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# Analysis of Composite Bands in the Electronic Absorption Spectra of Compounds in Solutions

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**Abstract**—Appearance of composite bands consisting of two individual bands with different half-widths in the course of resolution of absorption spectra was analyzed.

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Electronic absorption spectra bear information important for describing coordination compounds of transition metals in solutions. Data on the presence of *d*–*d*-transition and charge-transfer bands in the spectra, along with the other characteristics, are useful for elucidating the structure of the complexes [1–3]. In our opinion, in such cases it is necessary to use the parameters of individual bands of the initial spectra, which makes the analysis more informative [2–4]. Various resolution procedures are applied to determine the characteristics of individual bands, frequently used both for studying complexation processes in solutions and for analytical purposes [5–11]. All these procedures are based essentially on properties of functions chosen for describing the band shape; we use the Gaussian function. It is known that spectra of complexes in solutions have bands with half-width from 500 to 2000 $cm^{-1}$, but for some complexes of 4*d* and 5*d* transition metals broader bands with the half-width exceeding 3000 $cm^{-1}$ were also found [1]. However, in such cases a sum of two or more closely located bands could be considered as one band. Such bands were termed composite bands. In the course of spectrum resolution, they arise in the vicinity of broad or asymmetric maxima when the edges of these maxima are inaccessible to analysis. Previously it was suggested to use the "lognormal" distribution function for describing the shape of such bands [12]. However, by now certain evidence has been accumulated that the asymmetric shape of the bands may be due to the presence of closely located bands in the spectrum. In [4] we considered various cases of the appearance of composite bands and the possibility of their resolution into individual bands for the case when these bands have the same half-width. In this paper we analyze composite bands for the case when the half-widths of their components are different.

Consider a model spectrum that is the sum of two bands with different half-widths. Actually this may be a part of the experimental spectrum or its residue obtained by resolution of the experimental spectrum. Such a spectrum is described by an equation of type (1):

$$\varepsilon_{comp}(\nu) = \varepsilon_{1max}\cdot\exp\left[-\frac{(\nu - b_1)^2\ln 2}{\delta_1^2}\right] + \varepsilon_{2max}\cdot\exp\left[-\frac{(\nu - b_2)^2\ln 2}{\delta_2^2}\right], \quad (1)$$

where $\varepsilon_{1max}$, $\varepsilon_{2max}$, $b_1$, $b_2$, $\delta_1$, and $\delta_2$ are the parameters of the individual bands (molar extinction coefficient in the maximum, position, and half-width of each band, respectively). It is appropriate to consider the signs of the appearance of composite bands and the criteria of their resolution into individual bands using the ratios, rather than absolute values, of the parameters of the individual bands [4]. Therefore, we transform Eq. (1), replacing the constants $\varepsilon_{imax}$, $b_i$, and $\delta_i$ in this equation by dimensionless quantities. For this purpose, we divide both sides of Eq. (1) by $\varepsilon_1$ and denote as $r_1$ the ratio of the extinction coefficients of the individual bands in the maxima ($r_1 = \varepsilon_2/\varepsilon_1$). Let us express the difference between the wavenumbers of the band maxima through the half-width of the first band and a

certain positive quantity $r_2$: $b_2 - b_1 = 2r_2\delta_1$, provided that $b_2 > b_1$. Using the quantity $r_3 = \delta_2/\delta_1$ characterizing the ratio of the half-widths of the individual bands, let us replace the half-width of the second band by the product $\delta_2 = \delta_1 r_3$. Then let us apply the scaling and centering procedures and pass from the wavenumber ($\nu$) scale to the scale of relative numbers $\nu'$ using the substitution $\nu^* = \nu\sqrt{2}\ \ln 2/\delta_1$; $b^* = b\sqrt{2}\ \ln 2/\delta_1$. Let us shift the origin of the new scale of $\nu'$ to the center of the segment between the band maxima: $\nu' = \nu^* - (b_1^* + b_2^*)/2$. Then, after all the transformations, Eq. (1) will take form (2):

$$\varepsilon'_{comp}(\nu') = \exp\left[-\frac{(\nu' + r_2')^2}{2}\right] + r_1\exp\left[-\frac{(\nu' - r_2')^2}{2r_3^2}\right], \quad (2)$$

where $\varepsilon'_{comp}(\nu') = \varepsilon_{comp}(\nu)/\varepsilon_{1max}$ and $r_2' = r_2 \ldots 2\ln 2$.

