Inorganica Chimica Acta, 11 (1974) 217–222

Low Valence States of Metal Chelates.
VII. Bis[bis(2′-quinolyl)-2,6-pyridine]iron(II) Perchlorate

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Received May 25, 1974

The electrochemical reductions of Fe(II) complex with bis(2′-quinolyl)-2,6-pyridine has been studied in acetonitrile by polarography and cyclic voltammetry, using tetraethyl ammonium perchlorate as supporting electrolyte. The iron(II) complex gave a five-step reduction wave in the range of potentials from 0 to –2.5 V vs SCE. The first three steps were diffusion controlled and involved the transfer of one electron for each step; the last two steps regarded the discharge of the ligand. Low valence states of iron have been formed on dme surface, in particular at the third step the species $Fe(DQP)_2^-$ was obtained. The results are discussed in comparison with the recent studies on the low valence states of metal chelates, that we previously carried out at this laboratory.

Introduction

In recent years many workers studied the problem of the low valence states of metal chelates. In particular the class of the complexes with heterocyclic diimines have been extensively investigated, preparing complexes in formal low valence states[1–3] and observing their spectral and magnetic behaviour.[4–8] A question always arises in explaining the properties of these compounds: are the electrons in excess fully localized on the metal atom or delocalized on the total metal–ligand system? Moreover can the low oxidation states be obtained by a certain ligand or more generally by a certain class of ligands[9]? Because of our interest about the transition metal complexes with the ligands 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen) and 2,2′,2″-terpyridine (terpy), some years ago we began to study this problem by voltammetric techniques in aprotic solvents.[10–16] In particular, carrying out investigation on the reduction of $M(terpy)_2^{2+}$ (where M is a generic transition metal) we were greatly surprised to find that these complexes were different from those with $(bipy)_3$ and $(phen)_3$, because with the former we only obtained the two states of +1 and 0, regarding the species $M(terpy)_2^+$ and $M(terpy)_2$, while with the latter ligands the reduction processes continued up to the state of –1, regarding the species $M(bipy)_3^-$ and $M(phen)_3^-$. We tried to explain this diversity, considering that the structure of an α-diiminic complex ion was slight different from the structure of a triiminic one (from the spectral pattern of these compounds it is evident a lowering of the symmetry) and assuming that the only central metal ion was responsable for the reduction steps observed in the polarograms of these complexes, namely the electronic changes were localized on the metal atom of the complex ion. If these assumptions were true, the lowering of the symmetry should cause a different splitting of metal ion d orbitals and consequently the possibility of accepting electrons should be varied. This simple approach was very useful in explaining the order of half-wave potentials experimentally found in the case of $Fe(terpy)_2^{2+}$ [15] and $Co(terpy)_2^{2+}$ [13] voltammetric behaviour.

We must also consider that a certain loss of the planarity of the ligand should occur, when terpy is forced to occupy the relative positions of the complex ion, during the chelation, because of the steric conditions imposed by the ligand itself. Hence, the possibility of electron delocalization over the whole aromatic system can decrease. As low valence states of metal complexes may also be regarded like states in which the metal is bonded to molecules of ligands negatively charged,[4–8] it is evident that any factor that decreases the possibility of delocalization of the ligand in the complex ion, influences indirectly the formation of these states. This consideration accounted for the fact that even in the case of the voltammetric behaviour of the complex ions $Cr(terpy)_2^{3+}$ and $Mn(terpy)_2^{2+}$,[14] the reduction process stopped again to the low valence state of 0.

These facts together contributed to explain the different behaviour found in the case of the complex ions $M(terpy)_2^{n+}$ and these results are in agreement with those found by many authors that carried out studies on this problem. However, we thought that these hypothesis needed many experimental data before reaching a general conclusion. Therefore, we begun to study complexes of the transition metals with an other tri-

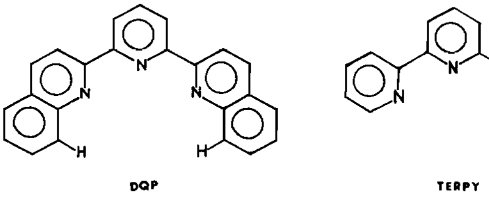

Figure 1. Structure formulas of DQP and terpy.

