MO STUDY OF T_d—D_{4h} EQUILIBRIUM IN COMPLEXES OF TRANSITION METALS. II. EQUILIBRIUM IN TETRAFLUORO AND TETRABROMO COMPLEXES OF ATOMS OF THE FIRST TRANSITION ROW

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Received February 22nd, 1984

The CNDO method for transition metals in the UHF version has been used to study the equilibrium of configuration isomers of tetrahedral and square-planar tetrafluoro and tetrabromo complexes of the first transition row atoms in the oxidation degree II (Mn(II), Fe(II), Co(II), Ni(II), Cu(II)) both in low-spin and in high-spin states. The results show that the ability (given by electronic structure of the central atom) to form the square-planar complexes decreases monotonously in the series: Mn(II) > Fe(II) > Co(II) > Ni(II) > Cu(II). With respect to the effect of electronic structure of ligands, the same ability decreases in the series: F^- > Cl^- > Br^-.

The present communication forms an extension of the previous work[1] (dealing with the study of chloro complexes) to analogous complexes with the halogenide ligands F^- and Br^-. The aim of the previous work was to study the effect of electronic structure of the central atom on the ability to form the T_d – D_{4h} isomers. The respective semi-empirical calculations of the equilibrium constants K_p of model equilibria

$$MCl_4^{2-}\ (T_d) \overset{K_p}{\longleftrightarrow} MCl_4^{2-}\ (D_{4h})$$

showed that the ability to form the square-planar complexes decreases in the series: Mn(II) > Fe(II) > Co(II) > Ni(II) > Cu(II).

Investigation of effects of the quality of directly bound atoms of the coordinated ligands on this property forms a logical continuation of the previous studies. The extension of the set studied by the fluoro and bromo complexes gives a model enabling – in the sections for the individual central atoms – to estimate the effect of quality of the directly bound coordinated atom on the possibility of formation of the square complexes, and, from a more general view, to estimate the superposition of the both effects, *viz.* that of electronic structure of the central atom with that of quality of the ligand. The factor which determines quality in the series of the ligands studied

is represented by electronegativity of the individual halogen atoms. The quantity adopted for the said analysis is (as it was in the previous case, too) the equilibrium constant K_p of the model reversible isomerization reaction in ideal gas phase.

CALCULATION METHOD

The K_p equilibrium constant of a gas phase chemical reaction

$$\sum_i a_i A_i \leftrightarrow \sum_j b_j B_j$$

can be expressed by means of the apparatus of statistical thermodynamics in the following form

$$K_p = \left(\prod_{j=1}^{N_J} (Q^0_{B_j}/N_A)^{b_j} / \prod_{i=1}^{N_I} (Q^0_{A_i}/N_A)^{a_i}\right) \exp\left(-\Delta H^0_0/RT\right),$$

where ΔH^0_0 is the reaction enthalpy at the absolute zero temperature, T is absolute temperature, N_i and N_j are numbers of reactants and products, resp., N_A is the Avogadro number, R means the universal gas constant, and $Q^0_{X_k}$ is the partition function of the X_k component in the standard state ($p_{X_k} = 101\ 325$ Pa). The partition functions were calculated with the presumption of validity of the Born–Oppenheimer approximation, in the form of product of the translational, rotational, vibrational, and electronic partition functions. Detailed procedure of the calculation is given in ref.[1].

The calculation was carried out in the way usual in quantum chemistry[2]:

1) The minima were found at the energy hypersurfaces of the reactants and products. The equilibrium geometries corresponding to these minima were used in the calculation of the rotational component of the overall partition function.

2) In the equilibrium geometries of the individual components, the second derivatives were calculated of the total energy with respect to the geometry coordinates, and these derivatives were submitted to the FG analysis[3] to give the frequences of normal vibrational modes and, hence, also the vibrational partition function and energy of the normal vibrational modes at absolute zero temperature.

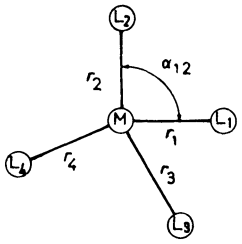

FIG. 1
Definition of coordinate system in the tetrahedral molecule

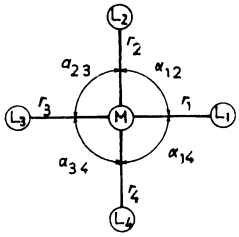

FIG. 2
Definition of coordinate system in the square-planar molecule

3) The stoichiometric difference of the calculated energies of the reactants and products was corrected with respect to the vibrational energy at the absolute zero temperature (ZPV correction) and used for determination of the reaction enthalpy ΔH_0^0 at the absolute zero temperature.

The necessary points of the energy hypersurfaces were calculated by means of the CNDO method in UHF version modified for compounds of transition elements[4-6]. The equilibrium geometries were determined by minimizing the total energy with regard to the bond lengths in the arrangements of given geometry and spin multiplicity.

The calculation of the vibrational frequences of the normal modes was carried out by the FG analysis in symmetrical coordinates[3,7]. The force constants were determined from the changes of the energy accompanying the changes in the symmetrical coordinates due to shifts of the valence coordinates by $\Delta r = 0{\cdot}05 \,.\, 10^{-10}$ m and/or to changes in the deformation coordinates by $\Delta\alpha = 2{\cdot}5$.

The calculation of the force constants in the tetrahedral molecules (Fig. 1) started from the SCF energy values in nine geometries obtained by various deformations of the equilibrium geometry according to Table I. The corresponding force constants F were calculated from the following relations:

$$2\,\Delta E_1 = F(A_1)\,.\,S^2(A_1)$$
$$2\,\Delta E_2 = F(A_1)\,.\,S^2(A_1)$$
$$2\,\Delta E_3 = F_1(T_2)\,.\,S_{1a}^2(T_2)$$
$$2\,\Delta E_4 = F_2(T_2)\{S_{2a}^2(T_2) + S_{2b}^2(T_2) + S_{2c}^2(T_2)\}$$
$$2\,\Delta E_5 = F_2(T_2)\{S_{2a}^2(T_2) + S_{2b}^2(T_2) + S_{2c}^2(T_2)\}$$
$$2\,\Delta E_6 = F(E)\{S_a^2(E) + S_b^2(E)\}$$
$$2\,\Delta E_7 = F(E)\{S_a^2(E) + S_b^2(E)\}$$
$$2\,\Delta E_8 = F_1(T_2)\,.\,S_{1a}^2(T_2) + 3F_2(T_2)\,.\,S_{2a}^2(T_2) + 2F_{1,2}(T_2)\,.\,S_{1a}(T_2)\,.\,S_{2a}(T_2)$$
$$2\,\Delta E_9 = F_1(T_2)\,.\,S_{1a}^2(T_2) + 3F_2(T_2)\,.\,S_{2a}^2(T_2) + 2F_{1,2}(T_2)\,.\,S_{1a}(T_2)\,.\,S_{2a}(T_2)\,,$$

where ΔE_i is the difference of the SCF energies between the i-th deformed geometry and the equilibrium T_d geometry. The symmetrical coordinates are defined according to Cyvin[7].

