Study of the equilibrium of formation of arsenic(III) lacunar heteropolytungstates by Raman spectroscopy

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The formation of lacunar heteropolyanions (HPA): $[AsW_9O_{33}]^{9-}$, $[As_2W_{19}O_{67}(H_2O)]^{14-}$, and $[As_2W_{20}O_{68}(H_2O)]^{10-}$ in aqueous solutions was investigated by Raman spectroscopy at $[Na_2HAsO_3]_0 = 0.1$, $[Na_2WO_4]_0 = 0.9$ mol L^{-1} and pH 9.4–1.6. The $[AsW_9O_{33}]^{9-}$ HPA is characterized by the most intense band ν_s (W=O) at 948 cm^{-1} retaining its position in the pH range from 8.9 to 7.5. Under these conditions, the equilibrium constant of $[AsW_9O_{33}]^{9-}$ formation from $H_2AsO_3^-$ and WO_4^{2-} ions was estimated ($\log K = 87.0\pm1.0$). The asymmetrical band at 952 cm^{-1} corresponding to $H_x[As_2W_{19}O_{67}(H_2O)]^{(14-x)-}$ shifts to 960 cm^{-1} as the pH decreases from 6.5 to 5.5, which is due to the change in HPA protonation. The $[As_2W_{20}O_{68}(H_2O)]^{10-}$ HPA is formed at pH 3.1—1.6; it is characterized by a band at 972 cm^{-1}.

Key words: heteropolytungstates, heteropolyanions, arsenic(III); ion equilibria, equilibrium constant; Raman spectroscopy, IR spectra.

Progress in the chemistry of tungsten(VI) and arsenic(III) heteropolycompounds (HPC) is due to the synthesis of new compounds, which find use as biologically active substances[1] and catalysts.[2]

In aqueous solutions, arsenic(III) and tungsten(VI) form HPC whose composition depends on the As^{III} to W^{VI} ratio, their concentrations, the nature of the cation in the initial As^{III} and W^{VI} salts, pH, and the temperature. Previously, it was found that acidification of solutions of sodium arsenite and tungstate ($[W^{VI}] : [As^{III}] \approx (9—10) : 1$) results in the formation of several heteropolyanions (HPA): $[AsW_9O_{33}]^{9-}$ (below, AsW_9) (pH 7.5—9.0), $[As_2W_{19}O_{67}(H_2O)]^{14-}$ (As_2W_{19}) (pH 4.0—7.5),[3] $[NaAs_4W_{40}O_{140}]^{27-}$ ($NaAs_4W_{40}$) (pH ~4), and $[As_2W_{20}O_{68}(H_2O)]^{10-}$ (As_2W_{20}) (pH 2—3).[4] The heteropolyanions $[KAs_4W_{40}O_{140}]^{27-}$ (KAs_4W_{40}) and $[KAs_4W_{42}O_{144}]^{23-}$ (KAs_4W_{42}) were obtained from $NaAs_4W_{40}$.[5] The saturated $[As_2W_{21}O_{69}(H_2O)]^{6-}$ HPA (As_2W_{21}) is formed from stoichiometric amounts of As_2O_3 and Na_2WO_4 at pH < 1.[6] The crystals of the salt $(NH_4)_7[H_2AsW_{18}O_{60}]\cdot16H_2O$ were prepared from a solution of Na_2WO_4 and As_2O_3 at pH ~3 and at an $[As^{III}] : [W^{VI}]$ ratio of 1 : 18.[7] The potassium salt of the $[AsW_8O_{30}AsOH]^{7-}$ complex crystallizes from a solution of KH_2AsO_3 and K_2WO_4 ($[W^{VI}] : [As^{III}] = 9 : 1$) at pH 8—9.[8] The addition of sodium tungstate to a solution of this complex with lowering the pH to 4.2 gave the heteropolytungstate $[As_4W_{20}O_{72}(H_2O)_2]^{12-}$.[9] The crystals of the $Na_3[As_3W_3O_{15}]\cdot10H_2O$ complex precipitate from a solution containing Na_2HAsO_3 and $WO_3\cdot H_2O$ when the initial $[As^{III}] : [W^{VI}]$ ratio is 1 : 1.[10]