iminic ligand, the bis(2′-quinolyl)-2,6-pyridine (DQP), the structure of which resembles the one of terpy, as shown in Figure 1. This ligand was firstly used by Harris *et al.*,[17] who prepared the bis complex of the iron(II) and studied the spectral and magnetic behaviour in comparison with the one of $Fe(terpy)_2^{2+}$. From their data it is possible to conclude that DQP is a weaker ligand than terpy, but for our purposes is a very interesting ligand because of the presence of the two quinolinic rings in substitution of the terminal pyridines of terpy. The latter condition should assure a great possibility of delocalization of DQP molecule than terpy one; in fact the two complexes of iron(II) show presumably the same distorted octahedral structure, but in the molecule of DQP chelated to the metal ion, the quinolinic rings remain flat.

For these reasons we will report here the voltammetric behaviour of the bis[bis(2′-quinolyl)-2,6-pyridine]iron(II) perchlorate in acetonitrile; the experimental results will be discussed in conjunction with the recent studies of the analogous complexes of cobalt(II) and manganese(II).[17]

Experimental

Chemicals

Acetonitrile and tetraethyl ammonium perchlorate were the same as previously described.[12] The ligand bis(2′-quinolyl)-2,6-pyridine was prepared according to a method known in literature.[17] The complex $Fe(DQP)_2(ClO_4)_2$ was prepared according to a procedure that will be described elsewhere.[18] All compounds were dried in vacuum, before the use.

Apparatus

Conventional dc polarograms were recorded in acetonitrile with an Amel polarecorder type 463, using 0.05*M* tetraethyl ammonium perchlorate as supporting electrolyte. A three-electrode system was employed for all conventional dc measurements, using an Amel assembly type 460. The reference electrode was an aqueous saturated (with NaCl) calomel electrode, the connection of which with the cell was performed by an agar-salt bridge with sodium chloride. The auxiliary electrode was a platinum wire. The dropping mercury electrode had the following characteristics in air-free water at a mercury column heigh of 49 cm, with no applied potential: flow rate of mercury, m = 0.779 mg/sec; drop-time, t = 2.92 sec. Cyclic voltammograms were obtained by an Amel multifunction plug-in system type 448 and a Polaroid Land camera type CU/5. The experimental system was the same used for polarographic measurements with a long drop-time (20–30 sec) capillary.

The complex was dissolved in acetonitrile, the concentrations employed in the test solutions ranged from 0.1 to 0.6 m*M*.

Test solutions were degassed with nitrogen which was previously passed trough a tube filled with sulfur-free copper wire heated to 450° C, a H_2SO_4 filled wash bottle and six acetonitrile filled wash bottles. Constant drop-time was obtained by an electromagnetic hammer. All solutions were thermostated in bath at the temperature of 25° ± 0.1 °C.

Results and Discussion

The complex ion $Fe(DQP)_2^{2+}$ is reduced in five steps in 0.05*M* tetraethyl ammonium perchlorate, going from 0 to –2.5 V *vs* SCE, as shown in Figure 2. Half-wave potentials of the five steps together with the slopes of log-plot analysis for the first three steps are reported in Table I. The limiting current of the first three steps was a linear function of the complex concentration over the range from 0.1 to 0.6 m*M*. The limiting current of the same steps was also linearly dependent on the square root of mercury pressure between 37 cm and 57 cm, and to the temperature between 23° and 35 °C; the increments per cent of the limiting current for degree were: 1.5% deg; 1.7% deg; 1.3% deg, respectively for the first, second and third step.[20] This behaviour is characteristic for a faradaic process diffusion controlled without any kinetic complication. Further confirmation that limiting current of the first three steps is diffusion controlled, was obtained examining the time-dependence of the limiting current, changing the time over the range from 1 to 6 seconds with the use of a mechanical device.[21] Plotting $\log i_l$ *vs* logt we obtained straight lines, the slopes of which were: 0.20; 0.20; 0.18 respectively for the first, second and third step. These values are very near to the theoretical values of 0.17–0.20 and to the value of 0.20 experimentally found for lead ion in 1 N HCl at this laboratory.

Plots of –E against $\log i/(i_d-i)$ were linear with slopes, reported in Table I, that are in agreement with theoretical value of 59/n mV. Moreover half-wave potentials were not dependent from drop-time, confirming the reversibility of the reduction processes.

