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A New Series of Organochromium Complexes Formed in Aqueous Solutions

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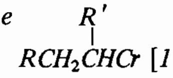
Chromous ion reacts with 3-pyridineacrylic acid, 4-pyridineacrylic acid, maleic acid and fumaric acid to give remarkably inert organochromium(III) species. These species were isolated by ion exchange from acidic aqueous media and were characterized by a variety of techniques. An organochromium(III) compound was even isolated from the Cr(III)–3-pyridineacrylic acid aqueous mixture in solid form. In all the organometallic compounds reported in this paper chromium(III) is believed to be σ-bonded to carbon by the general scheme

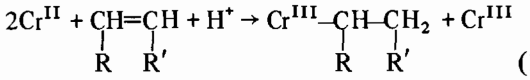


$RCH_2\overset{R'}{C}HCr$ [*1*].

Introduction

Organochromium compounds with σ carbon to metal bond can generally be prepared [2] from other organometallic compounds by replacement of the metal by Cr(III) or by addition to Cr(II) of an organic free radical. In aqueous media, all σ-bonded organochromium compounds reported in the literature [3] were prepared by free radical addition to Cr(II), but the method for generating these free radicals generally varied.

In this paper we report on the preparation, separation and characterization of some new organochromium species, differing from those known until now both in the method of preparation and in lability. The method of preparation involves what can be considered as a two-step oxidative addition to Cr(II), of an olefinic double bond, according to the overall reaction:



$$2Cr^{II} + \underset{R}{CH}=\underset{R'}{CH} + H^+ \rightarrow Cr^{III}-\underset{R}{CH}-\underset{R'}{CH_2} + Cr^{III} \qquad (1)$$

The species obtained by this reaction are remarkably inert towards aquation. In acid aqueous solution they last for days, even for months. In fact we were able in one case to obtain in the solid form a species retaining the Cr–C σ-bond – the first species of this kind obtained from a strongly complexing solvent such as water.

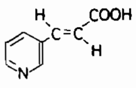
The findings of this paper have also mechanistic implications for electron transfer reactions between metal ions, mediated by unsaturated ligands, since they imply that this transfer may proceed through formation of transient organochromium species.

Experimental

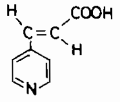
Materials and Composition of Reaction Mixtures

The reagents used were of analytical grade. Chromous perchlorate solutions were prepared electrolytically on a mercury pool cathode. Reaction mixtures containing Cr(II) were prepared and kept under an argon atmosphere.

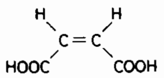
The unsaturated organic compounds investigated are (in parenthesis the abbreviations):



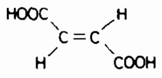
1. 3-pyridineacrylic acid (3-PA)



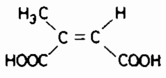
2. 4-pyridine-acrylic acid (4-PA)



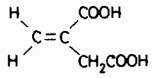
3. maleic acid (MA)



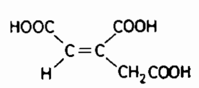
4. fumaric acid (FA)



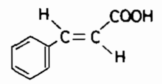
5. citraconic acid (CA)



6. itaconic acid (IA)



7. aconitic acid (AA)



8. cinnamic acid (CNA)

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*Author to whom correspondence should be addressed.

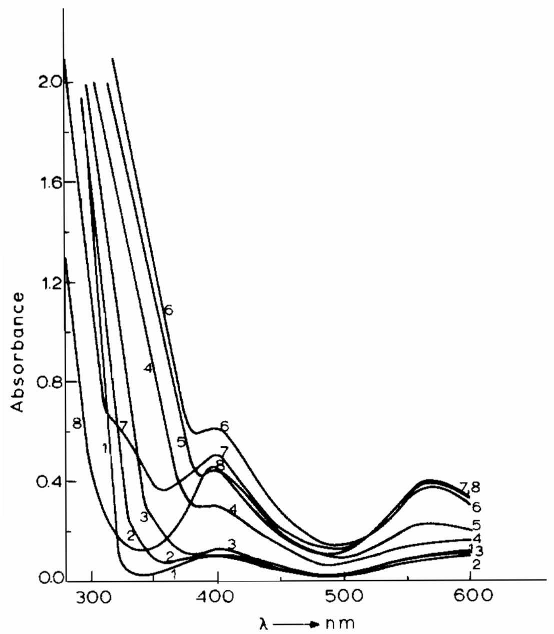


Fig. 1. Spectra of a typical 3-PA–Cr^{II} mixture at various times after mixing; $[3\text{-PA}]_0 = 4.29 \times 10^{-4}$ *M*, $[Cr^{2+}]_0 = 2.1 \times 10^{-2}$ *M*, $[HClO_4]_0 = 1$ *M*, 1 cm cell, 23 °C. (1) 23 min, (2) 57 hr, (3) 7 d, (4) 48 d, (5) 127 d, (6) 195 d, (7) 212 d, (8) 233 d.

The organochromium species are generally formed in strongly acidic solutions. At very low acidities ($[H^+] < 0.05$ *M*) and low concentrations of the organic reagent organochromium species are not formed in detectable amounts.

All organochromium compounds reported in this paper were red.

Ion Exchange Separation

Ion exchange separations were done at various times after mixing, using a Dowex 50WX2 resin, deaerated if necessary. Solutions of $HClO_4$ and $NaClO_4$ at various molarities were used for elution.

