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Synthesis and Structure of Cobalt(II) Complexes with Nitrilotris(methylenephosphonic) Acid $[Co(H_2O)_3\{NH(CH_2PO_3H)_3\}]$ and $Na_4[Co\{N(CH_2PO_3)_3\}]\cdot 13H_2O$

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Abstract—Nitrilotris(methylenephosphonato)triaquacobaltum(II) and tetrasodium nitrilotris(methylenephosphonato)cobaltate(II) tridecahydrate were synthesized and studied. The crystals of $[Co(H_2O)_3\{NH(CH_2PO_3H)_3\}]$ (**I**) are monoclinic, space group $P2_1/c$, $Z = 4$, $a = 9.2092(2)$, $b = 16.0540(2)$, $c = 9.7445(2)$ Å, $\beta = 115.778(3)°$. The coordination polyhedron of cobalt is a distorted octahedron formed by oxygen atoms. The organophosphorus ligand bridges the neighboring cobalt atoms. The crystals of $Na_4[Co\{N(CH_2PO_3)_3\}]\cdot 13H_2O$ (**II**) are triclinic, space group, $P\bar{1}$, $Z = 2$, $a = 11.2240(8)$, $b = 11.2663(8)$, $c = 12.3296(8)$ Å, $\alpha = 108.513(6)°$, $\beta = 97.261(6)°$, $\gamma = 117.056(7)°$. The cobalt atom is coordinated to form a distorted trigonal bipyramid. Complex **II** is a chelate in which the cobalt atom closes three five-membered N–C–P–O–Co rings sharing the Co–N bond. The Co atom is incorporated in the Co–O–Co–O ring. Upon dissolution in water, this ring is opened and cobalt(II) atom is hydrolyzed.

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INTRODUCTION

The paramagnetic Co^{2+} ion with the $3d^7$ configuration is efficiently stabilized in various ligand field configurations. As a result, coordination compounds of cobalt(II) are distinguished by structural diversity and have a high practical value. Cobalt(II) complexes with organophosphonic acids are biologically active compounds and catalysts [1]. The magnetic properties of cobalt(II) phosphonate complexes are diverse and depend on their structure [2]. The Co(II) coordination compounds with 1-hydroxyethylidenediphosphinic acid stabilized by tetra- and pentadiamines are linear [3]. The cobalt(II) complexes with phosphonohydroxyacetic [4, 5], phosphonomethyliminodiacetic [6], and benzyliminodiphosphonic [7] acids are two-dimensional layered structures. The Co(II) compound with ethylenediphosphonic acid has a structure of three-dimensional framework with flattened nanosized through channels [8]. Cobalt metal is one of the most important doping elements of dispersion-hardening steels and hard-magnetic alloys [9]. In view of the fact that organopolyphosphonic acids find wide use as corrosion inhibitors for steel [10, 11], the structures of the products of reactions of organopolyphosphonic acids with the Co^{2+} are of obvious interest for applied tasks of corrosion protection of materials. Nevertheless, the structure and properties of Co(II) complexes with organopolyphosphonic acids are far from being adequately investigated. Indeed, out of the 1439 references concerning coordination compounds of cobalt in a fundamental monograph in coordination chemistry [12], only one reference is to Co(II) compound with organophosphorus oxoanion [13].

The Co(II) complexation with nitrilotris(methylenephosphonic) acid $N(CH_2PO_3)H_6$ (NTP) was studied by NMR [14]. Some of the complexes were isolated and investigated by optical spectroscopy [15] but their crystal structures were not determined. According to powder X-ray diffraction [16], one of cobalt(II) complexes with NTP is isostructural to the corresponding complexes with Mn(II), Ni(II), Cu(II), Zn, and Cd in which the metal atoms are coordinated to oxygen atoms at the octahedron vertices. However, the structure and the properties of complexes formed by NTP with Zn [17, 18] and Cu(II) [19, 20] in acidic and alkaline media are considerably different. Spectroscopic investigations of the reaction between Co^{2+} and NTP over a broad pH range [21] also attest to different structures of the complexes in acidic and alkaline media. In [21], structure models for the Co(II) complexes of NTP in acidic and alkaline media were proposed relying on the hypothesis that the Co^{2+} and Ni^{2+} complexes are isostructural. These models differ from the models proposed in [16, 17] by inclusion of the nitrogen atom into the octahedral coordination sphere of the metal. However, earlier, M.A. Porai-Koshits and co-workers [22], who performed X-ray diffraction study of Co^{2+} and Ni^{2+} complexes with ethylenediaminetetraacetic acid, demonstrated [23] that the structural analogy between complexes of these metals is limited: in a number of cases, cobalt(II) is coordinated in a seven-vertex configuration unlike nickel, which has an octahedral coordination. In a known Co complex with 4,4,10,10-tetramethyl-1,3,7,9-tetraazaspiro[5.5]undecane-2,8-dione [24], the metal atom is coordinated by five oxygen atoms in the trigonal bipyramid geometry. According to spectroscopic data, this structure is fairly labile and, upon hydration, water molecule is incorporated in the inner coordination sphere of cobalt. The opinion stated in [21] that complex formation in acid media would involve the coordination of the N(NTP) atom to Co(II) atom seems unreasonable. Thus, the structure of Co(II) coordination compounds with NTP is currently a debatable issue and, hence, a direct experimental study of this structure appears pertinent.