For the square-planar complexes (Fig. 2) the force constants were calculated from the SCF energies of nine deformed energies defined in Table II. In analogy to the above case, the individual force constants were calculated from the following relations:

$$2\,\Delta E_1 = F(A_{1g})\,.\,S^2(A_{1g})$$
$$2\,\Delta E_2 = F(A_{1g})\,.\,S^2(A_{1g})$$
$$2\,\Delta E_3 = F(B_{1g})\,.\,S^2(B_{1g})$$
$$2\,\Delta E_4 = F(A_{2u})\,.\,S^2(A_{2u})$$
$$2\,\Delta E_5 = F(B_{2g})\,.\,S^2(B_{2g})$$
$$2\,\Delta E_6 = F(B_{2u})\,.\,S^2(B_{2u})$$

TABLE I

The geometries used for calculation of the force constants matrix of the tetrahedral molecules MX_4[a]

Geometry number	Symmetry	Δr_1	Δr_2	Δr_3	Δr_4	$\Delta\alpha_{12}$	$\Delta\alpha_{13}$	$\Delta\alpha_{14}$	$\Delta\alpha_{23}$	$\Delta\alpha_{24}$	$\Delta\alpha_{34}$
1	T_d	0·05	0·05	0·05	0·05	0	0	0	0	0	0
2	T_d	−0·05	−0·05	−0·05	−0·05	0	0	0	0	0	0
3	C_{2v}	0·05	−0·05	0·05	−0·05	0	0	0	0	0	0
4	C_{3v}	0	0	0	0	2·5	2·5	2·5	−2·6116	−2·6116	−2·6116
5	C_{3v}	0	0	0	0	−2·5	−2·5	−2·5	2·3801	2·3801	2·3801
6	D_{2d}	0	0	0	0	2·5	−1·2354	−1·2354	−1·2354	−1·2354	2·5
7	D_{2d}	0	0	0	0	−2·5	1·2643	1·2643	1·2643	1·2643	−2·5
8	C_s	0·05	−0·05	0·05	−0·05	2·5	2·5	2·5	−2·6116	−2·6116	−2·6116
9	C_s	0·05	−0·05	0·05	−0·05	−2·5	−2·5	−2·5	2·3801	2·3801	2·3801

[a] Δr_i means the deviation of the bond length in MX_i from the equilibrium distance R in 10^{-10} m, $\Delta\alpha_{ij}$ is the deviation in ° of the valence angle X_iMX_j from the tetrahedral value.

TABLE II

The geometries used for calculation of the force constants matrix of the square-planar molecules MX_4[a]

Geometry number	Symmetry	Δr_1	Δr_2	Δr_3	Δr_4	$\Delta\alpha_{12}$	$\Delta\alpha_{23}$	$\Delta\alpha_{34}$	$\Delta\varphi_{c14}$	Δz_1	Δz_2	Δz_3	Δz_4
1	D_{4h}	0·05	0·05	0·05	0·05	0	0	0	0	0	0	0	0
2	D_{4h}	−0·05	−0·05	−0·05	−0·05	0	0	0	0	0	0	0	0
3	D_{2h}	0·05	−0·05	0·05	−0·05	0	0	0	0	0	0	0	0
4	C_{4v}	0	0	0	0	−0·1090	−0·1090	−0·1090	−0·1090	R isn 2·5	R sin 2·5	R sin 2·5	R sin 2·5
5	D_{2h}	0	0	0	0	2·5	−2·5	2·5	−2·5	0	0	0	0
6	D_{2d}	0	0	0	0	0·1090	0·1090	0·1090	0·1090	$-R$ sin 2·5	R sin 2·5	$-R$ sin 2·5	R sin 2·5
7	C_{2v}	0·05	−0·05	0·05	−0·05	0	0	0	0	0	0	0	0
8	C_{2v}	0	0	0	0	0	2·5	0	−2·5	0	0	0	0
9	C_{2v}	0·05	−0·05	−0·05	0·05	0	2·5	0	−2·5	0	0	0	0

[a] Δr_i means the deviation of the bond length MX_i from the equilibrium distance R in 10^{-10} m, $\Delta\alpha_{ij}$ is the deviation in ° of the valence angle X_iMX_j from the right angle, Δz_i is the perpendicular deviation of the X_i ligand from the square plane in 10^{-10} m.

$$2\,\Delta E_7 = 2F_1(E_u)\,.\,S_{1a}^2(E_u)$$

$$2\,\Delta E_8 = 2F_2(E_u)\,.\,S_{2a}^2(E_u)$$

$$2\,\Delta E_9 = 2F_1(E_u)\,.\,S_{1a}^2(E_u) + 2F_2(E_u)\,.\,S_{2a}^2(E_u) + 2F_{1,2}(E_u)\,.$$
$$.\,\{S_{1a}(E_u)\,.\,S_{2a}(E_u) + S_{1b}(E_u)\,.\,S_{2b}(E_u)\}\,.$$

RESULTS AND DISCUSSION

This study deals with a series of tetrahalogeno complexes MX_4^{2-}, where X = F^-, Br^-, and M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II). We tried to find the trend of the equilibrium constants in this series and, therefore, attempts were made to find the effect of the spin state of the complex anion on the calculated order. Each of the complex anions was considered in the states with the maximum and with the minimum spin multiplicities. These states were determined from such schemes of distri-

TABLE III

The equilibrium geometries of the tetrafluoro and tetrabromo complexes studied (10^{-10}) m

System	Multiplicity	$R_{eq}(T_d)$	$R_{eq}(D_{4h})$
MnF_4^{2-}	2	2·081	2·071
	6	2·102	2·104
FeF_4^{2-}	1	2·048	2·033
	5	2·055	2·062
CoF_4^{2-}	2	1·962	1·938
	4	1·962	1·964
NiF_4^{2-}	1	1·892	1·865
	3	1·892	1·890
CuF_4^{2-}	2	1·876	1·867
$MnBr_4^{2-}$	2	2·471	2·485
	6	2·477	2·502
$FeBr_4^{2-}$	1	2·437	2·448
	5	2·440	2·464
$CoBr_4^{2-}$	2	2·384	2·393
	4	2·384	2·405
$NiBr_4^{2-}$	1	2·339	2·347
	3	2·339	2·358
$CuBr_4^{2-}$	2	2·352	2·336

bution of the *d* electrons of the cations at five one-electron levels which had the minimum and the maximum numbers of the unpaired electrons[1].

