

THE ELECTRONIC SPECTRA OF IRON(II) COMPLEXES WITH α -PICOLINIC ACID AND QUINALDIC ACID

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In the paper the spectra of iron(II) complexes with α -picolinic acid and quinaldic acid are studied. In the spectra of these complexes very weak bands ($\epsilon = 18.5 \text{ l cm}^{-1} \text{ mol}^{-1}$) were found with wave numbers 11.8 kK at FeP_3^- and 12.5 kK at $\text{FeQ}_2 \cdot 2 \text{ H}_2\text{O}$. These bands were identified as $d-d$ transitions between the states ${}^5T_{2g}$ and 5E_g . The intensive bands, which are present in the spectra, were resolved as $t_{2g} \rightarrow \pi^*$ and $\pi \rightarrow e_g$ transitions. On the basis of so called coupled-chromophore model, the states, between which the electron-transfer transitions occurs, are qualitatively described in the paper.

It is very well known, that α -picolinic acid (HP) and quinaldic acid (HQ) react with iron(II) ions, which originates intensive red complex compounds¹⁻¹⁵. Studying complex equilibria it was found that in case of picolinate complex the particles FeP^+ , FeP_2 and FeP_3^- exist in solution¹³, while the quinaldic acid form FeQ^+ and FeQ_2 (ref.¹⁵). The results of magnetic moment study show, that these complexes are high spin^{16,17}. The electronic spectra of these complexes were measured in the region 17.0–25.0 kK and it was found that the absorption maximum has the complex with α -picolinic acid^{5,7,14} at wave number 22.7 kK and in case of quinaldiate complex^{3,14} at 19.66 kK. In both cases these bands were resolved as electron-transfer bands¹⁸.

As the gained informations are not satisfactory for the theoretical study of electronic structure of these complexes, we measured the spectra of these compounds in whole range of electron transfer transitions and further we studied the spectra in long-wave region, where we have found out the presence of $d-d$ transitions in both cases.

EXPERIMENTAL

Materials and instruments. The hydrochloride of α -picolinic acid was prepared by oxidation of α -picoline (Lachema, Brno) with potassium permanganate¹⁹. Others compounds were products (Merck or Lachema), mostly analytical grade. For the study of spectra, sodium salts of α -picolinic acid and quinaldic acid have been used.

The spectra were measured with spectrophotometer SF-4 (SSSR). For the study of electron-transfer bands the 1 cm cells have been used and $d-d$ transitions were measured in 10 cm cells. pH of solutions was measured with compensation pH-meter PHK-1 (Mikrotechna, Prague), using glass and calomel electrode. For the calibration of glass electrode buffer solutions recommended from NBS were used²⁰.

Spectra. The spectra of α -picolinic acid, quinaldic acid and electron-transfer spectra of Fe(II) complexes of these compounds were studied at pH 4, 5, 7 and 8. To hold the pH 4 and 5 Kolthoff acetate buffer were used, for the pH 7 Kolthoff-Vleeschhouwer borax-phosphate buffer solution and for the pH 8 buffer solution of Clark-Lubs. The spectra of solutions were measured immediately after mixing solutions. The order of solutions mixing were ligand-buffer solution-Mohr salt.

Composition of quinaldate complex. To find out the composition of complex which arises by reaction of Fe(II)-quinaldate ion, the method of nonequimolar continuous variation²¹ was used for the study. For the measurement the $5 \cdot 10^{-3} \text{M}$ solution of Mohr salt was used and the measurement was carried out for $p = 40, 100$ and 200 (p is defined as c_L/c_M , where c_L is the starting concentration of ligand solution and c_M the starting concentration of metal ion solution). The solutions were measured at wave length 510 nm and the results are given in Table I. From these data Job curves were constructed from which the stability constants β_2 were calculated. The values of $\log \beta_2$ (4.97 for $p = 40$; 5.20 for $p = 100$; 5.23 for $p = 200$) are in a good agreement with tabulated value (5.44) (ref.²²). The analysis showed that the value $\beta_3 = 0$, and we can say, that in case of great excess of ligand the complex, having only two quinaldate ions bounded to Fe(II) exists in solution.

RESULTS AND DISCUSSION

The electronic spectra of Fe(II) complexes with α -picolinic acid and quinaldic acid are given in Fig. 1 and 2. In both cases these spectra were gained under the conditions responsible for existence of complex particle with maximum number of π -electronic ligands. For the complex with α -picolinic acid this complex is FeP_3^- and for quinaldate complex $\text{FeQ}_2 \cdot 2 \text{H}_2\text{O}$. For being certain that in the studied solutions complexes of composition FeP_3^- and $\text{FeQ}_2 \cdot 2 \text{H}_2\text{O}$ exist, the 0.1M solutions of ligand and $3 \cdot 10^{-4} \text{M}$ solution of Fe(II) have been used for measurement. Using tabulated stability constant values of iron complexes with these ligands²² it may be find out, that under these conditions the complex FeP_3^- is formed from 99.5% and the complex $\text{FeQ}_2 \cdot 2 \text{H}_2\text{O}$ from 73%.

