDS program package [21]. The structure was solved by dual space algorithm (SHELXT [22]) and refined by the full-matrix least squares technique (SHELXL [19]) in the anisotropic approximation (except hydrogen atoms).

Journal Pre-proofs Positions of nydrogen atoms of organic ligands were calculated geometrically and refined in the riding model. The crystallographic data and details of the diffraction experiments for compounds 3a and **3b** are summarized in Table 1.

Full tables of interatomic distances and bond angles, atomic coordinates and atomic displacement parameters for structures 3a and 3b have been deposited with the Cambridge Crystallography (CCDC 2013822 2012709 (**3b**) Data Center (3a)and https://www.ccdc.cam.ac.uk/structures/).

| Parameter | NbI ₄ (OPPh ₃) ₂ (3a) | NbI ₄ (OPPh ₃) ₂ (3b) |
|---|---|---|
| M, g/mol | 1157.05 | 1157.05 |
| <i>a</i> , Å | 9.5795(8) | 10.204(2) |
| b, Å | 9.7287(8) | 16.039(2) |
| <i>c</i> , Å | 11.2337(9) | 11.857(2) |
| α, ° | 107.984(2) | 90 |
| β, ° | 104.061(3) | 102.663(9) |
| γ, ° | 95.500(3) | 90 |
| Space group | <i>P</i> -1 | P2 ₁ |
| Z | 1 | 2 |
| Crystal size, mm | $0.28 \times 0.24 \times 0.16$ | 0.03 	imes 0.03 	imes 0.02 |
| Temperature, K | 150(2) | 100(2) |
| V, Å ³ | 949.24(14) | 1893.3(5) |
| $P_{calc}, g/cm^3$ | 2.024 | 2.030 |
| μ , mm ⁻¹ | 3.684 | 4.969 |
| Reflections measured/ independent | 12918/5311 | 15285/8633 |
| $R_{\rm int}/R_{\sigma}$ | 0.0221/0.0286 | 0.0608/0.0782 |
| GooF | 1.033 | 1.024 |
| R_1/wR_2 for $I > 2\sigma(I)$ | 0.0202/0.0416 | 0.0525/0.1210 |
| R_1/wR_2 for all data | 0.0243/0.0432 | 0.0720/0.1321 |
| Residual electron density (peak/hole), <i>e</i> Å ⁻³ | 0.525 / -0.553 | 1.172 / -2.014 |

Table 1. Experimental X-ray single crystal data for compounds 3a and 3b.

3. Results and Discussion

3.1. Synthesis

Compounds 3a and 3b were prepared by the method of ampoule synthesis, using niobium iodides Nb₃I₈ (for 3a) and NbI₅ (for 3b) as starting compounds. In the case of 3a, we didn't add an oxygen source on purpose; we consider that product of the partial hydrolysis of the starting Nb₃I₈ (presumably, niobium oxohalides) presented as an oxygen source in the reaction. Using of Nb₃I₈ in

Journal Pre-proofs such a way does not yieid analytically pure material. In this case we obtained only a tew crystals **3a** in the mixture of unreacted starting species.

First, we studied the reaction of Nb_3I_8 with PPh₃ which resulted in crystals **3a**. Further, for obtaining pure product 3a, we used NbI₅, OPPh₃ and PPh₃ as starting reagents, and this experiment resulted in 3b, not 3a. Unfortunately, attempts to find experimental conditions for the synthesis of 3a failed.

Powder of 3b was obtained in reactions of niobium pentaiodide with the melt of triphenylphosphine and triphenylphosphine oxide with yield of 98% referred to Nb. We assume that triphenylphosphine reduces niobium to +4 oxidation state:

 $2NbI_5 + 4OPPh_3 + PPh_3 = 2NbI_4(OPPh_3)_2$ (**3b**)+ I_2PPh_3

In general, compounds **3a** and **3b** were obtained in similar way – in ampoule syntheses, as **1** and 2 which were synthesized by us earlier [10].

