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Complex species in the oxidation of cobalt(II) with sodium peroxide in the presence of quinolinic and lutidinic acids

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Chimica. — *Complex species in the oxidation of cobalt(II) with sodium peroxide in the presence of quinolinic and lutidinic acids* (*).

Nota di Roberto Bedetti, Ugo Biader Ceipidor, Vincenzo Carunchio e Antonella Messina, presentata (**) dal Corrisp. G. Sartori.

RIASSUNTO. — È stato preso in esame il processo di ossidazione del cobalto(II) in soluzione acquosa in presenza degli acidi chinolinico e lutidinico, per ottenere informazioni che permettono di confrontare i dati ottenuti con quelli relativi al sistema cobalto(II)–acido picolinico già studiato, in modo da evidenziare l'influenza dei gruppi carbossilici e della loro posizione sull'anello piridinico.

Sono state trovate specie del tipo ML_2 con entrambi i leganti: i quozienti di concentrazione all'equilibrio a $-5°$ C, pH 2.4 e $\mu = 1{,}2$ M per $NaClO_4$ sono $1{,}6 \cdot 10^6\,M^{-2}$ e $10^7 \div 10^8\,M^{-2}$ e le assorbività molari $85\,M^{-1}\,cm^{-1}$ e $90\,M^{-1}\,cm^{-1}$, rispettivamente nei due casi.

Non sono state individuate specie dinucleari contrariamente a quanto è stato trovato con l'acido picolinico, e di questa differenza viene presentata una interpretazione.

INTRODUCTION

In the oxidation of aqueous solutions of cobalt(II) in the presence of picolinic acid [1] carried out with peroxides, the hypothesis was advanced that the reaction could occur through the formation of dinuclear peroxo-bridged species. The presence of the aza-group in the ligand and the α-position of the carboxylic group make possible a five-membered chelating ring to be formed [2, 3], with a likely stabilization of the above mentioned dinuclear species. When another carboxylic group is located in the eterocyclic ligand molecule, steric and electronic effects are promoted which could influence both the oxidative process of cobalt(II) and the properties of complex species which are formed [4]. In this view, in the present work we have investigated the oxidation reaction of cobalt(II) in the presence of quinolinic (pyridine-2,3-dicarboxylic) and lutidinic (pyridine-2,4-dicarboxylic) acids, hereafter indicated as H_2quin and H_2lut, respectively.

The analysis was performed by visible absorption spectrophotometry as in the previous work [1].

EXPERIMENTAL

Materials and apparatus.

All chemicals were analytical grade products. The quinolinic and lutidinic acids were crystallized from water-ethanol mixtures, purified in the usual

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(*) Coordination in the oxidation of cobalt(II) compounds in aqueous solutions, part III. Previous papers see ref. [1]. This work was presented in part at VI Convegno Nazionale di Chimica Inorganica, 24–29 settembre 1973, Firenze (Italy).

(**) Nella seduta del 23 giugno 1974.

manner and controlled by their melting points and UV absorption spectra. The aqueous solutions of the two above acids were standardized by a potentiometric method. The cobalt(II) perchlorate was dissolved in water and standardized by complexometric titration. Cl^-, CO_3^{2-} and Fe^{3+} were absent in all the solutions. Sodium peroxide contained no stabilizing agent.

Spectrophotometric measurements were performed on DU and DK-2 A Beckmann apparatus equipped with quartz cells with 10.00 and 5.00 cm path length in thermostatic compartment (Ultrathermostat Colora NB/DS 695 and Cryostat Colora TK 64). pH determinations were carried out with a pH-meter Radiometer "pH-M2 2r" using satured calomel and glass electrodes and an external agar-sodium perchlorate bridge.

Operative conditions.

The solutions have been prepared following the same procedure employed for the study of the cobalt-picolinic system [1]. The oxidation process was carried out by a large excess of sodium peroxide, corresponding to about 100 times the stoichiometric amount.

The temperature was always kept constant at $-5 \pm 0.5^\circ$ C; the freezing of the solutions was prevented by a ionic strength buffer ($NaClO_4$ 1.2 M).

We have not used a pH buffer to avoid any side-reactions; the pH values remained constant within 0.05 unit for at least 36 hours in each sample.

Every measurement was performed within 10 minutes after the adding of the oxidant solutions. The spectrum does not change for 36 hours at least, if the solutions under examination stand at -5° C.

RESULTS

Quinolinic acid.