The limiting currents of the first three steps had approximately the same height as can be seen in Figure 2; the ratios of the five limiting currents were: 1.00: 1.03: 1.12: 6.95: 8.73, considering the first wave

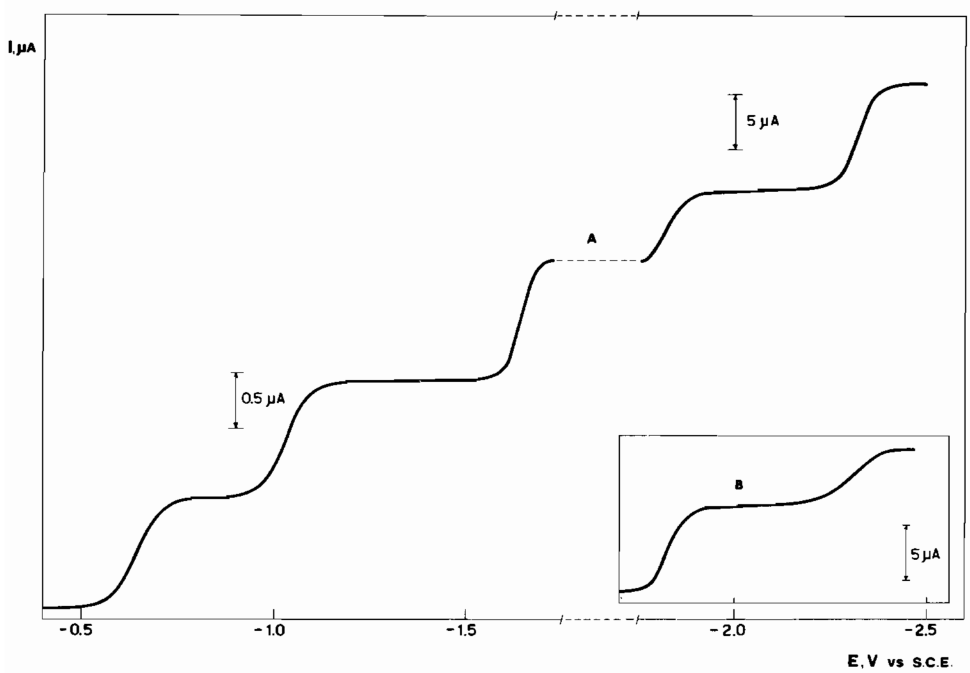

Figure 2. Polarograms taken in acetonitrile with 0.05*M* TEAP, using an aqueous SCE (with NaCl) reference electrode. A) 0.5 m*M* $Fe(DQP_2(ClO_4)_2$; B) 0.5 m*M* DQP; at the temperature of 25° ± 0.1 °C.

TABLE I. Half-wave potentials of $Fe(DQP)_2(ClO_4)_2$ reduction steps, in acetonitrile solutions containing 0.05 *M* TEAP as supporting electrolyte; slopes of log–plot analysis for the first three steps; half-wave potentials of the free ligand reduction steps. Potentials are referred to SCE (with NaCl) at the temperature of 25° ± 0.1 °C.

		I	II	III	IV	V
$Fe(DQP)_2(ClO_4)_2$	$E_{1/2}$, V	–0.637	–1.025	–1.640	–1.825	–2.300
	Slope, mV	60	58	58		
					I	II
DQP	$E_{1/2}$, V				–1.815	–2.295

height equal to the unity. The diffusion current constant of the first step is 1.95, that is nearly equal to the value found for the complex of iron(II) with terpy,[15] to the values of the analogous complexes of cobalt(II) and manganese(II) with DQP[19] and to the values found for various metal ions in acetonitrile.[22]

The free ligand gave a two-step reduction wave in the range of potentials between –1.8 and –2.5 V vs SCE. Its half-wave values, reported in Table I, were very similar to that of the fourth and fifth step in $Fe(DQP)_2^{2+}$ polarograms. Polarograms of the complex with the addition of a certain quantity of the free ligand (practically we prepared a saturated solution of DQP, stirring the solution of the complex together with the supporting electrolyte for two days in contact with DQP and filtering the excess before the use, because of the low solubility of the DQP in acetonitrile) showed that the first three steps were not affected, while the last two underwent modifications, in particular their limiting currents increased and their half-wave values shifted to less negative potentials. From these proofs we can reasonable assume that the last two steps regarded the discharge of the ligand.