The structures of lacunar HPA, AsW_9, As_2W_{19}, As_2W_{20}, and As_4W_{40}, were established by X-ray diffraction analysis in complexes with metal cations, namely, $K_{12}[As_2W_{18}O_{66}Cu_3(H_2O)_2]\cdot11H_2O$,[11] $K_5Cs_5[(Hg_2)_2WO(H_2O)(AsW_9O_{33})_2]$,[12] $Rb_8[As_2CoW_{20}O_{68}(H_2O)_2]\cdot10H_2O$,[13] and $(NH_4)_{23}[NH_4As_4W_{40}O_{140}Co_2(H_2O)_2]\cdot nH_2O$ ($18 \le n \le 20$).[14] Supramolecular heteropolytungstates containing 3, 4, and 12 $[AsW_9O_{33}]^{9-}$ groups have been obtained, in particular, $[Ce_2(H_2O)_7(AsW_9O_{33})_3(WO_2)_2]^{17-}$, $[Ce_4(H_2O)_{4-4x}(AsW_9O_{33})_4As(WO_3)_{2+x}(WO_5)]^{25-}$ ($x < 0.5$), and $[Ln_{12}(H_2O)_{36}(AsW_9O_{33})_{12}(WO_2)_4(W_2O_6)_8(W_5LnO_{18})_4]^{76-}$ ($Ln = Ce^{III}, La^{III}$).[15]

Previously, it was found that Raman spectroscopy allows one to identify iso- and heteropolyanions both in the solid state[16] and in solution[17—19] and in some cases, to determine the concentrations of various forms of HPA.[20] However, the lacunar HPA AsW_9, As_2W_{19}, and As_2W_{20}, which form the basis for the synthesis of metal-containing heteropolycomplexes, have not been characterized by Raman spectroscopy. In this work, we studied the equilibrium involved in the formation of heteropolycompounds in the Na_2HAsO_3—Na_2WO_4—HCl system, $As^{III} : W^{VI} = 1 : 9$, pH 9.4—1.6, by Raman spectroscopy and estimated the equilibrium constant for the formation of the $[AsW_9O_{33}]^{9-}$ HPA from the $H_2AsO_3^-$ and WO_4^{2-} ions.

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Experimental

Samples of Na_2HAsO_3 (0.170 g) and analytical grade $Na_2WO_4 \cdot 2H_2O$ (2.97 g) (molar ratio As : W = 1 : 9) were dissolved with heating in ~8 mL of H_2O, and a specified amount of 10 *N* HCl was added dropwise to the hot solution. The mixture was heated to boiling and cooled to room temperature, and the solution volume was brought to 10 mL. The total concentration of As^{III} was 0.1 mol L^{-1} and that of W^{VI} was 0.9 mol L^{-1}; the solution pH was varied from 9.4 to 1.6 by adding different amounts of HCl.

The pH was measured using a pH-121 instrument with an accuracy of ±0.02 pH units. The equilibration in the Na_2HAsO_3—Na_2WO_4—HCl system was monitored based on the time variation of the pH and the relative band intensity in the Raman spectra of WO_4^{2-} (932 cm^{-1}) and the HPA (948—972 cm^{-1}). The pH values and the Raman spectra of HPC measured at room temperature 5 days after the preparation of the solutions remained unchanged for three months.

The Raman spectra of solutions of HPC (with a 0.1 *M* solution of $NaNO_3$ (ν = 1049 cm^{-1}) as an internal standard) were recorded on a DFS-24 spectrometer with an ILM-120 laser excitation source (λ = 514 nm, linear polarization). The accuracy of determination of Raman band maxima was ±(2—3) cm^{-1}. In the Raman spectra of HPC, individual Gauss components were distinguished, similarly to the deconvolution procedure described previously.[20]

IR spectra of samples as pellets with KBr were recorded on a Specord IR-75 instrument. Phase analysis of solid HPC samples was carried out by the differentiating dissolution (DD) method as described previously.[21] The accuracy of determination of the Na, As, and W elements was ±10% (w/w).