The fig. 1 shows the absorption spectrum in the visible region of solutions containing cobalt(II) and quinolinic acid with initial molar concentration ratio $C_L/C_M = 10$ and oxidized by sodium peroxide at -5°C, then adjusted to pH 2.4.

The spectral behaviour suggested us to choose the 530 nm wavelength to study the system, since it corresponds to the maximum in the visible absorption spectrum for Co(III)—H_2 quin system where pH values lie in the range $1 \div 4$.

At such wavelength the absorption of the ligand (which was controlled not to be altered by oxidizing agent in our experimental conditions by means of the U.V. spectrum), of free metal and of sodium peroxide solutions are negligible.

It is noteworthy that moving to higher pH values the λ_{max} shifts progressively towards 550 nm values probably because of hydrolysis reactions [5]. In fig. 2 the absorbance variations of the solutions containing the metal, ligand and oxidant are reported as a function of pH. The trend of the curve shows no singular point in the pH range $1 \div 4$, so that it was possible to choose pH = = 2.4 for the systematic investigation, in order to compare the results obtained in the present work with those relative to cobalt(III)-picolinic acid system [1].

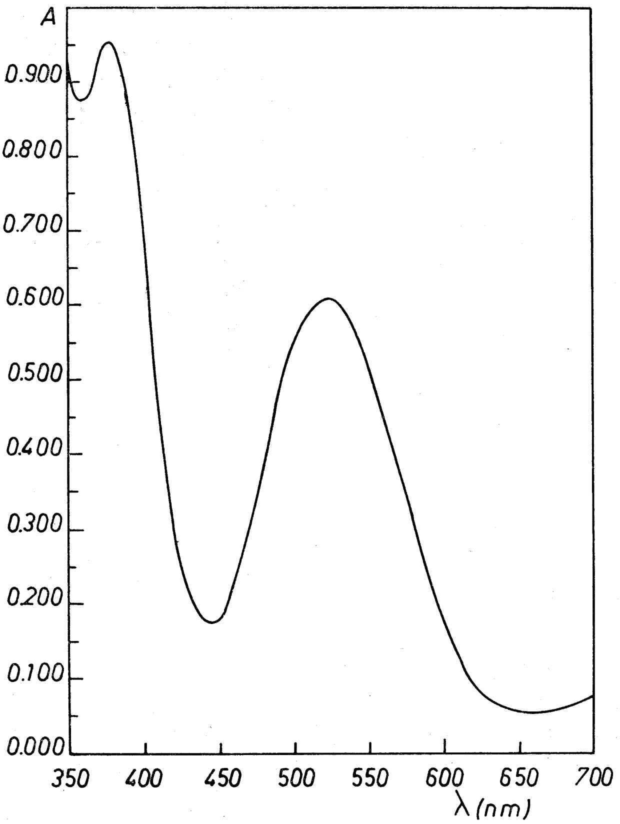


Fig. 1. – Absorption spectrum of the oxidized cobalt-H_2quin system at —5° C, pH = 2.4, μ = = 1.2 M, b = 10.00 cm; cobalt (II) perchlorate = 7.0 · 10^{-4} M; H_2quin = 7.0· 10^{-3} M.

The complexation ratios, the concentrations quotients at equilibrium and the molar absorptivity values of the present species were determined analyzing the spectrophotometric data through the suitable methods. In the applications of the mole ratio [6], the study of the two functions $A = f(C_M)_{C_L, pH}$

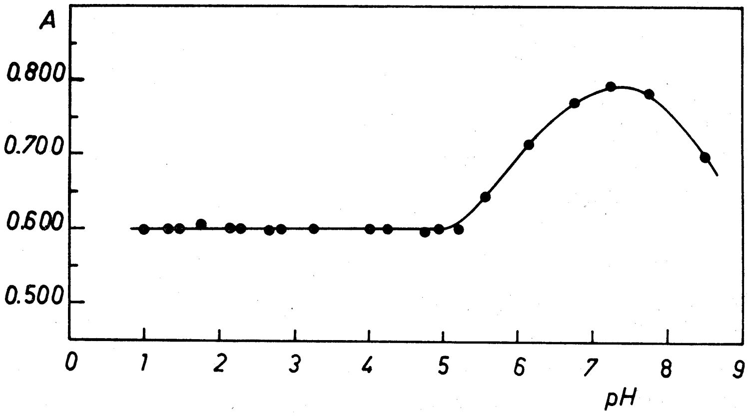


Fig. 2. – Absorbance at 530 nm at different pH values of the oxidized cobalt-H_2quin system at —5° C, μ = 1.2 M, b = 10.00 cm; cobalt(II) perchlorate = 7.0· 10^{-4} M; H_2quin = 7.0· 10^{-3} M.