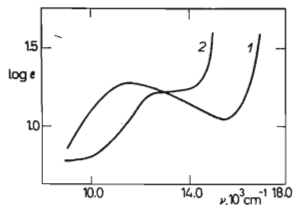


FIG. 1
 $d-d$ Spectra of FeP_3^- (1) and $\text{FeQ}_2 \cdot 2 \text{H}_2\text{O}$ (2)

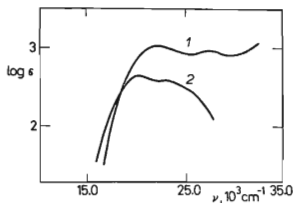


FIG. 2
Electron-Transfer Spectra of FeP_3^- (1) and $\text{FeQ}_2 \cdot 2 \text{H}_2\text{O}$ (2)

From Figs 1 and 2 it may be seen, that in both cases spectra are composed from the bands with low value of extinction coefficients ($\epsilon = 18.5 \text{ l cm}^{-1} \text{ mol}^{-1}$) and from the bands with the value of extinction coefficient $1000 \text{ l cm}^{-1} \text{ mol}^{-1}$ for FeP_3^- and $500 \text{ l cm}^{-1} \text{ mol}^{-1}$ for $\text{FeQ}_{2.2} \text{H}_2\text{O}$. As the d -electron system is one of the chromophore, we identify low intensity transitions as $d-d$ transitions between orbitals t_{2g} and e_g . The half-band width, $\delta = 2.5 \text{ kK}$, indicates this type of transitions, too. From the study of magnetic properties follows, that the electronic configuration of the ground state is $(t_{2g})^4 (e_g)^2$ and the excited state has the configuration $(t_{2g})^3 (e_g)^3$. The only terms, resulting from the approximation of octahedral microsymmetry from these states are the terms ${}^5T_{2g}$ and 5E_g and therefore in the $d-d$ spectra only one band can be expected, connected with the transition ${}^5T_{2g} \rightarrow {}^5E_g$. The wave number of these transitions is simultaneously the value Δ and is in case of FeP_3^- 11.8 kK and in case of $\text{FeQ}_{2.2} \text{H}_2\text{O}$ 12.5 kK . These values are in agreement with those observed in other high spin complexes of Fe(II) ion with octahedral microsymmetry^{23,24}.

Identification of electron-transfer transitions which appear in both cases as a broad band with two maxima is a little complicated. As in these complexes iron is in the

TABLE I
Nonequimolar Continuous Variation^a

	NaQ ml	Mohr salt, ml	Absorbance for p		
			40	100	200
	0.0	10	0.008	0.004	0.006
	0.2	9.8	0.256	0.709	1.119
	0.4	9.6	0.538	1.131	1.300
	0.6	9.4	0.790	1.207	1.341
	0.8	9.2	0.962	1.250	1.357
	1.0	9.0	1.051	1.256	1.342
	2.0	8.0	1.086	1.182	1.247
	3.0	7.0	1.000	1.067	1.111
	4.0	6.0	0.895	0.945	0.965
	5.0	5.0	0.750	0.805	0.833
	6.0	4.0	0.615	0.648	0.669
	7.0	3.0	0.470	0.492	0.511
	8.0	2.0	0.321	0.338	0.350
	9.0	1.0	0.171	0.178	0.192
	10.0	0.0	0.013	0.016	0.026

^a 10 ml of the acetate buffer (pH 5) was added to each solution. The total volume of the solution was 25 ml.

oxidation state +2 and both ligands are π -electronic systems, the transitions connected with transition t_{2g} event. e_g electron into the antibonding orbital of ligand (e.g. transition $t_{2g} \rightarrow \pi^*$ and $e_g \rightarrow \pi^*$) and the transitions connected with transition of electron from bonding orbital of ligand into the partly filled t_{2g} or e_g metal orbital (e.g. transition $\pi \rightarrow t_{2g}$ and $\pi \rightarrow e_g$) may be expected²³. From these transitions only transitions $t_{2g} \rightarrow \pi^*$ and $\pi \rightarrow e_g$ are taken into account. Remaining two transitions are symmetrically forbidden. The wave number of the $t_{2g} \rightarrow \pi^*$ transition is always lower than the transition $\pi \rightarrow e_g$ (ref²⁵). To distinguish these transitions qualitatively and to determine between which states the transitions occur, we use for the description of these systems so called coupled chromophore model²⁶⁻²⁸. This model was proposed for theoretical study of organic compounds containing interacting chromophore groups. At this model the ground state belongs to the state, in which no interaction occurs among chromophore groups. On applying this model on a molecule of mononuclear complex this ground state is described with function