Table III gives the calculated equilibrium distances and the SCF energies for the systems studied. As the CNDO method used does not differentiate between orbital degenerated states of different multiplicity, the calculated equilibrium distances

TABLE IV
Wave numbers of normal vibrations (cm^{-1}) of MF_4^{2-} complexes

System	MnF_4^{2-}	FeF_4^{2-}	CoF_4^{2-}	NiF_4^{2-}	CuF_4^{2-}
			T_d Symmetry		
Multiplicity	2	1	2	1	2
$\omega(a_1)$	666·6	71·70	802·6	888·2	931·0
$\omega(e)$	JT	JT	JT	JT	JT
$\omega(t_2)$	(596·7)	(459·4)	(547·0)	(653·2)	(894·2)
$\omega(t_2')$	(115·9)	JT	JT	JT	(173·4)
Multiplicity	6	5	4	3	2
$\omega(a_1)$	667·5	720·0	802·6	888·4	931·0
$\omega(e)$	140·4	(135·3)	174·9	JT	JT
$\omega(t_2)$	759·0	815·4	90·28	(831·1)	(894·2)
$\omega(t_2')$	187·7	199·3	218·3	(156·3)	(173·4)
			D_{4h} Symmetry		
Multiplicity	2	1	2	1	2
$\omega(a_{1g})$	655·9	699·3	789·0	874·2	913·9
$\omega(b_{1g})$	592·5	620·9	702·2	781·0	815·1
$\omega(b_{2g})$	368·3	253·8	474·1	611·7	594·5
$\omega(a_{2u})$	216·2	218·9	243·0	266·2	240·2
$\omega(e_u)$	808·2	852·9	966·7	1 080·2	1 075·2
$\omega(e_u')$	383·4	404·7	478·6	551·0	510·0
Multiplicity	6	5	4	3	2
$\omega(a_{1g})$	663·0	708·6	791·0	872·6	913·9
$\omega(b_{1g})$	596·7	614·5	715·2	774·1	815·1
$\omega(b_{2g})$	414·1	428·3	500·5	497·8	594·5
$\omega(a_{2u})$	179·2	193·4	220·5	239·0	240·2
$\omega(e_u)$	799·6	(851·1)	938·5	1 034·1	1 075·2
$\omega(e_u')$	355·3	(375·1)	421·6	472·4	510·0

and SCF energies are equal for the high- and the low-spin complexes CoX_4^{2-} and NiX_4^{2-}.

Some of the tetrahedral systems considered do not represent orbital singlets. The theory of the Jahn–Teller effect[7–10] for these systems states that the real equilibrium geometries have lower symmetry. However, as it was shown in the previous

TABLE V

Wave numbers of normal vibrations (cm^{-1}) of MBr_4^{2-} complexes

System	$MnBr_4^{2-}$	$FeBr_4^{2-}$	$CoBr_4^{2-}$	$NiBr_4^{2-}$	$CuBr_4^{2-}$
			T_d Symmetry		
Multiplicity	2	1	2	1	2
$\omega(a_1)$	337·7	362·8	395·0	425·6	437·8
$\omega(e)$	JT	JT	JT	JT	JT
$\omega(t_2)$	(484·4)	(489·1)	(546·6)	(608·0)	(624·5)
$\omega(t_2')$	(107·9)	(103·8)	(115·2)	(127·4)	(146·6)
Multiplicity	6	5	4	3	2
$\omega(a_1)$	336·9	362·3	395·0	425·6	437·8
$\omega(e)$	80·4	(79·2)	95·1	44·2	58·9
$\omega(t_2)$	522·2	552·6	591·6	(613·9)	(624·5)
$\omega(t_2')$	122·3	131·5	141·9	(141·4)	(146·6)
			D_{4h} Symmetry		
Multiplicity	2	1	2	1	2
$\omega(a_{1g})$	333·7	359·0	391·3	421·2	437·4
$\omega(b_{1g})$	257·6	294·1	320·1	343·6	349·1
$\omega(b_{2g})$	293·3	319·9	348·7	375·1	383·8
$\omega(a_{2u})$	188·9	203·3	214·1	228·6	223·8
$\omega(e_u)$	593·3	632·5	675·7	727·9	711·8
$\omega(e_u')$	276·7	296·6	323·4	348·3	355·0
Multiplicity	6	5	4	3	2
(a_{1g})	331·1	354·9	387·6	417·1	437·4
$\omega(b_{1g})$	266·2	284·4	295·1	331·8	349·1
$\omega(b_{2g})$	289·9	310·9	336·7	367·5	383·8
$\omega(a_{2u})$	177·2	189·3	204·3	222·1	223·8
$\omega(e_u)$	576·7	(612·1)	648·3	696·8	711·8
$\omega(e_u')$	269·2	(288·6)	315·7	340·0	355·0

work[1] this fact will not cause a change in relative order of any two equilibrium constants in the studied series of complex anions.

Tables IV and V give the calculated values of frequences of normal vibrational modes in the systems studied. The symbol JT denotes the values which could not be obtained due to the Jahn–Teller effect. The vibration frequency values given in brac-

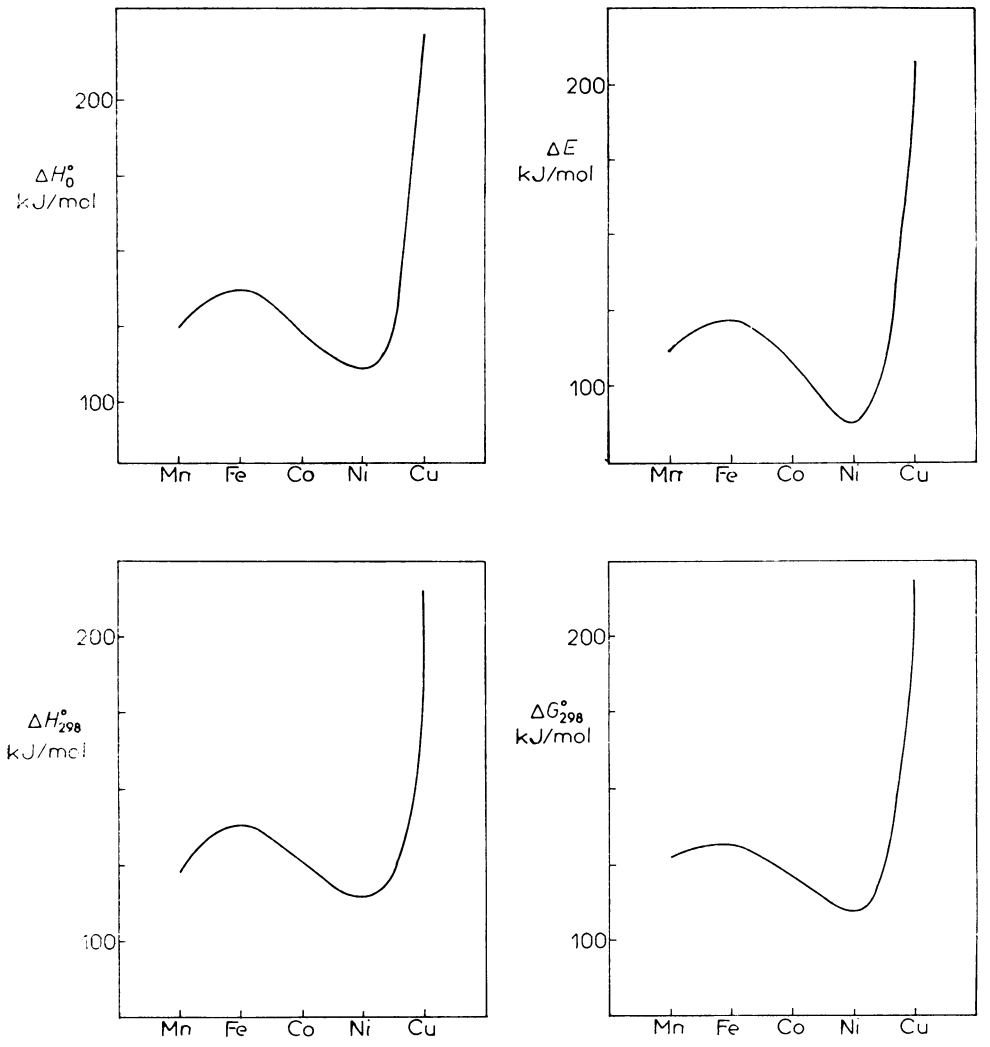

FIG. 3

Thermodynamical characteristics of the equilibrium: MF_4^{2-} (T_d, low-spin) $\leftrightarrow$ MF_4^{2-} (D_{4h}, low-spin

kets correspond to the modes which, in principle, would be able to interact vibronically with the electronic ground state, but no such interaction has been numerically proved. The vibration frequency values of the b_{2u} symmetry are not given for the square-planar complexes in Tables IV and V, because the motion along this vibrational coordinate stabilizes the system. The magnitude of excitation energies of elec-

