

Vibrational Spectra of Platinum Superoxo Complexes

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Abstract—Aqueous alkaline (KOH, KOD) solutions of hexahydroxoplatinate and "blue" superoxohydroxoplatinate complexes were studied by Raman spectroscopy. The spectra of superoxo complexes shows the bands at 1020 and 1060 cm^{-1} that arise from the O_2^- moiety. Solid samples of platinum hydroxide and the precipitates isolated from "blue" solutions were studied by IR and Raman spectroscopy. The spectra of hexahydroxoplatinate(IV) were assigned assuming the C_{3i} symmetry of the $\text{Pt}(\text{OH})_6^{2-}$ group. The Raman spectra of the decomposition products of the solid superoxo complex ($\nu(\text{O}-\text{O}) = 1080 \text{ cm}^{-1}$ for O_2^-) show the bands that arise from a platinum peroxo complex ($\nu(\text{O}-\text{O}) = 829 \text{ cm}^{-1}$ for O_2^{2-}).

Ozonizing alkaline solutions ($c_{\text{OH}^-} = 1\text{--}20 \text{ mol/l}$) of hexahydroxoplatinate yields platinum complexes, which predominantly exist in solutions [1, 2]. Based on electronic absorption spectroscopy and EPR evidence, these complexes were formulated as superoxohydroxoplatinate complexes [3–6]. Both methods provide only indirect evidence on the composition and electronic structure of complexes; therefore, an additional confirmation of their structure or, at least, of the occurrence of the superoxo group in these compounds is required. The same also refers to the platinum hydroxo compound incorporating a superoxo complex [7].

In this work, the above compounds were studied by IR and Raman spectroscopy with the major objective of interpreting the experimental vibrational spectra of hydroxo derivatives of platinum.

EXPERIMENTAL

Solutions containing the so-called "blue" platinum superoxo complexes [1] were prepared by ozonization of solutions of $\text{Pt}(\text{OH})_6^{2-}$ in aqueous KOH (0.1–4 M); the overall platinum concentration in these solutions was $(6.0\text{--}15) \times 10^{-3} \text{ mol/l}$. The nascent complexes were identified by electronic absorption spectroscopy and EPR, as described in [3, 4, 6]. The isolation of solids from initial and ozonized (blue) solutions was described elsewhere [5, 7]. The resulting solids were characterized by IR and Raman spectroscopy, as well as by EPR and X-ray powder diffraction [7].

IR spectra of solids were recorded on Perkin-Elmer 1700X (50–700 cm^{-1}), UR-20 (400–4000 cm^{-1}), and Specord-IR (200–3600 cm^{-1}) spectrophotometers. Samples were mineral oil or HCB mulls or KBr or

polyethylene pellets. Raman spectra of solutions and solids were recorded on a Nicolet Raman-950 FT spectrophotometer in the range 0–4000 cm^{-1} (Ge detector cooled with liquid nitrogen), on a Jobin-Yvon U-1000 spectrophotometer using the 457.9- and 514.5-nm lines of a Karl Zeiss Ar-ILA-120 argon laser (in the range 650–1200 cm^{-1}), and on a DFS-24 spectrophotometer at a wavelength of 514.5 nm (in the range 450–1200 cm^{-1}).²

RESULTS AND DISCUSSION

Alkaline solutions. Studying alkaline solutions by Raman spectroscopy has some specific features. An increase in alkali concentration in a solution from 0 to 20 M KOH leads to a considerable decrease in spectral intensity and even to the complete disappearance of spectra. This is presumably associated with the enhancement of the interaction between the electrolyte and the solvent as the concentration of the former increases. This leads to the formation of bulky structure-ordered fragments, whose mass increases with a decrease in solvent concentration.