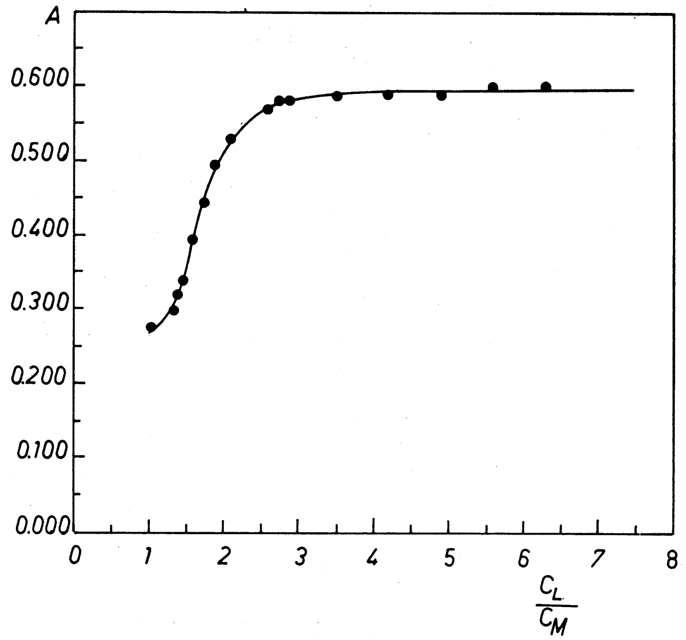


Fig. 3. – Mole Ratio plot with constant metal concentration of the oxidized cobalt–H_2quin system at — 5° C, $\mu = 1.2$ M; $\lambda = 530$ nm, pH = 2.4, $b = 10.00$ cm; cobalt(II) perchlorate: $C_M = 7.0 \cdot 10^{-4}$ M; H_2quin: $C_L = (0.70\text{-}4.4) \cdot 10^{-3}$ M.

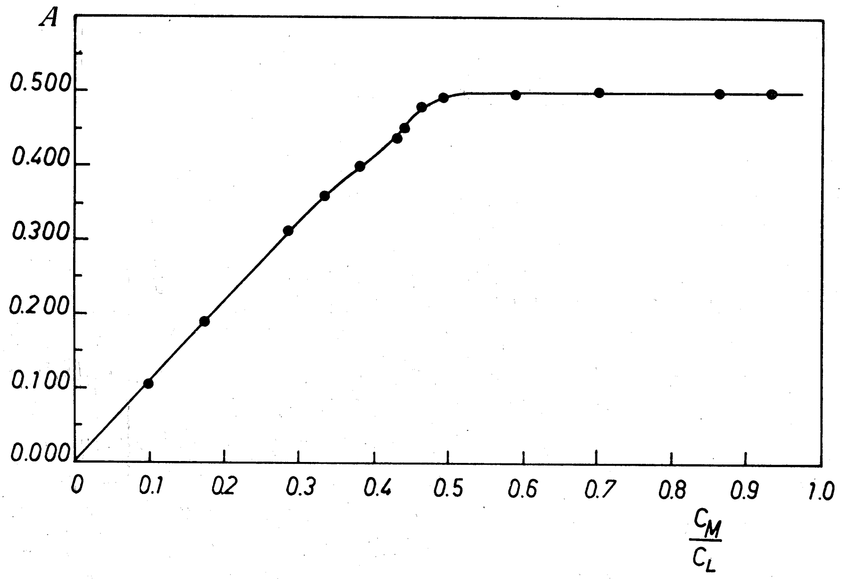


Fig. 4. – Mole Ratio plot with constant ligand concentration of the oxidized cobalt-H_2quin system at —5° C, $\mu = 1.2$ M, $\lambda = 530$ nm, pH = 2.4, $b = 10.00$ cm; cobalt(II) perchlorate: $C_M = -01.1 \cdot 10^{-3}$ M ; H_2quin: $C_L = 1.2 \cdot 10^{-3}$ M.

and $A = f(C_L)_{C_M, pH}$ has suggested the presence of species with complexation ratio $L/M = 2$ in the range $C_L/C_M = 1.5 \div 3.5$ (figs. 3 and 4).

