Extraction and Spectrophotometric Determination of Molybdenum with \( o \)-Hydroxythiophenols and Aromatic Amines

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Abstract

The interaction of molybdenum (VI) with \( o \)-hydroxythiophenol derivatives (HTPDs) and aromatic amines (AAs) was studied. The following three HTPDs, which contain different halogen atoms at position 5, were used: 2-hydroxy-5-chlorothiophenol (HCTP), 2-hydroxy-5-bromothiophenol (HBTP), 2-hydroxy-5-iodothiophenol (HITP). The examined AAs were aniline (An), N-methylaniline (mAn) and N,N-dimethylaniline (dAn). The obtained ternary complexes have a composition of 1:2:2 \{Mo(V):HBTP:AA\}. Optimal conditions for their liquid-liquid extraction (LLE) were found: organic solvent (chloroform), pH (4-6), concentration of the reagents (\((1.3-1.5) \times 10^{-3} \text{mol dm}^{-3}\) (HTPD) and \((1.2-1.5) \times 10^{-3} \text{mol dm}^{-3}\) (AA)) and extraction time (colour develops almost immediately after the reagents addition). The absorbance of the extracts is stable for at least 48 hours. The optimum shaking time is 10 min.). Under the optimal conditions, the complexes have absorption maxima (\(\lambda_{\text{max}}\)) at 515-538 nm and molar absorptivities (\(\varepsilon_{\text{max}}\)) between \(3.1 \times 10^{4} \text{dm}^{3} \text{mol}^{-1} \text{cm}^{-1}\). The degrees of extraction were \(\geq 98.4\%\). The results suggested that linear relationships exist between the spectral characteristics (\(\lambda_{\text{max}}\) or \(\varepsilon_{\text{max}}\)) and some fundamental properties of the halogen substituent in the HTPD (atomic mass and electronegativity). The effect of foreign ions on the LLE-spectrophotometric determination of molybdenum was examined and two sensitive, selective and precise procedures for molybdenum determination were proposed. The relative standard deviations for Mo content of (3-5) \(\times 10^{-4}\%\) were 4\% (HCTP-An procedure) and 3\% (HBTP-An procedure).

Keywords: Molybdenum(V); Solvent extraction; Ternary complex; Soil analysis; Plant analysis; Linear relationship

Introduction

Molybdenum has been recognized as an essential trace element for plants, animals and humans. In plants, molybdenum has a key function in the fixation of the atmospheric nitrogen [1]. In mammals, it is important for the activity of the enzymes xantine oxidase, sulphite oxidase, and aldehyde oxidase. Beneficial effects of molybdenum on patients with sulphite sensitivity and asthma have been observed. It has also been stated that molybdenum reduces the incidence of dental caries [2]. On the other hand, molybdenum can be toxic at high concentrations [3,4]. In humans, it increases the lability of blood pressure, disturbs the cholesterol transport and causes bone deformation. Effects of acute molybdenum toxicity include diarrhoea, anaemia and gout. Chronic occupational exposure has been associated with weakness, fatigue, lack of appetite, anorexia, joint pain and tremor [2].
Despite its relative rarity in the Earth’s crust (estimated abundance in the range 0.05-40 mg kg$^{-1}$ with a mean value of 1.5 mg kg$^{-1}$) [5,6], geochemical anomalies leading to molybdenum deficiencies in plants are not common [7,8] and are mostly of concern for leguminous crops. Molybdenum fertilization is often based on visual deficiency symptoms and/or history of crop rotation [8]. However, in order to assess the need for fertilization and the molybdenum dosage it is preferable to use analytical methods [5,6].

Recently, several techniques have been used for molybdenum determination: UV-Vis spectrophotometry, inductively coupled plasma mass spectrometry (ICP-MS), flame atomic absorption spectrophotometry (FAAS), electrothermal atomic absorption spectrometry (ETAAS), adsorptive anodic stripping voltammetry, and inductively coupled plasma optical emission spectrophotometry (ICP-OES) [9-15]. The methods involving spectrophotometry are rather popular due to their simplicity, inexpensive instrumentation and easy automation. In many cases, they are based on ion-association reaction between heavy organic cations and anionic complexes of Mo(VI) with thiocyanate or organic reagents containing hydroxyl groups in ortho-position to each other [15-24].