Figure 1 shows the Raman spectra of water and KOH solutions (as well as of their deuterated congeners, D_2O and KOD). In a long-wavelength region of the spectrum of KOH, the band due to O–H stretching vibrations "is extinguished." A similar phenomenon

¹ Raman spectra were acquired by repeatedly scanning the frequency range (the number of scans was no less than 600).

² Some Raman spectra of blue platinum superoxo complexes were obtained by V.V. Berdyugin and P.P. Shorygin (Institute of Organic Chemistry, RAS) and by N.A. Chumaevskii (Institute of General and Inorganic Chemistry, RAS), which is gratefully acknowledged.

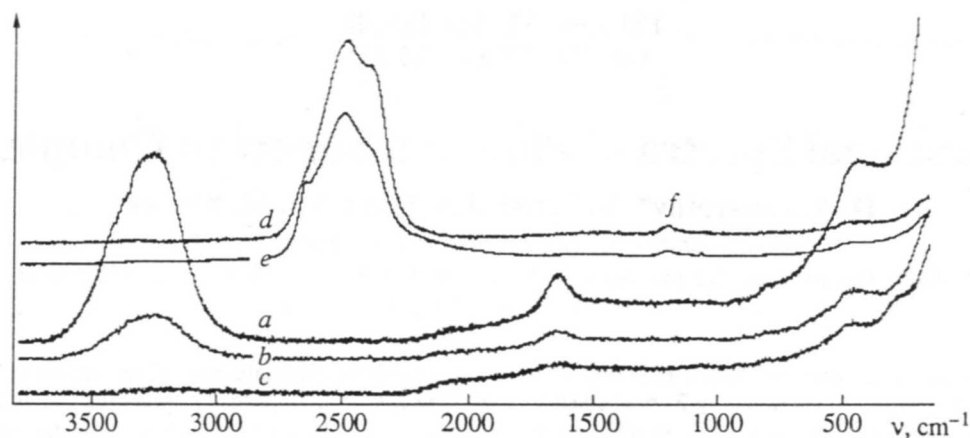


Fig. 1. Band extinction in the Raman spectra of solutions of supporting electrolytes: (a) H_2O , (b) 3 M KOH, (c) 10 M KOH, (d) D_2O , and (e) 3 M KOD; (f) the peak corresponding to the impurity CO_3^{2-} ion.

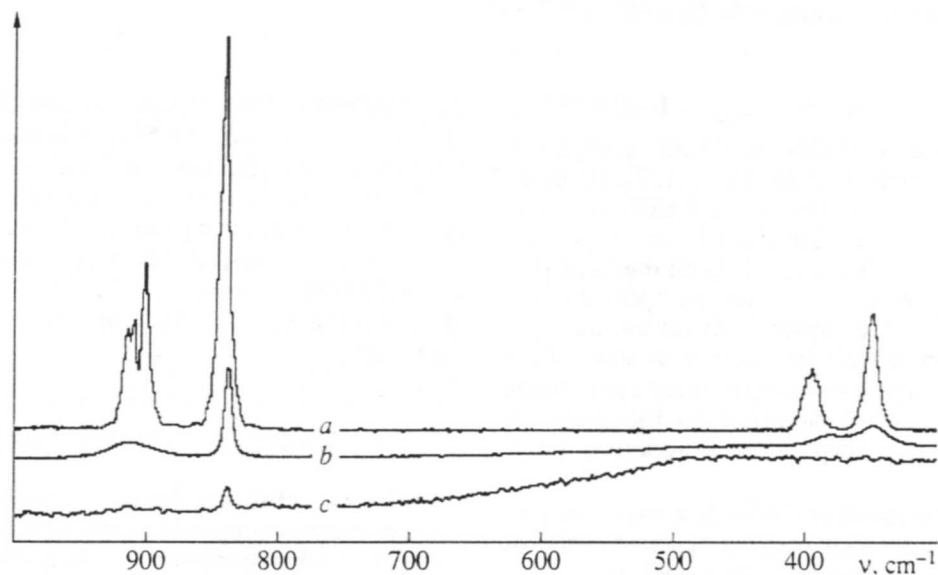


Fig. 2. Raman spectra of (a) KMnO_4 and its solutions in (b) water and (c) 3 M KOH.

