

ELECTRONIC SPECTRA AND CHEMICAL PROPERTIES OF ACETONE SOLUTIONS OF CHLORONITRATO AND CHLOROTETRAMETHYLTHIOUREACOPPER(II) COMPLEXES

E. HORVÁTH, J. KOVÁČOVÁ, J. SÝKORA and J. GAŽO

*Department of Inorganic Chemistry,
Slovak Institute of Technology, Bratislava*

Received January 25th, 1971

The absorption spectra of chloro-, chloronitrato- and chlorotetramethylthiourea-copper(II) complexes dissolved in acetone were studied in visible and near ultraviolet regions. The chloronitrato-copper(II) complexes give an absorption band at 25670 cm^{-1} . The 21100 cm^{-1} absorption band of chlorocopper(II) complexes is by formation of the chloronitrato-copper(II) complexes slightly shifted towards longer wavelengths. The chlorotetramethylthiourea-copper(II) complexes are characterized by three bands with maxima at 19010 , 21000 , and 24390 cm^{-1} . The absorption band at 19010 cm^{-1} can be considered a charge-transfer band $\text{Cu} \leftarrow \text{S}$. Absorption bands in the region of $20750\text{--}21000\text{ cm}^{-1}$ observed for the systems of chloro- and chloronitrato-copper(II) complexes can be interpreted as the charge-transfer bands $\text{Cu} \leftarrow \text{Cl}$. The absorption bands at 25670 and 24390 cm^{-1} in the presence of nitrate and tetramethylthiourea ligands, respectively, have the character of the charge-transfer bands $\text{Cu} \rightarrow \text{ligand}$. The π -acceptor nature of the tetramethylthiourea and the nitrate group deduced from the analysis of the electronic spectra is in good agreement with the previous experimental results concerning the effect of these ligands upon the intramolecular changes in the coordination sphere.

It was experimentally proved^{1,2} that the nitrate group enters the inner coordination sphere of the chlorocopper(II) complexes in acetone solution. An increase of the NO_3^- concentration affects the intensity of the absorption band in the region $20750\text{--}21100\text{ cm}^{-1}$, which is characteristic for the chloro copper(II) complexes. The absorbancy value of the system $[\text{Cu}(\text{II})]:[\text{Cl}^-]:[\text{NO}_3^-] = 1:2:0.5$ is nearly four times greater than that of the analogous system without nitrate ions. This effect was not yet explained. The existence of multinuclear complexes was assumed in the above mentioned papers. A remarkable effect of the nitrate ligand upon inner complex redox processes in chlorocopper(II) complexes was found in the works^{3,4}. The experimental evidence brought in these papers^{3,5,6} showed that an effect comparable to that of the nitrate group have also ketones, alcohols, thiourea and some of its derivatives, thiocyanates, etc. Theoretical explanation was given⁷, where the effect of these ligands upon the redox properties of the chlorocopper(II) complexes is explained by their π -accepting ability. For these reasons, it was important to collect further information about the heterogeneous coordination sphere of the investigated Cu(II) complexes, to obtain objective data of the π -accepting

ability of the ligands and of the nature of their effect upon the electronic system of the complex.

EXPERIMENTAL

Acetone (p.a. quality, Lachema) used for the preparation of the solutions was purified by treatment with permanganate⁸, rectified and dried over a molecular sieve (Nalsit)⁹. Commercial thiourea, $\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$, LiCl (Lachema), and $\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$ (Chemapol) were of p.a. quality. Anhydrous copper(II) chloride was prepared by dehydration of the dihydrate in hydrogen chloride atmosphere. Tetramethylthiourea was prepared according to the described method¹⁰. The instantaneous Cu(II) concentration in the system VI (see below) was determined in the following way: the absorbancy of the system was measured at appropriate time intervals and simultaneously an excess of thiourea was added to the solution of the same composition. An acetone insoluble precipitate of the dichloride of bis(aminoiminomethyl) disulphide formed by reaction of Cu(II) with thiourea³ was weighed (Fig. 1, Table I). The copper concentration was determined electrolytically, the concentration of chlorides potentiometrically, and the sulphur content both gravimetrically and by Škramovský's method¹¹. The measurements were performed on a Zeiss-Jena monochromator and on the spectrophotometers SF-10 (USSR, 400–750 nm), Unicam SP-700 (England, 200–3300 nm), and Spekord UV-VIS (DDR, Zeiss-Jena, 200–800 nm). The air humidity and the temperature ($\pm 0.5^\circ$) were kept constant.

