

Aquanitrilotris(methylenephosphonato)bis(dimercury(I)) Hydrate, [(Hg₂)₂(H₂O)N(CH₂PO₃)₃H₂] · H₂O: Synthesis, Structure, and Properties

N. V. Somov^{a, *}, F. F. Chausov^{b, c}, R. M. Zakirova^c, M. A. Shumilova^d,
V. A. Aleksandrov^d, and V. G. Petrov^d

^aLobachevsky State University, Nizhny Novgorod, Russia

^bPhysical-Technical Institute, Ural Branch, Russian Academy of Sciences, Izhevsk, Russia

^cUdmurt State University, Izhevsk, Russia

^dInstitute of Mechanics, Ural Branch, Russian Academy of Sciences, Izhevsk, Russia

*e-mail: somov@phys.unn.ru

Received March 30, 2015

Abstract—A reaction of dimercury(I) dinitrate with nitrilotris(methylenephosphonic acid), N(CH₂PO₃)₃H₆, gave the complex [(Hg₂)₂(H₂O){N(CH₂PO₃)₃H₂}] · H₂O. The crystals of the complex are triclinic, space group *P* $\bar{1}$, *Z* = 2, *a* = 8.3436(3), *b* = 9.0744(3), *c* = 11.1124(4) Å, α = 91.875(3)°, β = 104.452(3)°, γ = 92.195(3)° (CIF file CCDC no. 1051860). The atoms of either dimercury cation are coordinated differently, making up a distorted tetrahedron and a distorted trigonal bipyramid. The ligand is coordinated to the Hg atoms through seven donor atoms: six (out of nine) O atoms and a N atom. The coordination involves the formation of chelate rings: two four-membered, three five-membered, a six-membered, and an eight-membered ring (CIF file CCDC no. 1051860).

DOI: 10.1134/S107032841601005X

INTRODUCTION

Mercury is a prevalent ecotoxicant ubiquitously used in engineering applications [1]. Mercury complexes are less toxic than soluble mercury salts [2]. For this reason, binding of mercury ions in stable complexes is of current interest. Mercury compounds find use in medicine, veterinary practice, and agriculture as antiseptics, bactericides, and fungicides [3–5]. So the preparation of mercury compounds that would exhibit high antibacterial and fungicidal activity but would be nontoxic to warm-blooded animals is a challenge [6, 7]. The use of mercury compounds as corrosion inhibitors and self-discharge inhibitors in chemical current sources [8] necessitates searching for new Hg complexes with high anticorrosion activity and low toxicity.

Despite its closed electronic shell (5d¹⁰6s²), mercury forms complexes with many ligands, its complexes often having unique structures difficult to explain [9, 10]. Mercury shows an unusual tendency to form polycations; the dimercury(I) cation, (Hg–Hg)²⁺, is most commonly encountered [11, 12]. This tendency is due to relativistic effects [13] having impact on the binding mechanism in the excited linear complexes and polycations of mercury [14, 15].

Complexes of soft acids of Hg²⁺ and Hg₂²⁺ with soft C, N, S, Se, and halogen electron-donating centers are most stable [16, 17].

Some Hg(II) complexes with oxophosphate ligands have been obtained and studied; the mercury atoms in those complexes are coordinated by O atoms to form an octahedral environment. For instance, the coordination octahedra of the mercury(II) atoms in Hg₂P₂O₇ constitute an island structure in which the octahedra are linked in edge-sharing pairs [18]. Mercury(II) polymetaphosphate, Hg(PO₃)₂, is a linear-chain coordination polymer containing parallel polyphosphate chains linked by the skew edges of the oxygen octahedra of the mercury atoms [19]. Dimercury(I) oxophosphate complexes show a wider structural variety. Dimercury(I) orthophosphate, (Hg₂)₃(PO₄)₂, exist as two polymorphic modifications differing in unit cell parameters. In both structures, either mercury atom in Hg₂ is surrounded by three O atoms in such a way that the coordination polyhedron of the mercury atom is a strongly distorted tetrahedron [20]. The same coordination of dimercury(I) is found in dimercury(I) dihydroarsenate, Hg₂(H₂AsO₄)₂, and dimercury(I) diarsenate, Hg₂As₂O₆ [21]. In contrast, in dimercury(I) diphosphate, (Hg₂)₂P₂O₇, one of the two symmetrically nonequivalent Hg₂ groups is also

Table 1. Crystallographic parameters and the data collection and refinement statistics for HgNTP