was observed in the Raman spectra of MnO_4^- ions in neutral and alkaline solutions. For example, a 0.1 M KMnO_4 aqueous solution gives rise to well-defined peaks at 346, 386, 834, and 902 cm^{-1} (Fig. 2, spectrum *b*) assigned, in accordance with [8], to ν_2 , ν_4 , ν_1 , and ν_3 , respectively. In the Raman spectrum of a KMnO_4 solution in 3 M KOH, the intensities of these peaks abruptly decrease: The ν_1 and ν_3 frequencies persist in the spectrum, and the remaining peaks are unobservable (Fig. 2, spectrum *c*). We observed a similar effect in some other systems— SO_4^{2-} , CO_3^{2-} , NO_3^- , and H_2O_2 —in aqueous and aqueous alkaline solutions.

Therefore, Raman spectra of alkaline solutions can show only rather strong bands of stretching vibrations, whereas weak bands and/or the bands caused by bend-

ing vibrations, which are theoretically Raman active and are observable for diluted solutions, cannot be detected at all.

Solutions of platinum hydroxo complexes. Solutions of the $\text{Pt}(\text{OH})_6^{2-}$ complexes and of the products of the ozonization of $\text{Pt}(\text{OH})_6^{2-}$ in alkaline media (which are actually platinum superoxo hydroxo complexes [1–3]), as well as solutions of alkali-metal carbonates were obtained in a KOH medium of varied concentration.

Raman spectra of some hydroxoplatinate samples prepared in air may show a band at 1066 cm^{-1} , corresponding to the stretching vibration ν_2 of the carbonate ion [9]. A similar band was observed for solutions in deuterated systems because of the contamination of KOD with carbonate. Dedicated experiments showed

