MO STUDY OF T_d–D_{4h} EQUILIBRIUM IN COMPLEXES OF TRANSITION METALS. EQUILIBRIUM IN TETRACHLORO COMPLEXES OF ATOMS OF THE FIRST TRANSITION ROW

Petr PELIKÁN[a] and Marek LIŠKA[b]

[a] Department of Physical Chemistry and
[b] Department of Inorganic Chemistry,
Slovak Institute of Technology, 880 37 Bratislava

The CNDO method in UHF version has been used for study of equilibrium of configuration iso-mers of tetrahedral and square-planar tetrachloro complexes of the first transition row atoms in the oxidation degree II (Mn(II), Fe(II), Co(II), Ni(II), Cu(II)). From the results it follows that the ability (conditioned by electronic structure of the central atom) to form the square-planar complexes decreases in the series Mn(II) > Fe(II) > Co(II) > Ni(II) > Cu(II). Several authors state the fact that the most important task of quantum chemistry is to develop procedures for calculation of rate and equilibrium constants of chemical reactions[1,2]. At the same time it is emphasized that these procedures should be independent of experimental data. By this term the authors mean such experimental data which are in some way connected with the reaction studied, and not the general experimental experience which (after transformation into axioms) can re-present a basis of the used method.

Results of calculations of equilibrium constants of chemical reactions in gas phase involving molecules composed of light atoms showed[1–4] that accuracy of usual semiempirical methods type CNDO, INDO, MINDO is sufficient for determination of rotation and vibration partition functions. The greatest problem of semiempi-rical calculation of equilibrium constants consists in calculation of reaction enthalpy. Whereas the calculation results of the vibration and rotation partition functions affect relatively little the value of equilibrium constant K_p, an error of 12 kJ mol^{-1} in determination of the reaction enthalpy can change the equilibrium constant value by as much as two orders of magnitude at lower temperatures. No semi-empirical method of sufficient accuracy and general applicability is available at present. Problems of this type are still more obvious when using the semiempiri-cal methods for compounds containing atoms of transition elements[5]. This fact, however, does not exclude application of the semiempirical methods in calculat-ions of K_p with the aim of comparison and selection of the optimum in chemically similar systems[1]. It is known[5] that numerical results of the semiempirical methods relate correct trends in sets of similar molecules. In this sense the semiempirical calculation of equilibrium constants has been used in the present paper for ob-

taining the K_p trend of equilibria tetrahedron–square in a series of tetrachloro complexes of Mn(II), Fe(II), Co(II), Ni(II), and Cu(II). As far as the authors know, no paper has been published so far dealing with calculation of equilibrium or rate constants of chemical reactions of compounds containing atoms of transition elements.

This field was chosen as the study object, because many papers deal with configuration isomerism of coordination compounds of elements of the first transition row, the most frequent type of configuration isomers of such compounds being the square--planar and tetrahedral complexes (see the review[6]). In this field experimental works always concern the individual isomers in condensed phases (solid, solution[6]), where conditions of formation and relative stabilities are determined not only by structure of the inner coordination sphere but also by many other interactions (effects of solid phase, solvent effects *etc*). The aim of this work was to abstract the inner coordination sphere and therewithin to study effect of kind of the central atom on formation of the individual isomers.

CALCULATION METHOD

For equilibrium constant of a gas phase chemical reaction

$$\sum_{i}^{N_i} a_i A_i \leftrightarrow \sum_{j}^{N_j} b_j B_j \qquad (1)$$

(where N_i and N_j are numbers of reactants and reaction products, respectively), presuming ideal behaviour of all components, it can be written

$$K_p = \prod_{j=1}^{N_j} (p_{B_j})^{b_j} / \prod_{i=1}^{N_i} (p_{A_i})^{a_i}, \qquad (2)$$

where p_{X_i} is partial pressure of the component X_i (equal to fugacity under the presumption of ideal behaviour), and K_p is thermodynamic equilibrium constant. For a given temperature T it is possible to express K_p in terms of statistical thermodynamics:

$$K_p = \left(\prod_{j=1}^{N_j} (Q_{B_j}^0/N_A)^{b_j} / \prod_{i=1}^{N_i} (Q_{A_i}^0/N_A)^{a_i}\right) \exp\left(-\Delta H_0^0/RT\right), \qquad (3)$$

where ΔH_0^0 is the reaction enthalpy at the temperature of absolute zero, R is the universal gas constant, N_A is the Avogadro number, and $Q_{X_i}^0$ is partition function of the component X_i in standard state ($p_{X_i} = 101\ 325$ Pa). With respect to the present state of quantum-chemical methods it is possible for the partition functions to be expressed in the easily calculated most simple statistical thermodynamic way taking individual motions in a molecule as independent and describing them by the simplest quantum-mechanical models (rigid rotor, harmonic oscillator).

