ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2023, Vol. 49, No. 4, pp. 195–205. © Pleiades Publishing, Ltd., 2023.
Russian Text © The Author(s), 2023, published in Koordinatsionnaya Khimiya, 2023, Vol. 49, No. 4, pp. 195–204.

Binuclear Vanadium(V) Complex with the Ligand Based on Isonicotinic Acid Hydrazide and 1-Phenyl-1,3-Butanedione: Synthesis and Crystal Structure

P. Bourosh[a, *], **M. Cocu**[b], **O. Danilescu**[b], **and I. Bulhac**[b]
[a] *Institute of Applied Physics, Chisinau, MSU, Republic of Moldova*
[b] *Institute of Chemistry, Chisinau, MSU, Republic of Moldova*
**e-mail: pavlina.bourosh@ifa.md*

Received May 16, 2022; revised July 26, 2022; accepted August 2, 2022

Abstract—A new molecular binuclear vanadium(V) complex $[VO(L)(OCH_3)]_2$ (**I**) is synthesized in which ligand H_2L is prepared by the reaction of isonicotinic acid hydrazide (INAH, isoniazide) with 1-phenyl-1,3-butanedione. Ligand H_2L and complex **I** are studied by elemental analysis, IR spectroscopy, mass spectrometry, and X-ray diffraction (XRD) (CIF files CCDC nos. 2172124 and 2172125, respectively). The composition and structure of the ligand in the free state is additionally studied by NMR spectroscopy. The bideprotonated organic ligand L^{2-} coordinates to the metal atom via the tridentate mode through a set of donor atoms ONO to form two conjugated metallocycles. Different tautomeric forms are stabilized in H_2L and in the corresponding coordinated ligand.

Keywords: vanadium, coordination compound, isonicotinoyl hydrazone, XRD, IR spectroscopy, NMR spectroscopy

DOI: 10.1134/S1070328423700409

INTRODUCTION

Vanadium plays an important role in biological systems, since it is a significant element for the most part of living beings and is found in soil, oil, water, and air [1]. The role of vanadium in biological systems is manifested as both structurally stabilizing diverse biological forms of compounds and functionally providing the key activity of various sites of protein, enzyme, and coenzyme molecules [2]. Although the biological significance of vanadium has been acknowledged long ago [3] and this element is a component of many drugs for the treatment of diabetes, cancer, and parasite-induced diseases, vanadium is also interesting in the area of coordination chemistry as a metallic site with different oxidation states, coordination numbers, and preferences to donor atoms.

Pyridinecarbonyl coordinating agents, especially Schiff bases, are flexible and universal ligands with high and diverse capabilities of coordinating to metal ions with the formation of complexes with various molecular architectures [4]. In addition, it is known that isonicotinic acid hydrazide itself (isoniazide, INAH) is an antituberculous remedy and, hence, is frequently used for studying the formation of complexes with biological properties. Isoniazide is a polydentate ligand and can be coordinated in both keto and enol forms depending on the reaction conditions. The reactions of INAH with β-diketones afford Schiff bases forming, in the presence of metal ions, mono-, bi-, and polynuclear coordination compounds in which these ligands can coordinate as bridging ligands via the polydentate mode to both one and two metal atoms [5–12]. We synthesized the ligand 5-hydroxy-3,5-dimethyl-4,5-dihydro-1*H*-pyrazol-1-yl)(pyridin-4-yl)methane by the reaction of isonicotinic acid hydrazide with 2,4-pentadione due to the additional condensation of one terminal fragment. The ligand reacted with $[Co(DfgH)_2Br(H_2O)]$ ($DfgH_2$ is diphenylglyoxime) to form a complex in which this ligand substituted the water molecule [13]. It was revealed that the condensation of the same organic molecules afforded 2,4-pentanedione isonicotinoyl hydrazone, which reacted with the vanadium salts to for both mono- and binuclear complexes [6, 7].

In this work, we present both the new vanadium(V) complex $[VO(L)(OCH_3)]_2$ (**I**) with the ligand synthesized by the reaction of isonicotinic acid hydrazide with 1-phenyl-1,3-butanedione (H_2L) and the ligand itself in the free state.

EXPERIMENTAL

Commercially available reagents (including solvents) from Sigma-Aldrich were used as received: isonicotinic acid hydrazide (98%) (HPLC), 1-phenyl-1,3-butanedione (99%), oxovanadium acetylacetonate (98%), ethanol (95%), and methanol (99.8%).

Synthesis of 1-phenyl-1,3-butanedione isonicotinoyl hydrazone (H_2L) [14]. 1-Phenyl-1,3-butanedione (1.62 g, 10.0 mmol) was added to a warm solution of isonicotinic acid hydrazide (1.37 g, 10.0 mmol) in ethanol (7 mL). The resulting solution was heated at 75–78°C until a brown color appeared (~20 min). After 12 h, a yellow crystalline substance (1.45 g) was formed, filtered off, washed with ethanol and diethyl ether, and dried in air. The crystals are soluble in chloroform, dimethylformamide, dimethyl sulfoxide, and ethyl and methyl alcohols, and partially in water. The yield was ~50%.

For $C_{16}H_{15}N_3O_2$

Anal. calcd., %	C, 68.31	H, 5.37	N, 14.94
Found, %	C, 67.97	H, 4.99	N, 14.94

IR (ν, cm^{-1}) for H_2L: 3220 m, 3200 sh, 3058 w, 3039 w, 3026 w, 2967 vw, 2927 w, 2837 w, 1664 s, 1596 s, 1574 m, 1550 vs, 1528 vs, 1507 vs, 1483 s, 1431 s, 1410 m, 1378 m, 1305 s, 1281 s, 1272 s, 1214 s, 1187 s, 1113 m, 1086 m, 1063 s, 1039 m, 1027 m, 1022 w, 972 w, 925 m, 870 w, 845 s, 833 s, 800 w, 738 s, 714 s, 691 w, 665 m, 648 s, 620 w, 613 m, 565 m, 540 w, 529 w, 490 w, 485 w, 432 m, 413 w, 406 w.