Cyclic voltammograms at dme produced results consistent with those obtained from polarographic analysis. Typical voltammogram of the complex is shown in Figure 3; the study was only performed on the first three steps. In Table II are reported the peak potentials for cathodic and anodic processes, the separation of the peak values and the ratios of cathodic to anodic

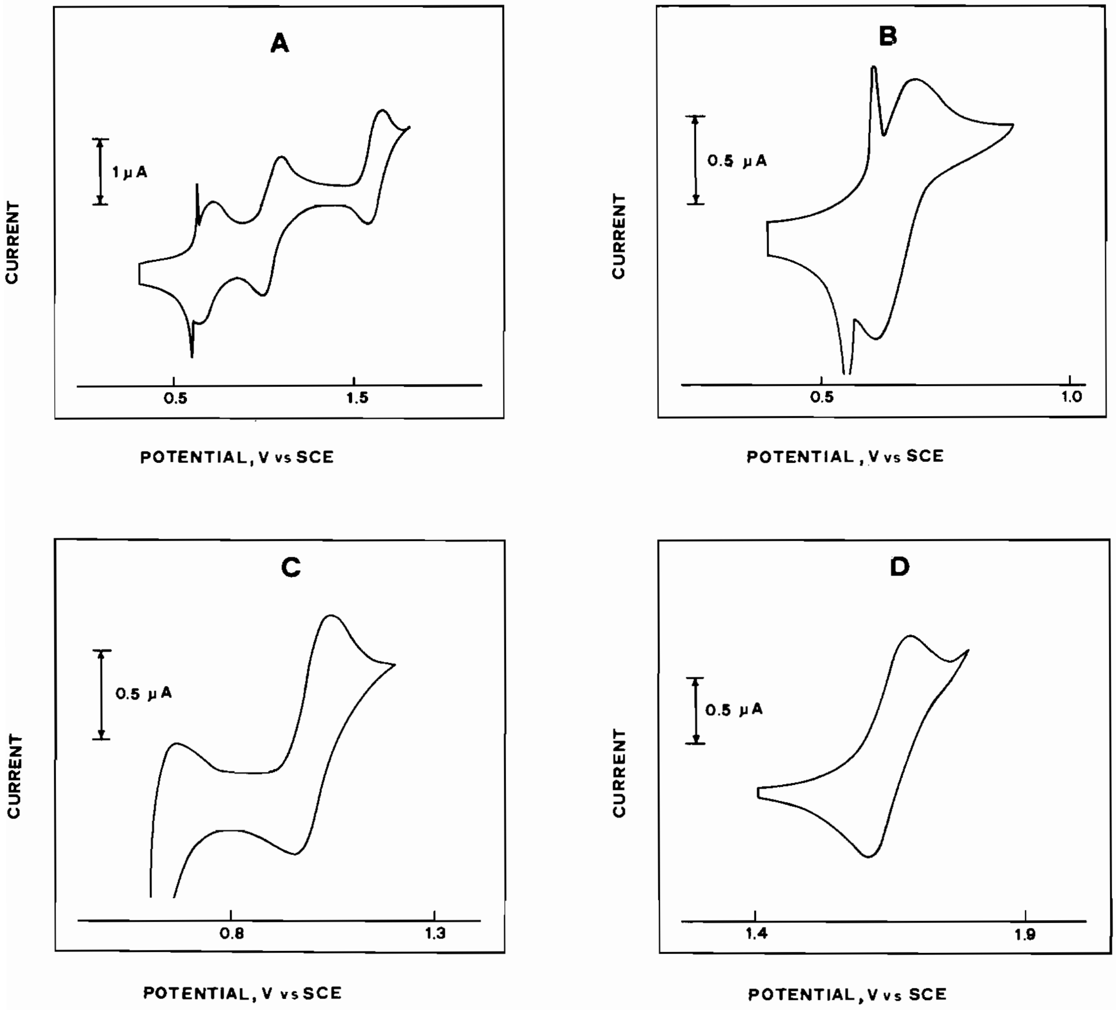

Figure 3. Cyclic voltammograms of 0.5 m*M* $Fe(DQP)_2^{2+}$ reduction processes in acetonitrile solution at the temperature of 25° ± 0.1 °C; A) together at the scan rate of 0.25 V/sec; B) first step alone at the scan rate of 0.25 V/sec; C) second step alone at the scan rate of 0.25 V/sec; D) third step alone at the scan rate of 0.25 V/sec.