The following systems were studied: CuCl_2 -LiCl-acetone (I), CuCl_2 -LiCl-LiNO₃-acetone (II), $\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$ -LiCl-acetone(III), $\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$ -LiCl-LiNO₃-acetone (IV), $\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$ -LiCl-acetone (V), and CuCl_2 -tetramethylthiourea-acetone (VI).

RESULTS AND DISCUSSION

The absorption spectra of the systems containing chlorocopper(II) complexes in the visible region were thoroughly studied in the papers^{5,6,12,13}. The plots of absorbancy

TABLE I

Rate of the Oxidation-Reduction Changes in the System CuCl_2 -Acetone-Tetramethylthiourea
 $c_{\text{Cu(II)}} 0.02\text{M}$; $c_{\text{T}} 0.05\text{M}$; $c_{\text{thiourea}} 0.15\text{M}$; $[\text{Cu(II)}] : [\text{Cl}^-] : [\text{T}] = 1 : 2 : 2$; $[\text{Cu(II)}] : [\text{thiourea}] = 1 : 5.26$.

| <i>t</i> min | A ^a % | P ^b % | A - P % | <i>t</i> min | A ^a % | P ^b % | A - P % |
|-----------------|---------------------|---------------------|------------|-----------------|---------------------|---------------------|------------|
| 0 | 100.0 | 100.0 | — | 10 | 91.0 | 92.0 | 1.0 |
| 2 | 97.5 | 98.0 | 0.5 | 16 | 86.5 | — | — |
| 4 | 95.5 | — | — | 20 | 84.5 | 86.0 | 1.5 |
| 8 | 92.5 | — | — | | | | |

^a Relative absorbancy value with respect to A at $t = 0$. ^b Relative weight amount of the precipitated bis(aminoiminomethyl) disulphide with respect to that amount precipitated at $t = 0$.

against wavelength show for all systems a very similar character (the position of the maximum of the absorption band and its intensity, Fig. 2). Substantial differences in the courses of the spectra were found in the near ultraviolet and near infrared regions.

Even the dried acetone contains some amount of water which influences the studied absorption spectra. However, this amount could be taken as constant, provided that the measurement was performed at constant temperature and air humidity. In connection with the studied problems the effect of water on the absorption spectra was negligible. It is known that the systems I—V undergo spontaneous redox processes^{3,5,6,14,15}. The absorbancy of all these systems was therefore measured immediately after the preparation and mixing of the solutions (within 1 minute). The decrease in the Cu(II) concentration in this time interval could be considered to be negligible.

The presence of the nitrate group in the system affects the intensity of the absorption band at $21050-21100\text{ cm}^{-1}$. Two new bands are observed on the absorption curves 1 and 2 of the system II: one at 25670 cm^{-1} (Fig. 3) and the second in the region of $28900-29400\text{ cm}^{-1}$ (approximately of double intensity). The nature of the last band remains unexplained. Acetone itself absorbs in this region. The symmetry of these bands indicates a superposition of several bands. An attempt to decompose these spectra to their components was made using a graphic method¹⁶. The result of such a decomposition of the absorption curve for the system IV is shown in the Fig. 4. The maxima found by this procedure are located at 21050 and 25670 cm^{-1} .

The absorption band with the maximum at 25670 cm^{-1} is present only in the spectra of systems containing the nitrate group. This fact is in agreement with the so far obtained results on the nitrate group participation in the Cu(II) coordination sphere^{1,2}. The information about the complex composition in the isomolar system $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}-\text{LiNO}_3$ -acetone was obtained by the method of Job¹⁷ and Ostromyslenskij¹⁸. The curve 1 on the Fig. 5 corresponds to the frequency 25670 cm^{-1} ,

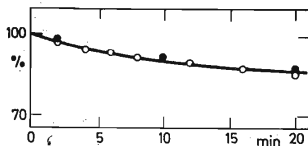


FIG. 1

Time Dependence of the Decrease in Absorbancy and Cu(II) Concentration in the System CuCl_2 -Acetone-Tetramethylthiourea

○ The absorbancy value relative to A at time $t = 0$; ● The amount of precipitated bis(aminoiminomethyl) disulphide relative to the amount formed in the reaction of the system VI with thiourea at time $t = 0$.