Parameter	Value
<i>M</i>	1131.39
Crystal system; space group; <i>Z</i>	Triclinic; $P\bar{1}$; 2
<i>a</i> , Å	8.3436(3)
<i>b</i> , Å	9.0744(3)
<i>c</i> , Å	11.1124(4)
α , deg	91.875(3)
β , deg	104.452(3)
γ , deg	92.195(3)
<i>V</i> , Å ³	813.36(5)
ρ_{calcd} , g/cm ³	4.62
Radiation, λ , Å, monochromator	MoK α , 0.71073, graphite
μ , mm ^{−1}	37.978
<i>T</i> , K	293(2)
Sample dimensions, mm	0.268 × 0.145 × 0.060
Diffractometer	Xcalibur, Sapphire3, Gemini
Scan mode	ω
Absorption correction, <i>T</i> _{min} / <i>T</i> _{max}	[31], 0.027/0.190
<i>F</i> (000)	976
$\theta_{\text{min}}/\theta_{\text{max}}$, deg	3.461/30.507
Ranges of <i>h</i> , <i>k</i> , <i>l</i> indices	−11 ≤ <i>h</i> ≤ 11, −12 ≤ <i>k</i> ≤ 12, −15 ≤ <i>l</i> ≤ 15
Number of measured/unique (<i>N</i> ₁)/with <i>I</i> > 2 σ (<i>I</i>) (<i>N</i> ₂) reflections (<i>R</i> _{int})	18092/4942/4477 (0.0392)
Number of parameters refined/constraints	211/7
GOOF	1.146
<i>R</i> ₁ / <i>wR</i> ₂ on <i>N</i> ₁	0.0361/0.0710
<i>R</i> ₁ / <i>wR</i> ₂ on <i>N</i> ₂	0.0308/0.0689
$\Delta\rho_{\text{min}}/\Delta\rho_{\text{max}}$, e/Å ³	−2.776/1.852
Programs	CrysAlisPro [31], SHELX [32], WinGX [33]

coordinated by six O atoms, while the other, by four O atoms [20]. Dimercury(I) hydroorthophosphate, (Hg₂)₂(H₂PO₄)(PO₄), shows different coordination environments for two mercury atoms making up either Hg₂ dumbbell: one Hg atom is coordinated by three, while the other, by four O atoms [22].

Organopolyphosphonic acids as ligands allow wide variation of the coordination fashion and provide a wide stereochemical variety of the resulting complexes

[23]. Many of these compounds are highly efficient corrosion inhibitors [24]; however, their mercury complexes have not been studied. When mercury compounds react with organophosphonates, the mercury atom becomes bound to the P rather than O atom [6, 7] to give alkyl derivatives of bis(phosphonomercury) structurally characterized using X-ray diffraction and NMR spectroscopy [25, 26].

Nitrilotris(methylenephosphonic acid), N(CH₂PO₃)₃H₆ (NTP), and its metal complexes inhibit the corrosion of steel and some other metals [27, 28]. For this reason, a study of the structures and properties of mercury(I) complexes with NTP are of current interest. Here we describe the synthesis, crystal structure, spectral features, and thermal stability of aquanitrilotris(methylenephosphonato)bis(dimercury(I)) hydrate, [(Hg₂)₂(H₂O){N(CH₂PO₃)₃H₂}] · H₂O (HgNTP).

EXPERIMENTAL

Synthesis of HgNTP was carried out in silica gel [29, 30]. A U-shaped tube was charged with a mixture of 14% AcOH (12.5 cm³) and aqueous Na₂SiO₃ (ρ = 1.06 g/cm³, 30.0 cm³). After the reaction produced silica gel, a 0.1 M solution of Hg₂(NO₃)₂ in 2.5% HNO₃ (5 cm³) was added to one arm of the tube, and 0.1 M NTP (prepared from twice recrystallized NTP; 5 cm³) was added to the other arm; both arms were closed with stoppers. After a month, the silica gel bulk adjoining the solution of Hg₂(NO₃)₂ and their interface showed transparent, colorless or yellowish, tabular triclinic crystals of HgNTP up to several millimeters in size. The product was mechanically separated, washed with water, ethanol, and diethyl ether, and dried at room temperature.

X-ray diffraction study. Crystallographic parameters and the data collection and refinement statistics for HgNTP are given in Table 1. The primary structural fragment of HgNTP was determined by a direct method. The non-hydrogen atoms were located in difference electron-density maps and refined anisotropically by the least-squares method on $|F|^2$. The hydrogen atoms were located geometrically and refined by imposing mixed constraints. The absorption correction was applied considering a polyhedron-given shape of the sample [31]. The imperfection of the sample as well as the impossibility of complete absorption correction are responsible for the considerable peaks of residual electron density (1.75–1.83 e/Å³) near the centers of the mercury atoms (0.77–0.96 Å).