This communication describes the synthesis and X-ray diffraction structure determination for two cobalt(II) complexes with NTP (1 : 1).

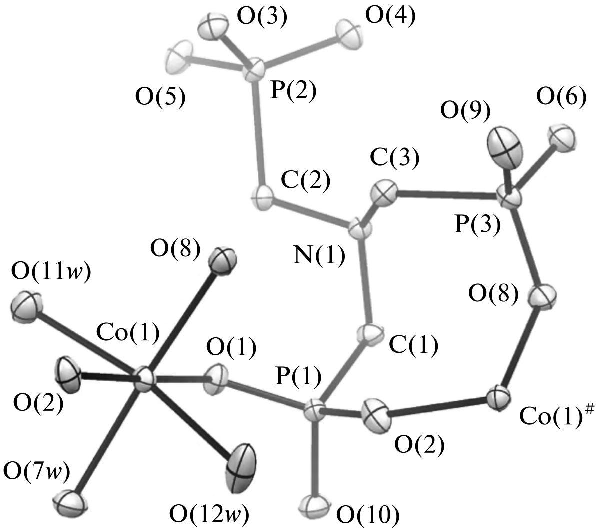

Fig. 1. Fragment of structure **I** ($^{\#}$ x, $1/2 - y$, $1/2 + z$).

EXPERIMENTAL

Synthesis of nitrilotris(methylenephosphonatotriaquacobalt(II), [Co(H$_2$O)$_3$(NTP)] (I). A stoichiometric amount of a 0.1 M aqueous solution of NTP (imp., twice recrystallized) was added dropwise with continuous vigorous stirring to a 0.1 M aqueous solution of reagent grade CoCl$_2$ until a transparent bright pink-colored solution of **I** formed. The complex was crystallized from the solution upon slow solvent evaporation. The crystals were washed with water containing 45% of ethanol. The monoclinic crystals of **I** were transparent and had an intense pink color.

Synthesis of tetrasodium nitrilotris(methylenephosphonato)cobaltate(II) tridecahydrate Na$_4$[Co(NTP)] · 13H$_2$O (II). A slight excess of reagent grade NaOH was added dropwise at 90–100°C with continuous vigorous stirring to a 0.1 M aqueous solution of CoCl$_2$ to precipitate Co(OH)$_2$. After Co(OH)$_2$ was washed up to complete removal of chloride ions, an equimolar amount of a 0.1 M aqueous solution of tetrasodium NTP salt was added until a transparent dark violet-colored solution of **II** formed. The complex was crystallized from the solution upon slow solvent evaporation. The crystals were washed with water containing 45% of ethanol. The crystals of **II** were transparent and violet-blue-colored.

UV/Vis spectra were recorded on an SF-56 spectrophotometer in the 190–1100 nm range in quartz cells with 1 cm-thick absorption layer; aqueous solutions of **I** and **II** and a mineral oil mull of **II** were used.

The Raman spectra of the Co(NTP) crystals were recorded in the 470–570 nm range on a Centaur U-HR microscope/microspectrometer with laser excitation at $\lambda = 473$ nm.

X-ray diffraction. The crysrallographic characteristics and details of the X-ray diffraction experiment and structure refinement for **I** and **II** are summarized in Table 1.

The primary fragments of the atomic structures of **I** and **II** were found by the direct method. The atom (including hydrogen) positions were determined using the difference Fourier electron density maps and refined by the least squares method on $|F|^2$. The hydrogen atom parameters for **I** were refined in the isotropic approximation without constraints together with other structure parameters. Some hydrogen atom parameters in the atomic structure of **II** were subject to constraints; the isotropic thermal parameters of the hydrogen atoms were considered equivalent.