Results and Discussion

Figure 1 shows the Raman spectra of aqueous solutions of Na_2HAsO_3 and Na_2WO_4 (molar ratio 1 : 9) at different pH in the region of 1100—800 cm^{-1}, which is the most characteristic for HPA.[16] The Raman spectrum at pH 9.4 (see Fig. 1, spectrum *a*) exhibits bands due to the WO_4^{2-} ion: 932 cm^{-1} (the W=O vibration) and 833 cm^{-1} (the W—O—W asymmetric vibration).[22] No Na_2HAsO_3 was found at this concentration. On the addition of HCl to a mixture of Na_2HAsO_3 and Na_2WO_4, a band at 948 cm^{-1} appears in the Raman spectra, in addition to the WO_4^{2-} band at 932 cm^{-1}, and becomes more and more intense (see Fig. 1, spectra *b* and *c*). The position of this band remains the same as the pH varies from 8.9 to 7.5, while the intensity of the band at 932 cm^{-1} decreases. When solutions of Na_2HAsO_3 and Na_2WO_4 are acidified to pH 6.5, the Raman spectrum exhibits a strong asymmetric band at 952 cm^{-1} (see Fig. 1, spectrum *d*). At pH 5.6 and 5.0, the spectral pattern is the same; however, the absorption maximum shifts to 956 and 960 cm^{-1}, respectively. When pH is 3.1—1.6, the Raman spectra contain a strong band at 972 cm^{-1}, the spectral pattern remaining similar to that shown in Fig. 1 (spectrum *d*).

In order to interpret the Raman spectra, aqueous solutions of Na_2HAsO_3 and Na_2WO_4 with different pH were concentrated to dryness at room temperature and the resulting solid specimens were studied by the differentiating dissolution procedure and by IR and Raman spectroscopy. The contents of the major compound in the solid specimens and its fragmentary formula determined from the dissolution stoichiograms are listed in Table 1. The DD data showed that Na, As, and W occur mainly (by 76—88% w/w) within the same phase with the stoichiometry Na_9AsW_9 (pH 7.6), $Na_6AsW_{9.5}$ (pH 5.6), and Na_5AsW_{10} (pH 3.1).

The IR spectra of solids (Fig. 2) confirm the formation of As^{III} and W^{VI} HPC.[21] The spectra exhibit

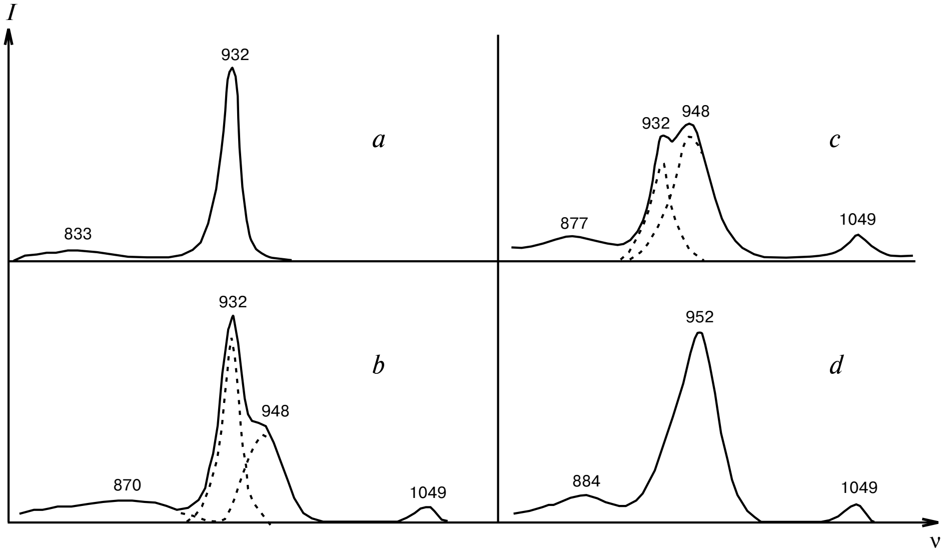

Fig. 1. Fragments of the Raman spectra of solutions of Na_2HAsO_3 and Na_2WO_4 at pH 9.4 (*a*), 8.4 (*b*), 7.9 (*c*), and 6.5 (*d*). $[As^{III}]_0$ = 0.1 mol L^{-1}, $[W^{VI}]_0$ = 0.9 mol L^{-1}. (1049 cm^{-1} is the line for the $NaNO_3$ standard).