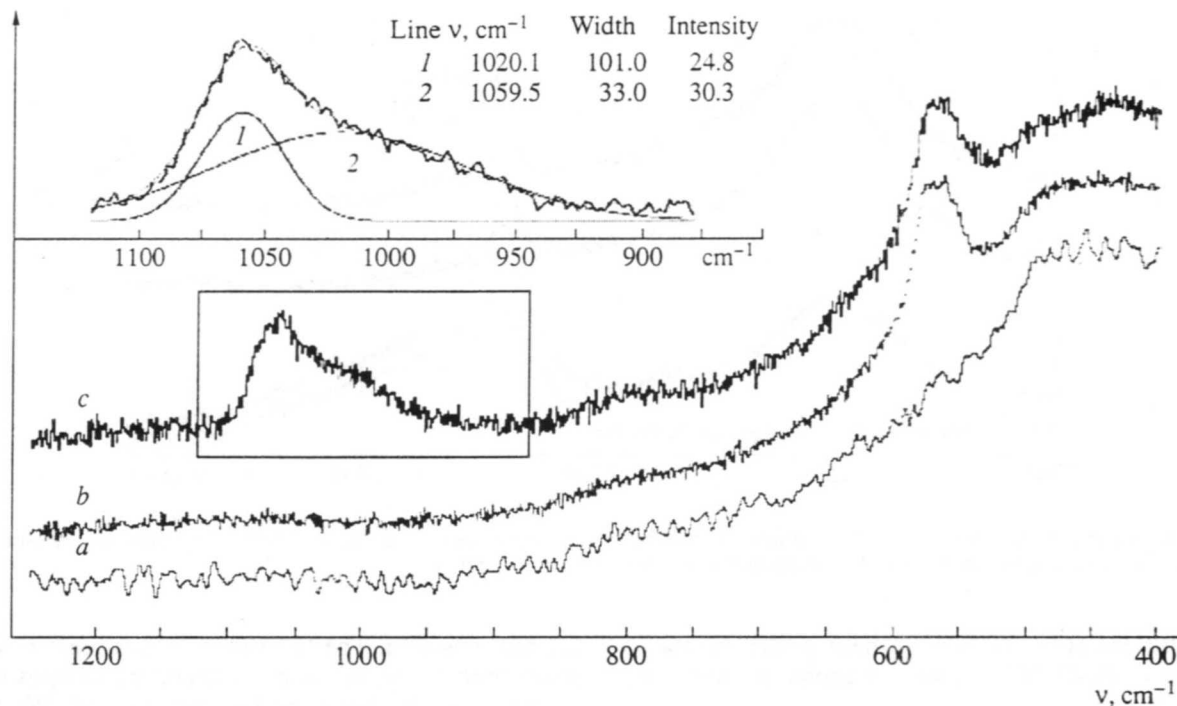


Fig. 3. Raman spectra of (a) 3 M KOH and solutions of (b) hexahydroxoplatinate(IV) and (c) a superoxo platinum(IV) complex in 3 M KOH.

that, in the Raman spectra of alkaline solutions of alkali-metal carbonates, the bands due to other CO_3^{2-} vibrations (for this ion, the ν_3 and ν_4 vibrations in the range 1350–1450 and 700–730 cm^{-1} , respectively, are Raman active) were not observed. Taking into account that the line of the carbonate ion falls into the frequency range typical of the O_2^- moiety, the experiments were carried out in a CO_2 -free atmosphere. The CO_3^{2-} content of initial solutions and of the decomposition products of superoxo complexes was monitored by observing the spectra. The lack of vibrations due to the carbonate ion in these spectra allowed us to state that the solutions were free of CO_3^{2-} . Hence, we could rule out the distortion of the spectra in question.

In addition, we studied the systems containing potassium carbonate. We obtained the Raman spectra of (i) initial $\text{Pt}(\text{OH})_6^{2-}$ solutions, (ii) the same solutions after ozonization, and (iii) the latter solutions after decomposition to the initial species (both spontaneously and under the action of a 0.1×10^{-3} M hydrogen (deuterium) peroxide solution in the alkali of appropriate concentration). We found that, even in the presence of CO_3^{2-} impurities in solutions, subtracting the spectra reliably revealed the lines caused by oscillators other than CO_3^{2-} .

Studying alkaline solutions of $\text{Pt}(\text{OH})_6^{2-}$ (or $\text{Pt}(\text{OD})_6^{2-}$) in H_2O (or D_2O), their ozonization products, and the decomposition products of the latter showed that, in a region above ca. 1150 cm^{-1} , the Raman spectra of these solutions are roughly the same as the spectra of supporting potassium hydroxide solutions of appropriate concentration.

The spectra of $\text{Pt}(\text{OH})_6^{2-}$ show weak (especially for more than 3 M KOH) peaks at 470, 570, and 820 cm^{-1} (Fig. 3, spectrum b). Similar spectra arise from solutions that form upon decomposition of ozonized blue solutions.

The Raman spectra of ozonized solutions of $\text{Pt}(\text{OH})_6^{2-}$ in less than 5 M KOH (blue complexes [1, 3]) show a strong asymmetric band in the range 920–1100 cm^{-1} (Fig. 3, spectrum c). The line shape is approximated by a sum of two Gaussian curves with maxima at 1020.1 and 1059.5 cm^{-1} taken in a ca. 4 : 5 intensity ratio (Fig. 3, spectrum c). The first line is ca. three times as broad as the second line. Whatever the conditions of preparing the samples and recording the spectra, these lines retain their position and intensity ratio. Studying the ozonized and initial solutions of $\text{Pr}(\text{OH})_6^{2-}$ in D_2O showed that the position and intensity ratio of these lines remained unaltered for deuter-