3.2. X-ray crystal structures of 3a and 3b

Crystal structures of both compounds **3a** and **3b** include complexes *trans*- $[NbI_4(OPPh_3)_2]$ but differ in the packing arrays as well as geometries of the complexes (Fig. 1). Compound 3a crystallizes in space group P-1, it is isostructural with 1 and 2 [10]. Coordination environments of Nb atoms are octahedral (4I+2O) with trans-positions of oxygen atoms. In the structures, the complexes [NbI₄(OPPh₃)₂] themselves differ by mutual orientations of coordinated molecules OPPh₃. Complex $[NbI_4(OPPh_3)_2]$ in **3a** is located in a special position with an inversion center on Nb atom, and P-O-Nb-O-P fragment has a zigzag form. Complex [NbI4(OPPh₃)₂] in **3b** is located in a general position, and P-O-Nb-O-P fragment has a bow form.

Selected values of bond lengths and angles in structures 3a and 3b are listed in Tables 2 and 3. Bond lengths Nb–I in structures **3a** and **3b** are in the range 2.77 - 2.83 Å, that is 0.1Å longer than bonds Nb-I (terminal) in the structure of NbI₄ (2.65-2.70Å) [23]. Bond lengths Nb-O in the structures **3a** and **3b** differ from the analogous Nb–O lengths not more than 0.02 Å. The angles on Nb atoms in **3a** and **3b** are very close; they differ by no more than 3°.



Figure 1. Structures of the complexes trans-[NbI₄(OPPh₃)₂] in **3a** (a) and **3b** (c), and their packing motifs in **3a** (b) and **3b** (d).

| Bond | Length, Å | Bond | Length, Å | Bond | Length, Å | Bond | Length, Å |
|--------|------------|--------|------------|--------|------------|-------|------------|
| 3a | | | | | | | |
| Nb1 I1 | 2.8191(2) | Nb1 I2 | 2.8110(2) | Nb1 O1 | 1.9788(14) | O1 P1 | 1.5412(14) |
| | 3b | | | | | | |
| Nb1 I1 | 2.8305(19) | Nb1 I2 | 2.8088(19) | Nb1 O1 | 2.003(11) | O1 P1 | 1.518(12) |
| Nb1 I3 | 2.7732(19) | Nb1 I4 | 2.8093(19) | Nb1 O2 | 1.985(12) | O2 P2 | 1.546(12) |
| | | | | | | | |

Table 2. Selected bond lengths in X-ray crystal structures of **3a** and **3b**.

Table 3. Selected angle values in X-ray crystal structures of **3a** and **3b**.

| Angle | value, ° | Angle | value, ° | Angle | value, ° | Angle | value, ° |
|-----------|-----------|-----------|----------|-----------|----------|-----------|------------|
| 3a | | | | | | | |
| I1-Nb1-I2 | 89.888(7) | 01-Nb1-I1 | 90.09(4) | O1-Nb1-I2 | 90.84(4) | P1-O1-Nb1 | 165.91(10) |
| 3b | | | | | | | |
| I1-Nb1-I2 | 90.15(5) | O1-Nb1-I1 | 89.8(3) | O1-Nb1-I2 | 91.7(3) | P1-O1-Nb1 | 163.5(8) |

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|--------------------|----------|-----------|---------|-----------|---------|-----------|----------|
| 13-Nb1-I4 | 90.75(6) | O1-Nb1-I3 | 88.9(3) | OÎ-Nb1-I4 | 93.2(3) | P2-O2-Nb1 | 159.6(8) |

As a result, we have a series of niobium(IV) complexes with very similar X-ray crystal structures. Moreover, these complexes $[NbX_4(OPPh_3)_2]$ (X=Cl, Br, I), having one unpaired electron per Nb atom, could serve as convenient objects for the study of magnetic properties. We examined the magnetic properties of the compounds $NbX_4(OPPh_3)_2$ by EPR and magnetic susceptibility measurements.

3.3. EPR spectra of the complexes 1, 2, 3b

The $[NbX_4(OPPh_3)_2]$ (X=Cl, Br, I) complexes were studied by EPR spectroscopy. Q-band experimental and simulated EPR spectra of these complexes are given in Fig. 2.