^{1}H NMR (400 MHz, 25°C, $CDCl_3$; δ, ppm): 2.10 (s, 3H, CH_3), 3.01 (d, 1H, CH_2, J = 18.6 Hz), 3.37 (d, 1H, CH_2, J = 18.6 Hz), 5.32 (s, 1H, NH), 8.71 (d, 2H, Py, J = 3.7 Hz), 7.76 (d, 2H, Py, J = 4.5 Hz), 7.45 (d, 2H, Ph, J = 7.7 Hz), 7.38 (d, 2H, Ph, J = 7.4 Hz), 7.31 (t, 1H, Ph, J = 7.0 Hz). ^{13}C NMR (400 MHz, 25°C, $CDCl_3$; δ, ppm): 16.1 (1C, CH_3), 53.8 (1C, CH_2), 94.6 (1C, Ph), 123.5 (2C, Py), 123.9 (2C, Ph), 128.3 (1C, Ph), 128.8 (2C, Ph), 141.2 (1C, Py), 143.03 (1C, >C=N), 149.7 (2C, Py), 156.4 (1C, >C=O (benzacet.)), 165.5 (1C, >C=O (hydr.)). ^{15}N NMR (400 MHz, 25°C, $CDCl_3$; δ, ppm): 213 (1N, =N–), 315 (1N, –NH–) (Bruker scale).

Synthesis of $[VO(L)(OCH_3)]_2$ (I) [13]. Oxovanadium acetylacetonate ($VO(Acac)_2$) (0.06 g, 0.24 mmol) in methanol (10 mL) was added to a solution of H_2L (0.07 g, 0.24 mmol) in methanol (10 mL) on heating (60–65°C). After 2–3 days, a black crystalline substance (0.07 g) was formed and washed with methanol and diethyl ether. The crystals are soluble in chloroform, dimethylformamide, and dimethyl sulfoxide, poorly soluble in ethanol and methanol, and insoluble in water. The yield of compound **I** was ~55%.

For $C_{34}H_{32}N_6O_8V_2$

Anal. calcd., %	C, 54.12	H, 4.27	N, 11.14
Found, %	C, 53.60	H, 3.80	N, 11.09

IR (ν, cm^{-1}) for $[VOL(OCH_3)]_2$: 3070 w, 3028 m, 2964 w, 2923 m, 2817 m, 1599 sh, 1589 m, 1574 s, 1534 vs, 1472 vs, 1455 vs, 1426 s, 1407 vs, 1393 vs, 1368 m, 1337 s, 1314 m, 1294 s, 1231 m, 1210 vw, 1182 m, 1146 m, 1110 m, 1076 w, 1060 m, 1015 vs, 978 vs, 889 m, 881 m, 837 s, 796 w, 762 vs, 744 s, 704 m, 692 m, 683 vs, 647 m, 611 vs, 600 vs, 569 m, 504 m, 454 m, 425 m, 403 vw.

The composition and structure of the ligand were determined from elemental analysis, IR spectroscopy, NMR spectroscopy, and XRD. The structure of the complex was solved using elemental analysis, mass spectrometry, IR spectroscopy, and XRD.

IR spectra were recorded on a FT-IR Perkin-Elmer Spectrum 100 instrument in Nujol in a range of 4000–400 cm^{-1} and in the attenuated total reflectance (ATR) mode in a range of 4000–650 cm^{-1}. ^{1}H, ^{13}C, and ^{15}N NMR spectra were detected on a Bruker Avance III instrument (400 MHz, 25°C, $CDCl_3$).

Mass spectra were measured on an Agilent 6520 Series Accurate-Mass Quadrupole Time-of-Flight (Q-TOF) LC/MS mass spectrometer. Solutions were injected into an ion source by the electrospray method (ESI) using a syringe pump at a flow rate of 0.01 mL/min. Data were collected and processed using the MassHunter Workstation Data Acquisition software (series 6200/6500, version B.01.03).

XRD of H_2L and **I** was carried out on an Xcalibur E diffractometer (MoK_α radiation, λ = 0.71073 Å, graphite monochromator, ω scan mode) at room temperature. The experimental data for compound **I** were refined taking into account a twin sample. The unit cell parameters were refined taking into account the full set of experimental data. The crystal structures were solved by direct methods and refined by least squares in the anisotropic full-matrix version for non-hydrogen atoms (SHELX-97) [15]. The positions of hydrogen atoms were partially calculated geometrically, partially determined in the Fourier syntheses, and isotropically refined by the rigid body model. The crystallographic data and experimental characteristics for H_2L and **I** are given in Table 1. Selected interatomic distances and bond angles are listed in Table 2. The geometric parameters of hydrogen bonds are given in Table 3.

Table 1. Crystallographic data and experimental characteristics for the structures of compounds H_2L and **I**

Compound	H_2L	**I**
Empirical formula	$C_{16}H_{15}N_3O_2$	$C_{34}H_{32}N_6O_8V_2$
FW	281.31	754.53
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a, Å	9.0853(18)	10.8850(8)
b, Å	9.970(2)	11.4822(8)
c, Å	16.0900(18)	15.9177(10)
α, deg	98.969(14)	72.427(6)
β, deg	98.833(13)	89.916(6)
γ, deg	90.033(18)	62.183(7)
V, Å^3	1422.2(5)	1654.3(2)
Z	4	2
ρ_{calc}, g/cm^3	1.314	1.515
μ, mm^{-1}	0.089	0.627
F(000)	592	776
Crystal sizes, mm	0.20 × 0.10 × 0.06	0.35 × 0.35 × 0.05
Range over θ, deg	3.03–25.25	2.90–25.05
Ranges of reflection indices	$-9 \le h \le 10$, $-7 \le k \le 11$, $-18 \le l \le 19$	$-9 \le h \le 12$, $-13 \le k \le 13$, $-18 \le l \le 18$
Number of measured/independent reflections (R_{int})	9234/5129 (0.0294)	6204/6204
Filling, %	99.8	99.7
Number of reflections with $I > 2\sigma(I)$	2714	3495
Number of refined parameters	379	456
GOOF	1.003	1.005
R factors ($I > 2\sigma(I)$)	$R_1 = 0.0422$, $wR_2 = 0.0774$	$R_1 = 0.0819$, $wR_2 = 0.1908$
R factors (for all data)	$R_1 = 0.0877$, $wR_2 = 0.0815$	$R_1 = 0.1334$, $wR_2 = 0.2103$
$\Delta\rho_{max}/\rho_{min}$, e Å^{-3}	0.191/–0.224	0.925/–0.736