Sulfur-containing analogues of the aforementioned catecholic reagents have been in our research interests for a long time because of their analytical potential and possibilities of obtaining new ternary complexes with desired properties [25-29].

In the present paper, we report results from liquid-liquid extraction-spectrophotometric experiments on 9 different systems, each of which containing Mo(VI), a $\sigma$-hydroxythiophenol derivative (HTPD) [2-hydroxy-5-chlorothiophenol (HCTP), 2-hydroxy-5-bromothiophenol (HBTP), and 2-hydroxy-5-iodothiophenol (HITP)], and an aromatic amine (AA) [aniline (An), N-methylaniline (mA), N,N-dimethylaniline (dAn)]. We propose new procedures for determining molybdenum in soils and plants, and show that linear relationships exist between the spectral characteristics of the ternary complexes (absorption maximum and molar absorptivity) and some fundamental properties of the halogen atom included in the HTPDs (atomic mass and electronegativity).

**Materials and Methods**

**Reagents and instrumentation**

A stock solution of Mo(VI) (1 dm$^3$) was prepared by dissolving 1.8402 g of (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O (Sigma-Aldrich, 99.98%) in distilled water. The solution was standardized gravimetrically. Working solutions (0.1 mg cm$^{-3}$) were prepared daily by appropriate dilution of the stock solution.

HTPDs were synthesized according to the procedure [30]; their purity was verified by paper chromatography and melting point determination. AAs were products of Sigma-Aldrich (98-99% purity). Chloroform solutions (0.01 moldm$^{-3}$) of HTPDs and AAs were used.

A masking solution (1 dm$^3$), containing 75 g of citric acid and 150 g of ascorbic acid, was prepared weekly and stored in a refrigerator [31]. A second masking solution was prepared from KI ($w=20\%$).

To create the optimum acidity, 0.1 moldm$^{-3}$ solutions of HCl or NaOH were used.

The absorbance of the extracts was measured using a KFK-2 photocolorimeter (USSR), a SF-26 spectrophotometer (USSR), and a Camspec M508 spectrophotometer (UK), equipped with 5 and 10 mm path-length cells. pH of aqueous phase was measured using an I-120.2 potentiometer with a glass electrode. Muffle furnace was used for dissolution of the samples.

**Procedure for determining the optimum conditions**

Aliquots of Mo(VI) solution, HTPD solution (up to 2.5 cm$^3$) and AA solution (up to 2.5 cm$^3$) were transferred in a 50 cm$^3$ calibrated tube with ground-glass stopper. pH of the aqueous phase was adjusted in the interval 3.5-7.9 by adding a small amount of HCl or NaOH solution. The volume of the aqueous phase was increased with water to 20 cm$^3$ and the volume of the organic
procedure for molybdenum determination

An aliquot containing molybdenum (no more than 90 μg when HTPD=HCTP or 85 μg when HTPD=HBTP) was placed in a calibrated tube. Chloroform solutions of HTPD (0.7 cm²) and An (0.7 cm³) were added and the organic phase was adjusted to 5 cm³ with chloroform. The volume and pH of the aqueous phase were adjusted to 20 cm³ and 5.3-5.8, respectively. The tube was closed with a stopper and after 10 minutes of shaking a portion of the organic extract was transferred through a filter paper into a cell. The absorbance was read at \( \lambda_{\text{max}} \) (535 nm when HTPD=HCTP or 530 nm when HTPD=HBTP) against a simultaneously prepared blank sample. The molybdenum content was found from a calibration graph.

Soil sample preparation for analysis

A soil sample (15 g) soil sample collected from depths of 15±5 cm was subjected to available molybdenum extraction procedure [31, 32] with an oxalate buffer of pH 3.3. Then the procedure [31] was followed: an aliquot of the obtained soil extract (50-100 cm³) was placed in a quartz beaker and evaporated to dryness on a hot plate. For dehydration of the residue and partial sublimation of the oxalates, the beaker was left on the plate for 30 more minutes. The beaker was transferred in a cold muffle furnace. The temperature was raised to 500 °C and held for 15 minutes. After cooling, 25 cm³ of 14% hydrochloric acid were added and the beaker was kept in a boiling water bath for 10-20 min. The obtained solution was quantitatively transferred to a volumetric flask of 50 cm³. 18
Masking solutions were added (4 cm³ of the citric acid – ascorbic acid solution and 2 cm³ of the KI solution) and the flask was filled to the mark with bidistilled water.