The X-ray diffraction data are deposited with the Cambridge Crystallographic Data Centre (CCDC no. 1046179 (**I**), 1046190 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCISSION

Figure 1 shows the structure of compound **I**. The interatomic distances and bond angles are summarized in Table 2. Each of the three phosphonate groups of the NTP ligand is monoprotonated (–PO$_2$OH). The nitrogen atom (also protonated) does not participate in Co coordination. Thus, in the electrically neutral complex **I**, the NTP ligand occurs as the zwitterion, as in the free NTP molecule [28]. The cobalt atom is coordinated at the vertices of a distorted octahedron. The Co coordination environment includes two oxygen atoms of different phosphonate groups of NTP (with closure of the Co–O–P–C–N–C–P–O chelate ring), an oxygen atom of the neighboring NTP molecule, and three water oxygen atoms (two of these occupy axial positions). One phosphonate group of

Table 1. Crystallographic characteristics and X-ray experiment and structure refinement details

Parameter	Value	
	I	**II**
M	406.98	678.09
System, space group, Z	Monoclinic, $P2_1/c$, 4	Triclinic, $P\overline{1}$, 2
a, Å	9.2092(2)	11.2240(8)
b, Å	16.0540(2)	11.2663(8)
c, Å	9.7445(2)	12.3296(8)
α, deg	90	108.513(6)
β, deg	115.778(3)	97.261(6)
γ, deg	90	117.056(7)
V, Å^3	1297.30(5)	1247.09(17)
ρ(calcd.), g/cm^3	2.084	1.806
Radiation; λ, Å	MoK_α; 0.71073	
μ, mm^{-1}	1.755	1.041
T, K	293(2)	293(2)
Sample size, mm	0.23 × 0.12 × 0.10	0.18 × 0.12 × 0.10
Diffractometer	Xcalibur, Sapphire III, Gemini S	
Scan mode	ω-scan	
Absorption connection, T_{min}/T_{max}	Empirical, Multi-scan 0.791/0.885	Empirical, Multi-scan 0.51841/1
$\theta_{min}/\theta_{max}$, deg	3.594/35.104	3.676/33.099
Ranges of h, k, l	$-14 \le h \le 14$, $-25 \le k \le 25$, $-15 \le l \le 15$	$-13 \le h \le 16$, $-17 \le k \le 15$, $-18 \le l \le 17$
The number of reflections measured/independent (N_1)	33238/5468	11359/7803
R_{int}	0.0265	0.0598
The number of reflections with $I > 2\sigma(I)$ (N_2)	4977	4470
Refinement method	Full-matrix least squares on F^2	
The number of parameters	233	404
S	1.087	0.941
R_1, wR_2 for N_1	0.0300, 0.0704	0.1238, 0.1131
R_1, wR_2 for N_2	0.0258, 0.0684	0.0600, 0.0882
$\Delta\rho_{min}/\Delta\rho_{max}$, e/Å^3	−0.342/0.855	−0.857/0.923
Software	CrysAlisPro [25], SHELX [26], WinGX [27]	

NTP does not participate in Co coordination. Complex **I** has a polymeric structure formed by zigzag-like chains $[-Co(H_2O)_3{=}NTPH_4-]_n$ arranged along the [001] direction.

The structure of **I** bears a similarity to the structure of the previously studied copper complex $[Cu(H_2O)_3(NTP)]$ (**III**) [20]. However, the properties of **I** differ substantially from the properties of copper complex **III**. Indeed, **III** is readily water-soluble, which is attributable to the 16% elongation of the Cu(II) coordination polyhedron (the axial Cu–O bond lengths are, on average, 2.30 Å, while these lengths in equatorial positions are 1.99 Å) due to the Jahn–Teller effect [29]. This weakens the Cu–O bonds in the polymer chain, resulting in easy dissolution of the coordination polymer. In cobalt complex **I**, the oxygen octahedron is compressed by 3.3%, which leads to poor solubility of the coordination polymer in water.

Figure 2 shows a fragment of **II**; the bond lengths and bond angles are given in Table 3. The NTP ligand is fully deprotonated including the N atom, which forms a donor–acceptor bond with cobalt. The metal atom has a distorted trigonal bipyramidal geometry, one axial site being occupied by nitrogen, the base being formed by oxygen atoms of three different phos-