Table 1. Composition of solid specimens of the As^{III}—W^{VI} HPC according to DD data

Solution pH	Composition of the major phase	Content (% w/w)		Molecular formula of the major substance
		Major phase	H_2O	
7.6	Na_9AsW_9	87.6	6.04	$Na_9[AsW_9O_{33}] \cdot 9H_2O$
5.6	$Na_6AsW_{9.5}$	84.5	7.17	$Na_{12}H_2[As_2W_{19}O_{67}(H_2O)] \cdot 20H_2O$
3.1	Na_5AsW_{10}	76.0	6.02	$Na_{10}[As_2W_{20}O_{68}(H_2O)] \cdot 17H_2O$

groups of bands corresponding to tungsten—oxygen bond vibrations in the heteropolyanions derived from the $[As_2W_{21}O_{69}(H_2O)]^{6-}$ anions:[23] ν_{as}(W=O) at 935—950 cm^{-1} and ν_{as}(W—O—W) at 883—890 and 795—727 cm^{-1}.

The Raman spectra of solid HPC specimens (Fig. 3) in the region of 1100—800 cm^{-1} are similar to the Raman spectra of the corresponding solutions, indicating that the compounds are similar in solutions and in the solid state. Thus, the band at 948 cm^{-1} observed in the Raman spectrum of solutions of Na_2HAsO_3 and Na_2WO_4 refers to the AsW_9 HPA. The band whose position changes from 952 to 960 cm^{-1} with pH variation from 6.5 to 5.0 was assigned to the partially protonated As_2W_{19} HPA and the band at 972 cm^{-1} was attributed to the As_2W_{20} HPA.

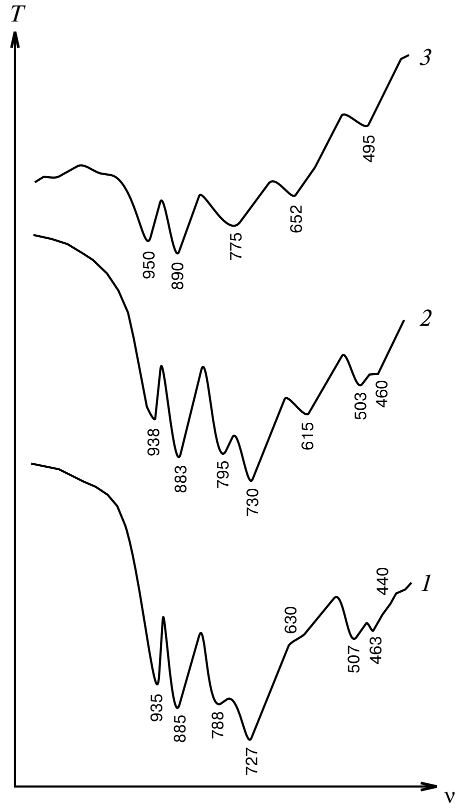

Fig. 2. IR spectra of solid specimens prepared by concentrating solutions of Na_2HAsO_3 and Na_2WO_4 with pH 7.6 (*1*), 5.6 (*2*), and 3.1 (*3*).

The Raman spectra recorded for As^{III}—W^{VI} HPC differ from the Raman spectra of the $[KAs_4W_{40}O_{140}]^{27-}$, $[KAs_4W_{42}O_{144}]^{23-}$,[5] or $[As_2W_{21}O_{69}(H_2O)]^{6-}$ HPA.[23] The frequencies of the strongest and the furthest short-wavelength band in the Raman spectra of KAs_4W_{40} and KAs_4W_{42} are 965 and 983 cm^{-1}, respectively, and that for As_2W_{21} is 986 cm^{-1}. In the case of AsW_9, As_2W_{19}, and As_2W_{20}, this band shifts to higher frequencies, from 948 to 952—960 and 972 cm^{-1}, respectively (see Fig. 3). This band is always present for tungsten HPA; it is due to symmetrical stretching vibrations of the terminal oxygen—tungsten bonds, which are strong double bonds in nature, ν_s(W=O).[24] The region of vibrations of the W—O—W bridge (800—500 cm^{-1}) [24] of the Raman spectra contains two bands in the case of KAs_4W_{40} (750 and 695 cm^{-1}) and one band for KAs_4W_{42} (741 cm^{-1}). In the case of AsW_9, As_2W_{19}, As_2W_{20}, and As_2W_{21},[23] the bands for the W—O—W bridge vibrations are rather weak. In the low-frequency region (230—200 cm^{-1}) showing the ν(W—O_a) vibrations,[24] the maximum of the strongest band is displaced to 228 cm^{-1} for AsW_9, 209 cm^{-1} for As_2W_{19}, and 202 cm^{-1} for As_2W_{20} (see Fig 3).