The positional and thermal parameters for H_2L and **I** were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 2172124 and 2172125, respectively; deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

In order to synthesize new 3*d*-metal complexes with Schiff bases based on the INAH nucleophilic agent, we synthesized ligand H_2L using 1-phenyl-1,3-butanedione (Scheme 1) and new dimeric complex

Table 2. Selected interatomic distances and bond angles in compounds H_2L and **I***

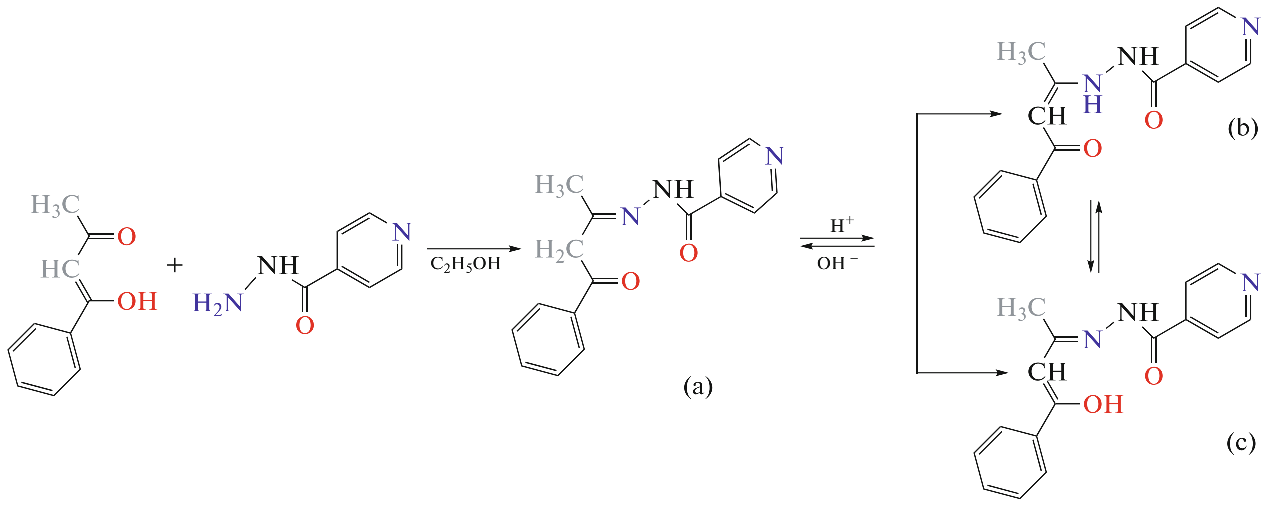
Bond	*d*, Å	Bond	*d*, Å
	H_2L		
O(1A)–C(6A)	1.227(2)	O(1B)–C(6B)	1.215(2)
C(6A)–N(2A)	1.333(2)	C(6B)–N(2B)	1.332(2)
N(2A)–N(3A)	1.386(2)	N(2B)–N(3B)	1.384(2)
N(3A)–C(7A)	1.341(2)	N(3B)–C(7B)	1.336(2)
C(7A)–C(8A)	1.366(2)	C(7B)–C(8B)	1.374(2)
C(8A)–C(9A)	1.420(3)	C(8B)–C(9B)	1.420(3)
C(9A)–O(2A)	1.246(2)	C(9B)–O(2B)	1.247(2)
	I		
V(1)–O(1A)	1.912(5)	V(2)–O(1B)	1.911(5)
V(1)–O(2A)	1.841(5)	V(2)–O(2B)	1.828(5)
V(1)–O(3A)	1.574(5)	V(2)–O(3B)	1.587(5)
V(1)–O(4A)	1.811(4)	V(2)–O(4B)	1.817(5)
V(1)–N(3A)	2.106(6)	V(2)–N(3B)	2.162(7)
V(1)–O(4A)$^{\#1}$	2.404(5)	V(2)–O(4B)$^{\#2}$	2.408(5)
O(1A)–C(6A)	1.317(8)	O(1B)–C(6B)	1.319(8)
C(6A)–N(2A)	1.314(9)	C(6B)–N(2B)	1.264(9)
N(2A)–N(3A)	1.385(8)	N(2B)–N(3B)	1.431(8)
N(3A)–C(7A)	1.247(9)	N(3B)–C(7B)	1.153(9)
C(7A)–C(8A)	1.424(10)	C(7B)–C(8B)	1.491(10)
C(8A)–C(9A)	1.357(10)	C(8B)–C(9B)	1.349(10)
C(9A)–O(2A)	1.339(8)	C(9B)–O(2B)	1.314(9)
Angle	**ω, deg**	**Angle**	**ω, deg**
	H_2L		
O(1A)C(6A)N(2A)	123.65(18)	O(1B)C(6B)N(2B)	124.14(18)
C(6A)N(2A)N(3A)	119.58(15)	C(6B)N(2B)N(3B)	120.53(16)
N(2A)N(3A)C(7A)	121.83(15)	N(2B)N(3B)C(7B)	121.15(16)
N(3A)C(7A)C(8A)	120.56(17)	N(3B)C(7B)C(8B)	121.20(18)
C(7A)C(8A)C(9A)	124.92(18)	C(7B)C(8B)C(9B)	124.56(18)
C(8A)C(9A)O(2A)	122.30(18)	C(8B)C(9B)O(2B)	122.85(18)
	I		
O(1A)V(1)O(2A)	153.2(2)	O(1B)V(2)O(2B)	153.3(2)
O(1A)V(1)O(3A)	98.1(3)	O(1B)V(2)O(3B)	97.0(3)
O(1A)V(1)O(4A)	94.7(2)	O(1B)V(2)O(4B)	93.9(2)
O(1A)V(1)N(3A)	75.0(2)	O(1B)V(2)N(3B)	76.3(2)
O(1A)V(1)O(4A)$^{\#1}$	81.98(19)	O(1B)V(2)O(4B)$^{\#2}$	83.01(19)
O(2A)V(1)O(3A)	100.4(3)	O(2B)V(2)O(3B)	101.4(3)
O(2A)V(1)O(4A)	99.9(2)	O(2B)V(2)O(4B)	100.8(2)

Table 2. (Contd.)