Table 2. Interatomic distances (*d*) and bond angles (ω) in **I***

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
Co(1)–O(1)	2.0668(9)	N(1)–C(2)	1.5053(15)	P(1)–O(10*H*)	1.5693(10)
Co(1)–O(2)#	2.0442(9)	N(1)–C(3)	1.5014(15)	P(2)–O(3)	1.5173(9)
Co(1)–O(7*w*)	2.1086(11)	C(1)–P(1)	1.8291(12)	P(2)–O(4)	1.4982(10)
Co(1)–O(8)	2.1171(10)	C(2)–P(2)	1.8324(12)	P(2)–O(5*H*)	1.5654(10)
Co(1)–O(11*w*)	2.1587(11)	C(3)–P(3)	1.8254(12)	P(3)–O(6)	1.5036(10)
Co(1)–O(13*w*)	2.0887(12)	P(1)–O(1)	1.5004(9)	P(3)–O(8)	1.5031(10)
N(1)–C(1)	1.5108(15)	P(1)–O(2)	1.4979(10)	P(3)–O(9*H*)	1.5654(10)
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
O(1)Co(1)O(2)#	177.02(4)	O(7)Co(1)O(13)	84.95(6)	O(8)P(3)C(3)	110.30(6)
O(1)Co(1)O(7)	93.27(4)	O(8)Co(1)O(11)	99.45(4)	O(9*H*)P(3)C(3)	99.02(6)
O(1)Co(1)O(8)	90.90(4)	O(8)Co(1)O(13)	89.67(5)	O(1)P(1)O(10)	109.60(6)
O(1)Co(1)O(11)	90.77(4)	O(11)Co(1)O(13)	169.86(5)	O(2)P(1)O(10)	110.70(6)
O(1)Co(1)O(13)	93.53(4)	O(1)P(1)C(1)	110.12(5)	O(1)P(1)O(2)	115.58(6)
O(2)Co(1)O(7)	86.75(4)	O(2)P(1)C(1)	109.54(6)	O(3)P(2)O(4)	115.37(6)
O(2)Co(1)O(8)	89.36(4)	O(10*H*)P(1)C(1)	100.21(6)	O(3)P(2)O(5)	107.17(5)
O(2)Co(1)O(11)	86.26(5)	O(3)P(2)C(2)	109.10(5)	O(4)P(2)O(5)	112.66(6)
O(2)Co(1)O(13)	89.44(5)	O(4)P(2)C(2)	107.49(6)	O(6)P(3)O(8)	114.98(6)
O(7)Co(1)O(8)	173.38(4)	O(5*H*)P(2)C(2)	104.48(5)	O(6)P(3)O(9)	112.08(6)
O(7)Co(1)O(11)	85.64(5)	O(6)P(3)C(3)	108.66(6)	O(8)P(3)O(9)	110.61(6)

* Symmetry codes : # *x*, 1/2 – *y*, 1/2 + *z*.

phonate groups of the ligand, and the other axial site being occupied by oxygen of the neighboring NTP residue. The Co coordination to NTP closes three five-membered chelate rings, N–Co–O–P–C, sharing the N–Co bond. The geometrical parameter τ [30] for the Co(II) environment is 0.63 (τ = 0 corresponds to an ideal tetragonal pyramid, τ = 1 corresponds to an ideal trigonal bipyramid). Thus, **II** has an island structure formed by dimeric complex anions $[Co(NTP)]_2^{8-}$, in which the coordination polyhedra of cobalt connected by shared edges form a planar parallelogram Co–O–Co–O.