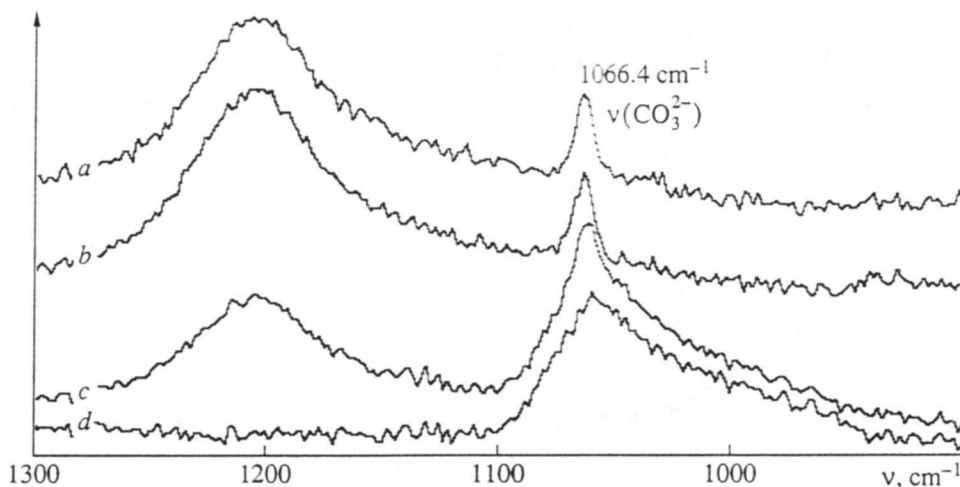


Fig. 4. Raman spectra of (a) 3 M KOD and solutions of (b) hexahydroxoplatinate(IV) and (c) a platinum(IV) superoxo complex in 3 M KOD; (d) the spectrum obtained by subtraction of spectrum *b* from spectrum *c*.

ated solutions (Fig. 4); hence, these peaks cannot be assigned to Pt–O–H bending vibrations, as was done previously in [10].

We assign the above bands to $\nu(\text{O–O})$ stretching vibrations of the superoxo group coordinated to platinum. The superposition of the lines at 1020 and 1060 cm^{-1} can be attributed to the occurrence of at least two complexes. This is consistent with EPR evidence on solutions of the blue complex [3]: These solutions contain three somewhat dissimilar superoxo platinum complexes. Two of these complexes are predominant, and the third one occurs as an admixture. It is likely that the major two complexes give rise to the above bands in the Raman spectrum.

The characteristic feature of the vibrational spectra of dioxygen compounds is the occurrence of the O–O stretching vibration ($\nu(\text{O–O})$) [9, 11], whose frequency is associated with the population of the oxygen π_g^* orbital. For peroxo compounds, this vibration manifests itself in a range of 750–920 cm^{-1} , whereas for superoxo derivatives (containing the O_2^- ion), this vibration is observed in a range of 1000–1200 cm^{-1} . The bands at 1020 and 1060 cm^{-1} in the Raman spectra of ozonized blue solutions evidently arise from stretching vibrations of platinum superoxo complexes.

EPR [3] and quantum-chemical [5] evidence, taken together, permits the assumption that differences in the shape and frequency of the bands under consideration can be caused either by the formation of mono- and binuclear superoxo complexes or by the formation of mono- and dibridged binuclear complexes (with the $(\mu\text{-O}_2^-)$ or $(\mu\text{-O}_2^-, \mu\text{-OH}^-)$ bridges); conformational isomerism of a binuclear superoxo complex and different compositions of the coordination sphere (for example, substitution of H_2O molecules for the OH^- groups)