Analysis and Spectra

Chromium was determined using a Perkin Elmer Model 303 Atomic Absorption Spectrophotometer. A Cary 14 was used for the electronic spectra and a Perkin Elmer 521 for ir (KBr pellets). Elemental analysis was done either after precipitation or after eluting with hydrochloric acid and evaporating to dryness. Polarographic studies were conducted on a Metrohm AG Herisau rapid polarograph.

Magnetic Measurements

Paramagnetic susceptibilities were measured in aqueous solutions by nmr [4].

Precipitation of the Chromium–3-Pyridineacrylic Acid and Chromium–4-Pyridineacrylic Acid Species

Red precipitates are obtained from the red solutions containing the organochromium complexes of 3-PA (*1*) and 4-PA (*2*) by alternate additions of small portions of n-butanol and 0.2 N NaOH up to pH 4. The precipitate can be redissolved by adding 1 *M* $HClO_4$ and heating mildly (35 °C), the resulting solution however is not identical to the original red one. Instead of n-butanol one can also use dioxane, but the products obtained then seem to have impurities.

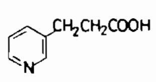
The solid compounds are filtered, washed with water, ethanol, and ether, and dried *in vacuum* at room temperature. They are highly hygroscopic and considerably more unstable than the corresponding solutions. In fact, the solid compound from 4-pyridineacrylic acid decomposes rapidly and could not be studied further. The compound from 3-pyridineacrylic acid lasts for several hours.

Organic Products

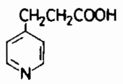
The final organic products in the reaction of Cr^{2+} (aq) with maleic (*3*) or fumaric acid (*4*) is succinic acid (*9*) [5] and with 3- and 4-pyridineacrylic acids (*1, 2*) the corresponding pyridinepropionic acids (*10, 11*), which were identified by nmr. Isomerization of maleic acid to fumaric is not observed.

$HOOCCH_2CH_2COOH$

9. succinic acid
(SA)



10. 3-pyridine-
propionic acid
(3-PPA)



11. 4-pyridine-
propionic acid
(4-PPA)

The overall stoichiometry is two chromous ions for each organic molecule reduced. Solutions of the organic products can be obtained by ion exchange separation directly from reaction mixtures at long times. They can also be obtained by refluxing the reaction mixtures with sodium pyrophosphate. Chromium is then removed by precipitation with sodium hydroxide and the organic products precipitated with acetone.

Results

3- and 4-Pyridineacrylic Acids

Figs. 1 and 2 illustrate the changes the UV–vis spectrum of 3-PA-Cr^{II} and 4-PA-Cr^{II} mixtures, respectively, undergo during the course of the reaction. It is seen from these figures that the absorbance in the UV region reaches maximum values and then decreases again. These maxima correspond to apparent absorptivities more than two orders of magnitude higher compared to the absorptivities of ordinary chromium (III) complexes (*e.g.* for Cr^{3+}(aq) $\epsilon_{408} = 15.6$ and $\epsilon_{574} = 13.4$ M^{-1} cm^{-1} [6]). Gener-

TABLE I. λ_{max} and ϵ_{max} of the Red Bands.[a]

	λ_{max}[b]	ϵ_{max}[b]	λ_{max}	ϵ_{max}	λ_{max}	ϵ_{max}
Excess organic acid[c]	512.5	62.04	400	386.9	287.5	5334.6
Excess chromous ion[d]	518.5	33.3	400	163.4	287.5	2258.6

[a] Eluted with 3 *M* $HClO_4$ (excess organic acid) and 2 *M* $HClO_4$ (excess chromous). [b] λ in nm, ϵ_{max} in M^{-1} cm^{-1}. Average absorptivities of the band. [c] $[3\text{-PA}]_o = 4.5 \times 10^{-2}$ *M*, $[Cr^{2+}]_o = 4.8 \times 10^{-3}$ *M*. [d] $[3\text{-Pa}]_o = 6.7 \times 10^{-2}$ *M*, $[Cr^{2+}]_o$ = 0.212 *M*.

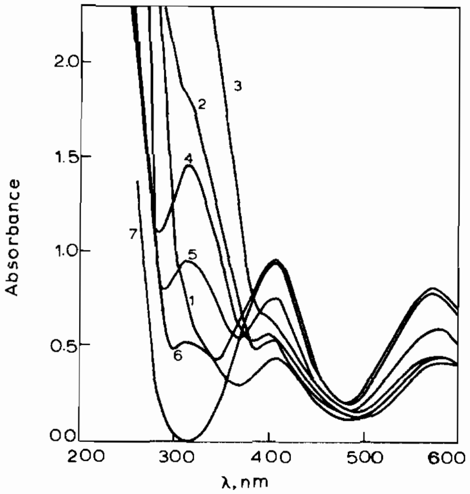


Fig. 2. Spectra of a typical 4-PA–Cr^{II} mixture at various times after mixing; $[4\text{-PA}]_o = 7.63 \times 10^{-5}$ *M*, $[Cr^{2+}]_o = 7.3 \times 10^{-3}$ *M*, $[HClO_4]_o$ = 1 *M*, 5 cm cell, 23 °C. (1) 2 min, (2) 53 min, (3) 89 hr, (4) 47 d, (5) 97 d, (6) 166 d, (7) 256 d.

ally speaking the increase in absorbance reflects an increase in the concentration of the organochromium species and the subsequent decrease results from their transformation into ordinary Cr(III) complexes. The continuing increase in absorbance around 550 nm at very long times can be attributed to the slow oxidation of the excess chromous by perchloric acid.