i.e. to the position of the absorption maximum. The value of ΔA shows its maximum at the ratio of $[\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}] : [\text{NO}_3^-] = 1 : 2$ and is negative for the ratios greater than $2 : 1$, which can be explained by the absence of the nitrate group in the coordination sphere. Maximum differences in the absorbancies due to the presence of the nitrate group were observed for $\bar{\nu} = 24690 \text{ cm}^{-1}$ (curve 2, Fig. 5). The values of ΔA are positive and exhibit the maximum difference at the ratio of $[\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}] : [\text{NO}_3^-] = 1 : 1$. At this ratio the effect of the nitrate group on the absorption spectrum in the region of $20750 - 21100 \text{ cm}^{-1}$ is the greatest. This finding agrees with the experimental results published earlier^{1,2}. The dihydrate of copper(II) chloride was used because of its better solubility in acetone. The effect of water in the studied spectral region is negligible. It was established in several papers^{5,6,12,13,19} that the acetone solutions of chloro- and chloronitratocopper(II) complexes show a maximum absorption in the region of $20750 - 21100 \text{ cm}^{-1}$. The position of the maximum depends on the Cu(II) concentration and the component ratio.

The conclusion that the nitrate-ligand has similar effect on the electronic system of the coordination sphere of the chlorocopper(II) complex as tetramethylthiourea(T) or some thiourea derivatives was drawn on the basis of experimental results^{3,7,14}. It can be expected that the absorption spectra of chloronitrate- and chlorotetramethylthiourecopper(II) complexes will show some similarity and analogous course of the curves, respectively. The absorption curves of the system VI for different ratios of $[\text{Cu(II)}] : [\text{T}]$ and the constant ratio of $[\text{Cu(II)}] : [\text{Cl}^-] = 1 : 2$ are shown in Fig. 6. The decomposition of a composite band as we made it by the method¹⁶ is shown in the Fig. 7. We were able to identify three bands with maxima

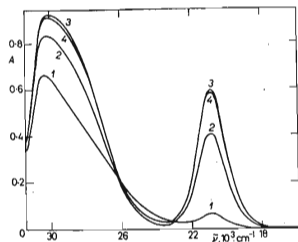


FIG. 2

Absorption Spectra of the System $\text{CuCl}_2 - \text{LiCl} - \text{Acetone}$

$[\text{Cu(II)}] : [\text{Cl}^-]$; 1 1 : 2; 2 1 : 3; 3 1 : 4, 4 1 : 6; $c_{\text{Cu(II)}}$; curve 1 $1 \cdot 10^{-3} \text{ M}$, curves 2-4 $5 \cdot 10^{-4} \text{ M}$; cell length 0.5 cm, temperature 24°C ; Unicam SP-700.

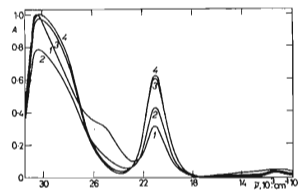


FIG. 3

Absorption Spectra of the System $\text{CuCl}_2 - \text{LiCl} - \text{LiNO}_3 - \text{Acetone}$

$[\text{Cu(II)}] : [\text{Cl}^-] : [\text{NO}_3^-]$; 1 1 : 2 : 2; 2 1 : 3 : 2; 3 1 : 4 : 2; 4 1 : 6 : 2; $c_{\text{Cu(II)}}$; curve 1 $1 \cdot 10^{-3} \text{ M}$; curve 2-4 $5 \cdot 10^{-4} \text{ M}$; cell length 0.5 cm; temperature 24°C ; Unicam SP-700.

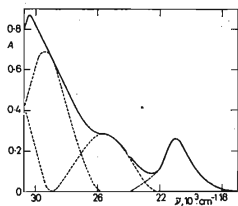


FIG. 4

Decomposition of the Absorption Band into Components

System $\text{CuCl}_2 \cdot 2 \text{H}_2\text{O} - \text{LiCl} - \text{LiNO}_3 - \text{acetone}$ $[\text{Cu(II)}] : [\text{Cl}^-] : [\text{NO}_3^-] : 1 : 2 : 2$; $c_{\text{Cu(II)}} = 1 \cdot 10^{-3} \text{M}$.