are also possible. The last two versions seem to be of lower probability, because the attendant changes in the spectral pattern should be less pronounced. We think that the narrower band can arise from the superoxo ion coordinated to the platinum atom either in a mononuclear complex or in a binuclear dibridged complex and a broader band is due to the superoxo ion in a binuclear monobridged superoxo complex. This assignment is not in conflict with EPR data (a solution of the blue complex contains at least three platinum superoxo complexes [3]) and with electronic absorption spectra (according to [5, 11, 12], mononuclear complexes cannot be identified against the background of binuclear complexes, whose electronic absorption spectra are little different from one another). The decrease in the $\nu(\text{O–O})$ frequency of the binuclear complex can be caused by an increase in the electron density in the antibonding orbitals of the dioxygen moiety because of its transfer from two platinum atoms. Note that, in both the mononuclear and binuclear dibridged complexes, this transfer is energetically less favorable because of steric hindrances. The broadening of the band at 1020 cm^{-1} in the Raman spectrum of the binuclear monobridged complex, compared to the mononuclear or binuclear dibridged complexes, is associated with the occurrence of several possible conformations with close geometrical parameters in a solution [5], as well as with a stronger interaction of the bulky and "flexible" binuclear complex with the medium.

Therefore, vibrational spectroscopy provides a piece of evidence on the formation of the platinum superoxo complexes in alkaline solutions.

Solid hydroxoplatinates. The Raman spectrum of platinum hydroxide (light yellow precipitate) shows the bands at 290 and 600 cm^{-1} , the latter being rather strong (Fig. 5). The gray solid isolated from ozonized complexes and containing the superoxo platinum complex.

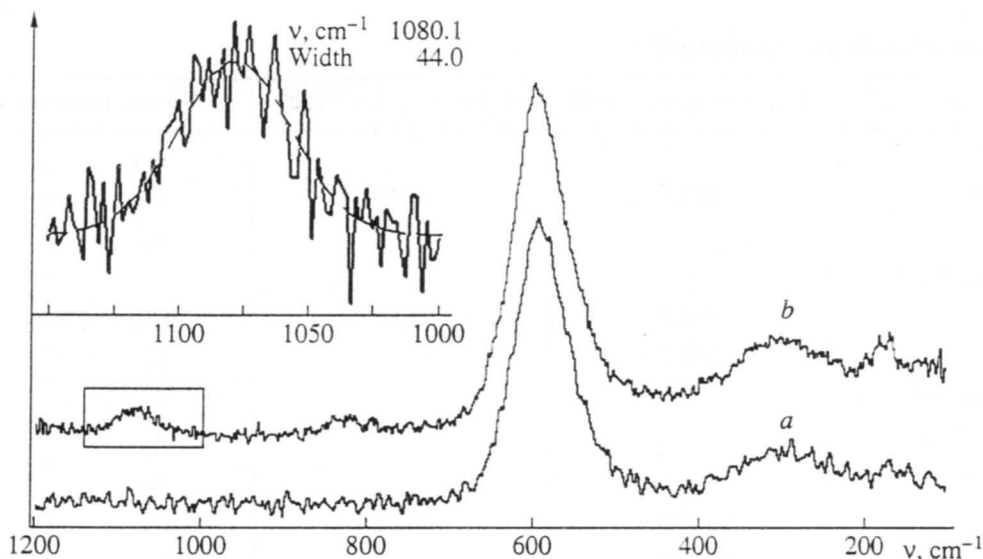


Fig. 5. Raman spectra of solid platinum(IV) (a) hydroxo and (b) superoxo complexes.

as determined in [7], gives rise to additional bands at 238, 829, and 1080 cm^{-1} .³ Spontaneous decomposition of this solid (monitored by its discoloration) is accompanied by a decrease in the intensity of the bands at 829 and 1080 cm^{-1} . Evidently, the latter band is due to the superoxo complex analogous to the complex in solutions. The band at 829 cm^{-1} corresponds to a platinum peroxy complex that forms as an intermediate product of the reduction of the superoxo complex; this intermediate is stabilized in the solid phase.