Using Raman spectra, we estimated the equilibrium constant for the formation of the $[AsW_9O_{33}]^{9-}$ HPA from the $H_2AsO_3^-$ and WO_4^{2-} ions according to the equation

$$H_2AsO_3^- + 9\,WO_4^{2-} + 10\,H^+ = [AsW_9O_{33}]^{9-} + 6\,H_2O. \quad (1)$$

The initial Na_2HAsO_3 is hydrolyzed in an aqueous solution at pH 8.5—7.5 to give the $H_2AsO_3^-$ ion.[25] The ionic strength of the solutions was ~3 g-ion L^{-1}. The equilibrium concentrations of the components for reaction (1) are related by the expressions: $[H_2AsO_3^-] = (0.1 - \alpha)$, $[WO_4^{2-}] = (0.9 - 9\alpha)$, and $[AsW_9] = \alpha$; hence, the equilibrium constant of reaction (1) can be written in the form

$$K = \alpha/\{(0.1 - \alpha)(0.9 - 9\alpha)^9[H^+]^{10}\}. \quad (2)$$

By taking the logarithm of Eq. (2) and by using pH instead of $-\log[H^+]$, we obtain the relation

$$\log K = \log K' + 10\mathrm{pH}, \quad (3)$$

where

$$\log K' = -8.6 + \log\alpha - 10\log(0.1 - \alpha). \quad (4)$$

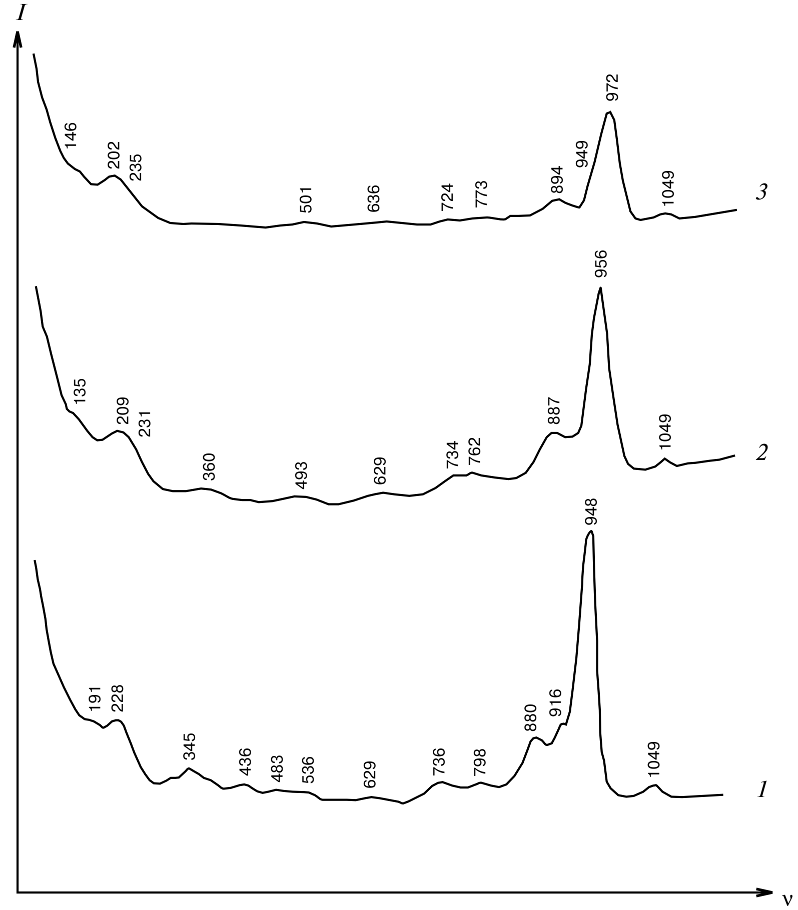

Fig. 3. Raman spectra of $Na_9[AsW_9O_{33}]\cdot 9H_2O$ (*1*), $Na_{12}H_2[As_2W_{19}O_{67}(H_2O)]\cdot 20H_2O$ (*2*), $Na_{10}[As_2W_{20}O_{68}(H_2O)]\cdot 17H_2O$ (*3*).