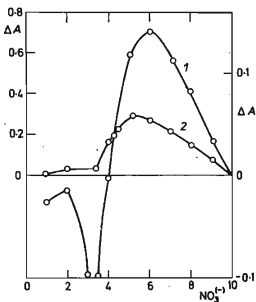


FIG. 5

The Changes in Absorbance of the Isomolar Systems $\text{CuCl}_2 \cdot 2 \text{H}_2\text{O} - \text{LiNO}_3 - \text{Acetone}$

$c_{\text{Cu(II)}} = c_{\text{NO}_3^-} = 7.5 \cdot 10^{-3} \text{M}$; the right-hand scale holds for the curve 1, $\bar{\nu} = 25670 \text{cm}^{-1}$, $\bar{\nu}$ for curve 2 is 24390cm^{-1} .

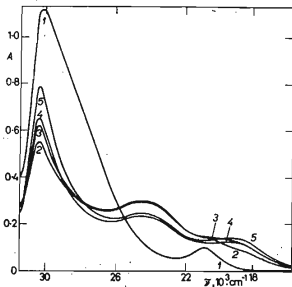


FIG. 6

Absorption Spectra of the System $\text{CuCl}_2 - \text{Tetramethylthiourea} - \text{Acetone}$

$[\text{Cu(II)}] : [\text{Cl}^-] : [\text{T}]$; 1 1 : 2 : 0; 2 1 : 2 : 2; 3 1 : 2 : 3; 4 1 : 2 : 4; 5 1 : 2 : 5; $c_{\text{Cu(II)}} = 1.25 \cdot 10^{-3} \text{M}$; cell length 0.5 cm; temperature 24°C ; Unicam SP-700.

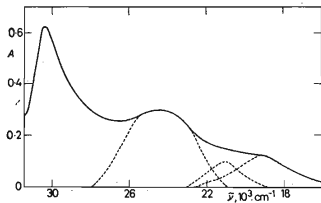


FIG. 7

Decomposition of the Absorption Band into Components. System $\text{CuCl}_2 - \text{Tetramethylthiourea} - \text{Acetone}$

$[\text{Cu(II)}] : [\text{Cl}^-] : [\text{T}]$; 1 : 2 : 2; $c_{\text{Cu(II)}} = 1 \cdot 10^{-3} \text{M}$.

at 19010, 21000, and 24390 cm^{-1} . The shape of the last one indicates its composite nature. Another band with its maximum at about 29850 cm^{-1} could be found on the absorption curves (Fig. 6). Its intensity rises with increasing concentration of tetramethylthiourea. For the reasons mentioned above this band was not further analysed. The presence of tetramethylthiourea in the coordination sphere of copper complexes markedly increases the rate of the oxidation-reduction process; the measured values of the absorbancies do not correspond to the analytically determined Cu(II) concentrations. The time dependence of the absorbancy was studied for the system VI (Fig. 8). The absorbancy at time $t = 0$ was obtained by graphical extrapolation. The error was 1%. The changes in absorbancy for $t = 2$ and $t = 5$ minutes corresponding to the decrease of intensity of the absorption bands in the region of 19000–21000 cm^{-1} are given in the Table II. A survey of the intensity increase of the band in the region of 19000–21000 cm^{-1} and its ratio to the intensity of an analogous band in the corresponding system not containing T is also incorporated in this Table. By chemical methods it was proved that the decrease in absorbancy observed for the system VI in the region of 19000–21000 cm^{-1} was caused by decrease of the Cu(II) concentration.