The IR spectra of all solid products are virtually the same. The IR spectrum of the yellow precipitate shows absorption bands at 350, 532, 585, 1070, 1616, and 3350 cm^{-1} ; the IR spectra of the ozonized derivatives show an extra band at 1740 cm^{-1} .

The vibrational data were interpreted assuming the C_{3i} point group of symmetry ($\Gamma = 5A_g + 5E_{2g} + 6B_u + 6E_{1u}$).⁴ The symmetry of $\text{Pt}(\text{OH})_6^{2-}$, lower than O_h , is evident if it is granted that the OH^- ions are linear rather than point ligands.⁵ The adequacy of such a description of the $\text{Pt}(\text{OH})_6^{2-}$ ion is supported by the crystal structure of $\text{K}_2\text{Pt}(\text{OH})_6$ [13]. The compound crystallizes in the rhombohedral symmetry system (space group $\bar{R}3m$). The oxygen atoms are located in parallel planes normal to the C_{3i} axis, and the metal atom resides on this C_{3i} axis between the planes [13].

³ Note that recording the Raman spectra at a rather high laser radiation power (>0.7 mV) leads to the decomposition of samples with the concurrent disappearance of spectral peaks.

⁴ This group of symmetry was chosen based on geometry optimization by molecular dynamics methods [5].

⁵ Since the orbitals of the oxygen atom in the OH^- ion are hybridized by the sp^3 type, the PtOH angle should differ from 180°.

Vibrational spectra of different hexahydroxo complexes (including $\text{K}_2\text{Pt}(\text{OH})_6$ and $\text{K}_2\text{Pt}(\text{OD})_6$) of symmetry C_{3i} have been interpreted based on group theoretical analysis and on changes in absorption frequencies for deuterated complexes [10]. Using a non-octahedral point group [10] made it possible to describe the vibrations associated with changes both in the relative positions of the central ion and the oxygen atoms and in the arrangement of the hydrogen atoms with respect to these atoms.

The assignment of vibrations for solid platinum(IV) hydroxide hydrate and solutions of $\text{Pt}(\text{OH})_6^{2-}$ is presented in the table. By analogy with [9, 10], we assigned the bands in the range 3000–3700 cm^{-1} to stretching vibrations $\nu(\text{OH})$ and the bands at 900–1100 cm^{-1} to bending vibrations $\delta(\text{PtOH})$ (in this case, $\nu_{3i}(B_u)$ and $\nu_{15}(E_{1u})$ are Raman inactive). In the region below 600 cm^{-1} , several different vibrations can occur; however, since the frequencies of these vibrations are insensitive to the isotope substitution for hydrogen atoms, the authors [10] have assigned them to stretching vibrations $\nu(\text{PtO})$ ($\nu_6(B_u)$ and $\nu_{12}(E_{1u})$) and bending vibrations $\delta(\text{OPTO})$ ($\nu_8(B_u)$ and $\nu_{16}(E_{1u})$).

Note that we studied platinum hydroxide rather than potassium hydroxoplatinate, which had been studied in [10]. This can be just the reason for some differences between our IR spectra and those in [10]. The $\delta(\text{HOH})$ bending vibration band at 1616 cm^{-1} is due to the occurrence of coordinated water molecules in the samples. Some long-wavelength displacement of bands (by ca. 20–45 cm^{-1}) is evidently caused by the lack of such a heavy counterion as K^+ . In the spectra of our samples, the stretching vibration bands of the hydroxide ion $\nu(\text{OH})$ are virtually lacking, which is likely associated with the formation of numerous hydrogen bonds

Vibrational spectra of hexahydroxoplatinates(IV)