Equation (2) differs from the analogous equation given in [4] by the coefficient $r_3$. Introduction of this coefficient makes this equation applicable to a wider group of spectra consisting of a sum of two Gaussian bands. By setting $r_1$ and $r_3$ from the ranges $0.1 \le r_1 \le 10$ and $0.5 \le r_3 \le 2$, from Eq. (2) and arbitrarily taken $r_2'$ it is possible to obtain any variant of the sum of individual bands, including the variants considered in [4] at $r_3$ 0. The set of $r_3$ values was chosen on the basis of data given in [1], and the set of $r_1$ values, on the basis of our experience of resolving experimental electronic absorption spectra. The program we use for resolving the electronic absorption spectra into individual bands analyzes the spectra plotted on the wavenumber scale in the ascending order from left to right. It should be noted, as it is important in resolution of composite bands, that at $r_3 < 1$ the first band to the left in the sum of the bands will be the broader band, and at $r_3 > 1$, the narrower band. In variation of $r_1$ within the above-indicated interval, the sums will differ in the contributions of the individual bands.

After taking logarithms and differentiating Eq. (2), we obtain

$$\frac{d\ln[\varepsilon'_{comp}(\nu')]}{d\nu'} = \frac{1}{\varepsilon'_{сост}(\nu')}\left\{-(\nu' + r_2')\exp\left[-\frac{(\nu' + r_2')^2}{2}\right] - r_1(\nu' - r_2')/r_3^2\exp\left[-\frac{(\nu' - r_2')^2}{2r_3^2}\right]\right\}. \quad (3)$$

Simulation showed that, in each variant, three main situations can arise in resolution of the band sum (2) into individual bands at any $r_3$ from the above-given interval. Let us discuss each situation with different values of $r_1$ and $r_2'$. First, let us consider the case when in curve *1* corresponding to the sum of two individual bands [Eq. (2)] there is a well-defined minimum between the bands (Fig. 1a). Then curve *1'* (Fig. 1a') reflecting in this case the behavior of the logarithmic anamorphosis (3) will contain two linear portions with negative slopes and three points of intersection with the abscissa. In this case, to find the parameters of the individual bands, we can use the linear part of any of the summands of Eq. (3), e.g., of the first summand:

$$\frac{d\ln[\varepsilon'_{comp}(\nu')]}{d\nu'} \cong -r_2' - \nu'. \quad (4)$$

The distance between the band maxima at the given values of $r_3$ and $r_1$ will correspond to the value of $r_2'$ at which in the range $\nu' \le -1.5r_2'$ the contribution of the second term in Eq. (3) is insignificant or on the error level and the factor $\exp[-(\nu' + r_2')^2/2]/\varepsilon'_{comp}(\nu')$ in the first term of this equation is virtually equal to unity. This provides the necessary and sufficient condition for finding the regression estimates of parameters $b_1$ (or $b_2$) and $\delta_1$ (or $\delta_2$) by Eq. (4) [7–10]. The second situation [4] arises when for each pair of the values of $r_3$ and $r_1$ the distance between the maxima of the constituent bands is equal to such a value of $r_2'$ at which in the region of the maximum of the spectrum a decrease or growth of the absorption intensity (curve *1*, Fig. 1b) leads to the formation of a shoulder in curve *1'* (Fig. 1b'), parallel to the abscissa. Within the limits of the given error model, this shoulder can be recognized as the linear segment for determining the parameters of one of the individual bands. However, the use for this purpose of the spectrum data from the range $-r_2' < \nu' < r_2'$ and of Eq. (4) leads in this case to considerable overestimation of the half-width $\delta_1$ and to the position of the maximum equal to $(b_1 + b_2)/2$. Nonrealistic estimate of the half-width can suggest the presence of two closely located bands. This problem is solved by imposing strict restrictions on the admissible values of $\varepsilon_{imax}$, $b_i$, and $\delta_i$. The third situation arises when the distance between the band maxima in sum (2) is smaller than the boundary value of $r_2'$ causing the appearance of composite bands. In this case, the shape of curve *1* in the region of the maximum is almost undistorted and is described quite satisfactorily within the framework of the initial error model by a single broad band (Fig. 1c). In the same region, the logarithmic anamorphosis (3) of this variant of the band sum contains a single linear portion necessary for