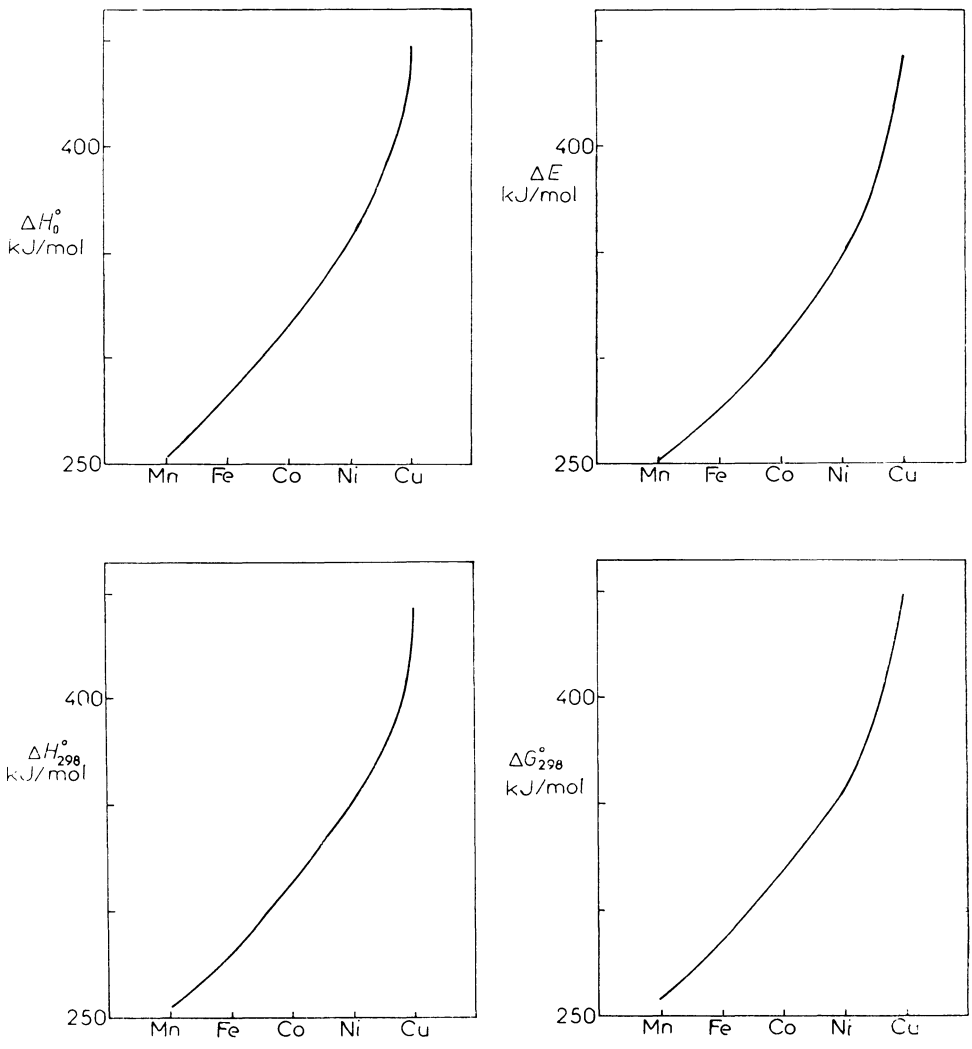

FIG. 4

Thermodynamical characteristics of the equilibrium: MBr_4^{2-} (T_d, low-spin) $\leftrightarrow$ MBr_4^{2-} (D_{4h}, low-spin)

tronic transitions was estimated in the zero order of the perturbation theory as a difference between the corresponding orbital energies. It was found that, in all the cases considered, the electronic partition function can be approximated by the statistical weight of the electronic ground state. As the orbital degeneration of symmetrical formations is removed by distorsion of the Jahn–Teller type, we calculated

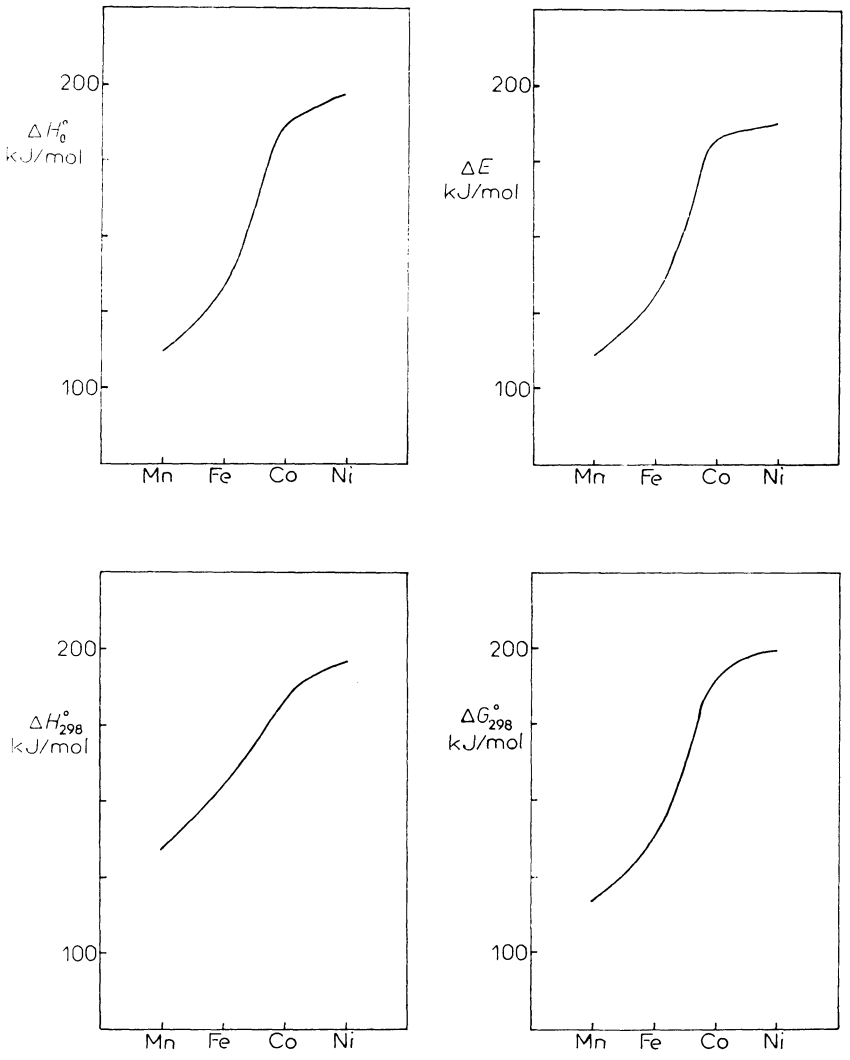

FIG. 5

Thermodynamical characteristics of the equilibrium: MF_4^{2-} (T_d, high-spin) $\leftrightarrow$ MF_4^{2-} (D_{4h}, high-spin)

the electronic partition function with the use of the unit value of orbital degeneration, *i.e.* statistical weights of the electronic ground states were identified with their spin multiplicities.