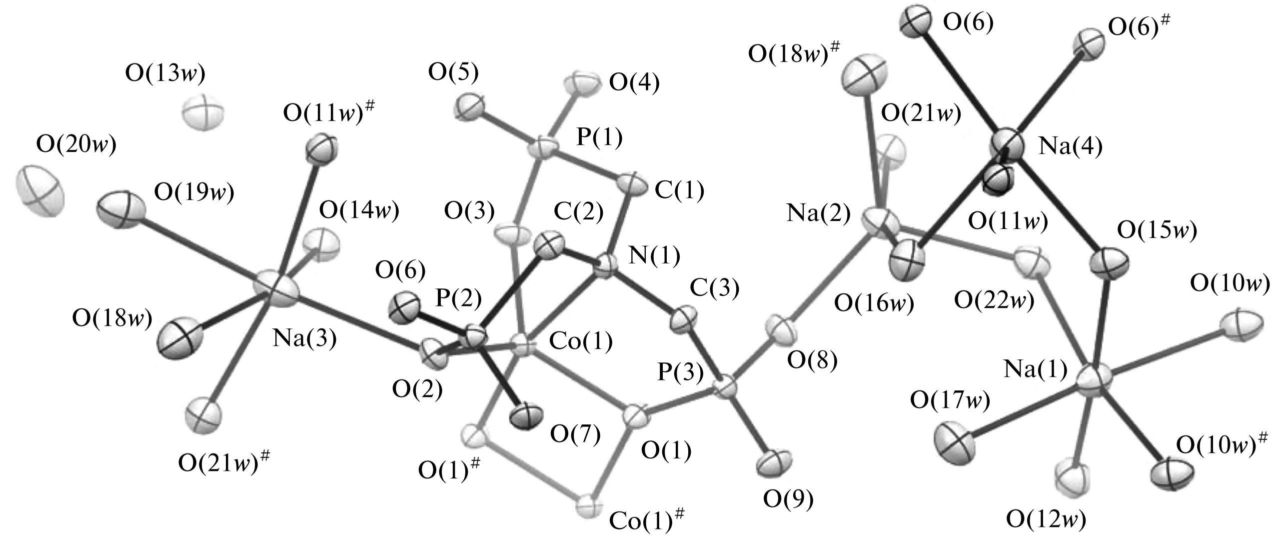

Fig. 2. Fragment of structure **II** (# –*x*, –*y*, –*z*).

Table 3. Interatomic distances (d) and bond angles (ω) in **II**

Bond	d, Å	Bond	d, Å	Bond	d, Å
Co(1)–N(1)	2.232(3)	N(1)–C(3)	1.491(4)	P(2)–O(2)	1.542(2)
Co(1)–O(1)	2.040(2)	C(1)–P(1)	1.820(4)	P(2)–O(6)	1.510(2)
Co(1)–O(1)$^{\#}$	2.056(2)	C(2)–P(2)	1.821(4)	P(2)–O(7)	1.514(2)
Co(1)–O(2)	2.020(2)	C(3)–P(3)	1.822(4)	P(3)–O(1)	1.559(2)
Co(1)–O(3)	1.991(2)	P(1)–O(3)	1.544(3)	P(3)–O(8)	1.514(3)
N(1)–C(1)	1.483(4)	P(1)–O(4)	1.511(3)	P(3)–O(9)	1.507(3)
N(1)–C(2)	1.492(4)	P(1)–O(5)	1.517(3)		
Angle	**ω, deg**	**Angle**	**ω, deg**	**Angle**	**ω, deg**
N(1)Co(1)O(1)	83.91(10)	Co(1)O(1)Co(1)$^{\#}$	98.05(9)	O(3)P(1)O(5)	111.10(15)
N(1)Co(1)O(2)	86.22(10)	O(3)P(1)C(1)	103.17(15)	O(3)P(1)O(4)	112.27(15)
N(1)Co(1)O(3)	86.64(10)	O(4)P(1)C(1)	107.72(16)	O(4)P(1)O(5)	112.68(15)
N(1)Co(1)O(1)$^{\#}$	165.86(10)	O(5)P(1)C(1)	109.37(16)	O(2)P(2)O(6)	112.38(14)
O(1)Co(1)O(2)	128.20(10)	O(2)P(2)C(2)	103.13(16)	O(2)P(2)O(7)	110.73(15)
O(1)Co(1)O(3)	115.75(10)	O(6)P(2)C(2)	108.45(16)	O(6)P(2)O(7)	113.24(15)
O(2)Co(1)O(3)	114.22(10)	O(7)P(2)C(2)	108.31(15)	O(1)P(3)O(8)	111.60(14)
O(2)Co(1)O(1)$^{\#}$	102.30(10)	O(1)P(3)C(3)	101.65(14)	O(1)P(3)O(9)	112.37(14)
O(3)Co(1)O(1)$^{\#}$	99.81(10)	O(8)P(3)C(3)	110.22(17)	O(8)P(3)O(9)	113.30(15)
O(1)Co(1)O(1)$^{\#}$	81.95(9)	O(9)P(3)C(3)	106.94(15)		

* Symmetry equivalent position: $^{\#}$ $-x$, $-y$, $-z$.

The outer coordination sphere of **II** comprises four sodium atoms coordinated by oxygen atoms in different ways. The Na(1) and Na(3) atoms have a highly distorted octahedral coordination (Na(1)–O, 2.332(3)–2.525(3) Å; ONa(1)O, 169.85(13)°–175.83(12)° and 84.42(12)°–100.36(12)°; Na(3)–O 2.342(3)–2.645(43) Å, ONa(3)O 162.20(12)°–168.87(12)° and 62.41(10)°–105.66(10)°). The Na(2) and Na(4) atoms are coordinated at the vertices of highly distorted tetragonal pyramids (Na(2)–O, 2.301(3)–2.428(3) Å; ONa(2)O, 162.26(13)°, 111.19(11)°–133.21(12)°, and 80.69(10)°–101.99(11)°, $\tau = 0.48$; Na(4)–O, 2.346(3)–2.437(3) Å; ONa(4)O, 172.25(12)°, 103.85(11)°–138.07(12)°, and 78.79(11)°–96.15(11)°, $\tau = 0.57$). The Na(3) and Na(4) atoms are coordinated by O(2) and O(6) atoms of the P(2) phosphonate group and by water molecules; Na(2) is coordinated by the O(8) atom of the P(3) phosphonate group and by water molecules. The Na(1) atom is coordinated only by water molecules. The P(1) phosphonate group is not involved in sodium coordination. Out of 13 water molecules, 11 molecules form hydrate bridges between the sodium atoms, while 2 are solvate molecules.