$$|G, A_1 S\rangle = |M\rangle \prod_g |L(g)\rangle,$$

where $|M\rangle$ is the function describing the electron state of metal, $|L(g)\rangle$ describes the state of the g^{th} ligand, A_1 marks the symmetry of the ground state and S is the total spin of a particle. The electron-transfer state, which arises from the transition of d -electron from the central field of the metal ion into the antibonding orbital of the ligand, was described with function

$$|CT, \Gamma_1 S\rangle = \left(\frac{1}{j}\right)^{1/2} \sum_j \sum_{h=1}^n D_h^{\Gamma_1} \left| \begin{matrix} L(h) \\ M_j \end{matrix} r \right\rangle \prod_{g=1}^n |L(g)\rangle,$$

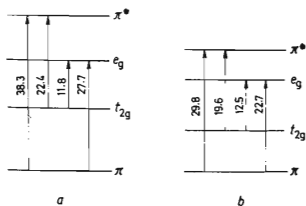


FIG. 3

One-electron Energetic Level Diagrams
a FeP_3^- , b $\text{FeQ}_2 \cdot 2\text{H}_2\text{O}$.

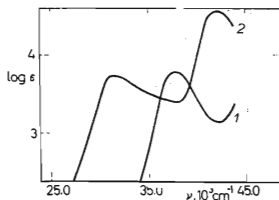


Fig. 4

Electronic Spectra of HP (1) and HQ (2) at
pH 5

where D_{λ}^{Γ} are group transformation coefficients and $|M_j^{L(h)}r\rangle$ is the function describing the state belonging to the transition of d -electron from the state with spin-orbital function $|M_j\rangle$ into the r^{th} antibonding orbital of the h^{th} ligand with spin-orbital function $|L(h)_r\rangle$. The prime at summation sign marks that the summation runs through those electron states of metal, which have the same quantum number λ , as the states of ligand atomic orbitals. In the same way we can write the function describing the electron transition from ligand bonding orbital into the partly filled metal orbital. As in this paper we are interested in the symmetry and number of new states, we determine only Γ for the given symmetry group. It is easy to find out, that the FeP_3^- complex can exist in the form *fac*- FeP_3^- or *mer*- FeP_3^- . In former case the symmetry of complex particle is C_3 and in latter case C_1 . From the character table of the point group C_3 we can find out, that the only representations of this group are representations A and E . As the orbitals $d\pi$ and $p\pi$ transform according to the representation E and $d\sigma$ and $p\sigma$ according to the representation A , we can expect in the electron transfer spectra one transition $t_{2g} \rightarrow \pi^*$ between states ${}^5A \rightarrow {}^5E$ and one transition $\pi \rightarrow e_g$ between the states ${}^5A \rightarrow {}^5A$. We notice, that the ground state of the particle is fully symmetrical. If the symmetry of the particle was C_1 , the number of transitions would be the same and in both cases between the states ${}^5A \rightarrow {}^5A$.

In case of quinaldate complex the particle with symmetry C_{2h} arises, *i.e.* *trans*- $\text{FeQ}_2 \cdot 2\text{H}_2\text{O}$ (the others ligand arrangements are excluded from the steric reasons and partly for the optical inactivity of the complex). In this symmetry group the orbitals $d\pi$ and $p\pi$ transform according to the representation B_g , and $d\sigma$ and $p\sigma$ according to the representation A_g . Therefore, there will be only one electron transfer transition $t_{2g} \rightarrow \pi^*$ between the states ${}^5B_g \rightarrow {}^5B_g$ and only one transition $\pi \rightarrow e_g$ between the states ${}^5A_g \rightarrow {}^5A_g$, too. As these transitions are between the states of the same parity, they are forbidden according to the Laporte rule and are allowed due to lowering of the symmetry, caused by vibrations of nuclei²⁹. In connection with this is the lower value of the extinction coefficients of these transitions. Basing on these considerations, the one-electron diagrams of energetic levels of complexes FeP_3^- and $\text{FeQ}_2 \cdot 2\text{H}_2\text{O}$ are given in Fig. 3. The wave numbers of the $\pi \rightarrow \pi^*$ transitions, given on this figure, were calculated from the experimental values obtained for electron-transfer transitions and $d-d$ transitions, and are in a very good agreement with the experimental values gained from the spectra of α -picolinic acid and quinaldic acid. These values are in case of picolinate ligand 37.9 kK and 21.2 kK in case of quinaldate ligand (Fig. 4).

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