The crystallographic data for HgNTP have been deposited with the Cambridge Structural Database (CCDC no. 1051860; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

The IR absorption spectra (KBr pellets) of HgNTP and its decomposition products were recorded on an

Table 2. Bond lengths (*d*) and bond angles (ω) in $[(\text{Hg}_2)_2(\text{H}_2\text{O})\{\text{N}(\text{CH}_2\text{PO}_3)_3\text{H}_2\}] \cdot \text{H}_2\text{O}$

Bond	<i>d</i> , Å	Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
N(1)–C(1)	1.495(7)	P(2)–O(5)	1.495(6)	Hg(2)–O(2)	2.369(4)
N(1)–C(2)	1.490(7)	P(2)–O(6)	1.493(6)	Hg(2)–O(9)	2.346(4)
N(1)–C(3)	1.497(7)	P(3)–O(7)	1.518(5)	Hg(2)–Hg(3)	2.5081(4)
C(1)–P(1)	1.817(6)	P(3)–O(8)	1.541(5)	Hg(3)–O(8)	2.940(6)
C(2)–P(2)	1.826(6)	P(3)–O(9)	1.512(4)	Hg(3)–O(8)*	2.121(4)
C(3)–P(3)	1.819(6)	Hg(1)–N(1)	2.370(5)	Hg(3)–O(2w)	2.918(6)
P(1)–O(1)	1.523(5)	Hg(1)–O(3)	2.495(4)	Hg(4)–Hg(1)	2.5274(3)
P(1)–O(2)	1.531(4)	Hg(1)–O(6)	2.457(5)	Hg(4)–O(2)	2.331(4)
P(1)–O(3)	1.528(5)	Hg(1)–O(8)	2.770(6)	Hg(4)–O(3)	2.337(4)
P(2)–O(4)	1.548(6)	Hg(2)–O(1)	2.281(4)	Hg(4)–O(9)	2.475(4)
Angle	ω , deg	Angle	ω , deg	Angle	ω , deg
C(1)N(1)C(2)	108.9(4)	O(4)P(2)O(6)	107.3(4)	O(2)Hg(2)Hg(3)	129.86(10)
C(1)N(1)C(3)	108.4(4)	O(5)P(2)O(6)	117.2(4)	O(9)Hg(2)Hg(3)	132.78(12)
C(2)N(1)C(3)	110.0(4)	O(7)P(3)C(3)	107.6(3)	O(1)Hg(2)O(2)	88.78(15)
Hg(1)N(1)C(1)	108.9(3)	O(8)P(3)C(3)	106.0(3)	O(1)Hg(2)O(9)	85.95(18)
Hg(1)N(1)C(2)	107.9(4)	O(9)P(3)C(3)	106.5(3)	O(2)Hg(2)O(9)	73.15(15)
Hg(1)N(1)C(3)	112.6(3)	O(7)P(3)O(8)	111.5(3)	O(8)Hg(3)Hg(2)	105.28(15)
N(1)C(1)P(1)	115.2(4)	O(7)P(3)O(9)	113.1(3)	O(8)*Hg(3)Hg(2)	173.01(12)
N(1)C(2)P(2)	114.9(4)	O(8)P(3)O(9)	111.6(3)	O(2w)Hg(3)Hg(2)	98.50(18)
N(1)C(3)P(3)	115.7(4)	N(1)Hg(1)Hg(4)	166.31(12)	O(8)Hg(3)O(8)*	84.51(15)
O(1)P(1)C(1)	104.3(2)	N(1)Hg(1)O(3)	78.81(15)	O(8)Hg(3)O(2w)	129.06(12)
O(2)P(1)C(1)	109.8(3)	N(1)Hg(1)O(6)	75.88(17)	O(8)*Hg(3)O(2w)	84.51(16)
O(3)P(1)C(1)	105.0(3)	N(1)Hg(1)O(8)	72.48(15)	O(2)Hg(4)Hg(1)	136.07(10)
O(1)P(1)O(2)	111.0(3)	O(3)Hg(1)O(6)	98.69(19)	O(3)Hg(4)Hg(1)	128.15(11)
O(1)P(1)O(3)	115.5(3)	O(6)Hg(1)O(8)	116.64(16)	O(9)Hg(4)Hg(1)	128.71(11)
O(2)P(1)O(3)	110.7(3)	O(3)Hg(1)O(8)	125.92(12)	O(2)Hg(4)O(3)	86.31(15)
O(4)P(2)C(2)	107.0(3)	Hg(4)Hg(1)O(3)	114.17(10)	O(2)Hg(4)O(9)	71.48(14)
O(5)P(2)C(2)	106.3(3)	Hg(4)Hg(1)O(6)	105.14(14)	O(3)Hg(4)O(9)	86.26(17)
O(6)P(2)C(2)	107.0(3)	Hg(4)Hg(1)O(8)	95.37(18)	Hg(3)O(8)Hg(3)	102.71(15)
O(4)P(2)O(5)	111.6(4)	O(1)Hg(2)Hg(3)	128.00(12)	Hg(2)O(2)Hg(4)	106.70(16)

* The symmetry operation is $-x, -y, -z$.

FSM-1202 FTIR spectrometer in the 450–5000 cm^{-1} range.

The Raman spectra of crystalline HgNTP were recorded on a Centaur U-HR microscope-microspectrometer in the 430–460 nm range (laser excitation at $\lambda = 432$ nm).

Thermogravimetric analysis of HgNTP was carried out on a Shimadzu DTG-60H automated derivatograph (air or argon, 30–500°C, heating rate 3°C/min).