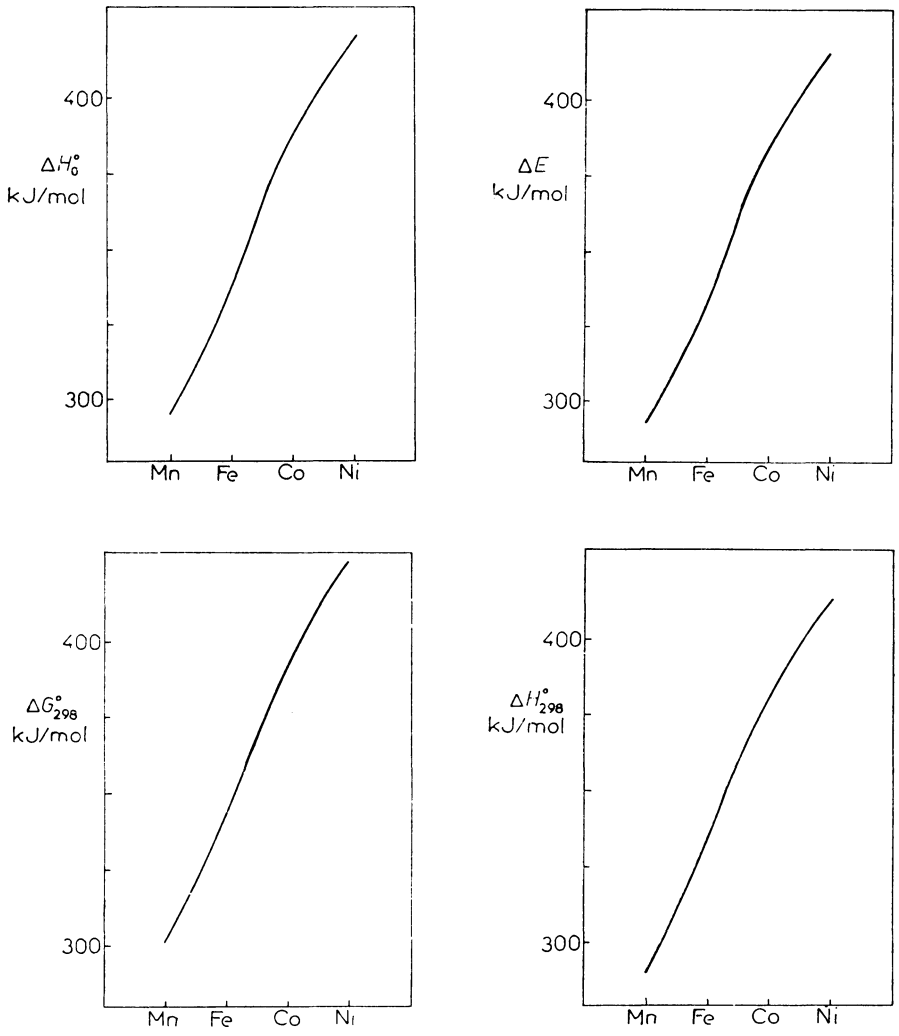

FIG. 6

Thermodynamical characteristics of the equilibrium: MBr_4^{2-} (T_d, high-spin) $\leftrightarrow$ MBr_4^{2-} (D_{4h}, high-spin)

Figs 3 and 4 represent the dependences of ΔE_{SCF}, ΔH_0^0, ΔH_{298}^0, and ΔG_{298}^0 on the central atom for the reactions:

$$MX_4^{2-} \ (T_d, \text{low-spin}) \leftrightarrow MX_4^{2-} \ (D_{4h}, \text{low-spin}),$$

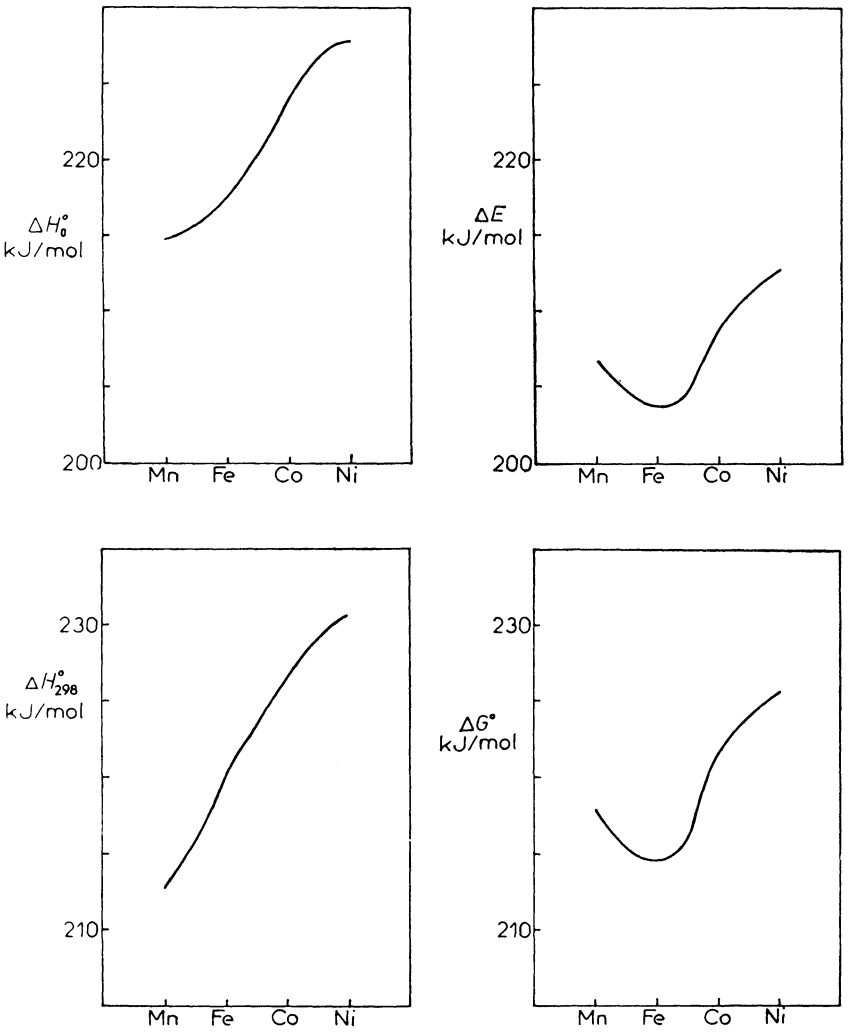

FIG. 7

Thermodynamical characteristics of the equilibrium: MF_4^{2-} (T_d, low-spin)$\leftrightarrow MF_4^{2-}$ (D_{4h}, high-spin)

where X = F^-, Br^-. Figs 5 and 6 give analogous dependences for the reaction in which the both components have the maximum spin multiplicity. The remaining two possibilities (low-spin tetrahedron – high-spin square, and high-spin tetrahedron – low-spin square) are represented in Figs 7, 8, and 9, 10, resp. Figs 11