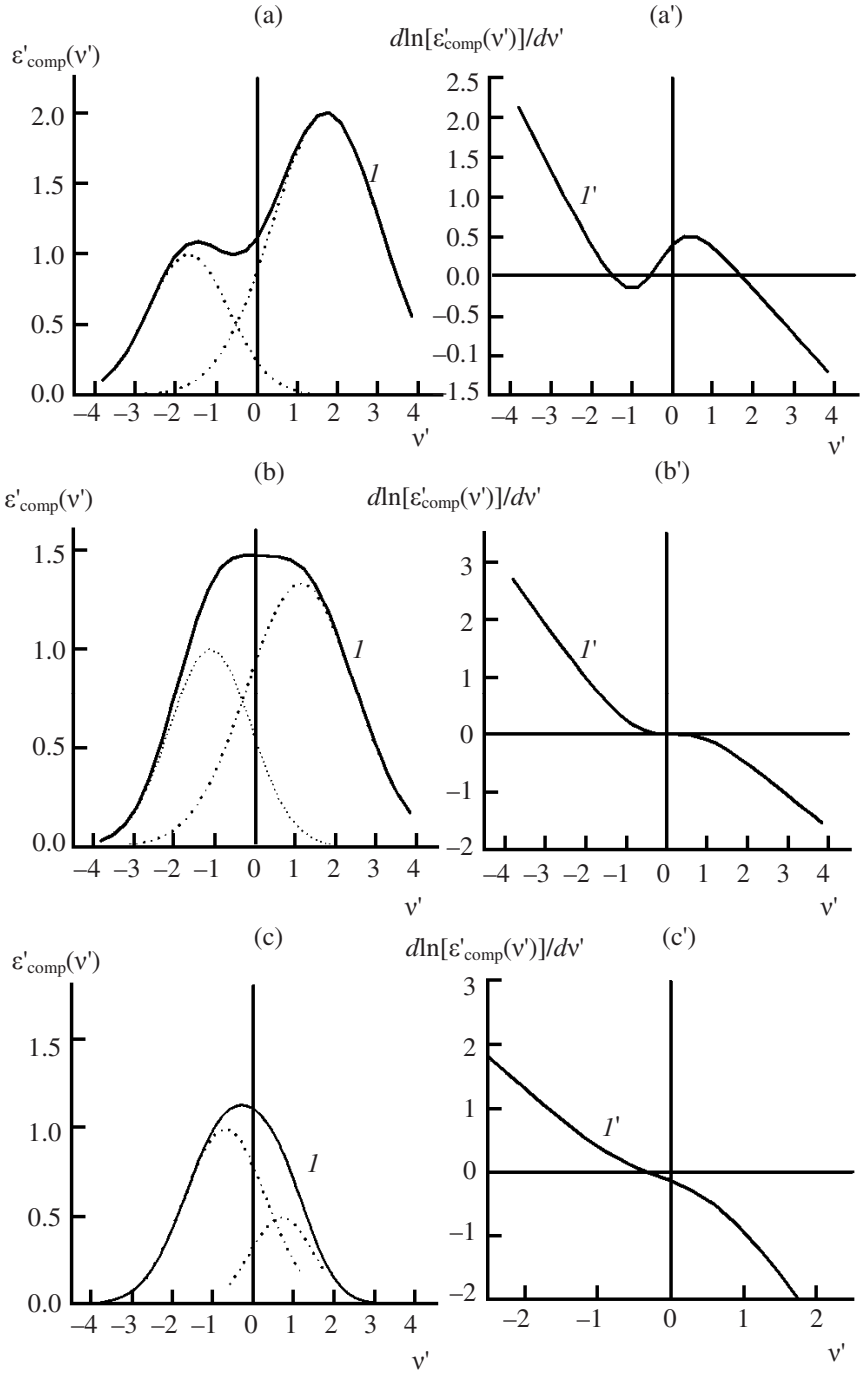


**Fig. 1**. (*1*) Sums of two individual bands and (*1'*) first derivatives of the corresponding semilog plots in the transformed coordinates (a, a') for $r_3$ 1.33 at $r_1$ 2.00 and $r_2'$ 1.70, (b, b') for $r_3$ 1.33 at $r_1$ 1.33 and $r_2'$ 1.12, and (c, c') for $r_3$ 0.75 at $r_1$ 0.5 and $r_2'$ 0.70. Dotted lines denote the individual bands.

determining the parameters (Fig. 1c'). The hypothesis that this band can be resolved into individual components can be based only on independent data on the existence of two bands in the region of the maximum under consideration.

As noted previously [4], the shoulder in curve *1'* [Eq. (3)], almost parallel to the wavenumber axis, can be a sign of the existence of composite bands. This shoulder is observed when, for the specific values of $r_3$ and $r_1$, the distance between the maxima corresponds