$$Q^0 = Q_{tr}^0 \cdot Q_{rot}^0 \cdot Q_{hind}^0 \cdot Q_{vib}^0 \cdot Q_{el}^0 \cdot Q_{nucl}^0. \qquad (4)$$

Thus, presuming validity of the Born–Oppenheimer approximation, the partition function is represented by the product of translation (Q_{tr}^0), rotation (Q_{rot}^0), hindered-rotation (Q_{hind}^0), vibration (Q_{vib}^0), electronic (Q_{el}^0), and nuclear (Q_{nucl}^0) partition functions. For chemical equilibria, the contributions of the nuclear partition functions are mutually canceled. In systems with free rotation it is $Q_{hind}^0 = 1$. If excitation energies of electronic transition are above $1 \cdot 2$ eV (*i.e.* $(E_i - E_0) \geqq 1 \cdot 2$ eV), then the electronic partition function Q_{el}^0 can be replaced by statistical weight of the ground electronic state. The tests carried out[7] in a set of 33 chemical reactions showed that accuracy of the used approximations is quite sufficient for chemical purposes.

The equilibrium constants were calculated in the usual way of quantum chemistry: *i*) The minima at the energy hypersurfaces of the reactants and products were found. The equilibrium geometries corresponding to these minima were used for calculation of the rotation component of the total partition function. *ii*) For the equilibrium geometries of the individual components the second derivatives of total energy with respect to the geometry coordinates were calculated, wherefrom the frequencies of normal vibration modes were obtained by **FG** analysis[8] (and hence also the vibration partition function and energy of the normal vibration modes at absolute zero). *iii*) From the stoichiometric difference of the calculated energies of the reactants and products corrected for the vibration energy at the temperature of absolute zero (ZPV correction) we determined finally the reaction enthalpy ΔH_0^0 for the absolute zero temperature.

The necessary points at the energy hypersurface were calculated by the CNDO method in UHF version modified for compounds of transition metals[9–11]. The equilibrium geometries were determined by minimization of the total energy with respect to bond lengths in the configurations with given geometry and spin multiplicity.
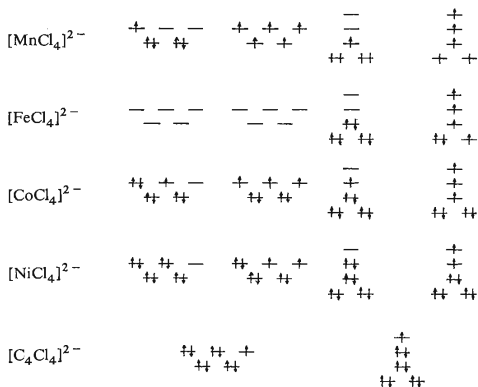

Fig. 1

Scheme of the considered occupations of one-electron levels in the studied systems

The vibration frequencies of normal modes were calculated by the **FG** analysis in symmetrical coordinates[8,12]. The force constants were determined from the total energy changes connected with the changes of symmetrical coordinates due to shifts of the valence coordinates by $\Delta r = 5$ pm or to changes of the deformation coordinates by $\Delta\alpha = 2.5°$. The used $\Delta\alpha$ value agrees with the tests carried out by Pulay[13,14], who suggested the value $\Delta r = 2.6$ pm. In our case it was proved that the calculated values of the force constants are stable with the Δr value used by us, too. The numerical values of the force constants were usually obtained at three points of the energy hypersurface corresponding to the equilibrium and two deformed geometries.