RESULTS AND DISCUSSION

A fragment of the crystal structure of HgNTP is shown in Fig. 1. Selected bond lengths and bond

angles are listed in Table 2. The structural unit of HgNTP is asymmetric; the unit cell comprises two formula units. Structurally, HgNTP is a 3D coordination polymer.

In the previously studied neutral NTP complexes with zinc [34], manganese [35], copper [36, 37], and other metals, the ligand molecule retains its zwitterionic structure characteristic of free NTP [38]. In contrast to those complexes, when NTP reacts with $(\text{Hg}_2)^{2+}$ in acidic medium, mercury(I) replaces the proton at the N atom. The ligand molecule undergoes slight deformations in the complex HgNTP: the bond angles at the N atom are 108.4(4)°–112.6(3)°, deviating from the ideal tetrahedral angle by no more than 3.1°. The deviations of the bond angles at the

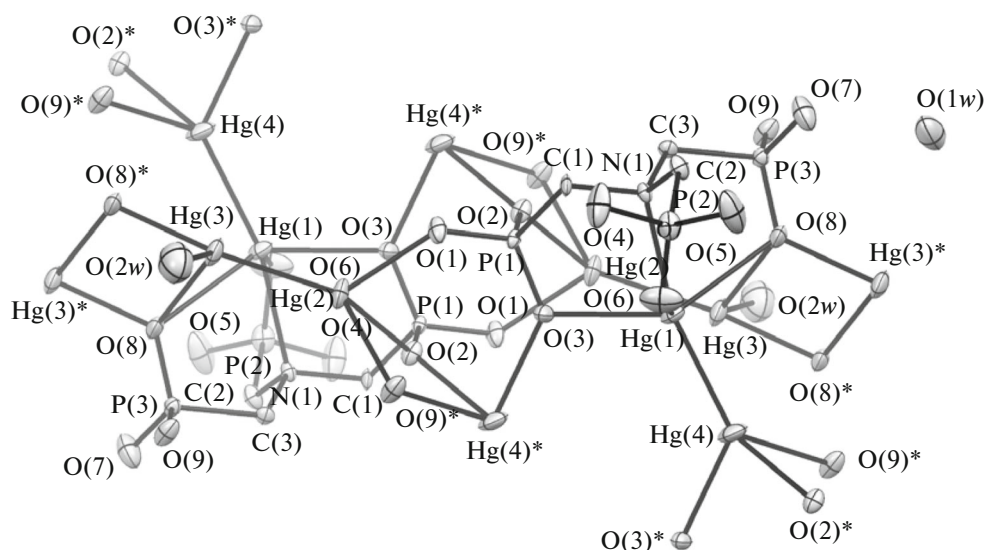


Fig. 1. Fragment of aquanitritoltris(methylenephosphonato)bis(dimercury(I)) hydrate; the symmetry-related equivalent atoms are asterisked.

C ($114.9(4)^\circ$ – $115.7(4)^\circ$) and P atoms ($106.0(3)^\circ$ – $117.2(4)^\circ$) do not exceed 6.2° and 7.7° , respectively. All three PO_3 groups of the ligand NTP^{4-} are symmetrically nonequivalent. The mercury atoms are coordinated by all three O atoms in one PO_3 group, by two O atoms in another group, and by only one O atom in a third group. A total of seven electron-donating centers of the ligand ($6\text{O} + \text{N}$) are involved in the mercury coordination. The structure of HgNTP contains several chelate rings, including three five-membered ones ($\text{Hg}(1)\text{--N}(1)\text{--C}(1)\text{--P}(1)\text{--O}(3)$, $\text{Hg}(1)\text{--N}(1)\text{--C}(2)\text{--P}(2)\text{--O}(6)$, and $\text{Hg}(1)\text{--N}(1)\text{--C}(1)\text{--P}(1)\text{--O}(8)$) with the $\text{Hg}(1)\text{--N}(1)$ bond in common. The Hg_2 dumbbell $\text{Hg}(2)\text{--Hg}(3)$ completes the seven-membered intramolecular ring $\text{Hg}(1)\text{--O}(3)\text{--P}(1)\text{--O}(2)\text{--Hg}(2)\text{--Hg}(3)\text{--O}(8)$. The formation of a coordination polymer structure gives rise to intermolecular chelate rings: two four-membered rings ($\text{Hg}(3)\text{--O}(8)\text{--Hg}(3)^*\text{--O}(8)^*$ and $\text{Hg}(2)\text{--O}(2)\text{--Hg}(4)^*\text{--O}(9)^*$), two six-membered rings ($\text{Hg}(1)\text{--Hg}(4)\text{--O}(3)\text{--Hg}(1)^*\text{--Hg}(4)^*\text{--O}(3)^*$ and $\text{O}(1)\text{--P}(1)\text{--O}(3)\text{--Hg}(4)^*\text{--O}(2)^*\text{--Hg}(2)^*$), and an eight-membered ring ($\text{O}(1)\text{--P}(1)\text{--O}(2)\text{--Hg}(2)\text{--O}(1)^*\text{--P}(1)^*\text{--O}(2)^*\text{--Hg}(2)^*$). The presence of many chelate rings makes the complex more stable.