The structure of complex **II** is similar to the structure of copper(II) complex $Na_8[CuN(CH_2PO_3)_3]_2 \cdot 19H_2O$ (**IV**) [20]. However, in this case, too, the cobalt(II) and copper(II) coordinations have differences, as in **I** and **III**. The coordination polyhedron of copper(II) in **IV** is compressed by 16% (the average lengths of Cu–O bonds ate 2.2220(14) Å for the equatorial bond and 1.9157(14) Å for the axial bond). In the cobalt complex, the difference between these distances is only 0.78% (2.040(2) and 2.056(2) Å, respectively), so that the Co(1)–O(1) and Co(1)–O(1)* bonds are almost equivalent in length. The N–Co–O–P torsion angles in **II** are 4.33(6)°–20.55(6)°. Hence, the chelate rings are not planar but have different and rather intricate spatial configuration. The crystal packing symmetry of **II** (M = Co; space group $P\bar{1}$) is lower than the symmetry of analogous copper(II) complex **IV** (M = Cu; space group $P2_1/c$).

The UV/Vis spectra of complexes **I** and **II** are summarized in Fig. 3. An aqueous solution of **I** exhibits a UV/Vis spectrum typical of octahedral complexes of high-spin Co(II) ion [31]. The spectrum shows a weak band with a maximum at 10500 cm^{-1} corresponding to the $^4T_{2g}$–$^4T_{1g}$ transition and a band with a maximum at 19080 cm^{-1} with a complex structure corresponding to the $^4T_{1g}(P)$–$^4T_{1g}$ transition. The charge transfer bands occur above 30000 cm^{-1}. They have a clear-cut multiplet structure in which at least three components can be distinguished corresponding apparently to three water molecules. The UV/Vis spectrum of an aqueous solution of **II** is typical of a trigonal bipyramidal coordination of high-spin Co(II) (C_{3v}) symmetry. The band at 12300 cm^{-1}is due to the $^4A_2$–^4E transition and the band having a maximum at 18700 cm^{-1} and a

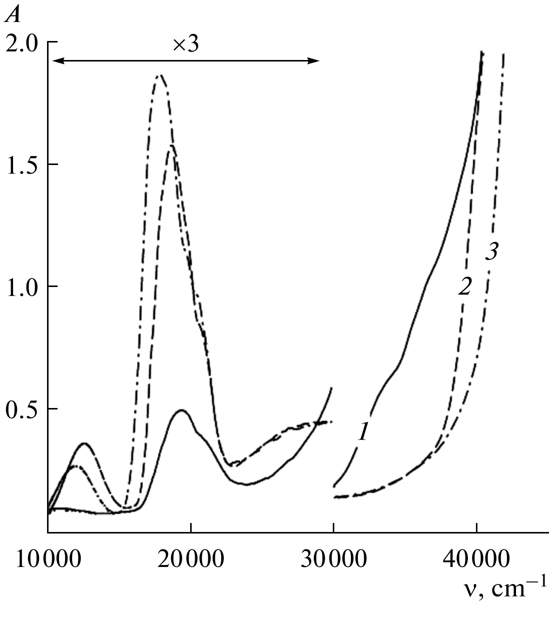

Fig. 3. UV/Vis spectra of aqueous solutions of (*1*) **I**, (*2*) **II**, and (*3*) crystalline **II** (mineral oil mull). (*1*) $c = 0.05$, (*2*, *3*) $c = 0.01$ mmol/cm^3.