RESULTS AND DISCUSSION

As the main purpose of this study of the tetrahedron–square equilibrium consisted in comparison of effect of electronic structure of the central atom with its ability to form the configuration isomers, we chose for this study a series of tetrachloro complexes MCl_4^{-2} where M = Mn(II), Fe(II), Co(II), Ni(II), and Cu(II). We tried to obtain a trend of the equilibrium constants in this series, and, therefore, an attempt was made to find the effect of spin state of the complex anion on the calculated order. Each of the complex anions was considered in the states with the maximum and the minimum spin multiplicities. These states were determined from such schemes of dislocation of d electrons of the cations M(II) in the five one-electron levels which

TABLE I

Equilibrium geometries and ground state energies of the studied tetrachloro complexes

Anion	Spin multiplicity	T_d			D_{4h}		
		$-E_{SCF}$[b]	R_{eq}^{CNDO}	$R_{eq}^{exp\,a}$	$-E_{SCF}$	R_{eq}^{CNDO}	R_{eq}^{exp}
$MnCl_4^{2-}$	2	2 074·2648	2·347	2·33—2·40	2 072·6463	2·357	—
	6	2 073·9440	2·364	2·33—2·40	2 072·0186	2·377	—
$FeCl_4^{2-}$	1	2 207·3682	2·310	2·27—2·30	2 205·6028	2·313	—
	5	2 207·2091	2·318	2·27—2·30	2 204·9493	2·330	—
$CoCl_4^{2-}$	2	2 370·8523	2·243	2·25	2 368·8964	2·242	—
	4	2 370·8523	2·243	2·25	2 368·2150	2·256	—
$NiCl_4^{2-}$	1	2 571·2659	2·185	2·27	2 569·0716	2·183	—
	3	2 571·2659	2·185	2·27	2 568·4178	2·194	—
$CuCl_4^{2-}$	2	2 802·0104	2·164	2·26	2 798·9683	2·170	2·30

[a] The interatomic distances are given in 10^{-10} m. The experimental values are taken from refs[22-24]. [b] The energies are given in eV.

had the maximum and the minimum numbers of unpaired electrons. The situation is schematically represented in Fig. 1 for all the considered transition metals and geometries.

Table I gives the calculated equilibrium distances and SCF energies for all the systems studied. For comparison it also contains the experimental values of the equilibrium distances obtained by X-ray analysis or their estimates used by other authors. However, comparison of the calculated and experimental bond lengths is not quite correct in this case. The calculated values concern the complex anions in ideal gaseous state at the temperature of absolute zero, whereas the experimental values are greatly influenced by the solid phase effects. In spite of that, the agreement between the given values is satisfactory. As the used CNDO method does not differentiate the orbital--degenerated states with various spin multiplicities, the calculated equilibrium distances and SCF energies are the same for high- $\left(CoCl_4^{-2}\right)$ and low-spin complexes $\left(NiCl_4^{-2}\right)$.

Many of the considered tetrahedral systems are not orbital singlets. From the theory of the Jahn–Teller effect[15,16] it follows for these systems that real equilibrium geometries possess lower symmetry. Strictly speaking, for these systems the energy hypersurface should be thoroughly investigated in the regions with the symmetry given by the vibration type interacting with the degenerated state of the symmetrical configuration. At the point of the absolute minimum corresponding to equilibrium geometry * the force constant matrix should be calculated, and the **FG** analysis should be solved. However, this procedure requires much machine time. Furthermore it was shown that the problem of the trend of equilibrium constants could be solved, with certain presumptions, also by a more passable way. It must be realized that a correct solution is obtained, if the simplification used does not cause any change in relative order of any two equilibrium constants in the studied series of complex anions.

The calculated frequency values of vibration modes are given in Table II. The symbol JT stands in place of the values which cannot be obtained due to operation of the Jahn–Teller effect. The vibration frequency values given in brackets correspond to the vibration modes which, in principle, could interact vibrationally with the ground electronic state, but the respective interaction was not found by the calculation. An interesting case is that of the high-spin complexes $FeCl_4^{-2}$ in both square and tetrahedral arrangement. In spite of being doubly orbital-degenerated, the two ground states do not show vibrational interaction E-e even when submitted to a detailed study. A likely reason thereof is that the orbital degeneration does not belong to the highest occupied molecular orbitals. A similar effect was also observed by Clack and coworkers in a study[19] of electronic structure and anomalous magnetic behaviour

---

*   In connection with the Jahn–Teller effect it should be mentioned that the newest quantitative results revealed that this effect was negligibly small in isolated systems[17,18].