Results and Discussion

Studies on the oxidation state of molybdenum

It is known that HTPDs have reducing properties in acidic medium [26,28,33]. Previous investigations with Mo(VI)-HCTP and Mo(V)-HCTP [26] suggested that only Mo(V) forms stable complexes with this reagent. To elucidate the oxidation state of molybdenum in the presence of other HTPDs (HBTP and HTP), we conducted two series of experiments. In the first series we used Mo(VI), while in the second series we used Mo(V) obtained by addition of a supplementary reducing agent (SnCl₂ or KI). The comparison of the obtained spectra showed that \( \lambda_{\text{max}} \) Mo(VI)-TPHHD=\( \lambda_{\text{max}} \) Mo(V)-TPHHD. This fact can be regarded as an indication [26,34] that Mo(VI) is reduced to Mo(V) by the reagent itself during the complex formation.
**Charge of the complexes**

The charge of the Mo(V)-HTPD binary complexes was determined by electromigration and ion-exchange. Experiments on electromigration in a U-shaped tube and on sorption on EDE-10P anion exchanger demonstrated the anionic nature of the complexes. Under the experimental conditions, these red binary complexes were insoluble in nonpolar organic solvents. However, when AAs were introduced the formation of electroneutral chloroform extractable ternary complexes was observed.

**Choice of organic solvent**

The following organic solvents were tested for the extraction of the ternary complexes: chloroform, dichloroethane, carbon tetrachloride, benzene, toluene, diethyl ether and n-butanol. Chloroform was found to be the most effective in terms of degree of extraction (R%) and rapid equilibration. As can be seen from (Table 1), chloroform provides R \( \geq 98.4\% \). At that, the nature of AA does not appreciably affect the extraction.

<table>
<thead>
<tr>
<th>Table 1. Characteristics of the extraction-chromogenic systems Mo(V)-HTPD-AA-water-chloroform.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Analytical characteristics</strong></td>
</tr>
<tr>
<td>Optimum pH interval</td>
</tr>
<tr>
<td>Degree of extraction / %</td>
</tr>
<tr>
<td>λ ( \text{max} ) / nm</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>ε ( 10^4 ) / dm³·mol⁻¹·cm⁻¹</td>
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<tr>
<td></td>
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<tr>
<td></td>
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<tr>
<td>Working range / μg</td>
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<td></td>
</tr>
</tbody>
</table>

**Absorption maxima, reagents concentrations, molar absorptivities and effect of time**

The absorption maxima (\( \lambda \text{max} \)) of the ternary Mo(V)-HTPD-AA complexes lie in the range of 527-538 nm (Table 1). All colour reactions are very contrast since the initial solutions are colourless (\( \lambda \text{max} \) HTPDs = 275-280 nm). Complete extraction is achieved at reagent concentrations not lower than (1.3-1.5) \( \times \) 10⁻³ moldm⁻³ (HTPD) and (1.2-1.5) \( \times \) 10⁻³ moldm⁻³ (AA). Mo(V) concentration ranges in which the Beer’s law is obeyed are listed in (Table 1). The calculated molar absorptivities (\( \varepsilon \text{max} \)) belong to the interval (3.2-4.2) \( \times \) 10⁴ dm³·mol⁻¹·cm⁻¹. Colour develops almost immediately after the reagents addition. The absorbance of the extracts is stable for at least 48 hours. The optimum shaking time is 10 min.