The value $\alpha = (0.1 - [WO_4^{2-}]/9)$ was found by determining the concentration of WO_4^{2-} from the normalized peak intensity of the band at 932 cm^{-1} after resolution of the Raman spectra into components, 948 and 932 cm^{-1} (see Fig. 1, spectra *b* and *c*): $[WO_4^{2-}] = (I_{932}/I_{1049})/k_w$, where $k_w = 22.3\pm0.7$ L g-ion^{-1},[26] and I_{1049} is the line intensity of the standard (0.1 *M* $NaNO_3$).

The resulting α values were used to calculate log*K′* from Eq. (4) and log*K* from Eq. (3) (Table 2); thus, it was found that log*K* = 87.0±1.0. Thus, the equilibrium constant for reaction (1) is of the same order of magnitude as other equilibrium constants for the formation of iso- and heteropolyanions from simple ions. For example, the logarithm of the constant for the formation of $[Mo_7O_{24}]^{6-}$ upon acidification of aqueous solutions of MoO_4^{2-}, found by Raman spectroscopy, equals 53.1±0.2,[27] while the logarithm of the equilibrium constant ($\log\beta_{15,9,1}$) for the formation of the $[PMo_9O_{31}(H_2O)_3]^{3-}$ HPA from the

Table 2. Data of the Raman spectra and α, log*K′* and log*K* values for the equilibrium of formation of AsW_9

Z*	pH	I_{1049}	I_{932}	I_{948}	$\alpha\cdot 10^2$ /mol L^{-1}	log*K′*	log*K*
			mm				
4.0	8.72	8.0	113	24	3.0	1.4	88.6
6.0	8.46	7.5	83	34	4.5	2.6	87.2
7.0	8.43	8.5	87	42	4.9	3.0	87.3
7.7	8.31	8.0	66	47	5.9	4.0	87.1
8.0	8.29	7.0	56	42	6.0	4.2	87.1
9.0	7.92	7.5	37	59	7.6	6.3	85.5
10.0	7.59	9.0	22	81	8.8	9.5	85.4

* $Z = [HCl]_0 : [Na_2HAsO_3]_0$.

HPO_4^{2-} and MoO_4^{2-} ions determined by potentiometry is 102.04.[28]

Table 2 also lists the intensities of the band at 948 cm^{-1} due to AsW_9 and the concentrations of AsW_9 (α) at different pH values. The dependence of I_{948}/I_{1049} on the AsW_9 concentration is linear; hence, it is possible to find the proportionality factor $k = (101\pm1)$ L mol^{-1} for the equation: $I_{948}/I_{1049} = k[AsW_9]$, which allows one to estimate the AsW_9 concentration in aqueous solutions from Raman spectra.

Thus, comparison of the Raman spectra of solutions and solid specimens of sodium salts characterized by the DD method and by IR spectroscopy demonstrated that lacunar As^{III} and W^{VI} HPA can be identified from the Raman spectra, because they markedly differ in the position of the strongest short-wavelength band corresponding to stretching vibrations of the bond between the W atom and the terminal O atom, $\nu_s(W=O)$: 948 cm^{-1} (AsW_9), 952—960 cm^{-1} ($H_xAs_2W_{19}$), and 972 cm^{-1} (As_2W_{20}). The resolution of Raman spectra into the components at 948 cm^{-1} (AsW_9) and 932 cm^{-1} (WO_4^{2-}) allowed us to estimate the equilibrium constant for the formation of AsW_9 from the $H_2AsO_3^-$ and WO_4^{2-} ions in an aqueous solution at pH 8.7—7.6 ($\log K = 87.0\pm1.0$).