TABLE II

Wave numbers of normal vibrations of the studied complexes[a]

Number of vibration	Multiplicity	$\omega(T_d)$	$\omega(D_{4h})$	Multiplicity	$\omega(T_d)$	$\omega(D_{4h})$
			$MnCl_4^{2-}$			
1	2	465	462	6	470	461
2		JT	379		100	393
3		(527)	346		591	347
4		(120)	175		144	165
5		—	640		—	627
6		—	324		—	315
			$FeCl_4^{2-}$			
1	1	505	500	5	508	497
2		JT	431		(99)	422
3		(530)	385		633	374
4		(105)	193		156	176
5		—	687		—	(672)
6		—	352		—	(341)
			$CoCl_4^{2-}$			
1	2	559	554	4	559	550
2		JT	477		123	446
3		(591)	432		687	412
4		(121)	208		170	195
5		—	749		—	724
6		—	395		—	379
			$NiCl_4^{2-}$			
1	1	609	601	3	609	596
2		JT	516		JT	502
3		(665)	472		(702)	457
4		(139)	223		(165)	212
5		—	813		—	783
6		—	432		—	410
			$CuCl_4^{2-}$			
1	2	639	628			
2		JT	529			
3		(734)	484			
4		(175)	218			
5		—	809			
6		—	436			

[a] The individual vibrations correspond to the following symmetries: ω_1- A_1, ω_2-E, ω_3-T_2, ω_4-T_2 (for the T_d symmetry); ω_1-A_{1g}, ω_2-B_{1g}, ω_3-B_{2g}, ω_4-A_{2u}, ω_5-E_u, ω_{6u}-E (for the D_{4h} symmetry).

of K_3NiF_6. The vibration frequency values of B_{2u} symmetry are not given in Table II for the square–planar complexes, because motion along this vibrational coordinate stabilizes these systems.
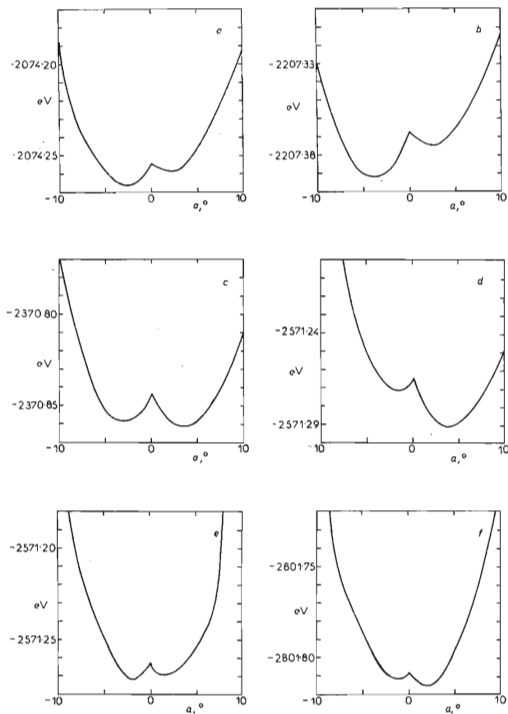

FIG. 2

Dependence of total energy of the tetrahedral complexes of deformation angle α for deformation of e symmetry. a [MnCl$_4$]$^{2-}$ $2S + 1 = 2$, b [FeCl$_4$]$^{2-}$ $2S + 1 = 1$, c [CoCl$_4$]$^{2-}$ $2S + 1 = 2$, d [NiCl$_4$]$^{2-}$ $2S + 1 = 1$, e [NiCl$_4$]$^{2-}$ $2S + 1 = 3$, f [CuCl$_4$]$^{2-}$ $2S + 1 = 2$

To verify the effect of the used vibration frequency values on the trends obtained, we calculated the equilibrium constants by two ways. In the former the vibration partition function was constructed of all frequences of the normal vibration modes given in Table II, the frequences denoted by the symbol JT being omitted. The other method used in the calculation unit values of the vibration partition functions, and the vibration frequency values were only used for calculation of the ZVP correction. These results are represented by dashed lines in Figs 5—9.