In mixtures of 3-PA and Cr(II) the results of the ion exchange separation depend on whether the organic acid or chromous ion is in excess. Thus, in excess organic acid and at the initial stages of the reaction only two colored bands appear on the resin, one red eluted with 3 *M* $HClO_4$ and one dark green, which could not be moved even with 6 *M* $HClO_4$. In more advanced stages a third (blue) band appears, eluted with 2 *M* $HClO_4$. The first species to come out (with 1 *M* $HClO_4$) are the colorless organic product and unreacted 3-PA.

In excess of chromous ion the situation is similar, except that the red band can be eluted with 2 *M* $HClO_4$, namely somewhat easier. In addition the spec-

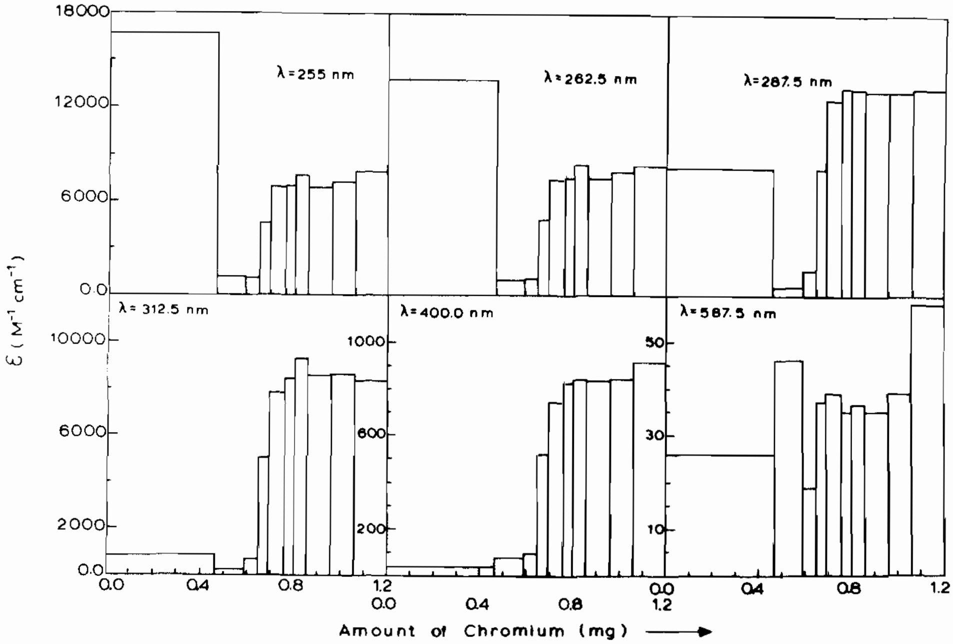


Fig. 3. Histograms of the fractional collection of the 'red band' in the 3-PA–Cr^{II} system when 3-PA is in excess. Each column represents a fraction. $[3\text{-PA}]_o = 5.7 \times 10^{-2}$ *M*, $[Cr^{2+}]_o = 2.96 \times 10^{-2}$ *M*, $[HClO_4]_o \approx 1$ *M*. Elution with 3 *M* $HClO_4$. Reaction time 25 hr.

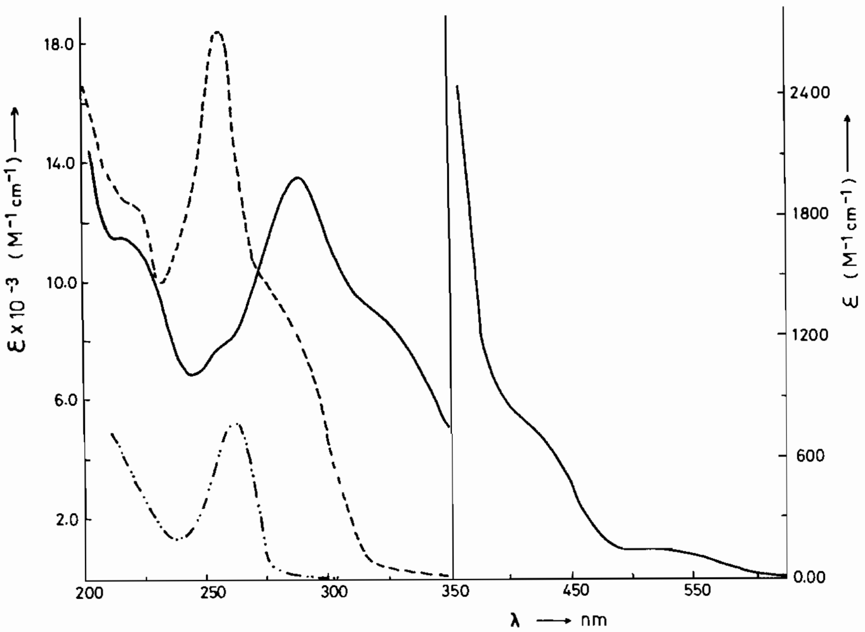


Fig. 4. Spectrum of the pure component obtained in excess 3-PA(–). Conditions similar to those of Fig. 3. Included are the spectra of 3-PA in 1 *M* $HClO_4$ (– – –) and of 3-PPA in 2 *M* $HClO_4$ (– · – · –).

tra of the isolated red bands in excess chromous and in excess 3-PA differ significantly in absorptivities (Table I).

The behavior of 4-PA is similar except that the red complexes are more reactive. Thus, in the absence of air the complexes obtained from 3-PA last in solution (in excess of Cr(II)) for several mounths. The corresponding species obtained from 4-PA decompose within days. In both cases oxygen has a profound effect in accelerating aquation. The red complexes also react with $HgCl_2$ and I_2, but not with Fe^{3+}.