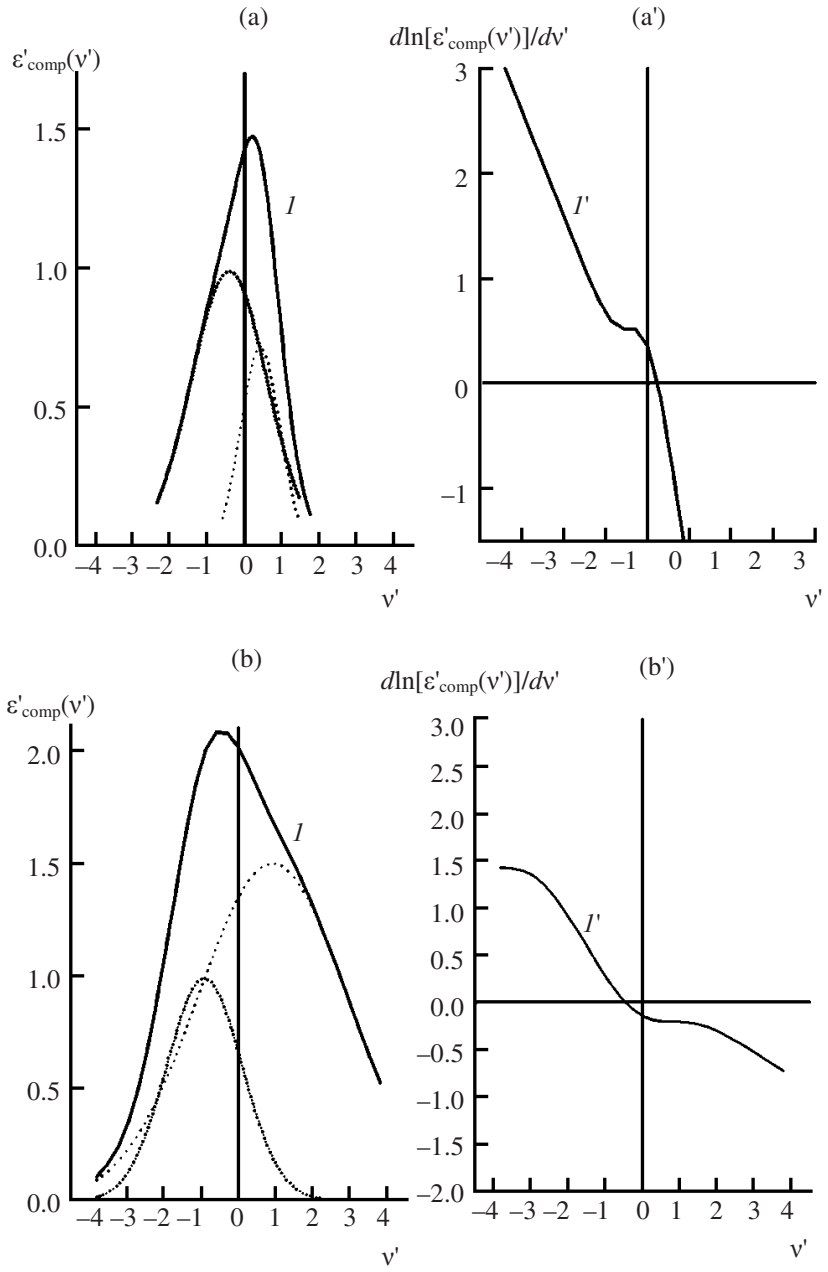


**Fig. 2**. (*1*) Sums of two individual bands and (*1'*) first derivatives of the corresponding semilog plots in the transformed coordinates (a, a') for $r_3$ 0.50 at $r_1$ 0.75 and $r_2'$ 0.42 and (b, b') for $r_3$ 2.00 at $r_1$ 1.50 and $r_2'$ 0.91. Dotted lines denote the individual bands.

to a quite definite value of $r_2'$. Therefore, based on Eqs. (2) and (3) and on the series of values (0.5, 0.75, 1.0, 1.33, and 2.0) set for $r_3$ and $r_1$, we performed simulation of such $r_2'$. The simulation results are given in the table, and curves *1* and *1'* for some of these cases are shown in Figs. 1 and 2. The variant shown in Fig. 1b corresponds to Eq. (2) when the ratio of the half-widths of the individual bands is equal to the ratio of their extinction coefficients in the maxima, $r_3 = r_1$. The $r_2'$ values corresponding to such pairs are arranged in the diagonal cells of the table. It is seen that composite bands in this case can appear in the region of the conventionally broad maximum. When in the sum of two bands the first band is broad (Fig. 2a) or narrow (Fig. 2b) and $r_3 \neq r_1$, composite bands can appear in the region of one of the branches of the asymmetric maximum if data on the second branch are inaccessible to analysis. However, resolution of the spectra and analysis of their logarithmic anamorphoses showed that there can also be other kinds of composite bands,