Magnitude of excitation energies of electronic transitions was assessed in the zero order of the perturbation theory as a difference of the respective orbital energies. It was found, that in all the cases considered the electronic partition function could
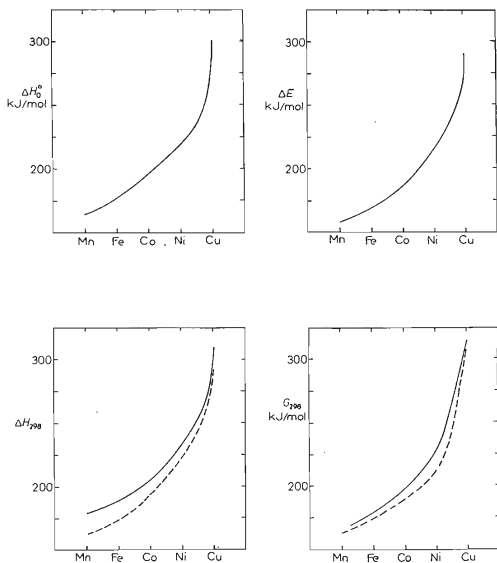
FIG. 3
Thermodynamic characteristics of the equilibrium MCl_4^{2-} (T_d, low-spin) $\leftrightarrow$ MCl_4^{2-} (D_{4h}, low-spin)

be approximated by statistical weight of the ground state. As orbital degeneration of symmetrical configurations is removed by distorsion of the Jahn–Teller type, unit values of orbital degeneration were used for calculation of the electronic partition function, *i.e.* statistical weights of the ground states were identified with their spin multiplicity.

The calculated values of the equilibrium constants are most sensitive to accuracy of determination of the reaction enthalpy. In our case it was necessary to establish whether the inaccuracy due to application of the SCF energy value corresponding to a configuration of T_d symmetry instead of that corresponding to the real equilibrium geometry could change the trend of the equilibrium constants in the series studied. Mapping of the energy hypersurface revealed that the vibrational interaction type
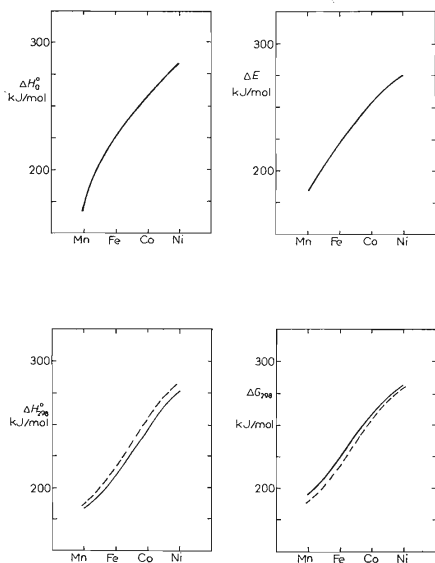

Fig. 4

Thermodynamic characteristics of the equilibrium MCl_4^{2-} (T_d, high-spin) $\leftrightarrow$ MCl_4^{2-} (D_{4h}, high-spin)

T-e is dominant even in triply degenerated ground states. Therefore, in all the degenerated ground states the total energy course was calculated in the section through energy hypersurface corresponding to tetragonal distorsion of e symmetry, the local energy being sought. The maximum difference between energy extremes of the total of the minimum at the tetragonal section through the energy hypersurface and the energy corresponding to the equilibrium geometry of T_d symmetry was considered a rough estimate of the error introduced into calculation of the reaction enthalpy. From graphical dependences given in Fig. 2 it is seen that the error estimate corresponds to about 3 kJ mol^{-1} (about $3 \cdot 10^{-2}$ eV) which, in the order of magnitude, makes $10^{-2}\%$ with respect to the reaction enthalpy values of the reaction considered. The problem of effect of correlation energy on the calculated reaction enthalpies
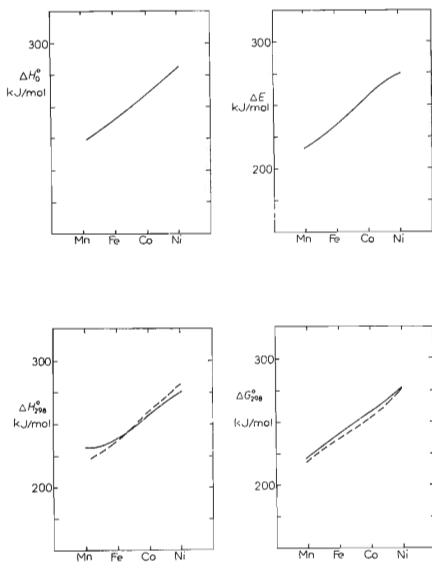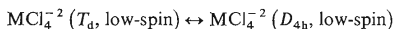

Fig. 5

Thermodynamic characteristics of the equilibrium MCl_4^{2-} (T_d, low-spin) $\leftrightarrow$ MCl_4^{2-} (D_{4h}, high-spin)

remains unsolved, and it could not be tested due to the considerable machine time required for the respective CNDO calculation. With respect to magnitude of the calculated ΔH_0^0 values and to magnitude of their changes accompanying transition from one system to the other, it seems reasonable to presume that involvement of the correlation energy will not change the studied trend of the thermodynamic quantities.