In order to elucidate the differences in elution behavior and in the spectra of the red bands (Table I) we repeated the experiments, but this time collecting what appeared like a single band fractionally. The results in excess 3-PA are summarized in the histograms of Fig. 3. This form of graphical presentation conveys important information in compact form. Thus, it is seen that the apparently single red band is clearly separated into two bands and that chromium is equally distributed among them. At 312.5 and 400 nm the separation is indicated by the sudden increase in absorptivity, at 255, 262.5, 287.5, and 587.5 nm by a minimum. The fractions in between contain the tails of these two bands and their absorptivities have intermediate values. It should also be noted that both bands have peaks (or shoulders) at 255 and 287.5 nm and around 580 nm, but only the second one has shoulder at 312.5 nm. The increased absorptivity of the second band at 400 nm is due to the peak at 312.5 nm, the tail of which extends into the visible. Finally, the fact that the spectra of the various fractions within each band are within experimental error identical (Fig. 4), strongly suggests that they contain only one component each.

Included in Fig. 4 are also the spectra of 3-PA and 3-PPA. In solvents of smaller polarity the absorptivities of these molecules increase and all maxima shift to longer wavelengths. The results with excess Cr(II) are summarized in the histograms of Fig. 5. Chromium in this case is not distributed equally among two bands. The first fractions (roughly up to half the total amount) differ from the corresponding fractions of Fig. 3 in that they do not seem to contain any organic ligand. The fractions in the second half of the histogram do not all have the same absorptivities. The spectrum of the fraction with maximum absorptivity in the uv (around 6 on the horizontal axis) is identical to that of Fig. 4, but the subsequent fractions contain another chromium (III) species having much smaller absorptivities.

The red complexes from 3-PA and 4-PA give polarographic waves with $E_{1/2}$ = –0.84 and –0.80 V, respectively (standard calomel electrode), as expected for Cr(III) species.

The Red Compound Obtained in Solid Form

In Fig. 6 we reproduce part of the ir spectrum of 3-PA, and the corresponding part of the spectrum of its red compound with chromium. The salient features of their spectra do not depend on whether

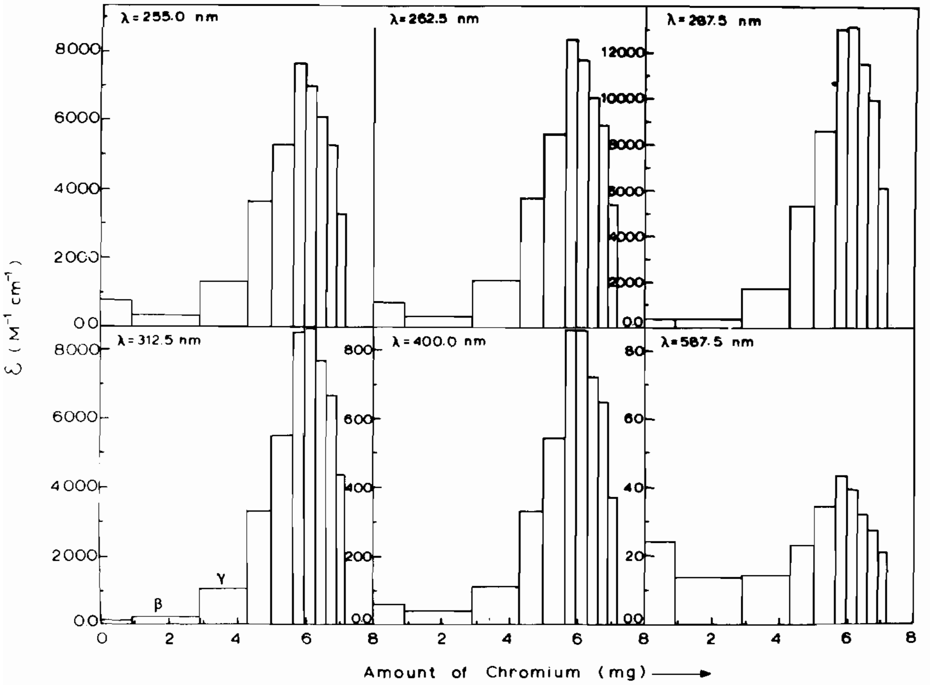


Fig. 5. Histogram of the fractional collection of the 'red band' in the 3-PA–Cr^{II} system when chromous ion is in excess. Each column represents a fraction. $[3\text{-PA}]_0 = 1.66 \times 10^{-2}$ *M*, $[Cr^{2+}]_0 = 0.375$ *M*, $[HClO_4]_0 = 1$ *M*. Elution with 2 *M* $HClO_4$. Reaction time 66 hr.

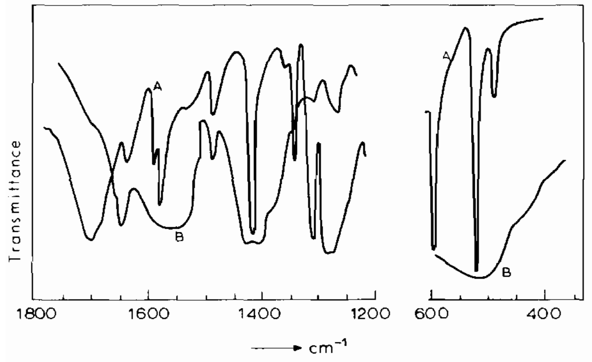


Fig. 6. IR spectra (in KBr) in the 1800–1200 cm^{-1} and 600–400 cm^{-1} regions. A) 3-pyridineacrylic acid. B) Red solid obtained by precipitation with n-butanol from 3-PA–Cr^{II} reaction mixtures.

the precipitate was obtained from solutions containing 3-PA in excess or from solutions containing Cr(II) in excess.