e.g., when the narrow band is almost fully located within the range of existence of the broad band (Fig. 2b). In this case, the parameters of the band being determined are found with the SPEKTR1 program as the mean parameters of the constituent individual bands, $\delta_{det} \approx (\delta_1 + \delta_2)/2$, $b_{det} \approx (b_1 + b_2)/2$, and $\varepsilon_{det\ max} \approx (\varepsilon_{1max} + \varepsilon_{2max})/2$. This band has realistic parameters, but its being a composite band follows only from the analysis of the behavior of the derivative of the logarithmic anamorphosis. In the case under consideration, all the composite bands consisting of individual bands with different half-widths are asymmetric relative to the ordinate. The results given in the table can be used for simulating, using Eq. (2), variants similar to certain portions of experimental spectra containing composite bands and also for choosing restrictions imposed on the parameters of individual bands when resolving composite bands into components. We used such procedures for resolving the experimental spectra of mercury(II) chloro complexes and of niobium(IV) complexes with sterically hindered β-diketones [13, 14]. Two variants of the resolution of the experimental spectrum of the niobium(IV) complex $NbL_4$, where HL is 1-(1-methoxycyclohexyl)-4-methyl-1,3-pentanedione, are shown in Fig. 3. In Fig. 3a, the spectrum is resolved into two composite bands with $\lambda_{max}$ 555.6 and 420.2 nm. The composite nature of these bands follows from analysis of the logarithmic anamorphosis of the initial spectrum