peak heights. As can be seen the separation of peaks respected approximately the theoretical value of 57/n mV and the ratios of peak heights were very near to the unity,[23] therefore from cyclic voltammetric data, as well as from polarographic ones, we can assume that the reduction processes undergone by the iron(II) complex are reversible and involve the transfer of one electron for each step. A pre-peak was also observed on the first step, as it is shown in Figure 3 B and it is ascribed to a strong absorption process due to the species $Fe(DQP)_2^+$,[24] a similar phenomenon was observed in cyclic voltammograms of $Fe(terpy)_2^{2+}$ too.[15]

Considering all the experimental results abovementioned, for the first three steps it is possible to write the following reactions:

first step $Fe(DQP)_2^{2+} + e^- \rightleftarrows Fe(DQP)_2^+$
second step $Fe(DQP)_2^+ + e^- \rightleftarrows Fe(DQP)_2$
third step $Fe(DQP)_2 + e^- \rightleftarrows Fe(DQP)_2^-$

the other two steps of iron(II) complex polarograms are to ascribe to the reduction of the ligand. We do not write any reaction for the fourth and fifth step, because the aim of this work is not the study of the organic ligand reduction, hence no quantitative analysis has been carried out in order to elucidate these reduction processes.

On the ground of the above reactions we admit the formation of low valence states of the iron at dme surface, during the reduction. This assumption can be considered reasonable enough, because the analogous

TABLE II. Voltammetric data for the first three reduction steps of 0.5 m*M* $Fe(DQP)_2(ClO_4)_2$ solution with 0.05*M* tetraethyl ammonium perchlorate at the temperature of 25° ± 0.1°C.

	Sweep Rate mV/sec	Epc, V *vs* SCE	Epa, V *vs* SCE	ΔEp, mV	Ipc/Ipa
First Step	250	−0.680	−0.617	63	0.90
	150	−0.680	−0.617	63	0.93
	100	−0.680	−0.617	63	0.93
	60	−0.680	−0.617	63	0.93
	40	−0.680	−0.617	63	0.95
Second Step	250	−1.040	−0.970	70	0.95
	150	−1.040	−0.970	70	0.95
	100	−1.038	−0.972	66	0.98
	60	−1.038	−0.974	64	1.00
	40	−1.038	−0.974	64	1.00
Third Step	250	−1.675	−1.610	65	1.04
	150	−1.675	−1.610	65	1.04
	100	−1.672	−1.610	62	1.06
	60	−1.672	−1.610	62	1.06
	40	−1.672	−1.610	62	1.06

complexes of cobalt(II) and manganese(II) with DQP showed the same voltammetric behaviour, furthermore $Fe(DQP)_2^{2+}$ behaved like $Fe(bipy)_3^{2+}$ and Fe $(phen)_3^{2+}$, because in the reduction processes we found the +1, 0 and −1 states. Previously we said that the complex ions with terpy and DQP have approximately the same distorted octahedral structure,[25–27,31] however we found that the two series of complexes show a different voltammetric behaviour, in that the reduction of a $M(terpy)_2^{n+}$ ion reached only the state with n = 0, while the reduction of a $M(DQP)_2^{n+}$ ion stopped to the state of n = −1. We think that this fact can be explained, considering that DQP has two quinolinic rings bonded to the central pyridine instead of the two terpy pyridinic rings and, hence, the stabilization of the state of −1 is probably due to the ability of electron delocalization increased in the DQP molecule. But this consideration presupposes the participation of the ligand π orbitals in the electron transfer undergone by the complex ion. A part from the conclusions of other workers on this problem, the voltammetric behaviour of transition metal complexes with DQP has a peculiarity that gives us an idea on the location of electronic changes over the metal–ligand system. In fact, if we examine the half-wave potentials of the reduction steps in $Fe(DQP)_2^{2+}$, Co $(DQP)_2^{2+}$ and $Mn(DQP)_2^{2+}$ polarograms reported in Table III, we can see that the first and second steps of all complexes have values quite different (the first much more than the second), whilst the third steps have values the maximum difference of which is 33 mV. Evidently the first and second steps regard an electron transfer that has the metal in the complex ion as the electroactive center, namely the molecular orbitals involved in the reduction process have some metal d character. The third steps regard an electron transfer that occurs in a molecular orbital which is, in large part, made up of ligand π orbitals.