The electronic spectra of chlorocopper(II) complexes in acetone were studied by several authors^{5,6,12,13,20}. Some absorption bands were only registered. Katzin²⁰ had assigned the two bands lying at 473 and 385 nm in the spectra of the system CuCl_2 -acetone to the charge-transfer bands $\text{Me} \rightarrow \text{L}$. This assignment disagrees with our assumption of the nature of the absorption band in the region of 20700–21000 cm^{-1} in the spectra of acetone solutions of chlorocopper(II) complexes¹⁴ and with the calculated absorption coefficient (2560 $\text{l mol}^{-1} \text{cm}^{-1}$)¹². We have ascribed to this band the character of a charge-transfer band type $\text{Me} \leftarrow \text{L}$. Our value of the absorption coefficient calculated for the systems II, IV, and V (the ratio of $[\text{Cu(II)}] : [\text{Cl}^-] : [\text{NO}_3^-] = 1 : 2 : 2$, $\bar{\nu} = 25670 \text{ cm}^{-1}$) is 564 $\text{l mol}^{-1} \text{cm}^{-1}$. The experimental results of spectrophotometric analyses^{5,6,12,14} prove the existence of an equilibrium between various Cu(II) complexes with heterogeneous coordination spheres. However, their equilibrium concentrations remain still unknown. The values of the absorption coefficients are incorrect since they are related to the analytical Cu(II) concentrations. The actual values will probably be somewhat higher. The changes in absorbancy of the isomolar system IV studied at $\bar{\nu} = 25670 \text{ cm}^{-1}$ and 24690 cm^{-1} suggest the formation of chloronitratocopper(II) complexes with various ratios of $[\text{Cu(II)}] : [\text{NO}_3^-]$. A shift of the absorption maximum in the region of 20750–21100 cm^{-1} towards the lower wavenumbers, caused by the substitution of one ligand in the chlorocopper(II) complex for a nitrate group brings another evidence in favour of the formation of chloronitratocopper(II) complexes and of the lowering of the energy required for a charge transfer in these complexes. Some of our results¹⁹ indicate that the nitrate group replaces an acetone ligand at low ratios of $[\text{Cl}^-] : [\text{Cu(II)}]$.

TABLE II

Time Dependence of the Decrease in Absorbancy in the System CuCl_2 -Acetone-Tetramethylthiourea

Measured on a SF-10 instrument at 24°C , the cell length 0.5 cm , $c_{\text{Cu(II)}} = 2 \cdot 10^{-3}$.

| [Cu(II)] [T] | -A ^a , % | | B ^b |
|-----------------|---------------------|-------|----------------|
| | 2 min | 5 min | |
| 1 : 0.25 | 13.0 | 22.0 | 0.480 |
| 1 : 0.50 | 14.5 | 22.0 | 0.525 |
| 1 : 1.00 | 11.5 | 16.7 | 0.692 |
| 1 : 1.25 | 16.0 | 23.0 | 0.577 |
| 1 : 1.50 | 12.1 | 19.2 | 0.930 |
| 1 : 2.00 | 12.6 | 20.0 | 1.080 |
| 1 : 2.50 | 14.2 | 21.2 | 1.420 |

^a Percentual decrease in absorbancy of the system VI at $\bar{\nu} = 19\,000\text{--}21\,000\text{ cm}^{-1}$. ^b The ratio of the absorbancies of the system VI to that of the analogous system not containing T at time $t = 0$.

The increase in the absorption band intensity in the region of $20750\text{--}21100\text{ cm}^{-1}$ after incorporation of the nitrate group in the coordination sphere of the chlorocopper(II) complex can be explained by the π -accepting ability of this group. The conditions for a charge transfer from a chloro-ligand to the central atom are favoured by a charge withdrawal from the non-bonding orbital of the central atom to the incompletely occupied or vacant π -orbitals of the nitrate-ligand in a heterogeneous sphere of the chloronitratecopper(II) complex⁷. The intensities of the charge-transfer bands reflect the probability of the transitions. The number of chloro-ligands

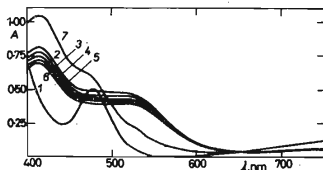


FIG. 8

The Time Dependence of the Changes in Absorbancy in the System CuCl_2 -Tetramethylthiourea-Acetone

[Cu(II)] : [Cl⁻] : [T]; 1 1 : 2 : 0; 2—6 1 : 2 : 2; 7 1 : 2 : 1; readouts taken after: 1, 2, 7 0.5 min; 3 2.5 min; 4 4.4 min; 5 6.4 min; 6 8.3 min. Cell length: 1—6 0.5 cm; 7 1.0 cm; spectrophotometer SF-10.

contributing to the transition at the mentioned wavenumbers due to the charge withdrawal from the central atom so increased (even if some chloro-ligands were replaced by nitrate groups) that an intensity enhancement is observed.