The carbonyl band of the ligand at 1700 cm^{-1} does not appear in its chromium compound, strongly suggesting presence in this compound of carboxylate ion rather than of the undissociated carboxyl group. The carboxyl ion absorption is presumably merged into the broad band between 1580 and 1530 cm^{-1}. It seems, therefore, that in the process of precipitation the protons of the ligands are removed. In fact, the elemental analysis indicates that most of the protons of the coordinated water have been removed. With large excess of Cr(II) in the initial reaction mixture the chromium to the organic ligand ratio in the precipitate is 1:1. Hydrogen, however, barely exceeds that corresponding to the organic ligand. It seems that precipitation involves extensive hydrolysis and condensation and this is probably the reason of the insolubility of the precipitate in water and other solvents and of the irreversibility of their formation. It is, therefore, remarkable that the precipitate retains the red color. The quite drastic chemical change which took place did not significantly affect the ligand field around chromium. It is particularly remarkable that this field does not seem to be affected drastically, in spite of the fact that the undissociated carboxyl group favored in the strongly acidic solutions was transformed into its anion.

The ir region between 600 and 400 cm^{-1} is also included in Fig. 6, because this is where the chromium–carbon bond is expected to absorb (around 450 cm^{-1}). The broadness of the peak in this region does not allow a definite statement to be made, but it is certainly consistent with the presence of such a bond in the isolated complex.

Maleic and Fumaric Acids

It is known that the reduction of maleic acid and related compounds by aqueous chromous ion

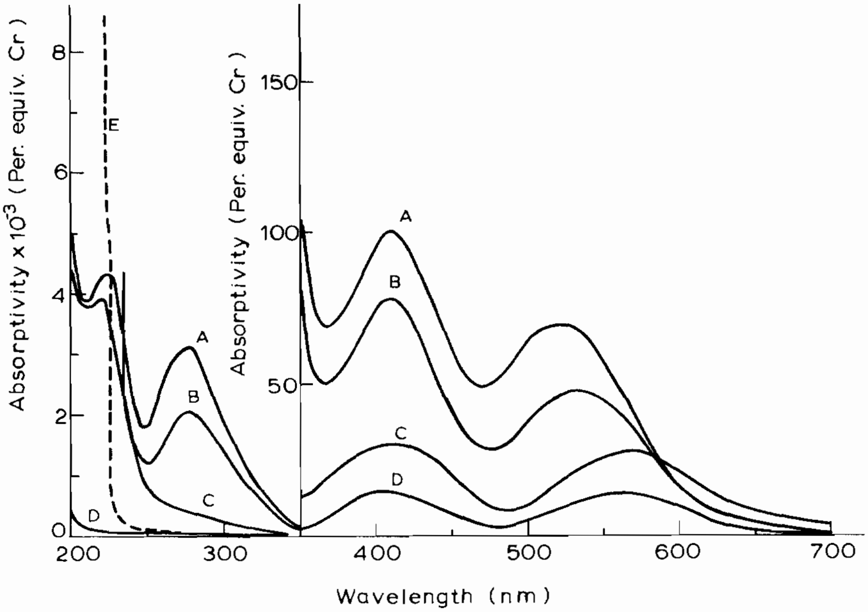


Fig. 7. UV–vis spectra of the red complexes obtained by ion exchange from reaction mixtures containing chromous ion and excess maleic acid. A) Red complex of lower charge. B) Red complex of higher charge. C) Blue complex of lower charge. D) Cr^{3+} (aq). E) (dotted line) maleic acid. Perchloric acid concentrations for spectra A and B: 0.11 *M*, 1 *M*, and 2 *M*. Within this acid concentration range the spectra do not change. Spectra C, D, and E were obtained in 1 *M* $HClO_4$.

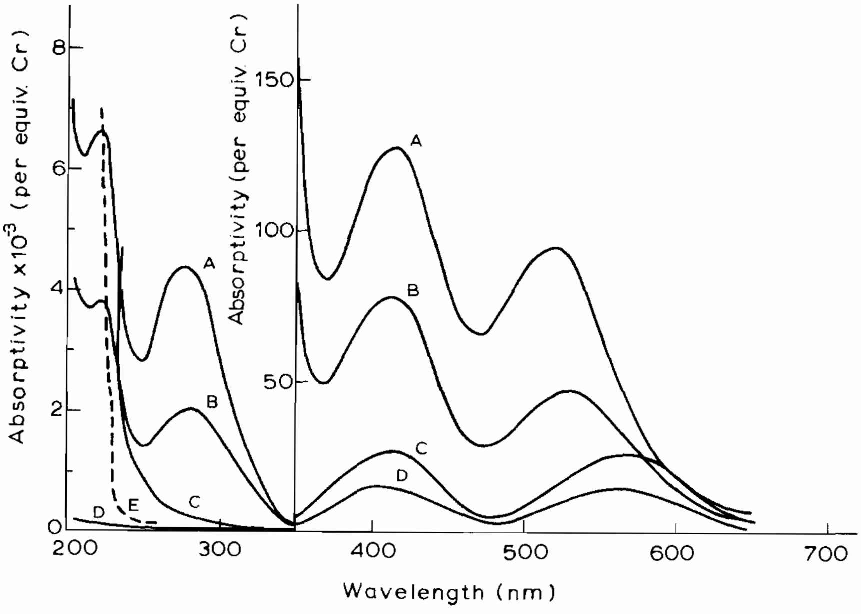


Fig. 8. UV–vis spectra of the red complexes obtained by ion exchange from reaction mixtures containing chromous ion and excess fumaric acid. A) Red complex of lower charge. B) Red complex of higher charge. C) Blue complex of lower charge. D) Cr^{3+} (aq). E) (dotted line) fumaric acid. Perchloric acid concentrations as in Fig. 7.

proceeds through formation of an intermediate red complex [5] (or complexes), but no attempt had been made to characterize it (them). Castro, Stephens and Mojé [7] assumed that the intermediate in the reduction is a chelate, in which chromium is attached to the oxygens of the two carboxyl groups forming a seven-membered ring. This assumption was later accepted by Ševčík and Treindl [8], but again direct supporting evidence was not given.