These results were confirmed by the straight-line method [7] and some of the Sommer functions [8] briefly described in the previous work [1], by which it was possible to evaluate the metal and ligand indices. The complex species are of ML_2 type. The concentration quotient at equilibrium is $K = [ML_2]/[M]\,[L]^2 = 1.6 \cdot 10^6\,M^{-2}$ and the molar absorptivity $\varepsilon = 85\,M^{-1}\,cm^{-1}$.

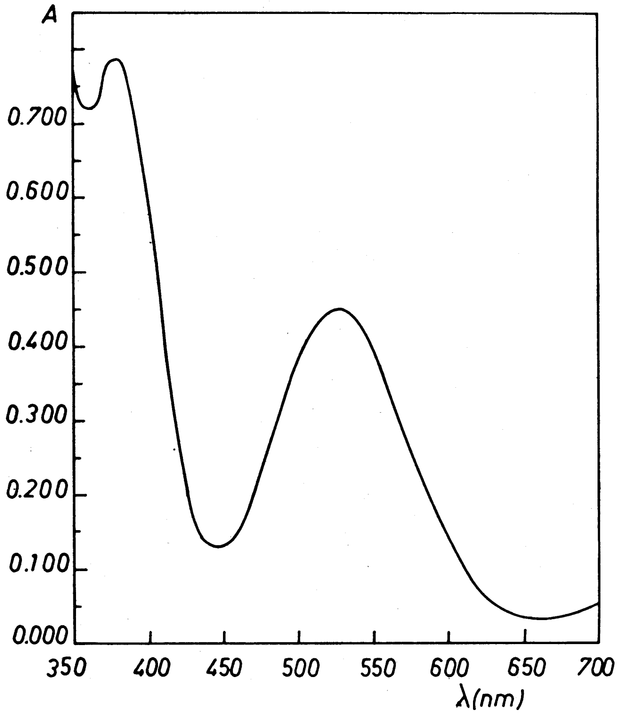


Fig. 5. – Absorption spectrum of the oxidized-H_2lut system at —5° C, pH = 2.4, $\mu = 1.2\,M$, $b = 5.00$ cm; cobalt(II) perchlorate $\leq 1.0 \cdot 10^{-3}$ M; H_2lut = $= 1.0 \cdot 10^{-2}$ M.

Lutidinic acid.

The spectrum at pH = 2.4 of a solution containing cobalt(II) and lutidinic acid with initial molar ratio $C_L/C_M = 10$, oxidized as above stated, is shown in fig. 5. It does not change, at least within 36 hours. The absorbance variation with varying pH at 530 nm is reported in fig. 6. The curve is strictly similar to that one shown in fig. 2. The analysis of the two functions $A = f(C_M)_{C_L, pH}$ and $A = f(C_L)_{C_M, pH}$ performed at pH = 2.4 (figs. 7 and 8) has shown that the complexation ratio of the present species is $L/M = 2$, but it was not possible to obtain information about the metal complexation index. The molar absorptivity was equal to $90\,M^{-1}\,cm^{-1}$, per cobalt atom. This species is characterized by a high value of the concentration quotient at equilibrium, the value of which cannot be directly determined even if it has been possible to estimate it in within the range $10^7 \div 10^8\,M^{-2}$ for the mononuclear species.

These features of the system do not allow the above cited methods [7, 8] to be satisfactorily employed, considering that the results do not change also with reducing to one half the metal concentration of the solutions. Further dilution is not possible because the absorbance becomes too small to be detected.

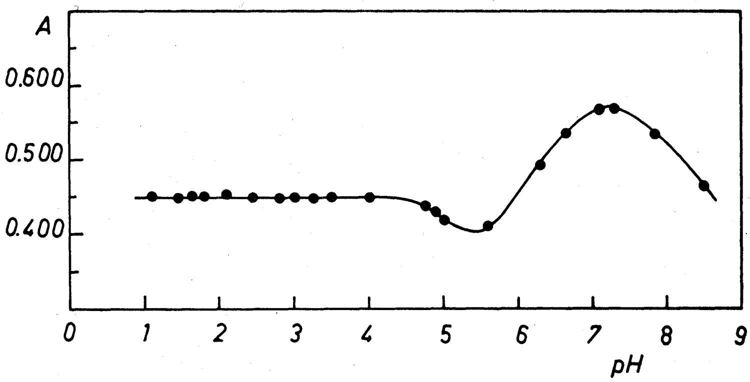


Fig. 6. – Absorbance at 530 nm at different pH values of the oxidized cobalt-H_2lut system at $-5°$ C, $\mu = 1.2$ M, $b = 5.00$ cm; cobalt(II) perchlorate $= 1.0 \cdot 10^{-3}$ M; H_2lut $= 1.0 \cdot 10^{-2}$ M.