The experimental results cited so far indicate that thiourea and some of its derivatives (*e.g.* tetramethylthiourea) show an effect on the properties of the Cu(II) complexes comparable to that of the nitrate group. Tetramethylthiourea was assumed to have some π -accepting ability^{3,7}. The changes of the absorption spectra caused by the nitrate group and by tetramethylthiourea are similar. This analogous behaviour is evident from the graphs shown in the Figs 6 and 8. A new band at 24390 cm^{-1} can be interpreted (similarly to the 25670 cm^{-1} band observed in the presence of nitrate groups) as the charge-transfer band Cu(II) \rightarrow ligand. The increase in the intensity of the band at 21000 cm^{-1} due to the presence of tetramethylthiourea (system VI) is not so expressive as in the case of the nitrate groups. This band is split into two components because of the different donor nature of the sulphur atom entering the coordination sphere. The intensities of the 19010 and 21000 cm^{-1} bands are nearly equal under the given conditions (Fig. 7) but their relative intensity depends on the ratio $[\text{Cu(II)}] : [\text{Cl}^-] : [\text{T}]$ (Fig. 8, Table II).

The data obtained by spectrophotometric measurements and especially the value of the absorption coefficient of the 25670 cm^{-1} absorption band (systems II, IV, and V) or the 24390 cm^{-1} band (system VI) allow us to suppose that the absorption at the wavelengths is due to the charge transfer from a nonbonding orbital of the central atom to some unoccupied MO level. The energy of this transition in the complex $\text{CuCl}_2 \cdot \text{H}_2\text{O}$ was calculated $3.2\text{ eV}^{21,22}$. A transition in the region of $19000\text{--}21000\text{ cm}^{-1}$ has the energy between 2.2 and $2.6\text{ eV}^{21,22}$. The value of the absorption coefficient and especially the existence of two absorption bands with maxima at 19010 and 21000 cm^{-1} in the system VI indicate that the charge transfer into the nonbonding orbitals of the central atom are involved. This assumption is further justified by an observed proportionality between the decrease of the intensity of this band and the decrease of the Cu(II) concentration (Table I, Fig. 1). The position of the absorption band at 19010 cm^{-1} corresponds to a shift of the original band towards lower wavenumbers after the replacement by a heavier ligand. Therefore this band can be assigned to the transition $\text{Cu} \leftarrow \text{S}$. More accurate conclusions will be formulated on the basis of further experimental data and especially after MO calculations of the respective complexes.

REFERENCES

1. Gažo J.: Sborník prác Chem. fakulty SVŠT I, 7 (1962).
2. Gažo J.: Chem. zvesti 15, 20 (1961).
3. Kováčová J., Horváth E., Gažo J.: Chem. zvesti 23, 15 (1969).
4. Gažo J., Serátorová K., Kováčová J., Serátor M.: Chem. zvesti 14, 497 (1960).
5. Gažo J.: Chem. zvesti 11, 107 (1957).

6. Gažo J.: Chem. zvesti 11, 143 (1957).
7. Gažo J.: Chem. zvesti 19, 826 (1965).
8. Keil B.: *Laboratorní technika organické chemie*. Published by Nakladatelství ČSAV, Prague, 1953.
9. Hýbl Č.: *Synthetické zeolity — molekulové sítě*. Výzkumný ústav pre ropu a uhl'ovodíkové plyny, Bratislava 1964.
10. Billeter O. C.: Ber. 43, 1857 (1910).
11. Škramovský S.: Čas. čes. lékárn. 21, 1 (1941).
12. Gažo J.: Chem. zvesti 10, 508 (1956).
13. Gažo J.: Chem. zvesti 10, 612 (1956).
14. Horváth E., Kováčová J., Gažo J.: Chem. zvesti 23, 81 (1969).
15. Ondrejovič G., Čislova J., Gažo J.: Chem. zvesti 20, 729 (1966).
16. Hocman G., Ličko V.: Acta Fac. Rerum Nat. Univ. Comenianae 11, 75 (1966).
17. Job P.: Ann. Chim. (Paris) 9, 113 (1928).
18. Ostromyslenskij I.: Ber. 44, 268 (1911).
19. Horváth E., Kováčová J., Sýkora J., Gažo J.: Unpublished results.
20. Katzin L. I.: J. Chem. Phys. 36, 3034 (1962).
21. Rundle R. E.: J. Phys. Chem. 61, 45 (1957).
22. Rundle R. E., Richardson J. W.: Lecture on the 129th Natl. ACS Meeting, Dallas 1956.

Translated by P. Sedmora.