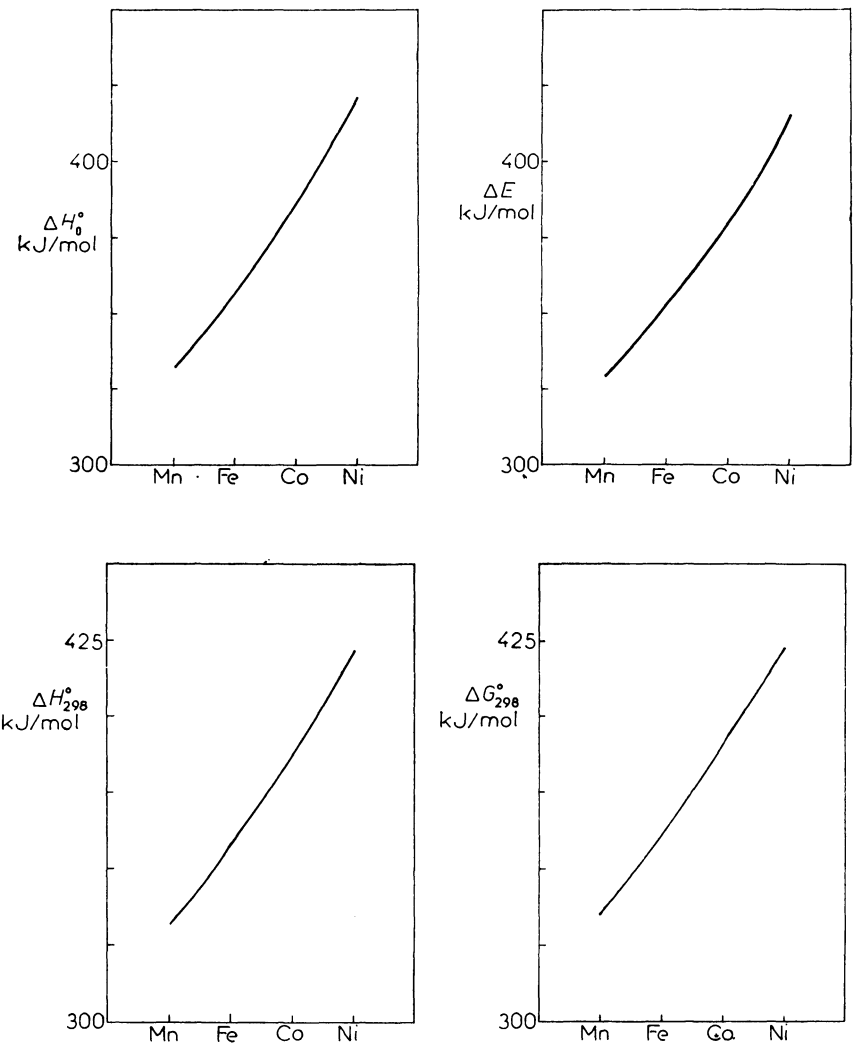

FIG. 8

Thermodynamical characteristics of the equilibrium: MBr_4^{2-} (T_d, low-spin) $\leftrightarrow$ MBr_4^{2-} (D_{4h}, high-spin)

and 13 give the dependence of pK_{298} on the central atom for the individual spin states of the tetrahedrons and squares. For comparison, Fig. 12 gives the same dependence for the series of chloro complexes studied in the previous work[1]. Comparison of the dependences in Figs 11–13 shows unambiguously that the pK values

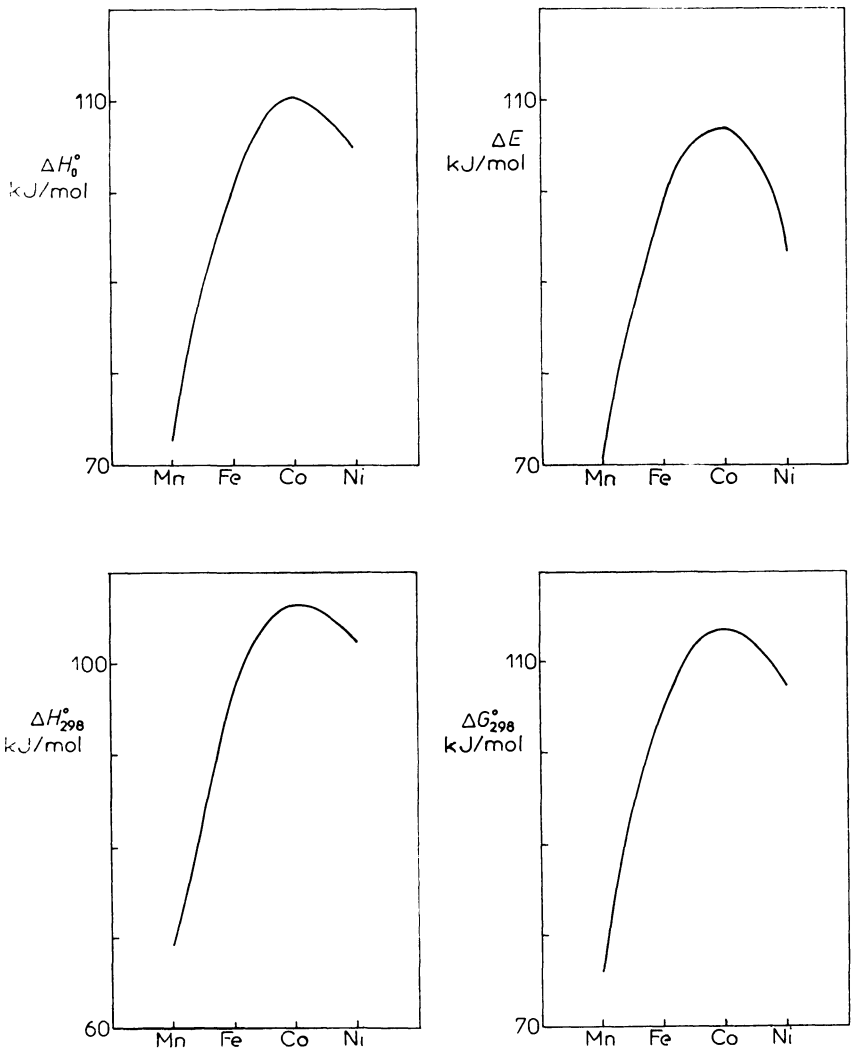

FIG. 9

Thermodynamical characteristics of the equilibrium: MF_4^{2-} (T_d, high-spin) $\leftrightarrow$ MF_4^{2-} (D_{4h}, low-spin)

increase monotonously in the series F, Cl, Br for each central atom and in each of the equilibrium type studied. This fact indicates that – in the systems studied – electronic structure of the halogenide ligands affects the ability to form the square--planar complexes, this ability being diminished in the series: $F^- > Cl^- > Br^-$, *i.e.* in the order of decreasing electronegativity of the ligands.