**Fig. 1. Absorbance of the ternary Mo(V)-HTPD-An complexes vs. pH of the aqueous phase. (1) HTPD=HCTP; (2) HTPD=HBTP; (3) HTPD=HITP. \( \varepsilon \text{Mo} = 4.16-10^3 \text{moldm}^{-3} \); \( \varepsilon \text{HTPD} = \varepsilon \text{AA}=1.4-10^3 \text{moldm}^{-3} \); \( l=0.5 \text{sm} \)**

**Influence of pH**

Fig. 1 represents the influence of pH on the absorbance of the Mo(V)-HTPD-An extracts. The optimum pH ranges are wide enough to ensure stable and reproducible results without using buffer solutions. The course of all pH curves supports the assumption that only one complex is formed in each of the extraction systems. The optimum pH intervals are listed in (Table 1). At higher pH values, the efficiency of the extraction is impaired, which relates to the lower degree of AA protonation. At lower pH values, the extraction is also impaired most probably due to decrease of the concentration of the anionic HTPDs forms.
Stoichiometry of the ternary complexes

The molar ratios of the components of the ternary complexes were established by the equilibrium shift method [35] and the method of Asmus [36] The results show a simple composition of 1:2:2 (Mo(V):HTPD:AA). Using the Nazarenko’s method [37] we found that the molybdenum complexation form is Mo(OH)\(^2\)\(^+\). Hence, the complexes can be regarded as ion associates between doubly charged anionic chelates \([\text{Mo}^\text{VII}(\text{OH})(\text{HTPD}^{2-})]^2\)\(^-\) and two protonated AA species:

\[(\text{AAH}^+)_2[\text{MoO(OH)}(\text{HTPD})_2].\]

Effect of foreign ions and masking reagents

The influence of foreign ions and reagents on the extraction-spectrophotometric determination of molybdenum with HCTP+An and HBTP + Anwas examined in details. It was found that great excesses of alkali, alkali earth, and rare earth cations do not interfere with determination. The same was valid for anions, such as F\(^-\), Cl\(^-\), Br\(^-\), SO\(_3\)\(^2-\), SO\(_4\)\(^2-\) and C\(_2\)O\(_4\)\(^2-\).

Table 2. Influence of foreign ions on the determination of molybdenum (50 µg) with HCTP\(^+\) and An.

<table>
<thead>
<tr>
<th>Foreign ion (FI)</th>
<th>FI-to-Mo ratio</th>
<th>Masking agent</th>
<th>Mo found / µg</th>
<th>RSD(^%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(III)</td>
<td>100</td>
<td>–</td>
<td>50.0</td>
<td>1.5</td>
</tr>
<tr>
<td>Bi(III)</td>
<td>40</td>
<td>–</td>
<td>49.5</td>
<td>4.5</td>
</tr>
<tr>
<td>Co(II)</td>
<td>55</td>
<td>–</td>
<td>50.4</td>
<td>4.2</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>70</td>
<td>–</td>
<td>49.6</td>
<td>2.3</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>25</td>
<td>KI</td>
<td>50.0</td>
<td>2.1</td>
</tr>
<tr>
<td>Fe(III)</td>
<td>50</td>
<td>Ascorbic acid</td>
<td>50.4</td>
<td>4.2</td>
</tr>
<tr>
<td>Hg(II)</td>
<td>35</td>
<td>Na(_2)S(_2)O(_3)</td>
<td>49.8</td>
<td>2.4</td>
</tr>
<tr>
<td>Nb(V)</td>
<td>45</td>
<td>Oxalic acid</td>
<td>50.2</td>
<td>1.5</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>50</td>
<td>Citric acid</td>
<td>50.0</td>
<td>1.5</td>
</tr>
<tr>
<td>Ta(V)</td>
<td>45</td>
<td>Ascorbic acid</td>
<td>49.7</td>
<td>2.3</td>
</tr>
<tr>
<td>Ti(IV)</td>
<td>20</td>
<td>Ascorbic acid</td>
<td>49.6</td>
<td>2.3</td>
</tr>
<tr>
<td>V(IV)</td>
<td>40</td>
<td>–</td>
<td>50.0</td>
<td>1.5</td>
</tr>
<tr>
<td>W(VI)</td>
<td>40</td>
<td>Citric acid</td>
<td>50.3</td>
<td>4.2</td>
</tr>
<tr>
<td>Zr(IV)</td>
<td>70</td>
<td>–</td>
<td>49.6</td>
<td>2.3</td>
</tr>
</tbody>
</table>

\(^{a}\)Statistically undistinguished results were obtained by using HBTP at the mentioned FI-to-Mo ratios
\(^{b}\)Relative standard deviation based on three determinations

Serious interferences were observed from small amounts (less than 200 µg) of Fe(III), Ti(IV), Cu(II), Nb(V), Ta(V), Hg(II) and W(VI). The interfering influence of these ions can be eliminated by using various masking agents (Table 2). For the sake of convenience, we used only two masking solutions in our further analytical work: 1) ascorbic acid + citric acid solution; and 2) KI solution.