A specific coordination environment of the Hg_2 dumbbells in HgNTP is shown in Fig. 2. Either of two covalently bound mercury atoms is differently coordinated. The $\text{Hg}(2)$ and $\text{Hg}(4)$ atoms are both coordinated by three O atoms making up the base of a trigonal pyramid. With the neighboring mercury atom taken into account, the coordination polyhedra of the

$\text{Hg}(2)$ and $\text{Hg}(4)$ atoms can be considered strongly elongated tetrahedra (the angles deviate from those in a regular tetrahedron by 26.63° – 38.01°). The coordination polyhedron of the $\text{Hg}(1)$ atom is a distorted trigonal bipyramid with three equatorial O atoms and axial N and Hg atoms (OHgO , $98.69(19)^\circ$ – $125.92(12)^\circ$; HgHgO and NHgO , $72.48(15)^\circ$ – $114.17(10)^\circ$; NHgHg , $166.31(12)^\circ$). The structural parameter τ [39] of the $\text{Hg}(1)$ atom is 0.67 (for a regular trigonal bipyramid, $\tau = 1$; for a regular tetragonal pyramid, $\tau = 0$). The $\text{Hg}(3)$ atom is coordinated by three O atoms and an adjacent Hg atom (OHgO , $129.06(12)^\circ$ and $84.51(16)^\circ$; HgHgO , $98.50(18)^\circ$ – $105.28(15)^\circ$ and $173.01(12)^\circ$; $\tau = 0.73$). The coordination polyhedron of the $\text{Hg}(3)$ atom can be most accurately described as a distorted trigonal bipyramid with an equatorial vacancy, or a bisphenoid. The bisphenoidic coordination environment is characteristic of complexes of the type AX_4E in which the lone electron pair (E) is localized on the central atom [40]; however, according to quantum chemical calculations [13, 14], the Hg_2^{2+} ion contains no such pairs. The equatorial angle OHgO of $129.06(12)^\circ$ cannot be accounted for by the orienting effect of the ligands because of the mobility of the water molecule $\text{O}(2w)$. However, there is an obvious structural similarity of two Hg_2 dumbbells in the complex HgNTP .

This similarity is also reflected by the ionic radii of the Hg(I) ions (Table 3). When calculating the ionic radii of the mercury ions ($r_{\text{Hg(I)}}$), we used the Shannon radii for other ions [41]. In particular, the ionic radius of O^{2-} for C.N. 2, 3, and 4 was taken to be 1.35, 1.36,

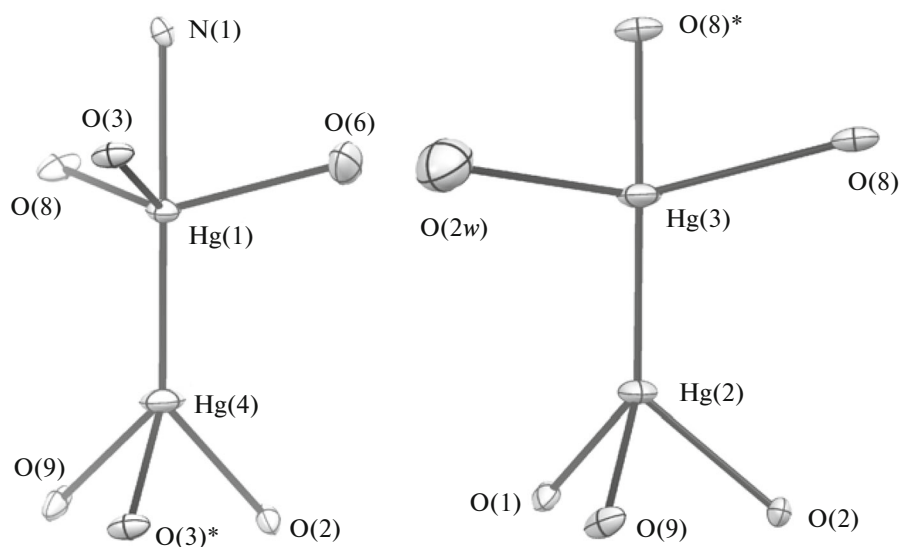


Fig. 2. Coordination environment of two Hg_2 dumbbells in HgNTP .

and 1.38 Å, respectively. For the $\text{Hg}(2)$ and $\text{Hg}(4)$ atoms, the calculated $r_{\text{Hg(I)}}$ values agree well with the literature data (0.97 Å for C.N. 3). For the $\text{Hg}(1)$ and $\text{Hg}(3)$ atoms, the calculated $r_{\text{Hg(I)}}$ values contrast with those for $\text{Hg}(2)$ and $\text{Hg}(4)$ but are consistent with the literature data ($r_{\text{Hg(I)}} = 1.19$ Å for C.N. 6). The standard deviations $\sigma(r)$ given in Table 3 allow estimating the scatter of the distances in the coordination spheres of, on the one hand, the $\text{Hg}(1)$ and $\text{Hg}(3)$ atoms and, on the other hand, the $\text{Hg}(2)$ and $\text{Hg}(4)$ atoms.