Angle	ω, deg	Angle	ω, deg
O(2A)V(1)N(3A)	83.5(2)	O(2B)V(2)N(3B)	82.5(2)
O(2A)V(1)O(4A)$^{\#1}$	81.5(2)	O(2B)V(2)O(4B)$^{\#2}$	80.3(2)
O(3A)V(1)O(4A)	102.6(2)	O(3B)V(2)O(4B)	102.3(2)
O(3A)V(1)N(3A)	97.4(3)	O(3B)V(2)N(3B)	96.3(2)
O(3A)V(1)O(4A)$^{\#1}$	174.3(2)	O(3B)V(2)O(4B)$^{\#2}$	174.9(2)
O(4A)V(1)N(3A)	158.6(2)	O(4B)V(2)N(3B)	160.0(2)
O(4A)V(1)O(4A)$^{\#1}$	71.76(19)	O(4B)V(2)O(4B)$^{\#2}$	72.6(2)
N(3A)V(1)O(4A)$^{\#1}$	88.07(19)	N(3B)V(2)N(4B)$^{\#2}$	88.65(18)
O(1A)C(6A)N(2A)	121.1(7)	O(1B)C(6B)N(2B)	123.7(7)
C(6A)N(2A)N(3A)	108.9(6)	C(6B)N(2B)N(3B)	111.1(6)
N(2A)N(3A)C(7A)	116.7(6)	N(2B)N(3B)C(7B)	117.1(7)
N(3A)C(7A)C(8A)	124.3(6)	N(3B)C(7B)C(8B)	119.6(7)
C(7A)C(8A)C(9A)	124.2(6)	C(7B)C(8B)C(9B)	124.5(7)
C(8A)C(9A)O(2A)	119.0(6)	C(8B)C(9B)O(2B)	121.4(7)

* Symmetry codes: $^{\#1}$ $-x + 1, -y + 1, -z + 1$; $^{\#2}$ $-x, -y, -z$ (**I**).

$[VO(L)(OCH_3)]_2$ formed due to the reaction with oxovanadium(IV) acetylacetonate. The tautomeric forms of H_2L obtained by the condensation of 1-phenyl-1,3-butanedione with INAH are shown in Scheme 1.



Scheme 1.

The IR and ^{1}H NMR spectral characteristics for the organic ligand [16] confirm the formation of H_2L in the more stable tautomeric form (a) [17].

The IR spectrum of H_2L exhibits medium-intensity absorption bands at 3200 cm^{-1} with a shoulder at the low-frequency side assigned to ν(NH) [18] and a series of lower-intensity absorption bands in a range of 3060–2800 cm^{-1} attributed to ν(C–H) of different origin: aromatic at 3058, 3038, and 3026 cm^{-1} and aliphatic at 2967, 2927, and 2837 cm^{-1} [19]. An intense

Table 3. Geometric parameters of hydrogen bonds in compounds H_2L and **I**

Contact D–H···A	Distance, Å			Angle DHA, deg	Coordinates of atoms A
	D–H	H···A	D···A		
		H_2L			
N(2A)–H(1)···O(1B)	0.86	2.05	2.820(2)	148	x, y, z
N(3A)–H(1)···O(2A)	0.86	1.99	2.650(2)	132	x, y, z
N(3A)–H(1)···O(2A)	0.86	2.31	2.963(2)	133	$-x + 1, -y + 1, -z + 2$
N(2B)–H(1)···O(1A)	0.86	2.05	2.816(2)	147	$x, y - 1, z$
N(3B)–H(1)···O(2B)	0.86	2.02	2.668(2)	132	x, y, z
N(3B)–H(1)···O(2B)	0.86	2.28	2.926(2)	132	$-x, -y, -z + 2$
C(16B)–H(16E)···O(1A)	0.96	2.66	3.482(2)	145	$x, y - 1, z$
		I			
C(17A)–H(17B)···N(1A)	0.96	2.68	3.568(10)	155	$x + 1, y - 1, z$
C(17A)–H(17C)···O(3A)	0.96	2.53	3.036(9)	1113	x, y, z
C(17A)–H(17C)···O(3B)	0.96	2.65	3.213(8)	156	$-x + 1, -y, -z + 1$
C(13A)–H(13A)···O(3A)	0.93	2.48	3.263(8)	132	$-x + 1, -y, -z + 1$
C(17B)–H(17E)···N(3B)	0.96	2.68	3.349(9)	127	$-x, -y, -z$
C(17B)–H(17F)···N(1A)	0.96	2.63	3.553(11)	161	$-x, -y + 1, -z + 1$

absorption band appears at 1664 cm^{-1} and can be ascribed to associated ν(C=O) [20]. Absorption bands at 1596, 1574, 1507, and 1483 cm^{-1} are attributed to planar skeletal vibrations (C=C) in the aromatic rings of H_2L [19]. An absorption band at 1528 cm^{-1} can be ascribed to the amide **II** vibrations (δ(NH) + ν(C–N)) [19]. The methyl groups absorb at 1431 cm^{-1} ($\delta_{as}(CH_3)$) and 1378 cm^{-1} ($\delta_s(CH_3)$) [21].

The positions of the δ(C–H) planar vibration absorption bands in aromatic compounds depend on the type of substitution and are specific [21]. The spectrum of the 1-substituted cycle (five unsubstituted adjacent hydrogen atoms) contains absorption bands at 1086 and 1063 cm^{-1}, whereas the spectrum of the 1,4-substituted aromatic cycle (two unsubstituted adjacent hydrogen atoms) exhibits one band at 1214 and two bands at 1039 and 1027 cm^{-1}, respectively [21]. Nonplanar C–H vibrations in aromatic rings also express the type of substitution, but the bands are substantially more intense in this case: the bands at 714 and 664 cm^{-1} are observed for the 1-substituted ring (five unsubstituted adjacent hydrogen atoms), whereas the band at 833 cm^{-1} is observed for the 1,4-substituted ring (two unsubstituted adjacent hydrogen atoms).

The ^1H NMR spectrum of compound H_2L exhibits eight groups of lines that were assigned to protons (δ, ppm) of one CH_3 group (2.10 s), one CH_2 group (3.02–3.38 d), and one NH group (5.32 s); five signals of the hydrogen atoms of the phenyl group (7.28–7.49) and four signals of the hydrogen atoms belonging to the pyridine ring (7.78–8.76).