Calibration graphs, analytical characteristics and application

Table 3 summarizes the calibration characteristics obtained with HCTP+An and HBTP+An. The procedures with these reagents were applied to the determination of molybdenum in samples of soil and pea. The accuracy of the results was checked by two independent methods [31]. The results are listed in (Table 4).

Table 3. Analytical characteristics for the extraction-chromogenic systems: Mo-HCTP-An-water-chloroform and Mo-HBTP-An-water-chloroform.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Mo-HCTP-An</th>
<th>Mo-HBTP-An</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear calibration range / µg cm(^{-3})</td>
<td>up to 4.5</td>
<td>up to 4.3</td>
</tr>
<tr>
<td>Slope ± Standard deviation / (Aµg^{-1} \text{cm}^2)</td>
<td>0.383±0.004</td>
<td>0.351±0.03</td>
</tr>
<tr>
<td>Intercept ± Standard deviation/A</td>
<td>0.007±0.011</td>
<td>0.007±0.008</td>
</tr>
<tr>
<td>Correlation coefficient (9 standards used)</td>
<td>0.9994</td>
<td>0.9997</td>
</tr>
<tr>
<td>Limit of detection (LOD) / ng cm(^{-3})</td>
<td>15(^a)</td>
<td>12(^a)</td>
</tr>
<tr>
<td>Limit of quantification (LOQ) / ng cm(^{-3})</td>
<td>50(^a)</td>
<td>40(^a)</td>
</tr>
<tr>
<td>Sandell’s sensitivity / ng cm(^{-2})</td>
<td>2.61</td>
<td>2.85</td>
</tr>
</tbody>
</table>

\(^{a}\)Defined as 3\(σ\)/a (LOD) or 10\(σ\)/a (LOQ), where a is the slope of the calibration plot

Table 4. Molybdenum content in soil and pea samples determined by different methods (\(N=3, P=95\%\)).

<table>
<thead>
<tr>
<th>Method</th>
<th>Mo-HCTP-An</th>
<th>Mo-HBTP-An</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Molybdenum content in soil</td>
<td>Molybdenum content in pea</td>
</tr>
<tr>
<td></td>
<td>(×10^7) %</td>
<td>RSD / %</td>
</tr>
<tr>
<td>Present methods</td>
<td>2.93</td>
<td>4.0</td>
</tr>
<tr>
<td>HBTP-An method</td>
<td>2.86</td>
<td>3.0</td>
</tr>
<tr>
<td>Thiocyanate method [31]</td>
<td>2.97</td>
<td>5.0</td>
</tr>
<tr>
<td>Dithiol method [31]</td>
<td>2.96</td>
<td>5.0</td>
</tr>
</tbody>
</table>

\(^{a}\)Statistically undistinguished results were obtained by using HBTP at the mentioned FI-to-Mo ratios
\(^{b}\)Relative standard deviation based on three determinations
Some linear relationships involving the spectral characteristics of the ternary complexes

The nature of the substituents and the molecular mass of the associating ions are important factors in the chemistry of ion-association [20,38]. Linear relationships have been described between the molecular mass of a particular class of cationic ion-association reagents [20,38] and some parameters, such as constant of association [38], temperature of decomposition [39], constant of extraction and molar absorptivity [40].