The experimental spectra can be well fitted with spin Hamiltonian (1)

$$H = g_{xx}\beta H_x S_x + g_{yy}\beta H_y S_y + g_{zz}\beta H_z S_z + A(Nb)_{xx}I_x S_x + A(Nb)_{yy}I_y S_y + A(Nb)_{zz}I_z S_z$$
(1)

with S = 1/2, I = 9/2, and the principal values of g- and A-tensors given in Table 4 (considering the natural abundance of ⁹³Nb isotope is 100%). The observed EPR spectra with the electron spin S = 1/2 and the HFS of one ⁹³Nb nucleus (I = 9/2) is typical for the 4*d*¹ electronic configuration of niobium ion niobium(IV). All spectra were simulated with the linewidths $\Delta H = 8.0$ mT (H || g_{zz}) and $\Delta H = 19.0$ mT (H±g_{zz}). The linewidths for parallel and perpendicular directions of NbX₄(OPPh₃)₂ EPR spectra are different probably due to the unresolved HFS of chlorine (chlorine isotopes ³⁵Cl and ³⁷Cl with natural abundance 75.78% and 24.22%, respectively, with the nuclear moment I=3/2), bromine (bromine isotopes ⁷⁹Br and ⁸¹Br with natural abundance 50.69% and 49.31%, respectively, with the nuclear moment I=3/2), and iodine atoms (iodine isotope ¹²⁷I with natural abundance 100% with the nuclear moment I=5/2).

EPR spectra are very similar for **2** and **3b**. They were simulated assuming $g_{xx}\neq g_{yy}$ for **3b**; the principal values $A(Nb)_{xx}$ and $A(Nb)_{yy}$ have been obtained from the wide perpendicular component of the spectrum. It should be noted that the lines are quite broad and it is impossible to estimate precisely the principal values $A(Nb)_{xx}$ and $A(Nb)_{yy}$ of the niobium A-tensor, as well as the possible contribution of superhyperfine interaction (SHFI) due to bromine or iodine atoms.



Fig. 2. The Q-band EPR spectra of the 1 (a), 2 (b), and 3b (c) complexes: 1 - experimental, 2 - simulated. EPR spectra of the 1 (a), 2 (b) complexes were recorded at 50K, and 3b (c) complexes at 300K.

| Compound | g-tensor | A-tensor of | g-tensor | A-tensor of | g-tensor | A-tensor of ⁹³ Nb, |
|--|-------------------------|----------------------|------------------------|-------------------------|------------------------|--|
| | | ⁹³ Nb, mT | (B3LYP, TZP, | ⁹³ Nb, mT | (B3LYP, TZP | mT (B3LYP, |
| | | | SO ZORA) | (B3LYP, | except of Nb | TZP except of |
| | | | | TZP, SO | with TZ2P-J, | Nb with TZ2P-J, |
| | | | | ZORA) | SO ZORA) | SO ZORA) |
| [NbCl ₄ (OPPh ₃) ₂] | g _{xx} =1.518, | $ A_{xx} =17.3,$ | g _{xx} =1.41, | A _{xx} =-15.1, | g _{xx} =1.48, | A _{xx} =-14.3, A _{yy} =- |
| | g _{yy} =1.518, | $ A_{yy} =17.3,$ | $g_{yy}=1.44,$ | A _{yy} =-14.6, | g _{yy} =1.50, | 14.0, A _{zz} =-21.9 |
| | g _{zz} =1.813 | $ A_{zz} = 28.5$ | g _{zz} =1.91 | $A_{zz} = -21.6$ | g _{zz} =1.91 | |
| [NbBr ₄ (OPPh ₃) ₂] | g _{xx} =1.658, | $ A_{xx} =15.0,$ | g _{xx} =1.51, | A _{xx} =-12.5, | g _{xx} =1.55, | A _{xx} =-12.2, A _{yy} =- |
| | g _{yy} =1.658, | $ A_{yy} = 15.0,$ | g _{yy} =1.52, | A _{yy} =-12.2, | g _{yy} =1.56, | 12.0, A _{zz} =-19.0 |
| | g _{zz} =1.990 | $ A_{zz} = 23.0$ | g _{zz} =2.02 | $A_{zz} = -18.8$ | g _{zz} =2.02 | |
| [NbI ₄ (OPPh ₃) ₂] | $g_{xx}=1.540,$ | $ A_{xx} =8.0,$ | g _{xx} =1.53, | A _{xx} =-10.5, | $g_{xx}=1.56,$ | A _{xx} =-10.3, A _{yy} =- |
| | g _{yy} =1.650, | $ A_{yy} =8.0,$ | g _{yy} =1.54, | A _{yy} =-10.3, | g _{yy} =1.57, | $10.2, A_{zz} = -14.1$ |
| | $g_{zz} = 2.098$ | $ A_{zz} = 16.0$ | $g_{zz}=2.18$ | $A_{zz} = -13.8$ | $g_{zz}=2.18$ | |

Table 4. Experimental and simulated EPR parameters of the 1, 2, 3b.