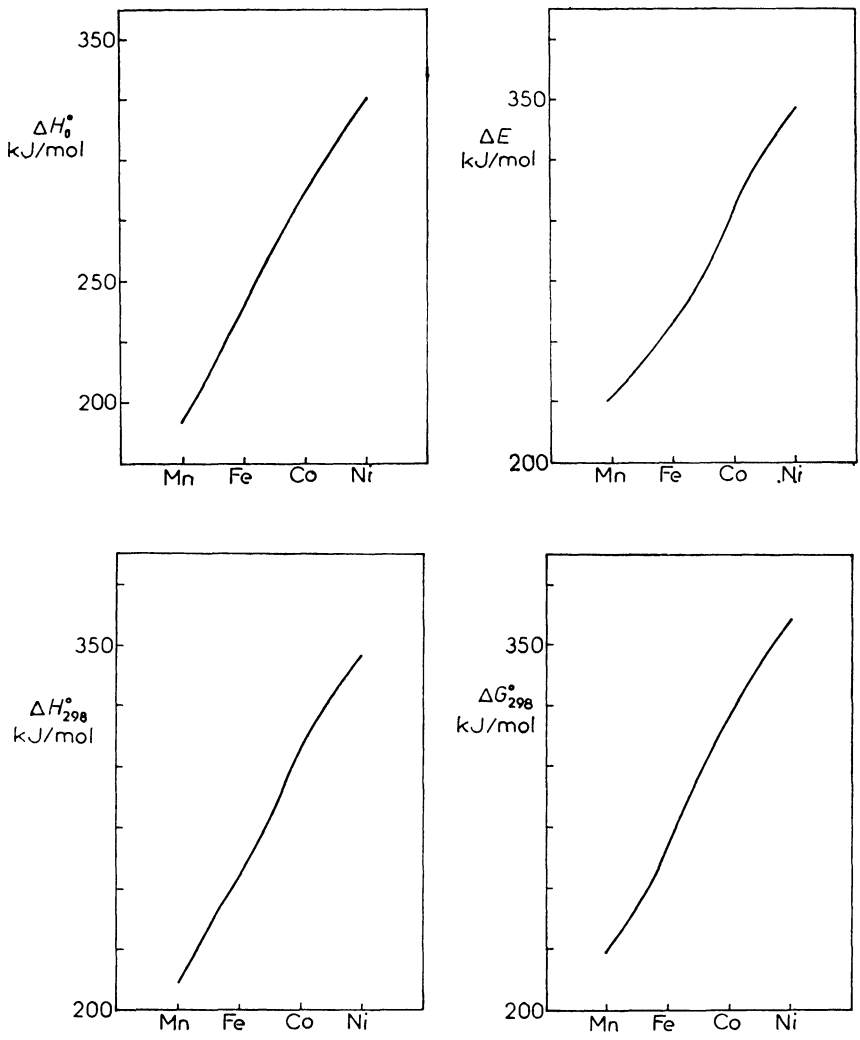

FIG. 10

Thermodynamical characteristics of the equilibrium: MBr_4^{2-} (T_d, high-spin) $\leftrightarrow$ MBr_4^{2-} (D_{4h}, low-spin)

The results obtained with the system of tetrabromo complexes (Fig. 13) agree well (with regard to the course of the individual dependences of pK on atomic number) with those obtained for tetrachloro complexes D_{4h} (Fig. 12), which fully confirms the trend of lowering of the ability to form the square-planar complexes in the series

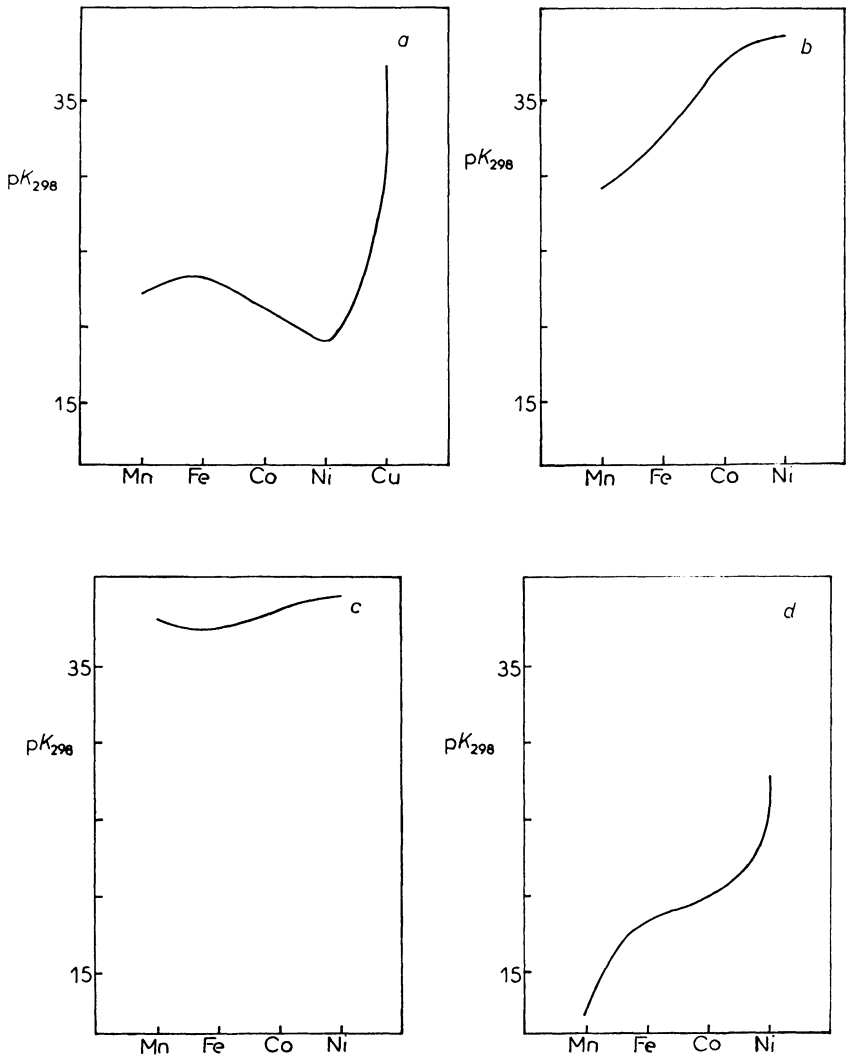

FIG. 11

The pK_{298} values of the equilibrium: MF_4^{2-} (T_d) $\leftrightarrow$ MF_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

of central atoms with different electronic structures, the decreasing order being: Mn(II) > Fe(II) > Co(II) > Ni(II) > Cu(II). This trend also stands in accordance with the results obtained in the series of tetrafluoro complexes for the equilibria: high-spin T_d – high-spin D_{4h} (Fig. 11*b*), and high-spin T_d – low-spin D_{4h} (Fig. 11*d*).