Clearly, the mercury atoms in either Hg_2 dumbbell are symmetrically nonequivalent to each other. However, we failed to explain in this study why the coordination of the $\text{Hg}(3)$ atom is unusual and why two Hg_2 dumbbells in the complex HgNTP are structurally similar.

The structure of HgNTP was confirmed by molecular vibrational spectroscopy (Fig. 3). The band at 82 cm^{-1} is due to the vibrations of the Hg_2 dumbbells as a whole, and the bands at 123 and 156 cm^{-1} relate to the bending and stretching $\text{Hg}-\text{Hg}$ vibrations, respectively [42, 43]. The assignments of the bands at 460, 480, and 570 cm^{-1} are still controversial in the literature. In [44, 45], the bands in the 400–500 cm^{-1} range are assigned to $\nu(\text{Hg}-\text{N})$, and the bands at 500–600 cm^{-1} , to $\nu(\text{Hg}-\text{O})$. In our case, the band at 460–480 cm^{-1} , which is split in the IR spectrum according to the molecular symmetry (this is confirmed by a forbidden component of this band in the Raman spectrum), should be assigned to the vibrations of the oxygen atoms (460 cm^{-1} , $\nu_{\text{as}}(\text{Hg}-\text{O})$; 480 cm^{-1} , $\nu_{\text{s}}(\text{Hg}-\text{O})$). The band at 570 cm^{-1} can be assigned to $\nu(\text{Hg}-\text{N})$, in agreement with the literature data [46, 47]. The bands at 680, 720, and 750 cm^{-1} are due to the bending

vibrations of the $\text{N}-\text{C}-\text{P}$ framework of the ligand NTP^{4-} . An incompletely resolved group of intense bands at 900–1300 cm^{-1} relate to the vibrations of three symmetrically nonequivalent PO_3 groups; the vibrations of the partially localized $\text{P}-\text{O}$ π -bonds appear as a shoulder at 1240–1260 cm^{-1} . The spectrum contains other characteristic bands (cm^{-1}): 1385 $\delta(\text{PO}-\text{H})$, 1435 $\delta_{\text{as}}(\text{CH}_2)$, 1465 $\delta_{\text{s}}(\text{CH}_2)$, 1580 $\delta_{\text{as}}(\text{H}_2\text{O})$, 1655 $\delta_{\text{s}}(\text{H}_2\text{O})$, 2928 $\nu_{\text{as}}(\text{CH}_2)$, 2965 $\nu_{\text{s}}(\text{CH}_2)$.

Thermogravimetric analysis of HgNTP (Fig. 4) shows that the sequential elimination of two water molecules at 45–140°C is accompanied by no appre-

Table 3. Estimation of the ionic radii of mercury(I)

Atom	C. N.	Bond	$r_{\text{Hg(I)}}, \text{\AA}$	$\langle r_{\text{Hg(I)}} \rangle, \text{\AA}$	$\sigma(r), \text{\AA}$
Hg(1)	5	Hg(1)–N(1)	0.910	1.135	0.386
		Hg(1)–O(3)	1.135		
		Hg(1)–O(6)	1.106		
		Hg(1)–O(8)	1.390		
Hg(2)	4	Hg(2)–O(1)	0.929	0.977	0.034
		Hg(2)–O(2)	1.007		
		Hg(2)–O(9)	0.995		
Hg(3)	4	Hg(3)–O(8)	1.560	1.289	0.412
		Hg(3)–O(8)*	0.750		
		Hg(3)–O(2w)	1.558		
Hg(4)	4	Hg(3)–O(2)	0.972	1.026	0.072
		Hg(3)–O(3)	0.977		
		Hg(3)–O(9)	1.128		

* The symmetry operation is $-x, -y, -z$.

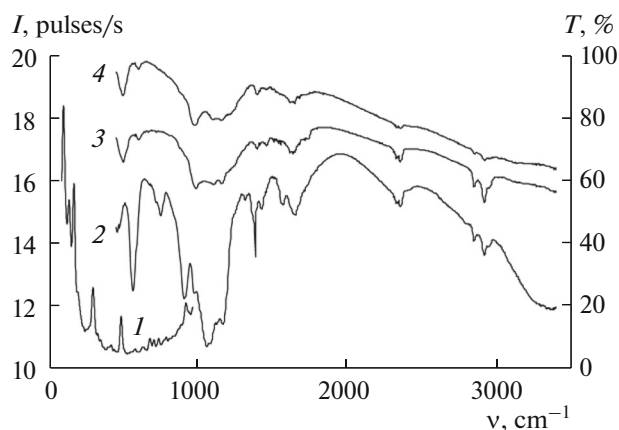


Fig. 3. Raman spectrum of HgNTP (1) (I is intensity) and IR spectra (T is transmittance) of HgNTP (2) and its thermal decomposition products at 500°C in air (3) and under argon (4).