3.4. Theory calculations

Theoretical calculation of the hyperfine interaction of the unpaired electron with the nuclear magnetic moment of niobium ⁹³Nb is discussed in [24]. The unpaired electron localized on the s-orbital gives $A_{iso} = 235.15$ mT, whereas the unpaired electron localized on the d-orbital gives $A_{aniso} = 6.527$ mT. Usually, the absolute values of the HFS tensor are about 10–30 mT for niobium(IV) compounds [3–6,25], which is consistent with our results.

The absolute values of niobium A-tensor decrease and the g_{zz} components of g-tensor increase simultaneously from X = Cl to I. At the same time, the Nb–X bond lengths increase from 2.433 – 2.421 Å for chlorine to 2.811 – 2.819 Å for iodine. Such change in geometry corresponds to increasing length of Nb-X bonds due to atomic radius of halogen atoms. But all three complex compounds have the same symmetry of the coordination environment of niobium atom. The reason for the changes in the g- and A-tensors may be the effect of spin-orbit interaction which is specified

Journal Pre-proofs by the sort of halogen. The spin-orbit coupling constant increases from chlorine to logine: $\lambda = 500$ cm⁻¹ (Cl), 2400 cm⁻¹ (Br), and 5000 cm⁻¹ (I) [26].

Only a few works can be found for comparison where a series of complexes with different halogenide ligands have been studied by EPR spectroscopy. One if not the only work is EPR study of presumably octahedral molybdenum (V) complexes (d^1) [MoOX₅]²⁻ (X = Cl, Br) and $[MoOI_4(H_2O)]$, which were obtained *in vitro* in concentrated HX (X = Cl, Br, I) [27]. The EPR spectra of these frozen solutions were measured and the g_{\parallel} revealed to increase from chlorine (1.948) to iodine (2.274) and, starting from the bromide complex (2.093), g_{||} was significantly higher than 2.0023. At that, the g₁ value does not change being equal to 1.9375 for chlorine, 1.945 for bromine, and 1.956 for iodine. The g- and A-tensors were calculated within the theory of molecular orbitals for C_{4V} symmetry, the spin-orbit coupling both of the ligands and the central ion was taken into account [28]. However, in this consideration, the optical absorption data and several empirical fitting parameters were used to match the calculated and experimental data. This made the calculations too bulky but in general evaluative. Following the data of Marov [28], the calculated gtensor values were in good agreement with the experimental ones.

The molecular orbital approach combined with complete diagonalization (of energy matrix) method and the perturbation theory method were used to simulate the EPR spectra of niobium(IV) in a tetrahedrally distorted oxygen octahedron in glasses [29]. In this case, the spin-orbit interaction due to the niobium and oxygen atoms was taken into account with the covalence effect and polarization varied. Additionally, the optical transitions data were used. As a result of such calculations, a good agreement was reached between the calculated ($g_{\parallel} = 1.88$, $g_{\perp} = 1.928$; $A_{\parallel} = -$ 26.8 mT, $A_{\perp} = -11.4 \text{ mT}$) and experimental (g || = 1.88, g_{\perp} = 1.92; A || = 26.2 \text{ mT}, A_{\perp} = 12.1 \text{ mT}) EPR parameters. The polarization of the niobium electron shell gave the negative values of the calculated principal values of the A tensor. We should note here that it is hard to determine the sign of the principal values of A tensor from the EPR experiments.

Niobium complex [NbCl₄(PEt₃)₂] was studied by EPR spectroscopy [30]. The EPR parameters for [NbCl₄(PEt₃)₂] (g || = 1.959, g_{\perp} = 1.912; A || = 21.85 mT, A_{\perp} = 10.3 mT) differ from that obtained in this work due to difference in donor properties of oxygen and phosphorus, but the g-tensor (g $|| > g_{\perp}$) and A-tensor (A $|| > A_{\perp}$) are characteristic for octahedral niobium complexes. As far as the authors know, the quantum chemical calculations of the EPR parameters of niobium complexes were not reported previously. Below, the quantum chemical calculations are given for the series $[NbX_4(OPPh_3)]$ (X = Cl, Br, I) performed with a hybrid functional B3LYP [13].