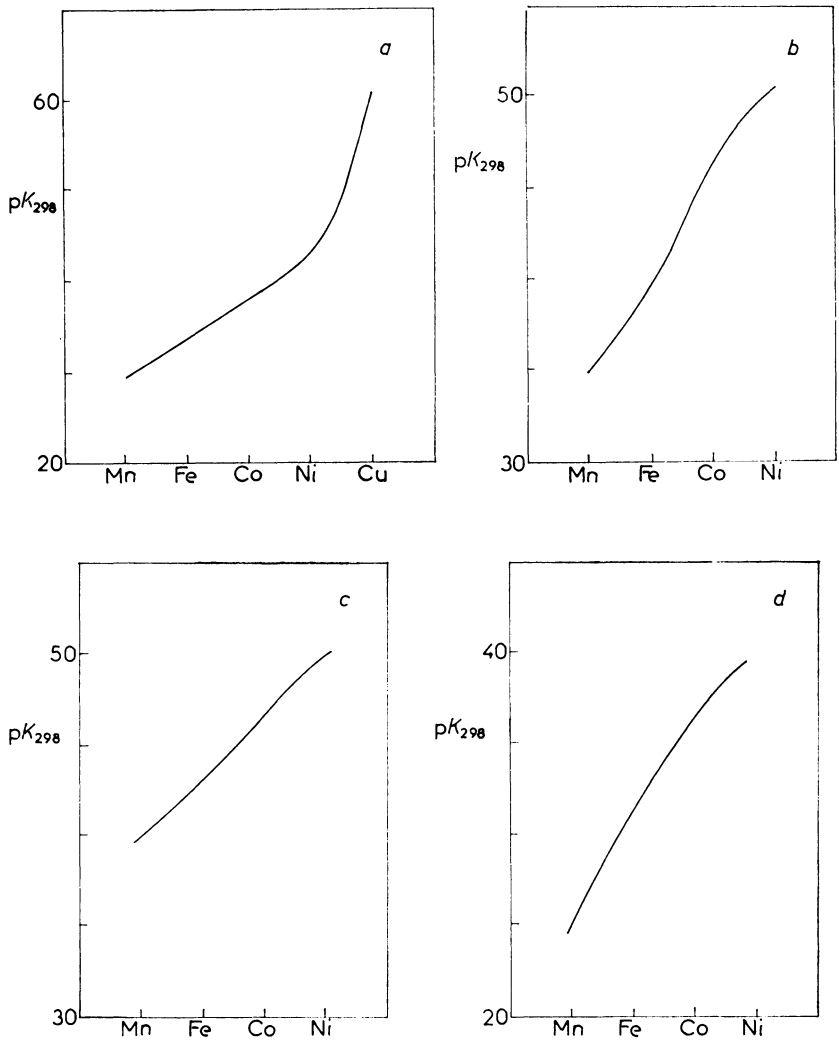

FIG. 12

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

In the equilibrium: low-spin T_d – high-spin D_{4H} (Fig. 11*c*) we found only a slight dependence of pK value on atomic number. This fact is due to decreasing energy requirements of the transition of the low-spin to the high-spin square-planar complexes in the series from Mn to Ni. This decrease becomes more distinct with increasing

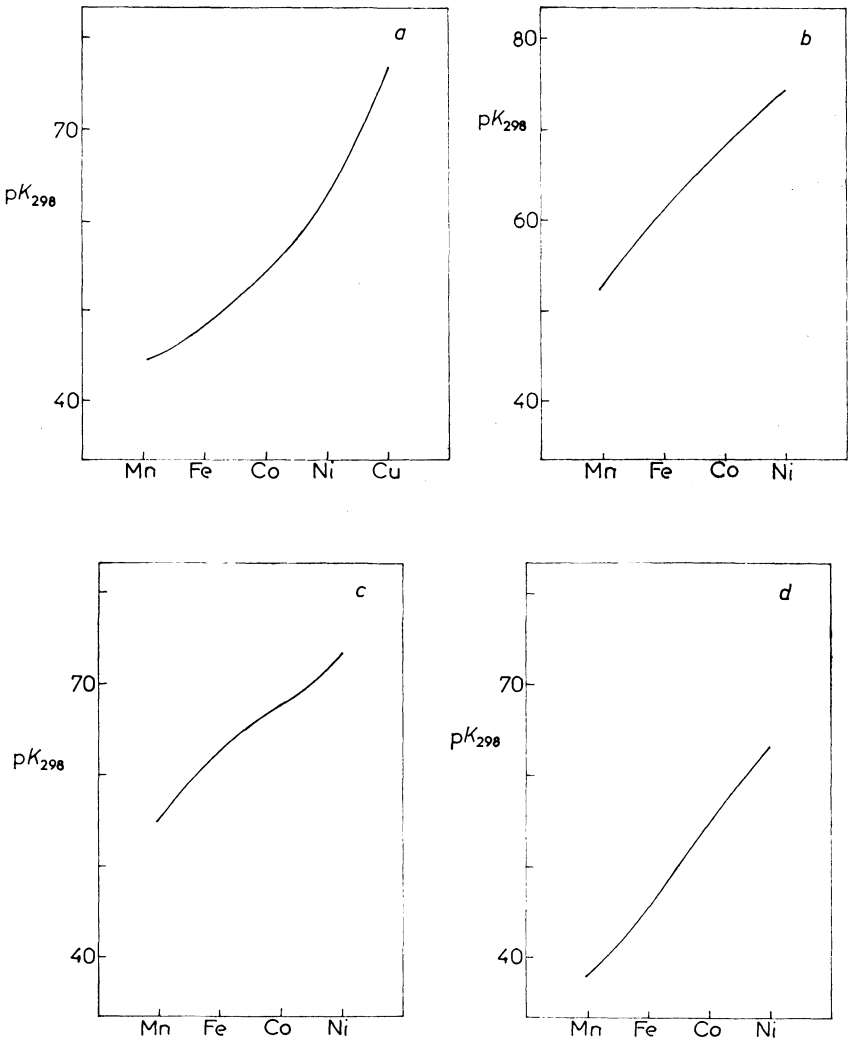

FIG. 13

The pK_{298} values of the equilibrium; MBr_4^{2-} (T_d) ↔ MBr_4^{2-} (D_{4h}) *a*) low-spin ↔ low-spin; *b*) high-spin ↔ high-spin; *c*) low-spin ↔ high-spin; *d*) high-spin ↔ low-spin

strength of the ligand field. With chloride and bromide ions this fact made itself felt in a decreased slope of the pK curve when going from the equilibrium: low-spin T_d – low-spin D_{4h} to the equilibrium: low-spin T_d – high-spin D_{4h} (Figs 12*a* – 12*c*, 13*a* – 13*c*). Thus the extremely strong ligand field of fluoride ion has the consequence of practically complete levelling of the pK *vs* atomic number dependence (Fig. 11*c*).

A rather surprising finding is that of decreasing order of K_p values obtained in the series of the tetrafluoro complexes in the iron triad (Fe, Co, Ni) when studying the equilibrium: low-spin T_d – low-spin D_{4h}.This result is obviously due to the marked change in the sequence of the individual electron levels caused by the extreme electronegativity of the fluoride ligand.

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Translated by J. Panchartek.