Figure 3 represents influence of the central atom M on the quantities ΔE_{SCF}, ΔH_0^0, ΔH_{298}^0, and ΔG_{298}^0 calculated for the reaction

$$\text{MCl}_4^{-2}\ (T_d,\ \text{low-spin}) \leftrightarrow \text{MCl}_4^{-2}\ (D_{4h},\ \text{low-spin})$$

with involvement of the vibration partition function. For comparison the figure also gives the dependences obtained with neglection of the vibration partition function
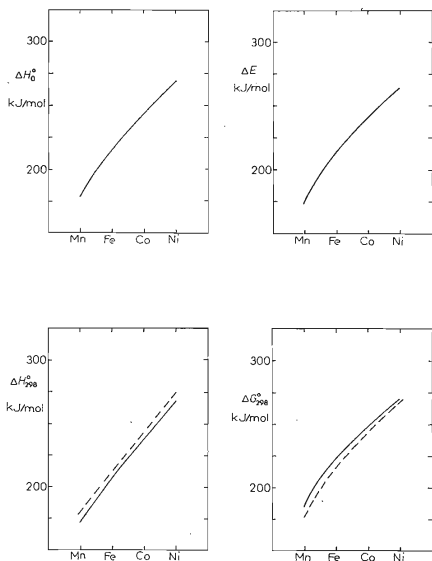

Fig. 6

Thermodynamic characteristics of the equilibrium MCl_4^{2-} (T_d, high-spin) $\leftrightarrow$ MCl_4^{2-} (D_{4h}, low-spin)

(dashed lines). From the point of view of the CNDO method which neglects the exchange integrals, the low-spin states are in all the cases energetically more favourable (or equivalent — in the degenerated state) than the corresponding states with the maximum multiplicity. Fig. 4 gives analogous dependences represented for a similar reaction in which the both components have the maximum multiplicities. The remaining two possibilities (the low-spin tetrahedron — the high-spin square and the high-spin tetrahedron — the low-spin square) are represented in Figs 5 and 6. Fig. 7 gives dependence of pK_{298} on the kind of the central atom for the individual spin states of tetrahedrons and squares. The same dependence neglecting the vibration partition function is given for comparison (dashed line).
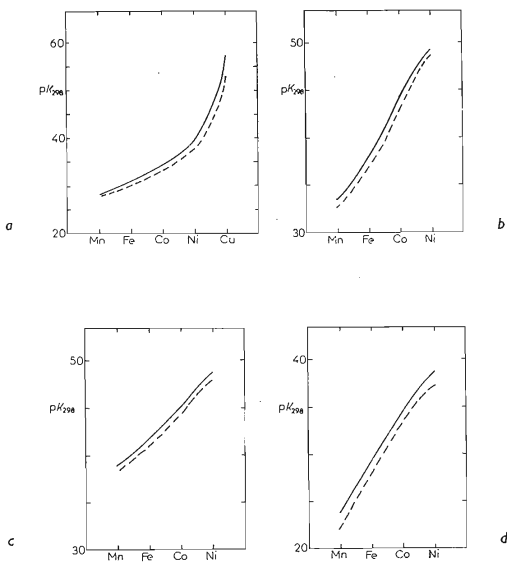

Fig. 7

pK_{298} values of the equilibrium MCl_4^{2-} (T_d) $\leftrightarrow$ MCl_4^{2-} (D_{4h}) a) low-spin $\leftrightarrow$ low-spin, b) high-spin $\leftrightarrow$ high-spin, c) low-spin $\leftrightarrow$ high-spin, d) high-spin $\leftrightarrow$ low-spin.