TABLE II. Chromium Distribution among Various Bands in the Ion Exchange Separation of MA–Cr(II) Reaction Mixtures.[a]

Fraction[b]	mg of Cr immediately after mixing	mg of Cr 75 min after mixing
Low charge red	1.7	3.2
Low charge blue	3.7	4.7
High charge red	5.6	5.0

[a] $[MA]_0 = 0.5$ *M*, $[Cr^{2+}]_0 = 0.16$ *M*, $[HClO_4]_0 = 0.5$ *M*. Elution with 2 *M* $HClO_4$. Total amount of chromium 16.3 mg. [b] There is another blue band of low chromium content and a band of brown-reddish color, which remains at the top of the column and cannot be eluted. The fact, however, that the total amount of chromium in the second column of the Table is larger than the total amount in the first, indicates that the highly charged species decompose as the reaction proceeds.

In the case of maleic and fumaric acids complexation through the carboxyl group will decrease the charge by one unit, whereas a similar complexation of 3-PA and 4-PA may not change the overall charge, because of the strong protonation of the pyridine nitrogen. If then different species are formed involving such complexation, in the case of maleic and fumaric acids they are expected to be resolvable on the ion exchange column.

From reaction mixtures containing Cr(II) and MA or FA at a 2:1 ratio, two distinct bands were separated. The lower was blue, the upper red. They were eluted with 1 *M* $HClO_4$ and 1 *M* $HClO_4$ + 1 *M* $NaClO_4$, respectively, and they contained *ca.* 80% of total chromium. The remaining chromium stayed at the top of the column, in the form of highly charged species. The spectra of the red complexes are given in Figs. 7B and 8B, for MA and FA, respectively.

When maleic or fumaric acids are in excess, a second red species is formed in each case in addition to the previously mentioned. This species has lower charge and is eluted with 0.5 *M* $HClO_4$. The corresponding spectra are included in Figs. 7 and 8 (curves A).

Elemental analysis of the complexes obtained from reaction mixtures containing excess maleic acid gives for the lower charge red complex, the ratio Cr:MA = 1:1 and for the other the ratio Cr:MA = 2:1. The values of maximum absorptivities are $\epsilon_{278} = 3071$, $\epsilon_{410} = 99$, $\epsilon_{520} = 69.5$ M^{-1} cm^{-1} for the low charge complex, and $\epsilon_{278} = 2040$, $\epsilon_{410} = 78$, $\epsilon_{520} = 47$ M^{-1} cm^{-1} for the other. Elemental analysis of the lower charge blue complex gives Cr:MA = 1:1 and values of maximum absorptivities $\epsilon_{410} = 29.5$, $\epsilon_{570} = 27.8$ M^{-1} cm^{-1}.

The spectrum of the lower charge red complex from fumaric acid is distinctly different from the spectrum of the corresponding complex of maleic. Maximum absorptivities have values $\epsilon_{278} = 4431$, $\epsilon_{410} = 120$, and $\epsilon_{520} = 95$ M^{-1} cm^{-1}. The spectrum, however, of the higher charge red complex obtained from fumaric acid is identical to that obtained from maleic acid (curves B in Figs. 7 and 8). The spectrum of the lower charge blue complex from fumaric acid differs very little from that of maleic acid. All the above extinction coefficients were calculated per equivalent chromium.

Illustrative data on the chromium content of the various fractions (maleic acid in excess) are given in Table II. These data are useful in choosing the conditions for obtaining higher yields, but are also helpful in establishing the time sequence of their formation. The light brown residue which is mentioned in this Table is obviously a highly charged species, but it is not identical to the green dimer or polymers obtained by boiling aqueous Cr(III) solutions [6].

Attempts to isolate the complexes with maleic and fumaric in the solid form either by using different organic solvents, or by precipitating them with a bulky anion failed. Increasing the pH above 2 caused immediate hydrolysis.

After ion exchange separation the solutions of the red complexes were subjected to a series of reactions in order to see whether they have the chemical properties of organochromium compounds. It was thus found that they are readily destroyed by $HgCl_2$ and I_2. In contrast, however, to the corresponding species from 3-PA and 4-PA, they are inert towards oxygen and excess chromous accelerates their decomposition. The relation between the two red complexes obtained from maleic acid and their lability was also explored chemically by simply adding more maleic acid to a solution containing the red complex of higher charge only. This complex is then partially transformed into that of the lower charge. The time scale of this transformation is of the order of a few hours, indicating lability intermediate to that of the ordinary Cr(III) and Cr(II) species. Nevertheless, chromium in the red complexes is surely in oxidation state III. This is clearly indicated by their spectra, but also by their polarographic behavior [8], and by their magnetic moments:

Complex	μ_{eff} (BM)
Low charge red	3.98
High charge red	3.76
Low charge blue	3.72
High charge blue	3.63

In order to compare the complexes formed in the chromous–maleic acid and in the chromous–fumaric