ciable thermal effect. An abrupt change at 160–180°C is due to the elimination of one Hg atom from two structural units of HgNTP, which is manifested as an intense exothermic peak. In air, this process is accompanied by attachment of an oxygen atom; this is evident from the corresponding differences between the sample weights as well as between the thermal effects measured in air and under argon. At 180–280°C, the mercury atoms are sequentially eliminated, with a slight endothermic effect. The nitrogen atom is eliminated at 330–340°C. Further heating results in gradual endothermic decomposition of mercury oxide, with evaporation of its decomposition products. The IR spectrum of the solid residue shows characteristic

bands due to mercury(II) oxide (503 and 604 cm^{-1}) [48], phosphate groups (995, 1110, 1170, and 1240 cm^{-1}), and organic fragments (cm^{-1}): 1430 $\delta_{\text{as}}(\text{CH}_2)$, 1470 $\delta_{\text{s}}(\text{CH}_2)$, 2930 $\nu_{\text{as}}(\text{CH}_2)$, 2960 $\nu_{\text{s}}(\text{CH}_2)$.

REFERENCES

1. Petrosyan, V.S., *Ekologiya i promyshlennost' Rossii* (Ecology and Industry of Russia) 1999, no. 12, p. 34.
2. Swaran, J.S.F. and Vidhu, P., *Int. J. Environ. Res. Publ. Health*, 2010, vol. 7, no. 7, p. 2745.
3. Morris, S.K., US Pat. 1672615, USPTO, 1928.
4. Pershin, G.N., Vovchenko, G.D., Milovanova, S.H., et al., USSR Inventor's Certificate no. 121544, *Byull. Izobret.*, 1959, no. 15, p. 4.
5. Gusev, S.N., Gusev, R.S., and Gramma, A.I., RF Patent no. 2456001, *Byull. Izobret.*, 2012, no. 20, p. 24.
6. Fox, R.B. and Venezky, D.L., *J. Am. Chem. Soc.*, 1953, vol. 75, no. 16, p. 3967.
7. Venezky, D.L. and Fox, R.B., *J. Am. Chem. Soc.*, 1956, vol. 78, no. 8, p. 1664.
8. Romanov, V.V. and Khashev, Yu.M., *Khimicheskie istochniki toka* (Chemical Current Sources), Moscow: Sovetskoe radio, 1968.
9. Magarill, S.A., Borisov, S.V., Pervukhina, N.V., and Pal'chik, N.A., *Priroda* (Moscow, Russ. Fed.), 2000, no. 6, p. 46.
10. Pervukhina, N.V., Romanenko, G.V., Borisov, S.V., et al., *Zh. Strukt. Khim.*, 1999, vol. 40, no. 3, p. 561.
11. Borisov, S.V., Magarill, S.A., Romanenko, G.V., and Pervukhina, N.V., *Zh. Strukt. Khim.*, 2000, vol. 41, no. 2, p. 335.

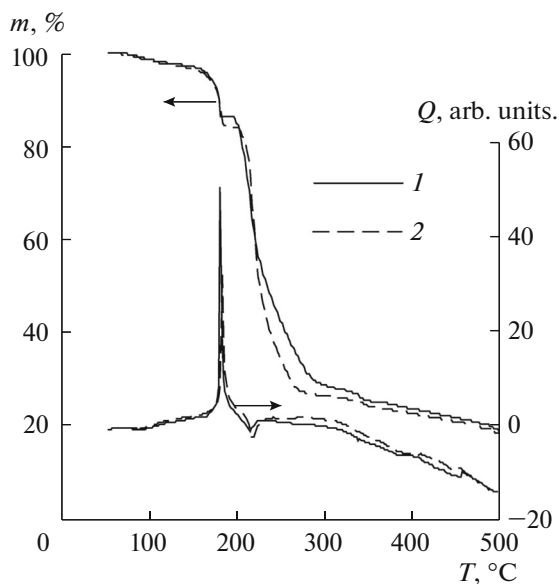


Fig. 4. TG curves of HgNTP. The plots of the sample weight (m) and the heat evolution (Q) vs. temperature (T) in air (1) and under argon (2).