On the other hand, when considerably increasing the temperature up to 60° C, we have found a well defined mononuclear ML_2 species with $K = 8.3 \ 10^5 M^{-2}$ and $\varepsilon = 90 M^{-1} cm^{-1}$.

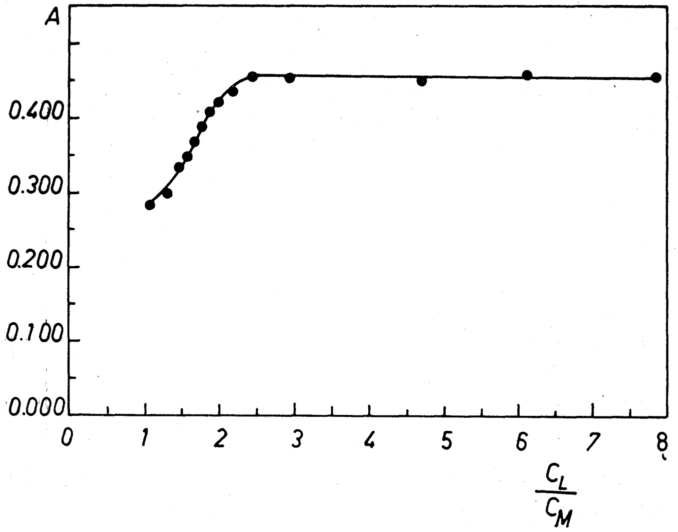


Fig. 7. – Mole Ratio plot with constant metal concentration of the oxidized cobalt-H_2lut system at $-5°$ C, $\mu = 1.2$ M, $\lambda = 530$ nm, pH $= 2.4$, $b = 5.00$ cm; cobalt(II) perchlorate: $C_M = 1.0 \cdot 10^{-3}$ M; H_2lut: $C_L = (1.1\text{-}7.9) \cdot 10^{-3}$ M.

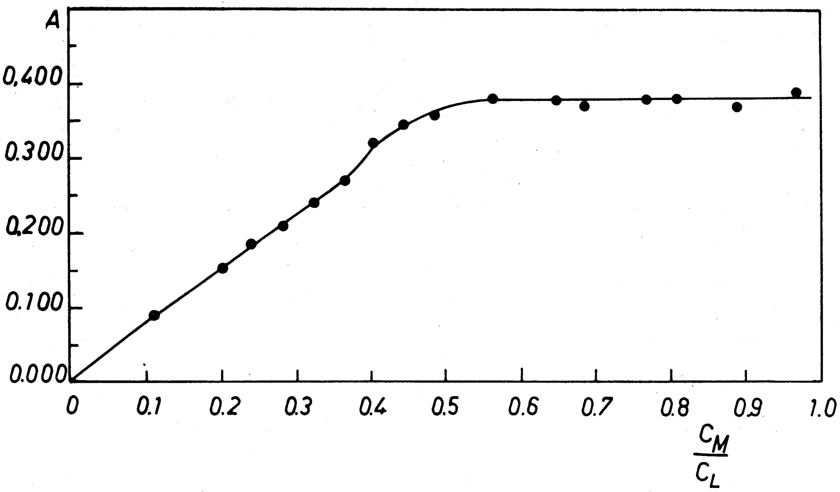


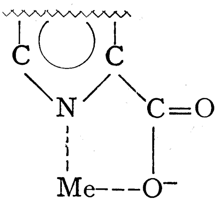
Fig. 8. – Mole Ratio plot with constant ligand concentration of the ozidized cobalt-H_2lut system at —5° C, $\mu = 1.2$ M, $\lambda = 530$ nm, pH = 2.4, $b = 5.00$ cm; cobalt(II) perchlorate: $C_M = 0\text{–}1.7 \cdot 10^{-3}$ M; H_2lut: $C_L = 1.8 \cdot 10^{-3}$ M.

DISCUSSION

The data relative to the two examined systems are very similar to each other, while they considerably differ with respect to those obtained for cobalt-picolinic acid (Hpic), as to concern some particular aspects. It is meaningful to compare A-pH functions of the systems particularly in the pH range $1 \div 4$. The absorbance values show a non-monotonic trend in the cobalt-Hpic system, while they describe a plateau in cobalt-H_2quin and cobalt-H_2lut ones.