Boundary values of $r_2'$ (on intersections of rows and columns) at which composite bands can arise

| $r_1$ | $r_3$ | | | | |
|---|---|---|---|---|---|
| | 2.00 | 1.33 | 1.00 | 0.75 | 0.50 |
| 2.00 | 1.25 | 1.19 | 1.00 | 0.73 | None |
| 1.33 | 0.98 | 1.12 | 1.00 | 0.77 | None |
| 1.00 | 0.70 | 1.07 | 1.00 | 0.81 | 0.35 |
| 0.75 | 0.25 | 1.05 | 1.00 | 0.85 | 0.42 |
| 0.50 | None | 0.94 | 1.00 | 0.90 | 0.57 |

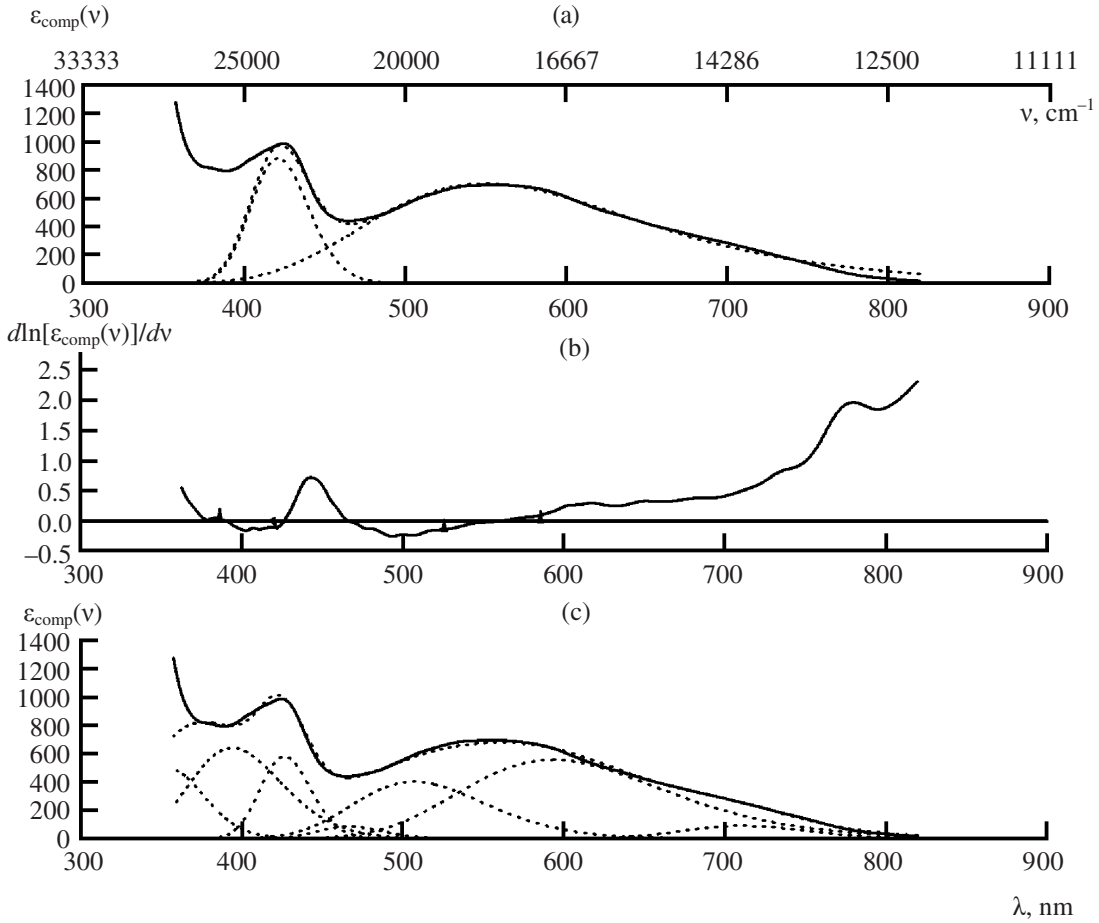


**Fig. 3**. (a) Solid line: electronic absorption spectrum of the complex $NbL_4$; dashed lines: composite bands obtained by its resolution; (b) first derivative of the experimental spectrum plotted in the semilog scale; (c) solid line: electronic absorption spectrum of the complex $NbL_4$; dashed lines: its Gaussian components obtained by resolution of the composite bands.