To confirm that both tautomeric forms of H_2L exist indeed (Scheme 1a and 1b), a droplet of trifluoroacetic acid was added to the sample containing H_2L dissolved in $CDCl_3$, after which the ^1H NMR spectrum was repeatedly detected. The band of the protons of the =CH– group (δ = 6.30 ppm (s)) enhanced in the spectrum, indicating the shift of the equilibrium toward the formation of tautomeric form (b), the concentration of which increased with decreasing pH of the medium [17].

The data of the ^{13}C NMR spectrum of a solution of compound H_2L indicate 16 carbon atoms, since the spectrum contains the lines belonging to one carbon atom of the CH_3 group (16.1 ppm), one carbon atom of the CH_2 group (53.8 ppm), and five carbon atoms of the pyridyl group: two carbon atoms in positions 2 and 6 (149.72 ppm), two carbon atoms in positions 3 and 5 (123.5 ppm), and one quaternary carbon atom (141.2 ppm); and six carbon atoms of the phenyl group: two in *ortho*- (123.9 ppm), two in *meta*- (128.8 ppm), and one in *para*-position (128.3 ppm) and one quaternary carbon atom (94.6 ppm). The ^{13}C NMR spectrum also contains lines characteristic of one azomethine carbon atom (143.03 ppm) and two

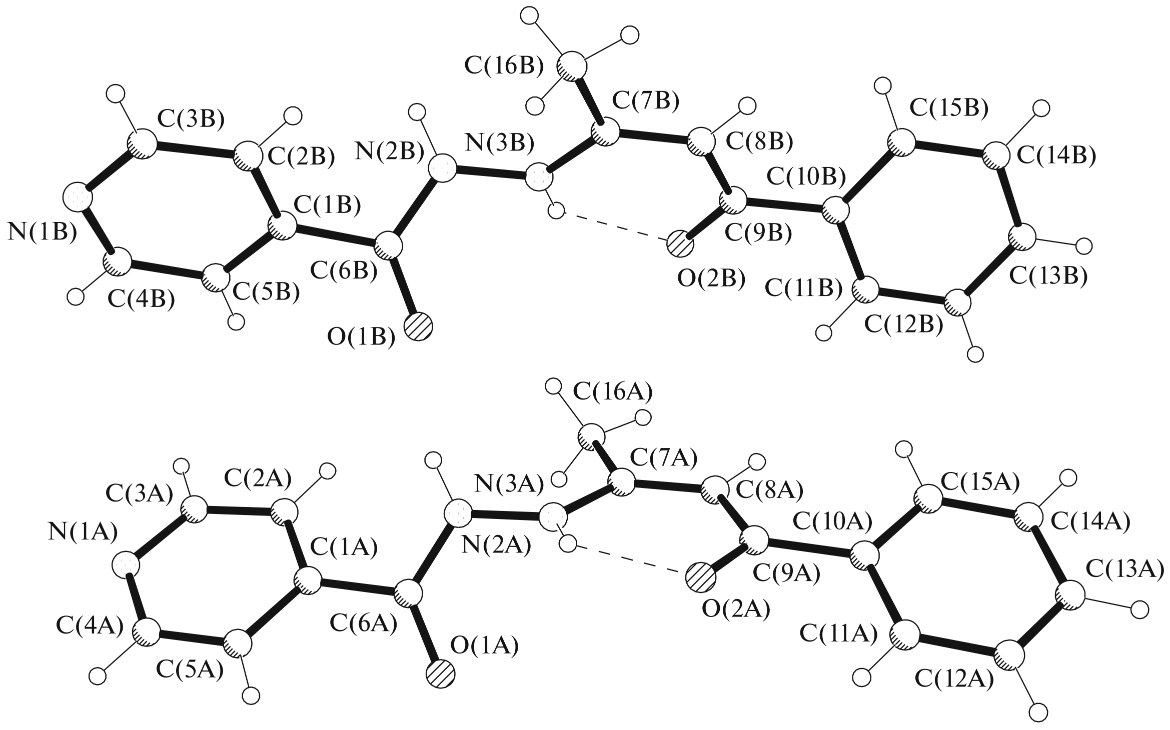


Fig. 1. Structures of crystallographically independent molecules **A** and **B** in the crystal of compound H_2L.

carbon atoms of the carbonyl groups belonging to 1-phenyl-1,3-butanedione (156.4 ppm) and INAH (165.5 ppm).

The ^{15}N NMR spectrum of a solution of compound H_2L contains two lines, which confirm the presence of two nitrogen atoms: =N– (213 ppm) and –NH– (315 ppm) (Bruker scale) [22].

The doubly deprotonated L^{2-} ligand is stabilized in the tautomeric form (c) during the coordination of H_2L to the vanadium ions. This fact is confirmed by the IR spectral and XRD data.

Unlike the spectrum of H_2L, the IR spectrum of $[VO(L)(OCH_3)]_2$ exhibits no absorption bands at 3220 (ν(NH)) and 1664 cm^{-1} (ν(C=O)). The most intense band appears at 978 cm^{-1} and is assigned to ν(V=O) [23–25]. Absorption bands of skeletal vibrations (ν(C=C), ν(C=N)) of the bonds of the aromatic rings are observed at 1599, 1589, 1574, and 1456 cm^{-1} [19]. The planar bending vibrations (δ(C–H)) of the 1-substituted ring appear at 1146 and 1076 cm^{-1}, and those of the 1,4-substituted ring are observed at 1231 and 1060 cm^{-1}. The nonplanar δ(C–H) vibrations of the 1-substituted aromatic rings are observed at 762 and 681 cm^{-1}, and those for the 1,4-substituted benzene ring are observed at 837 cm^{-1} [20, 21].

The metallocycles with electron delocalization are formed in the $[VO(L)(OCH_3)]_2$ complex and, hence, the spectrum exhibits absorption bands at 1574 and 1534 cm^{-1} attributed to ν(C$\overset{...}{-}$C) + ν(C$\overset{...}{-}$O) and ν(C$\overset{...}{-}$O) + ν(C$\overset{...}{-}$C), respectively [26, 27]. An absorption at 921 cm^{-1} can be ascribed to ν[V–(μ-O)–V] [23], that at 600 cm^{-1} is attributed to ν(V–N) [21], and that at 454 cm^{-1} belongs to ν(V–O) mixed with the C–CH_3 bending vibration, whereas a lower-frequency band at 425 cm^{-1} can be assigned to an almost unmixed stretching vibration ν(V–O) [24, 26].