12. Pervukhina, N.V., Magarill, S.A., Borisov, S.V., Romanenko, G.V., and Pal'chik, N.A., *Usp. Khim.*, 1999, vol. 68, no. 8, p. 683.
13. Kaupp, M. and von Schnering, H.G., *Inorg. Chem.*, 1994, vol. 33, no. 12, p. 2555.
14. Kaupp, M. and von Schnering, H.G., *Inorg. Chem.*, 1994, vol. 33, no. 18, p. 4179.
15. Volkova, L.M. and Magarill, S.A., *Zh. Strukt. Khim.*, 1999, vol. 40, no. 2, p. 314.
16. *Comprehensive Coordination Chemistry*, Wilkinson, G., Ed., Oxford: Pergamon, 1987, vol. 5.
17. *Comprehensive Coordination Chemistry II*, McCleverty, J.A., Meyer, T.J., and Fenton, D.E., Eds, Amsterdam: Elsevier, 2003.
18. Weil, M. and Glaum, R., *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1997, vol. 53, p. 1000.
19. Weil, M. and Glaum, R., *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2000, vol. 56, p. 133.
20. Weil, M. and Glaum, R., *Z. Anorg. Allg. Chem.*, 1999, vol. 625, no. 10, p. 1752.
21. Weil, M., *Z. Naturforsch., A: Phys. Sci.*, 2014, vol. 55, no. 8, p. 699.
22. Weil, M., *Z. Anorg. Allg. Chem.*, 2000, vol. 626, no. 8, p. 1752.
23. Dyatlova, N.M., Temkina, V.Ya., and Popov, K.I., *Kompleksy i kompleksy metallov* (Complexones and Metal Complexones), Moscow: Khimiya, 1988.
24. Kuznetsov, Yu.I., *Usp. Khim.*, 2004, vol. 73, no. 1, p. 79.
25. Mather, G.G. and Pidcock, A., *J. Chem. Soc., Dalton Trans.*, 1972, no. 5, p. 647.
26. Power, W.P., Lumsden, M.D., and Wasylishen, R.E., *Inorg. Chem.*, 1991, vol. 30, no. 15, p. 2997.
27. Kuznetsov, Yu.I. and Raskol'nikov, A.F., *Zashch. Met.*, 1992, vol. 28, no. 2, p. 249.
28. Naimushina, E.A., Chausov, F.F., Shabanova, I.N., and Kazantseva, I.S., *Izv. Akad. Nauk, Ser. Fiz.*, 2014, vol. 78, no. 4, p. 436.
29. Henish, H.K., *Crystal Growth in Gels*, Cambridge: Cambridge Univ., 1973.
30. Petrov, T.G., Treivus, E.B., Punin, Yu.O., and Kasatkin, A.P., *Vyrashchivanie kristallov iz rastvorov* (Crystal Growth from Solutions), Leningrad: Nedra, 1983.
31. CrysAlisPro. Agilent Technologies. Version 1.171.37.35 (release 13-08-2014 CrysAlis171.NET).
32. Sheldrick, G.M., *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, vol. 64, p. 112.
33. Farrugia, L.J., *J. Appl. Crystallogr.*, 1999, vol. 32, p. 837.
34. Demadis, K.D., Katarachia, S.D., and Koutmos, M., *Inorg. Chem. Commun.*, 2005, no. 8, p. 254.
35. Cabeza, A., Ouyang, X., Sharma, C.V.K., et al., *Inorg. Chem.*, 2002, vol. 41, p. 2325.
36. Chausov, F.F., Zakirova, R.M., Somov, N.V., et al., *Zh. Prikl. Khim.*, 2014, vol. 87, no. 8, p. 1046.
37. Somov, N.V. and Chausov, F.F., *Crystallogr. Rep.*, 2015, vol. 60, no. 2, p. 210.
38. Daly, J.J. and Wheatley, P.J., *J. Chem. Soc. A*, 1967, p. 212.
39. Addison, A.W., Rao, T.N., Reedijk, J., et al., *J. Chem. Soc., Dalton Trans.*, 1984, no. 7, p. 1349.
40. Gillespie, R.I., *Molecular Geometry*, New York: Van Nostrand Reinhold, 1972.
41. Shannon, R.D., *Acta Crystallogr., Sect. A: Cryst. Phys., Diff., Theor. Gen. Crystallogr.*, 1976, vol. 32, p. 751.
42. Russell, S.J., Tan, K.-H., and Taylor, M.J., *J. Raman Spectrosc.*, 1980, vol. 9, no. 5, p. 308.
43. Baran, E.J., Mormann, T., and Jeitschko, W., *J. Raman Spectrosc.*, 1999, vol. 30, no. 12, p. 1049.
44. Sahebalzamani, H., Ghamamy, S., Mehrani, K., and Salimi, F., *Chem. Sinica*, 2010, vol. 1, no. 1, p. 67.
45. Kriza, A., Dianu, M.L., and Dianu, G., *Analele universitatii Bucuresti—chimie*, 2002, vol. 11, no. 2, p. 33.
46. Canty, A.J. and Devereux, J.W., *Spectrochim. Acta, Part A*, 1980, vol. 36, no. 5, p. 495.
47. Rama, K., Reddy, K., Suneetha, P., Karigar, C.S., et al., *J. Chil. Chem. Soc.*, 2008, vol. 53, no. 4, p. 1653.
48. Pothoff, G.F. and Balt, S., *Z. Anorg. Allg. Chem.*, 1970, vol. 377, no. 3, p. 342.

Translated by D. Tolkachev