Comparison of the results shows that, in all the cases, the trends of all investigated quantities are the same in the studied series of transition metals. At the same time it can be stated that involvement of the vibration partition function constructed of available vibration frequencies did not change qualitative picture of the studied dependence. The pK_{298} values increase in all the cases with increasing atomic number of the transition metal, and the differences between pairs of subsequent transition elements also increase in the same series. Comparison of the differences of pK_{298} values in the two calculation methods (taking into account possible errors in calculation of the reaction enthalpy) indicates that the obtained trend can be considered correct. It is self-evident that the obtained values cannot be compared with any experimental dates of the equilibria tetrahedron–square which always involve implicitly influence of many other factors which were not taken into account in the given model calculation. On the other hand, however, the given results enable to determine the factor of influence of the central atom on a certain type of configurational isomerism. From the graphical dependences it follows that the ability to form square complexes (conditioned by electronic structure of the central atom) markedly decreases in the studied series of transition elements:

$$Mn(II) > Fe(II) > Co(II) > Ni(II) > Cu(II).$$
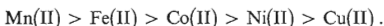
The relatively high pK or ΔG^0 values agree with the experimental experience[6] that establishing of the tetrahedron–square equilibria in solutions is always affected by special steric and bonding properties of ligands and solvents. In this context formation of chelate complexes with steric hindrance at axial coordination positions can be given as an example.

However, the obtained results are relatively surprising in connection with the known extraordinary plasticity of a coordination polyhedron of Cu(II) (refs[20,21]). With respect to the fact that, out of all the studied central atoms, copper possess the least tendency to change the geometric arrangement of the coordination polyhedron ($T_d \leftrightarrow \leftrightarrow D_{4h}$), it would be useful to specify with more precision what is meant by the word plasticity. It should be emphasized that this word is connected with non-rigidity of the coordination polyhedron and that it should not be connected with the tendency to global reorganisation of geometrical arrangement of the chromophore.

REFERENCES

1. Čársky P., Slanina Z., Zahradník R.: Chem. Listy *69*, 529 (1975).
2. Kellö V.: *Thesis.* Comenius University, Bratislava 1977.
3. Zahradník R., Slanina Z., Čársky P.: This Journal *39*, 63 (1974).
4. Slanina Z., Schlanger J., Zahradník R.: This Journal *41*, 1864 (1975).
5. Pelikán P., Turi Nagy L., Liška M., Boča R.: Chem. Listy *69*, 917 (1975).
6. Barefield E. K., Busch D. H.: Quart. Rev. *22*, 457 (1968).
7. Slanina Z., Zahradník R., This Journal *39*, 729 (1974).

8. Wilson E. B., Decius J. C., Cross P. C.: *Molecular Vibrations*. McGraw-Hill, New York 1955.
9. Pople J. A., Beveridge D. L.: *Approximate Molecular Orbital Theory*. McGraw-Hill, New York 1970.
10. Clack D. W., Hush N. S., Yandle J. R.: J. Chem. Phys. *57*, 3503 (1972).
11. Allen G. C., Clack D. W.: J. Chem. Soc. A *1970*, 2668.
12. Cyvin S. J.: *Molecular Vibrations and Mean Square Amplitudes*. Elsevier, Amsterdam 1968.
13. Pulay P.: Mol. Phys. *18*, 473 (1970).
14. Pulay P.: *Thesis*. Technische Hochschule, Stuttgart 1970.
15. Jahn H. A., Teller E.: Proc. Roy. Soc. *161*, 220 (1937).
16. Bersuker I. B.: Coord. Chem. Rev. *14*, 357 (1975).
17. Pelikán P., Breza M., Liška M.: Inorg. Chim. Acta *45*, L1 (1980).
18. Pelikán P., Breza M., Boča R.: Unpublished results.
19. Clack D. W., Smith W.: Mol. Phys. *29*, 1615 (1975).
20. Gažo J., Bersuker I. B., Garaj J., Kabešová M., Kohout J., Langferderová H., Melník M., Serátor M., Valach F.: Coord. Chem. Rev. *19*, 253 (1976).
21. Gažo J.: Pure Appl. Chem. *38*, 279 (1974).
22. Cusachs L. C., Reynolds J. W., Barnard D.: J. Chem. Phys. *44*, 835 (1966).
23. Helmholtz L., Kruh R. F.: J. Amer. Chem. Soc. *74*, 1176 (1952).
24. Demuyuck F., Veillard A.: Chem. Phys. Lett. *6*, 304 (1970).

Translated by J. Panchartek.