The electron impact mass spectrum of a chloroform–methanol solution of $[VO(L)(OCH_3)]_2$ exhibits an intense peak at m/z = 378.15 corresponding to the doubly protonated ion $[M + 2H]^{2+}$ and two low-intensity peaks at m/z = 400.13 and 777.22 corresponding to the $[M + 2Na]^{2+}$ and $[M + Na]^{+}$ ions (M is molecular weight of $C_{34}H_{32}N_6O_8V_2$).

The XRD study of H_2L shows that the compound crystallizes in the triclinic space group $P\bar{1}$ (Table 1), and its structure is presented in Fig. 1. The independent part of the unit cell contains two crystallographically independent molecules (**A** and **B**), which are stabilized in the crystal in the same tautomeric form (b). This fact is also confirmed by the C(6)–O(1), C(6)–N(2), N(2)–N(3), C(7)–N(3), C(7)–C(8), C(8)–C(9), and C(9)–O(2) distances between the atoms in the central fragments of molecules **A** and **B** (Table 2). An analysis of the Cambridge Structural Database (CSD) [4] shows that this compound is known, but another polymorphic form crystallizes in

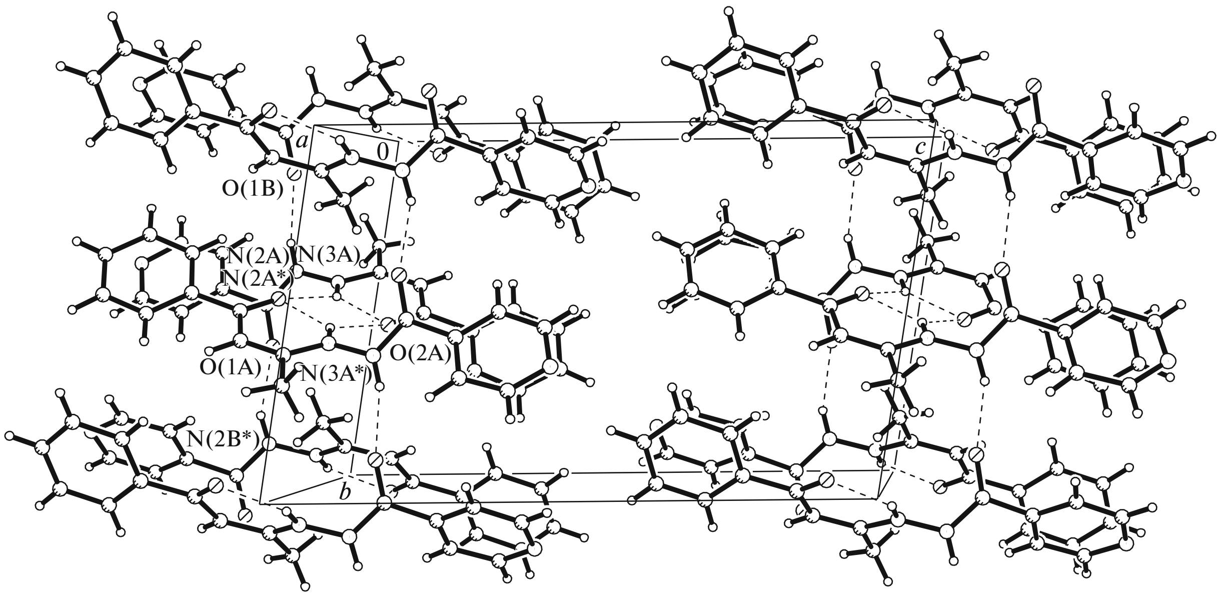


Fig. 2. Fragment of the crystal structure of compound H_2L.

the monoclinic space group $P2_1/c$ [22]. The same tautomeric form (b) was stabilized for H_2L in both the latter and our case. The conformation of the ligand allows it to coordinate to the metal as a tridentate chelate ligand using a set of donor atoms ONO (Fig. 1).

Strong intramolecular hydrogen bonds N(3)–H···O(2) can be emphasized in molecules **A** and **B** in the crystal of H_2L. One of two NH groups is involved as a donor in these hydrogen bonds (Table 3, Fig. 1) stabilizing their configuration by the formed pseudohexacycles. In addition, both molecules **A** and **B** are linked to each other by the intermolecular hydrogen bonds N(3)–H···O(2) (Table 3, Fig. 2). The second NH groups of molecules **A** and **B** participate in the formation of intermolecular hydrogen bonds N(2A)–H···O(1B) and N(2B)–H···O(1A) to form chains, and these molecules are additionally combined by weak intermolecular hydrogen bonds C(16B)–H···O(1A).

Molecular binuclear complex $[VO(L)(OCH_3)]_2$ (**I**) synthesized by the reaction of H_2L with $VO(Acac)_2$ (molar ratio 1 : 1) in a methanol medium crystallizes in the triclinic space group $P\overline{1}$ (Table 1). The independent part of the unit cell contains two 1/2 crystallographically independent vanadium(V) complexes **A** and **B**. The structures of these centrosymmetric complexes are shown in Fig. 3.

Two conjugated metallocycles are formed due to the coordination of one tridentate bideprotonated organic ligand L^{2-} to each metal atom via the ONO donor atoms: five-membered VNNCO metallocycle and six-membered VOCCCN metallocycle. The formation of the identical coordination metal polyhedra of V(1) and V(2) is supplemented by one oxo anion and two oxygen atoms of the deprotonated methanol ligands, which combine two metal atoms, and their bridging function induces the formation of dimers in the crystal (Figs. 3a, 3b). Since one methoxy anion lies in the equatorial plane of the polyhedron, another methoxy atom is localized in one of the axial positions, and the second axial position is occupied by the oxy atom, the coordination number of the metals is 4 + 1 + 1 and their coordination polyhedra in these complexes are square bipyramids. The V=O bond lengths in the V(1) and V(2) coordination polyhedra are 1.574(5) and 1.587(5) Å, respectively, and the V–OCH_3 bond lengths in **A** and **B** are 1.811(4), 2.404(5) and 1.817(5), 2.408(5) Å, respectively (Table 2). The V···V distance between two vanadium atoms in the centrosymmetric dimers is 3.432 and 3.422 Å. Note that these complexes are stabilized additionally by different intramolecular hydrogen bonds C(17A)–H···O(3A) and C(17B)–H···N(3B), respectively (Table 3). The bond lengths and bond angles in the V(1) and V(2) coordination polyhedra are close to analogous values in the mono- and binuclear complexes of this metal with tridentate 2,4-pentanedione isonicotinoyl hydrazone [6, 7]. The bond lengths in the central moieties of molecules H_2L and in organic ligands L^{2-} in compound **I** (Table 2) differ slightly, and higher values of some C=O groups indicate the stabilization of the coordinated ligand in tautomeric form (c).