The HTPDs used in this work provided an excellent opportunity to examine the influence of the halogen substituent (Cl, Br, I) on the spectral characteristics of the ternary complexes (molar absorptivity ε_max and absorption maximum λ_max). The results showed that straight lines can be obtained by plotting the atomic mass of the halogen atom (A_Hal) vs. λ_max (Fig. 2) or ε_max (Fig. 3). The experimental data plotted in coordinates λ_max – χ_Hal and ε– χ_Hal (where χ_Hal is the Pauling electronegativity of the halogen atom) also fit linear equations (Table 5) (the squared correlation coefficients R^2 are in the range of 0.9347-1.000). The differences in the slopes (a_i) of the straight-lines λ_max=a_i×A_Hal+b_i and λ_max=a_2×χ_Hal+b_2 can be attributed to the different nature of the AAs used. However, the slopes were relatively constant for the straight lines ε_max=a_i×A_Hal+b_i and ε_max=a_4×χ_Hal+b_4; a_1=-0.0060±0.0005 and a_1=1.08±0.09. This fact can be used for simple prediction of molar absorptivities of still uninvestigated ternary complexes.

Table 5. Equations and squared correlation coefficients (R^2) describing the linear relationships between the atomic mass (A_Hal) or Pauling electronegativity (χ_Hal) of the halogen atom in the HTPD and the spectral characteristics of the ternary complexes (λ_max and ε_max).

<table>
<thead>
<tr>
<th>AA</th>
<th>λ_max=f(A_Hal)</th>
<th>ε_max×10^2=f(A_Hal)</th>
<th>λ_max=f(χ_Hal)</th>
<th>ε_max×10^2=f(χ_Hal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>An</td>
<td>y=0.0873x+553.71</td>
<td>y=0.0065x+3.8739</td>
<td>y=15.526x+493.28</td>
<td>y=0.9737x+0.5837</td>
</tr>
<tr>
<td></td>
<td>R^2=0.9748</td>
<td>R^2=0.9829</td>
<td>R^2=0.9868</td>
<td>R^2=0.9481</td>
</tr>
<tr>
<td>mAn</td>
<td>y=0.0764x+539.5</td>
<td>y=0.0066x+4.1297</td>
<td>y=1.3684x+493.28</td>
<td>y=1.1842+0.1342</td>
</tr>
<tr>
<td></td>
<td>R^2=0.9904</td>
<td>R^2=0.9997</td>
<td>R^2=0.9616</td>
<td>R^2=0.9868</td>
</tr>
<tr>
<td>dAn</td>
<td>y=0.0437x+539.53</td>
<td>y=0.0065x+4.3947</td>
<td>y=7.8947x+512.89</td>
<td>y=1.1579+0.4779</td>
</tr>
<tr>
<td></td>
<td>R^2=0.9997</td>
<td>R^2=0.9581</td>
<td>R^2=0.9868</td>
<td>R^2=0.9098</td>
</tr>
</tbody>
</table>

Table 5 shows that the straight-line equations with participation of λ_max are characterised by relatively constant ordinate cuts b_i, (b_1=534±4 and b_2=485±12). This information can be important for predicting the absorption maxima of new ternary complexes after a single experimental step as outlined above.
Conclusions

Molybdenum(VI) forms well chloroform-extractable ternary complexes with HTPDs and AAs which can be used liquid-liquid extraction-spectrophotometric determination of molybdenum. The complexes have a composition of 1:2:2 (Mo:HTPD:AA) and can be regarded as ion associates between doubly charged anionic chelates of Mo(V) and protonated AA species: (AAH\(^{+}\))\(_2\)[MoO(OH)(HTPD)\(_2\)]. The collected information about the spectral characteristics (absorption maximum \(\lambda_{\text{max}}\) and molar absorptivity \(\varepsilon_{\text{max}}\)) of the complexes makes it possible to conclude that linear relationships exist between some fundamental properties of the halogen substituent in the HTPD (atomic mass \(A_{\text{Hal}}\) and electronegativity \(\xi_{\text{Hal}}\) and \(\lambda_{\text{max}}\) or \(\varepsilon_{\text{max}}\): i) The higher the atomic mass, the lower \(\lambda_{\text{max}}\) or \(\varepsilon_{\text{max}}\); ii) The higher the electronegativity \(\xi_{\text{Hal}}\), the higher the \(\lambda_{\text{max}}\) or \(\varepsilon_{\text{max}}\). The established constancy of the slopes or ordinate cuts of the obtained straight-line equations can facilitate the prediction of the mentioned spectral characteristics of new uninvestigated complexes of the same class.

References