DFT calculations were performed for compounds 1, 2, 3b. The simulated g- and A-tensor values are given in Table 4. These are of particular interest considering the specific EPR parameters discussed above. The g- and A-tensor principal axes are disoriented at an angle of approximately 10

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degrees. The calculated EPK parameters are reasonably close to the experimental ones considering the accuracy of the DFT approach [16,17,31,32], the A-values being negative. Previously, the negative HFS constants were obtained theoretically for Nb⁴⁺ in tetragonally compressed NbO₆^{8–} anion in glasses [29]. The negative isotropic HFS constant was reported for six-coordinate vanadium(IV) tris(maleonitriledithiolene) anion and it was proposed that negative contribution to the spin density at the nucleus is produced by spin polarization of inner *s* levels by the unpaired electron in a 3*d* level [33,34].

We performed calculations at the same level of theory but taking the TZ2P-J basis set with additional polarization and five extra tight (mainly 1*s*) functions for niobium atom in an attempt to obtain better agreement between the experimental and calculated g- and A-tensor values. Although the A-tensor values remained almost the same, the g-tensor values obtained in this way had noticeably better match with the experimental values.

3.5. Measurements of magnetic susceptibility

Magnetic susceptibility was measured in the temperature range of 80-300 K for the complexes **1**, **2**, **3b** (Fig. 3). For all examined complexes, the temperature dependence of magnetic susceptibility could be fitted using the Curie-Weiss law [35]:

$$\chi(T)=\frac{C}{T-\theta} ,$$

where T is temperature, C is the Curie constant and θ is the Weiss constant. The negative sign of the Weiss constant indicates a weak antiferromagnetic interaction in the samples at low temperatures.

The effective magnetic moment value increases in a series $[NbCl_4(OPPh_3)_2] < [NbBr_4(OPPh_3)_2] < [NbI_4(OPPh_3)_2]$. The effective magnetic moments are close to that of octahedral niobium(IV) complexes $NbX_4(CH_3CN)_2$ with $\mu = 1.81-1.79 \mu_B$ (X=Cl), $\mu = 1.59-1.40 \mu_B$ (X=Br), and $\mu = 1.45-1.24 \mu_B$ (X=I) [36,37].



Figure 3. Magnetic susceptibility dependences on temperature for the complexes 1 (a), 2 (b), and 3b (c).

| | C, cm ³ ·K·mol ⁻¹ | μ_{eff}, μ_{B} | θ, Κ |
|--|---|----------------------|-------|
| [NbCl ₄ (OPPh ₃) ₂] | 0.25(1) | 1.40(1) | -2(2) |
| [NbBr ₄ (OPPh ₃) ₂] | 0.31(1) | 1.57(2) | -7(3) |
| [NbI ₄ (OPPh ₃) ₂] | 0.35(1) | 1.68(3) | -9(5) |

| Table 5. | Parameters of | f magnetic | susceptibility | for the com | plexes 1, 2, and 3b. |
|----------|---------------|------------|----------------|-------------|----------------------|
| | | <i>L</i>) | | | |

4. Conclusions

In this work, we developed a convenient synthesis method of new niobium(IV) complex trans-[NbI₄(OPPh₃)₂] using ampoule synthesis approach; we studied magnetic properties of the series of complexes trans-[NbX₄(OPPh₃)₂] (X=Cl, Br, I). Experimental data and quantum-chemical calculations have shown that an increase of the spin-orbit coupling constant of the halogen from chlorine to iodine leads to an increase of the g-tensor values higher than g = 2.0023. Quantum chemical calculations made it possible to estimate the sign of the hyperfine tensor values for the niobium ion. The use of the correct values of g-factors in calculating the magnetic susceptibility showed the practical absence of exchange interactions in the structures of the studied niobium(IV) compounds.

Declaration of competing interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data. CCDC 2013822 and 2012709 contains the supplementary crystallographic data for compound **3a** and **3b**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving/html, or from the CambridgeCrystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223336-033; or e-mail: <u>deposit@ccdc.cam.ac.uk</u>. Supplementary data to this article can be found online at

Appendix B. Supplementary material. Supplementary material contains X-ray powder diffraction patterns and FTIR-spectra of compounds mentioned in the text.

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