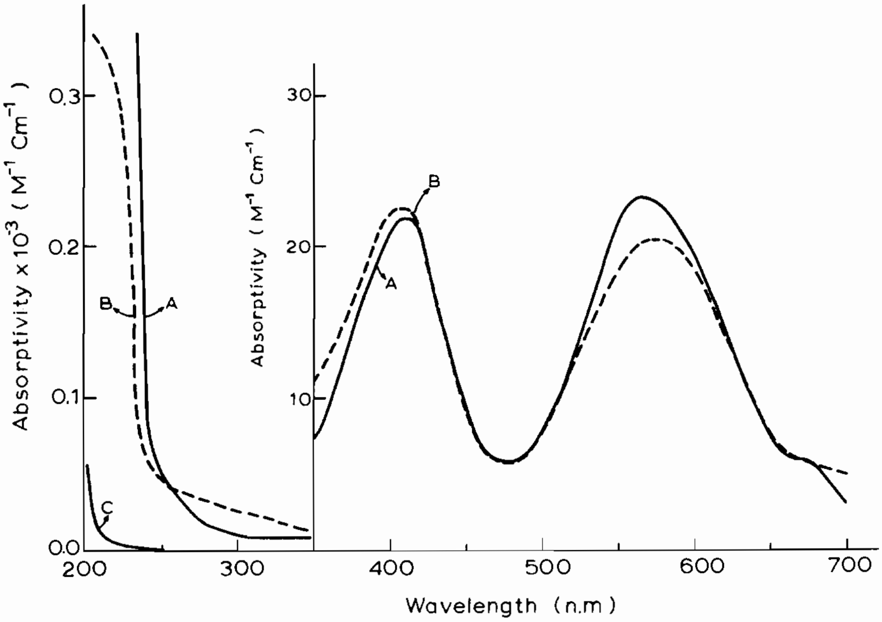


Fig. 9. UV–vis spectra of complexes obtained directly from Cr(III) and succinic acid. A) Lower charge band. B) Higher charge band. C) Succinic acid. All spectra were taken in 1 *M* $HClO_4$.

acid systems to those directly formed from Cr(III) and succinic acid, we heated (0.01–1 *M*) acidic solutions containing monomeric Cr^{3+} (aq) and excess succinic acid for several hours. Red complexes are not formed. Ion exchange separation yielded instead two blue-green bands, containing *ca.* 80% of the chromium, which were eluted with 0.5 *M* and 1 *M* $HClO_4$, respectively. Their spectra are shown in Fig. 9.

The following experiments were performed in order to obtain information about the structure of the low-charge red complexes:

– To the high-charge red complex formed during the reaction of chromous ion with fumaric acid and isolated by ion-exchange separation, a large excess of maleic acid was added. A low-charge red complex was then formed and isolated by ion-exchange, whose spectrum was identical to that of the low-charge red complex formed in the reaction of chromous ion with maleic acid in excess.

– To reaction mixtures containing maleic acid and chromous ion, where only the high-charge red complex is formed (excess chromous), a large amount of succinic or acetic acid was added after the end of the redox reaction. After one hour the reaction mixtures were allowed to pass through a Dowex 50W X 2 column. Red bands appeared in both cases corresponding to low-charge red complexes. The spectra of these complexes were similar to those formed in excess of maleic or fumaric acid, but the extinction coefficients were different: ϵ_{278} = 4309, ϵ_{410} = 127.2, ϵ_{520} = 99.4 M^{-1} cm^{-1} in the case of acetic acid, and ϵ_{278} = 2939, ϵ_{410} = 97.7, ϵ_{520} = 68.7 M^{-1} cm^{-1} in the case of succinic acid.

These complexes are obviously analogous to the low-charge red complexes formed in excess of maleic or fumaric acid. This shows that in addition to the carbon-bonded ligand the molecule contains a second organic ligand bonded through a Cr–O bond. This second ligand can be maleic or fumaric, or succinic, or acetic acid, or any other acid present in excess. The relatively fast rate of substitution by such a ligand shows that it is inserted in the coordination sphere of the chromium which carries the Cr–C bond. Taking into consideration the fact that the low-charge red complexes contain chromium and the organic ligand at a 1:1 ratio, we are thus led to the conclusion that the complexes are binuclear, that is the ratio is 2:2.

Citraconic, Itaconic, Aconitic, and Cinnamic Acids

Citraconic (methylmaleic) acid (*5*) reacted with Cr^{2+} (aq) fairly fast, but intermediate formation of red complexes was not found. Only the final ordinary (blue-green) complexes of Cr(III), were observed. Their spectra are given in Fig. 10. From a solution containing 0.02 *M* Cr^{2+} (aq), 0.09 *M* citraconic acid, and 1 *M* $HClO_4$, 45 min after mixing 75% of the chromium appeared in the form of these two ordinary complexes. The rest (25%) stayed at the top of the column as a light brown, high charge residue.

Under the conditions of our experiments itaconic acid (*6*) did not react with Cr^{2+} (aq), whereas aconitic (*7*) reacted very fast to give a blue complex.