References

1. J. T. Rhule, C. L. Hill, D. A. Judd, and R. F. Schinazi, *Chem. Rev.*, 1998, **98**, 327.
2. C. L. Hill and C. M. Prosser-McCartha, *Coord. Chem. Rev.,* 1995, **143**, 407.
3. C. M. Tourné, A. Revel, G. Tourné, and M. Vendrell, *C. R. Acad. Sci., Ser. C.,* 1973, **277**, 643.
4. M. Leyrie, J. Martin-Frère, and G. Hervé, *C. R. Acad. Sci., Ser. C*, 1974, **279**, 895.
5. M. Leyrie and G. Hervé, *Nouv. J. Chim.*, 1978, **2**, 233.
6. Y. Jeannin and J. Martin-Frère, *J. Am. Chem. Soc.*, 1981, **103**, 1664.
7. Y. Jeannin and J. Martin-Frère, *Inorg. Chem.*, 1979, **18**, 3010.
8. M. Leyrie, A. Tézé, and G. Hervé, *Inorg. Chem.*, 1985, **24**, 1275.
9. Y. Jeannin, *C. R. Acad. Sci., Ser. IIc*, 1999, **2**, 161.
10. J. Martin-Frère, Y. Jeannin, F. Robert, and J. Vaissermann, *Inorg. Chem.*, 1991, **30**, 3635.
11. F. Robert, M. Leyrie, and G. Hervé, *Acta Crystallogr.*, *Sect. B*, 1982, **38**, 358.
12. J. Martin-Frère and Y. Jeannin, *Inorg. Chem.*, 1984, **23**, 3394.
13. T. J. R. Weakley, *Inorg. Chim. Acta*, 1984, **87**, 13.
14. F. Robert, M. Leyrie, G. Hervé, A. Tézé, and Y. Jeannin, *Inorg. Chem.*, 1980, **19**, 1746.
15. M. T. Pope, X. Wei, K. Wassermann, and M. H. Dickman, *C. R. Acad. Sci., Ser. IIc*, 1998, **1**, 297.
16. E. N. Yurchenko, L. G. Detusheva, L. P. Solov´eva, G. N. Kustova, S. V. Tsybulya, and T. P. Lazarenko, *Zh. Strukt. Khim.*, 1992, **33**, 48 [*Russ. J. Struct. Chem.*, 1992, **33** (Engl. Transl.)].
17. K. Murata and S. Ikeda, *Polyhedron*, 1987, **6**, 1681.
18. S. Himeno, M. Hashimoto, and T. Ueda, *Inorg. Chim. Acta*, 1999, **284**, 237.
19. T. Ueda, K. Wada, and M. Hojo, *Polyhedron*, 2001, **20**, 83.
20. L. G. Detusheva, E. N. Yurchenko, and T. P. Lazarenko, *Koord. Khim.*, 1991, **17**, 1078 [*Sov. J. Coord. Chem.*, 1991, **17** (Engl. Transl.)].
21. L. G. Detusheva, L. I. Kuznetsova, V. A. Likholobov, A. A. Vlasov, N. N. Boldyreva, S. G. Poryvaev, and V. V. Malakhov, *Koord. Khim.*, 1999, **25**, 611 [*Russ. J. Coord. Chem.*, 1999, **25** (Engl. Transl.)].
22. Ng Ka Yuen Simon and E. Gulari, *Polyhedron*, 1984, **3**, 1001.
23. T. D. Gutsul and E. N. Yurchenko, *Koord. Khim.*, 1992, **18**, 944 [*Russ. J. Coord. Chem.*, 1992, **18** (Engl. Transl.)].
24. C. Rocchiccioli-Deltcheff, R. Thouvenot, and R. Franck, *Spectrochim. Acta*, *Part A*, 1976, **32**, 587.
25. Yu. Yu. Lur´e, *Spravochnik po analiticheskoi khimii* [*Handbook on Analytical Chemistry*], Khimiya, Moscow, 1971, 251 (in Russian)
26. L. G. Detusheva, S. Ts. Khankhasaeva, E. N. Yurchenko, T. P. Lazarenko, and I. V. Kozhevnikov, *Koord. Khim.*, 1990, **16**, 796 [*Sov. J. Coord. Chem.*, 1990, **16** (Engl. Transl.)].
27. K. Murata and S. Ikeda, *Spectrochim. Acta*, *Part A*, 1983, **39**, 787.
28. L. Pettersson, I. Andersson, and L.-O. Öhmann, *Inorg. Chem.*, 1986, **25**, 4726.

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