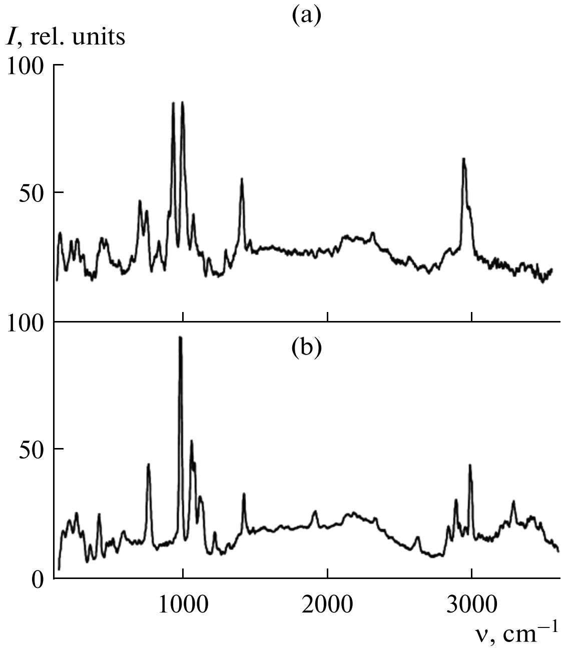

Fig. 4. Raman spectra of single crystals of (a) **I** and (b) **II**.

complex structure corresponds to the $^4A_2$–$^4E(P)$ transition. The charge transfer bands lie above 38000 cm^{-1}. Interestingly, the UV/Vis spectrum of crystalline **II** differs substantially from the spectrum of its aqueous solution. The $^4A_2$–^4E band shifts bathochromically to 11720 cm^{-1}; the $^4A_2$–$^4E(P)$ band sifts to 17700 cm^{-1}. The shape of the latter band substantially changes and the width and the maximum integral intensity increase, which can be attributed to the appearance of a new component. Visually, this difference is reflected in the fact that crystalline **II** is colored violet-blue, while the aqueous solution is dark violet. The charge transfer band shifts hypsochromically to the region above 40000 cm^{-1}. Apparently, in aqueous solution, the Co–O–Co–O ring is opened and the cobalt atom is hydrated in the apical position, while upon crystallization, the water molecule is split off and a quadrupole configuration is formed. This is consistent with X-ray diffraction data described above. However, the trigonal bipyramidal Co(II) coordination in **II** is retained in aqueous solutions, unlike that in the reported Co(II) complex with 4,4,10,10-tetramethyl-1,3,7,9-tetraazaspiro[5.5]undecane-2,8-dione [24].

The Raman spectra of single crystals of **I** and **II** are shown in Fig. 4. The bands below 400 cm^{-1} refer to mutual vibrations of separate structural units in the crystals. The group of bands in the 400–600 cm^{-1} range is due to vibrations of the Co(II) coordination sphere. The spectrum of complex **I** shows three relatively strong bands in this range (465, 490, and 585 cm^{-1}). For complex **II**, the band at 420 cm^{-1} corresponds to the apical Co–O bond; the 485, 500, and 520 cm^{-1} bands are due to equatorial Co–O bonds, while the band at 600 cm^{-1} is due to Co–N bond vibrations. The increase in the ligand configuration symmetry in **II** with respect to **I** is manifested as a decrease in the number of bands corresponding to PO_3 modes. The spectrum of **I** exhibits three δ(O–P–O) bands (670, 730, and 775 cm^{-1}), while in the case of **II**, there is only one such band (760 cm^{-1}). In the spectrum of **I**, one can distinguish the ν(P–O) modes at 840, 860, 885, 940, 955, 1020, 1150, and 1200 cm^{-1}; the spectrum of **II** contains ν(P–O) bands at 987, 1060, 1080, 1120–1140, and 1220 cm^{-1}. The band for the localized P–O π-bond (1200–1300 cm^{-1}) in the spectra of both **I** and **II** is shifted bathochromically, indicating a substantial delocalization of the P–O π-bond. This is consistent with X-ray diffraction data for both compounds, which fail to distinguish one P–O bond as being markedly shorter than the other two bonds. The band at 1320 cm^{-1} is due to δ(Co–O–H) vibrations. This band is very weak in the spectrum of **II** and seems to refer to the apically hydrated form present in minor amount and manifested in the UV/Vis spectrum of the solution. The CH_2 modes are not split ($\delta_{as}(CH_2)$ 1425, $\delta_s(CH_2)$ 1485, $\nu_{as}(CH_2)$ 2955, $\nu_s(CH_2)$ 2990 cm^{-1}). Of interest is the stretching vibration intensity distribution, indicating that the structural unit of **II** has a center of symmetry, which is missing in the structural unit of **I**. The shoulder at 3200 cm^{-1} in the spectrum of **I** corresponds to the $\nu(N^+–H)$ mode. The 2840, 2890, and 2913 cm^{-1} bands of **I** refer to water molecules in the outer coordination sphere, while the bands at 3284, 3390–3430, and 3470 cm^{-1} refer to the solvate water molecules.