An analysis of the crystal structure of compound $[VO(L)(OCH_3)]_2$ shows that the supramolecular architecture is formed only due to weak intermolecular hydrogen bonds involving the CH groups of both

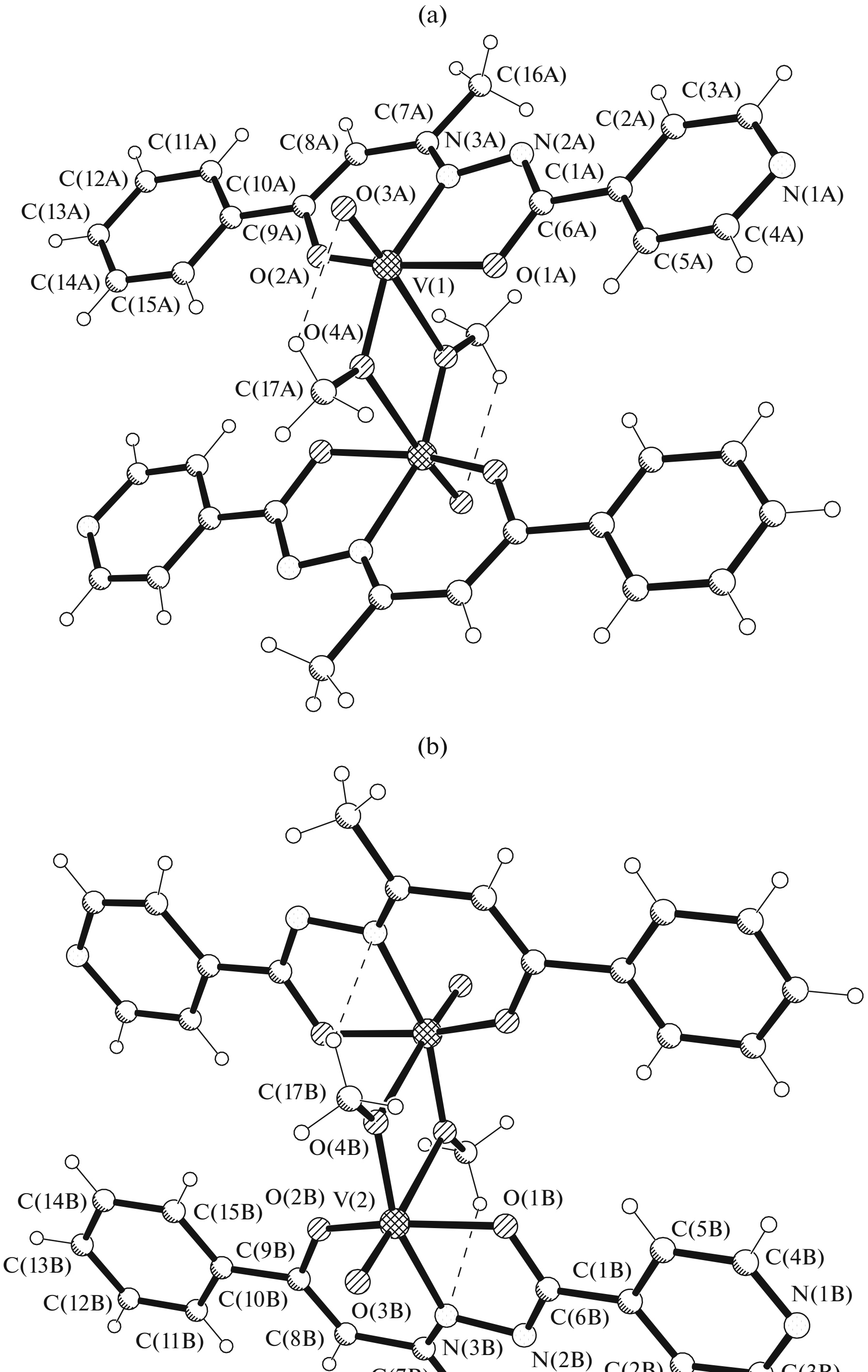


Fig. 3. Structures of the crystallographically independent vanadium(V) complexes in compound **I**.

methyl and phenyl groups as donors. Complexes **A** are linked to each other by weak intermolecular hydrogen bonds C–H···O to form a layer, and complexes **B** are combined by the same weak bonds with the latter (Table 3). In the layers of crystalline complexes **A**, chains can be emphasized between which complexes **B**