Dinuclear species may account for an explanation of the results obtained in the previous system [1]. Mononuclear species only have been found in the cobalt-H_2 quin system in the same experimental conditions so we may consider a tentative attribution of the non-monotonic trend in the A-pH function to protolitic equilibria of a bridging group [5]. Thus the species detected in the cobalt-H_2lut system (where it was not possible to obtain direct information about the ligand and metal indexes owing to the high strength of the complexes) may be assumed to be mononuclear since the A-pH curve is strictly similar to that of cobalt-H_2quin system and so different with respect to that of cobalt-Hpic. Further results relative to other similar ligands, actually under investigation in our laboratory, seem to confirm the previous assumptions. Of course other possibilities and interpretation cannot be excluded especially if considering the differences among the ligand agents, monocarboxylic and dicarboxylic acids, respectively.

As to concern the molecular arrangement of the evidenced species in the three systems under consideration, it is reasonable to suppose that the formation of a five-membered chelating ring occurs, where the cobalt is bound directly to a nitrogen donor atom and to the α-carboxylic group.



The spectral behaviour too (λ_{max} is the same for each system) seems to confirm the above statement.

The formation of the complex species Co(III)-H_2 quin and Co(III)-H_2lut probably occurs through the same mechanism invoked in most oxidation processes performed by peroxides [9], that may take place in three steps i) cobalt(II) complex, ii) cobalt(III) binuclear complex, iii)* cobalt(III) mononuclear complex.

In our systems it was not possible to evidence the formation of binuclear compounds, probably owing ot the high rate of the reaction ii) → iii).

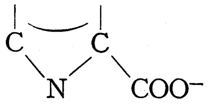
Our results may be explained when considering the different structures for H_2quin and H_2lut. In a way similar to that proposed by Taube [10] the attack of cobalt(II) in the former case could occur on the more acidic carboxylic group in the molecule (that in 3-position) and induces the activation of the side carboxylic group by electronic effect. The consequent cleavage of intramolecular hydrogen bond between nitrogen and carboxylic group in 2-position makes now the latter available to form a chelate with the two carboxylic groups and the cobalt. With the addition of sodium peroxide solution, the oxidation may occur with the formation of dinuclear peroxo-complexes. With the above mentioned ring the stabilizing power of the azagroup is lacking, so the peroxo bridge breaks fast and mononuclear species are formed.

A structural rearrangement may take place to get the formation of the five membered ring containing nitrogen atom. The fact that absorption maximum of cobalt-quinolinic acid complex does not differ from that of lutidinic and picolinic complexes may account for that hypotesis.

When considering the lutidinic acid, the attack of cobalt(II) would be directed to the most acidic carboxylic group (in 4-position) and may induce the activation of the azagroup of the pyridine ring which can bind another metal atom.

The oxidation could occur on such cobalt atom with the formation of dinuclear species. The electronic effect of the carboxylic group in 4-position on nitrogen would cause the strength of the N—Co bound to be decreased. In such a condition the dinuclear compound is destabilized too and rapidly transforms into the mononuclear species.

When comparing the K values for the 2/1 complexes with the two acids under investigation in this work, we may observe that the complex between cobalt and H_2quin results less stable than that between cobalt and H_2lut, in the above assumption that also the species found in the latter system is mononuclear. This fact may be tentatively explained by taking into account that the Lewis donor strength of the



group in the pyridine ring, which is decreased for the presence of another carboxylic group by a conjugation effect. In the case of H_2quin an inductive effect is also operating. The same K order for the two systems has been also observed with chromium(III) [11].

On the other hand it cannot be excluded that in the cobalt-H_2quin complex, the metal atom is bound to two oxygen atoms, while in the previous suggestion the linkages occur on one oxygen and one nitrogen atom, which contributes to stabilize the system. This conclusion, however, seems to be scarcely probable if considering the spectra which show in each system the same maximum at 530 nm.

Species with complexation ratio L/M = 1 are probably present too in the system, as it may be noted considering that the spectra show some weak inflections (figs. 3, 4, 7 and 8). It was not possible to ascertain their presence be using the methods stated above and the aims of the present work do not justify more complicated calculations to obtain further information about these species especially if considering the relevant overlapping with the 2 : 1 species.

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