Experimental data, cm ⁻¹	K ₂ Pt(OH) ₆ , cm ⁻¹ [10]	K ₂ Pt(OD) ₆ , cm ⁻¹ [10]	Normal modes of vibrations*	
290 (Raman)			E _{2g}	δ(OPtO)
328 (IR)	301.0	300.2	E _{1u}	δ(OPtO)
350 (IR)			B _u	τ(PtOH)
470 (Raman)**			A _g	τ(PtOH)
	515.3	513.5	E _{1u}	ν(PtO)
532 (IR)	538.3	535.0	B _u	ν(PtO)
570 (Raman)**			E _{2g}	ν(PtO)
600 (Raman)			A _g	ν(PtO)
820 (Raman)**			A _g	δ(PtOH)
	1058.0	803.5	B _u	δ(PtOH)
1070 (IR)	1076.0		E _{1u}	δ(PtOH)
3350 (IR)	3375.8	2507.8	B _u	ν(OH)
		3387.2	E _{1u}	ν(OH)

* The results of quantum-chemical calculations [5] were also used in assignment.

** Solution data (the remaining data refer to solids).

among the Pt(OH)₆²⁻ octahedra. In the Raman spectra of solid platinum hydroxide, only two stretching and bending vibrations—ν₂₁(E_{2g}) and ν₁(A_g), respectively—are active. Note that the absence of the bands in the range 900–1100 cm⁻¹ in the Raman spectra of platinum hydroxide hydrate is of crucial importance for identification of ozonized objects [5].

Therefore, our findings confirm the earlier conclusions [1–7] that platinum superoxo complexes exist in alkaline solutions and solid samples and permit some inferences concerning the structure of these complexes.

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REFERENCES

- Kiselev, Yu.M., Pankratov, D.A., Ezerskaya, N.A., *et al.*, *Zh. Neorg. Khim.*, 1994, vol. 39, no. 8, p. 1340.
- Kiselev, Yu.M., Pankratov, D.A., Kiseleva, I.N., and Shundrin, L.A., *Zh. Neorg. Khim.*, 1996, vol. 40, no. 12, p. 2069.
- Komozin, P.N., Pankratov, D.A., and Kiselev, Yu.M., *Zh. Neorg. Khim.*, 1999, vol. 44, no. 12, p. 2050.
- Pankratov, D.A. and Kiselev, Yu.M., Abstracts of Papers, XVI Mezhdunarodnaya Chernyaevskaya konferentsiya *po khimii, analizu i tekhnologii platinovykh metallov* (XVI Int. Chernyaev Conf. on Chemistry, Analysis, and Technology of Platinum Metals), Yekaterinburg, 1996, p. 81.
- Pankratov, D.A., *Cand. Sci. (Chem.) Dissertation*, Moscow: Moscow State Univ., 1998.
- Pankratov, D.A. and Kiselev, Yu.M., Abstracts of Papers, XVI Mendeleevskii s'ezd po obshchei i prikladnoi khimii (XVI Mendeleev Congr. on General and Applied Chemistry), Moscow: Nauka, 1998, vol. 1, p. 239.
- Pankratov, D.A., Komozin, P.N., and Kiselev, Yu.M., *Zh. Neorg. Khim.*, 2000, vol. 45, no. 10.
- Homborg, H. and Preetz, W., *Spectrochim. Acta, Part A*, 1976, vol. 32, p. 709.
- Nakamoto, K., *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, New York: Wiley, 1986. Translated under the title *IK-spektry i spektry KR neorganicheskikh i koordinatsionnykh soedinenii*, Moscow: Mir, 1991.
- Maltese, M. and Orville-Thomas, W.J., *J. Inorg. Nucl. Chem.*, 1967, vol. 29, p. 2533.
- Bratushko, Yu.I., *Koordinatsionnye soedineniya 3d-perekhodnykh metallov s molekulyarnym kislorodom* (Complexes of 3d Transition Metals with Dioxygen), Kiev: Naukova Dumka, 1987.
- Lever, A.B.P. and Gray, H.B., *Acc. Chem. Res.*, 1978, vol. 11, p. 348.
- Balitseva, T.G. and Kononova, M.A., *Koord. Khim.*, 1980, vol. 6, no. 3, p. 456.