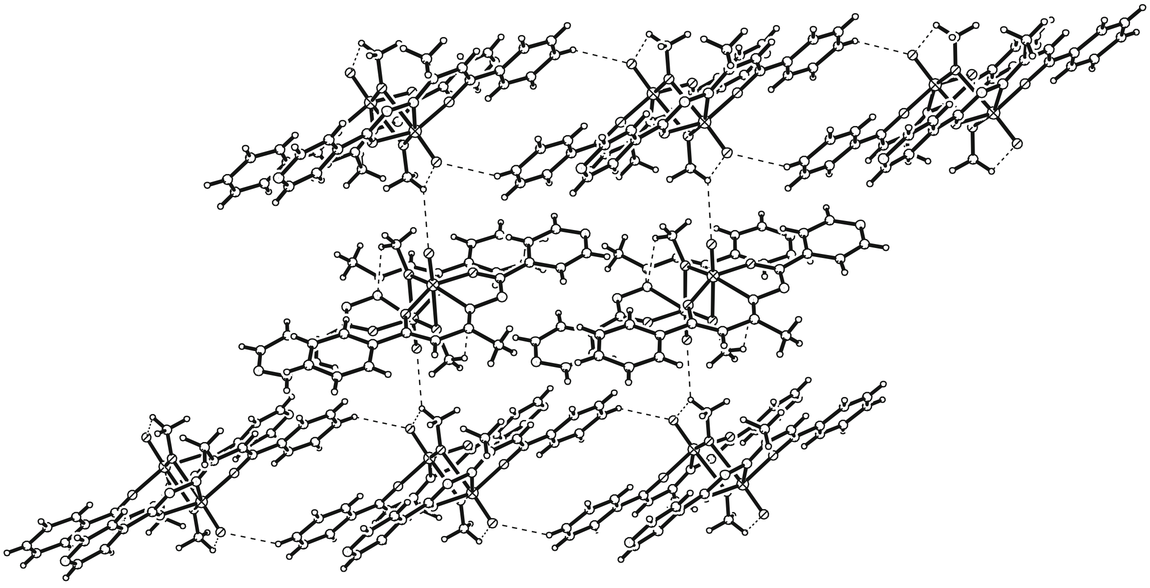


Fig. 4. Packing of vanadium(V) complexes (a) **A** and (b) **B** in the crystal.

are located and linked by the hydrogen bonds C—H···O to form a layer of alternating complexes **A** and **B** (Fig. 4).

Thus, the condensation of INAH with 1-phenyl-1,3-butanedione afforded another polymorphic form of organic ligand H_2L used for the synthesis of the new binuclear vanadium(V) complex. Different tautomeric forms of the ligand are stabilized in the crystal states of H_2L and coordinated L^{2-} in the vanadium(V) complexes.

FUNDING

This work was carried out in terms of two state assignments (2020–2023) financed by the National Agency for Research and Development of Republic of Moldova: "Applications of Principles of Crystal Engineering and X-ray Crystallography for Design and Preparation of Crystalline Hybrid Organic/Inorganic Materials with Promising Physical and Bioactive Functions" (project no. 20.80009.5007.15) and "Development of New Multifunctional Materials and Efficient Technologies for Agriculture, Medicine, and Technology and Formation System Based on Metal Complexes with *s* and *d* Metals with Polydentate Ligands" (project no. 20.80009.5007.28).

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

1. Gad, S.C. and Pham, T., *Encyclopedia of Toxicology*, New York: Academic, 2014, p. 909.
2. Krakowiak, J., Lundberg, D., and Persson, I., *Inorg. Chem.*, 2012, vol. 51, no. 18, p. 9598.
3. Rehder, D., *Angew. Chem., Int. Ed. Engl.*, 1991, vol. 30, p. 148.
4. Allen, F.H., *Acta Crystallogr., Sect. B: Struct. Sci.*, 2002, vol. 58, p. 380.
5. Nandy, M., Shit, S., Rizzoli, C., et al., *Polyhedron*, 2015, vol. 88, p. 63.
6. Monfared, H.H., Kheirabadi, S., Lalami, N.A., and Mayer, P., *Polyhedron*, 2011, vol. 30, p. 1375.
7. Monfared, H.H., Farrokhi, A., Alavi, S., and Mayer, P., *Transition Met. Chem.*, 2013, vol. 38, p. 267.
8. Yadav, S., Yousuf, I., Usman, M., et al., *RSC Adv.*, 2015, vol. 5, p. 50673.
9. Hosseini-Monfared, H., Bikas, R., Sanchiz, J., et al., *Polyhedron*, 2013, vol. 61, p. 45.
10. Bourosh, P., Bulhac, I., Mirzac, A., et al., *Russ. J. Coord. Chem.*, 2016, vol. 42, no. 3, p. 157. https://doi.org/10.1134/S1070328416030015
11. Croitor, L., Cocu, M., Bulhac, I., et al., *Polyhedron*, 2021, vol. 206, p. 115329.
12. Danilescu, O., Bulhac, I., Shova, S., et al., *Russ. J. Coord. Chem.*, 2020, vol. 46, no 12, p. 838. http://doi.org./10.1134/S1070328420090018
13. Cocu, M., Bulhac, I., Coropceanu, E., et al., *J. Mol. Struct.*, 2014, vol. 1063, p. 274.
14. Rotaru, M. and Cocu, M., *Acta et Comment. seria Științe Exacte și ale Naturii*, 2017, no. 1(3), p. 136.
15. Sheldrick, G.M., *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, no. 1, p. 112.
16. Tarasevich, B.N., *IK spektry osnovnykh klassov organicheskikh soedinenii. Spravochnye materialy* (IR Spectra of Main Classes of Organic Compounds. Reference Data), Moscow, MGU, 2012.

17. Hernández-Molina, R. and Mederos, A., *Comprehensive Coordination Chemistry*, *II*, 2003, p. 411. https://doi.org/10.1016/B0-08-043748-6/01070-7
18. Bellamy, L.J., *The Infrared Spectra of Complex Molecules*, New York: Wiley, 1958.
19. Kazitsyna, L.A. and Kupletskaya, N.B. *Primenenie UF-, IK- i YaMR-spektroskopii v organicheskoi khimii* (Apllications of UV, IR, and NMR Spectroscopy in Organic Chemistry), Moscow: Vyssh. shkola, 1971.
20. Nakanishi, K., *Infrared Absorption Spectroscopy—Practical*, Tokyo: Holden-Day, 1963.
21. Adams, D.M., *Metal–Ligand and Related Vibrations: A Critical Survey of the Infrared and Raman Spectra of Metallic and Organometallic Compounds*, Ltd. London, 1967.
22. Bikas, R., Anarjan, P.M., Aslekhademi, S., et al., *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2012, vol. 68, p. o412.
23. Kolawole, G.A. and Osowole, A.A., *J. Coord. Chem.*, 2009, vol. 62, no. 9, p. 1437.
24. Monfared, H.H., Kheirabadi, S., Lalami, N.A., and Mayer, P., *Polyhedron*, 2011, vol. 30, p. 1375.
25. Nakamoto, K., *Infrared Spectra and Raman Spectra of Inorganic and Coordination Compounds*, New York: Wiley, 1986.
26. Koksharova, T.V., *Visnik ONU. Khimiya*, 2014, vol. 19, no. 50, p. 27.
27. Bovey, F.A., *Nuclear Magnetic Resonance Spectroscopy*, New York: Academic, 1988, p. 461.

Translated by E. Yablonskaya