TABLE III. Half-wave potentials of the first three reduction steps from polarograms of $Fe(DQP)_2^{2+}$, $Co(DQP)_2^{2+}$ and $Mn(DQP)_2^{2+}$ in acetonitrile solutions with 0.05*M* tetraethyl ammonium perchlorate as supporting electrolyte.

		I	II	III
$Fe(DQP)_2^{2+}$	$E_{1/2}$, V *vs* SCE	−0.637	−1.025	−1.640
$Co(DQP)_2^{2+}$	$E_{1/2}$, V *vs* SCE[a]	−0.506	−1.305	−1.673
$Mn(DQP)_2^{2+}$	$E_{1/2}$, V *vs* SCE[a]	−0.875	−1.090	−1.650

[a] From reference 19.

These considerations are in agreement with the results of many workers who carried out studies on this field. Bond *et al.*[28,29] studying the polarographic behaviour of octahedral and planar dithioacetylacetone complexes of transition metals, found that these had a capacity to accept one or more electrons in a reversible way, the number of which varying systematically with the d-electron configuration and the structure of the complex ion. Dessy *et al.*,[30] studying the polarographic behaviour and ESR spectra of $FeL_2(NO_2)$, where L_2 is bipy or phen, found the formation of four distinct charge states with formal oxidation of −2, −1, 0 and +1. From their study the electron transfer that brings to the formation of the radical cation regards a molecular orbital having some metal s character, while in the formation of the radical anion and dianion it is evident the strong participation of $L_2\pi^*$ orbitals. Mines and Geiger[31] found that from the reduction of bis (malenonitrile dithiolato)nickel dianion it is possible to obtain the trianion, in the formation of which a primarily metal-based orbital is involved. On the other hand Tanaka *et al.*[32] concluded from ESR evidences that in Fe(bipy)$_3^+$, originated by the reduction in acetonitrile from Fe(bipy)$_3^{2+}$ there is Fe(II) (d^6 spin-paired), with an unpaired electron localized on the ligand orbitals, in Fe(bipy)$_3$ there is iron of d^8 configuration, in Fe(bipy)$_3^-$ it is only possible to deduce the formation of bipyridine or its anion radical formed by the dissociation of the product. These last results are in disagreement with those of Hanazaki and Nagakura,[7] who concluded from theoretical calculations, analysis of ESR and electronic absorption spectra, that excess electrons are localized on the metal for complexes with a large charge and are gradually transferred to the ligand π-electron system as the total charge of the complex decreases. The same conclusions were reached by Sayto *et al.*,[8] examining I.R. frequencies in a series of M(bipy)$_3^{n+}$ complexes with variable oxidation number, and by Konig and Herzog,[4–6] who studied the electronic spectra of the same compounds.

From voltammetric behaviour of (DQP)$_2$ complexes it is possible to draw other conclusions about the formation of low valence states. The first observation that we can do, is that low valence states do not depend from the spin-state, as one can see comparing polarographic behaviour of Fe(terpy)$_2^{2+}$ [15] and Fe(DQP)$_2^{2+}$; in fact the former complex, having a low spin d^6 configuration, reached the state of 0 in the electrochemical reduction, the latter, having a high spin configuration, reached the state of –1. This last state is also obtained in the reduction of Fe(bipy)$_3^{2+}$ [33] and Fe(phen)$_3^{2+}$,[12] where bipy and phen are ligands known to cause the spin pairing. The second observation is that no simple relation exists between the electrochemical formation of low valence states and the thermodynamic stability of metal chelates; in fact Fe(terpy)$_2^{2+}$ has a thermodynamic stability that resembles those of Fe(bipy)$_3^{2+}$ and Fe(phen)$_3^{2+}$,[34] while Fe(DQP)$_2^{2+}$ is a weak complex, because of the enormous steric hindrance of the two terminal quinolinic rings that oppose to the chelation.

In conclusion we can affirm that low valence states depend strickly from the possibility of electron delocalization shown by the ligand and from the structure of the complex ion.

According to the combination of these factors we can obtained in this class of complexes the state of 0 or even the state of –1. Hence, we may assert that low valence states depend strongly on the particular ligand to which the metal ion is bonded, rather than on a given class of ligands.

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