(Fig. 3b), in which there are portions almost parallel to the abscissa. In Fig. 3c, the composite bands are resolved using simulation, and each band is replaced by a sum of two individual bands.

Thus, composite bands consisting of the sum of two individual bands with different intensities and half-widths can arise in the course of resolution of the absorption spectra at $r_3 > 0.5$ and $r_1 \geq 0.75$, or at $r_3$ from the range $0.25 < r_3 \leq 0.5$ and $r_1 \leq 1.0$. At $r_3$ 0.25 and below, detection of composite bands seems impossible. We hope that further accumulation of information in this field will allow more correct resolution of composite bands of various kinds in experimental spectra. To conclude, the analysis we performed is also useful when using the Origin program for the search for Gaussian components.

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## REFERENCES

1. Lever, A.B.P., *Inorganic Electronic Spectroscopy,* Amsterdam: Elsevier, 1984. Translated under the title *Elektronnaya spektroskopiya neorganicheskikh soedinenii*, Moscow: Mir, 1987, part 1, p. 493.
2. Isci, H. and Mason. W.R., *Inorg. Chem.,* 1983, vol. 22, no. 16, p. 2267.
3. Makotchenko, E.V., Malkova, V.I., and Belevantsev, V.I., *Koord. Khim*., 1999, vol. 25, no. 4, p. 302.
4. Belevantsev, V.I., Malkova, V.I., and Makotchenko, E.V., *Koord. Khim*., 2006, vol. 32, no. 10, p. 764.
5. Morrey, J.R., *Anal. Chem*., 1968, vol. 40, no. 6, p. 905.
6. Grushka, E. and Israeli, D., *Anal. Chem*., 1990, vol. 62, no. 7, p. 717.
7. Yatsimirskii, K.B. and Mal'kova, T.M., *Zh. Neorg. Khim*., 1961, vol. 6, no. 4, p. 835.
8. Barker, B.E., Fox, M.F., Hayon, E., and Ross, E.W., *Anal. Chem*., 1974, vol. 46, no. 12, p. 1785.
9. O'Haver, T.C. and Begley, T., *Anal. Chem.*, 1981, vol. 53, no. 12, p. 1876.
10. Belevantsev, V.I., Malkova, V.I., Ryzhkov, V.D., and Peshchevitskii, B.I., Izv. *Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1972, issue 4, p. 19.
11. Malkova, V.I. and Belevantsev, V.I., in T*rudy Sibirskoi konferentsii po prikladnoi i industrial'noi matematike, posvyashchennoi pamyati L.V. Kantorovicha* (Proc. Siberian Conf. on Applied and Industrial Mathematics, Dedicated to the Memory of L.V. Kantorovich), Novosibirsk: Sib. Otd. Ross. Akad. Nauk, 1997, vol. 2, p. 146.
12. Siano, D.V. and Metzlier, D.E., *J. Chem. Phys*., 1969, vol. 51, no. 5, p. 1856.
13. Belevantsev, V.I., Malkova, V.I., Gushchina, L.V., and Obolenskii, A.A., *Koord. Khim.*, 2006, vol. 30, no. 7, p. 499.
14. Kandybin, M.V., Belaya, S.V., Malkova, V.I., Nadolinnyi, V.A., Semyannikov, P.P., Igumenov, I.K., Zanina, A.S., Shergina, S.I., and Sokolov, I.E., *Zh. Obshch. Khim.*, 1999, vol. 69, no. 6, p. 902.