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REFERENCES

1. Zheng, L.-M. and Duan, Y., in *Metal Phosphonate Chemistry. From Synthesis to Applications*, Clearfield, A. and Demadis, K., Eds., Cambridge: The Royal Society of Chemistry, 2012, p. 235.
2. Cai, Z.-S., Bao, S.-S., Ren, M., and Zheng, L.-M., *Chem.-Eur. J.*, 2014, vol. 20, p. 17137.
3. Zheng, L.-M., Gao, S., Yin, P., and Xin, X.-Q., *Inorg. Chem.*, 2004, vol. 43, p. 2151.
4. Zhang, Y.-Y., Zeng, M.-H., Qi, Y., Sang, S.-Y., and Liu, Z.-M., *Inorg. Chem. Commun.,* 2007, no. 10, p. 33.
5. Dai, L.-L., Huang, C.-Y., Li, R., Suna, Z.-G., et al., *Inorg. Chem. Commun.,* 2014, no. 40, p. 181.
6. Mao, J.-G. and Clearfield, A., *Inorg. Chem.*, 2002, vol. 41, p. 2319.
7. Cai, Z.-S., Bao, S.-S., and Zheng, L.-M., *Acta Chim. Sinica,* 2013, vol. 71, p. 555.
8. Fu, S.-J., Cheng, C.-Y., and Lin, K.-J., *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.,* 2007, vol. 63, p. 368.
9. Rzhevskaya, S.V., *Materialovedenie* (Materials Science), Moscow: MGGU, 2003.
10. Kuznetsov, Yu.I., *Usp. Khim.*, 2004, vol. 73, no. 1, p. 79.
11. Chausov, F.F., Shabanova, I.N., Kazantseva, I.S., and Naimushina, E.A., *Izv. Akad. Nauk, Ser. Fiz.*, 2014, vol. 78, no. 4, p. 436.
12. McCleverty, J.A., Meyer, T.J., and Fenton, D.E., *Comprehensive Coordination Chemistry* II, Vol. 6, *Amsterdam: Elsevier*, 2003, p. 1293.
13. Du, J.-L., Rettig, S.J., Thompson, R.C., and Trotter, J., *Canadian J. Chem.*, 1991, vol. 69, p. 277.
14. Sawada, K., Araki, T., Suzuki, T., and Doi, K., *Inorg. Chem.*, 1989, vol. 28, no. 13, p. 2687.
15. Lukeš, I., Rejšková, D., Odvárko, R., and Vojtišek, P., *Polyhedron*, 1986, vol. 5, no. 12, p. 2063.
16. Sharma, C.V.K. and Clearfield, A., *J. Am. Chem. Soc.*, 2001, vol. 123, p. 2885.
17. Demadis, K.D., Katarachia, S.D., and Koutmos, M., *Inorg. Chem. Commun.*, 2005, no. 8, p. 254.
18. Somov, N.V. and Chausov, F.F., *Kristallografiya*, 2014, vol. 59, no. 1, p. 71.
19. Chausov, F.F., Zakirova, R.M., Somov, N.V., Petrov, V.G., et al., *Russ. J. Appli. Chem.*, 2014, vol. 87, no. 8, p. 1031.
20. Somov, N.V. and Chausov, F.F., *Kristallografiya*, 2015, vol. 60, no. 2, p. 233.
21. Korobeinikova, E.Yu. and Merkulov, D.A., *Vestn. Udmurt. Un-ta. Fiz. Khim.*, 2013, no. 4, p. 11.
22. Porai-Koshits, M.A., Polynova, T.N., and Shkol'nikova, L.M., *Zh. Vses. Khim. O-va im. D.I. Mendeleeva*, 1984, vol. 29, no. 3, p. 43.
23. Bokii, G.B. and Porai-Koshits, M.A., *Kristallografiya*, 1960, vol. 5, p. 605.
24. Netreba, E.E., *Cand. Sci. (Chem) Dissertation*, Voronezh: Voronezh. State Univ., 2014.
25. CrysAlisPro. Agilent Technologies. Version 1.171.37.35 (release 13-08-2014 CrysAlis171.NET). 2014.
26. Sheldrick, G.M., *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, p. 112.
27. Farrugia, L.J., *J. Appl. Crystallogr.*, 1999, vol. 32, p. 837.
28. Daly, J.J. and Wheatley, P.J., *J. Chem. Soc. A*, 1967, p. 212.
29. Bersuker, I.B., *The Jahn-Teller Effect and Vibronic Interactions in Modern Chemistry*, Cham: Springer, 2013.
30. Addison, A.W., Rao, T.N., Reedijk, J., et al., *Dalton Trans.*, 1984, no. 7, p. 1349.
31. Lever, A.B.P., *Inorganic Electronic Spectroscopy*, Amsterdam: Elsevier, 1987, vol. 2.

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