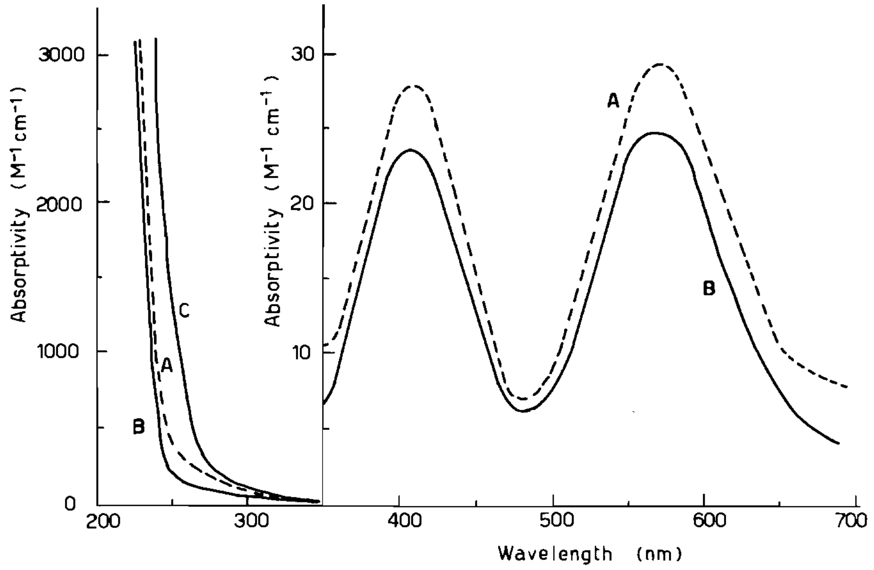


Fig. 10. UV–vis spectra of the blue complexes obtained in the Cr^{II}–citraconic acid system. A) Complex eluted with 0.5 *M* $HClO_4$. B) Complex of higher charge eluted with 1 *M* $HClO_4$. C) Citraconic acid in 1 *M* $HClO_4$.

Finally, cinnamic acid (*8*) reacted slowly even at elevated temperatures and there was no direct indication of formation of any intermediate red complex.

Discussion

Two kinds of complexes were isolated from the systems studied in this paper; the 'blue' and the 'red' ones, differing in important aspects of their physical and chemical behavior. In fact, the 'blue' complexes behave like any ordinary Cr(III) complex and are mentioned here only because they provide an internal basis for comparison. Thus, whereas the differences in spectra among the 'blue' complexes or among the 'red' complexes are rather minor, the differences between 'blue' and 'red' are striking.

Generally speaking the behavior of the 'red' complexes as contrasted to that of the ordinary 'blue' ones can only be understood if it is accepted that they contain chromium–carbon bonds of the σ-type. The more specific arguments supporting this general statement can be summarized as follows:

– The spectra, the polarographic behavior, and the magnetic moments show that chromium is in oxidation state III and that there is no metal-metal bond. Chromium (II) complexes of the tetraacetato type can in particular be ruled out, since the solutions are strongly acidic.

– The new peaks appearing in the near uv at 278 nm for MA and FA, at 287.5 and 325 nm for 3-PA, and at 312.5 nm for 4–PA, can be associated with the characteristic absorption of species having Cr–C bond [2f, 3a, 3b, 9].

– The lability is intermediate between that of the ordinary Cr(III) and Cr(II) complexes, as expected for organochromium species. The chemical behavior towards O_2, $HgCl_2$, I_2 *etc.* is also the expected for such compounds.

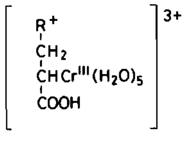
– In the base hydrolysis of the red Cr^{III}-3-PA complex occuring during its precipitation, complexation through the carboxyl group breaks down, but the Cr–C bonds persist. The ir spectrum is consistent with such bonds.

– In the case of MA and FA identification with ordinary complexes of succinic acid should be ruled out on the basis of direct evidence.

An important fact to point out too is that the formation of a red complex is always associated with the formation of at least one blue complex. A straightforward interpretation of this fact is provided by the two-step oxidative addition reaction (1) given in the Introduction. The overall stoichiometry requires formation of two Cr(III) species for each double bond reduced.

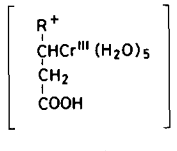
In view of the above discussion we propose the following tentative structures for the various red species isolated.

For the Cr^{III}-PA carbon bonded species:



$$\left[\begin{array}{l} R^+ \\ | \\ CH_2 \\ | \\ CHCr^{III}(H_2O)_5 \\ | \\ COOH \end{array}\right]^{3+}$$

or



$$\left[\begin{array}{l} R^+ \\ | \\ CHCr^{III}(H_2O)_5 \\ | \\ CH_2 \\ | \\ COOH \end{array}\right]^{3+}$$

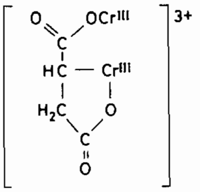
(9) (9')

where R^+ is the protonated pyridine ring. For steric reasons *9* seems more likely than *9'*.

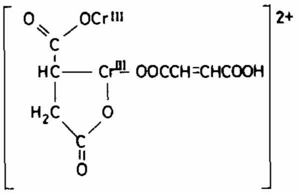
Complex *9* (or *9'*) is formed both in excess 3-PA and in excess chromous ion. The difference in the two cases is that the ordinary complex in excess 3-PA contains the unsaturated reagent (Fig. 3), whereas in excess chromous ion the ordinary chromium species formed is purely inorganic.

In view of the behavior of complex *9* on the ion exchange resin, as compared to the behavior of Cr^{2+} (aq) and the ordinary Cr^{III} species, it is unlikely that its overall charge is two. Chelation, therefore, involving removal of the hydroxyl proton, must be ruled out, although weak interaction with the carbonyl group is possible. The absence of chelation can be used as an argument in choosing structure *9* over *9'*.

For the species obtained from maleic acid and fumaric acid we propose the formulae:



10 High charge red complex



11 Low charge red complex

11 is formed *from 10* by replacement of one coordinated water molecule (not shown in the formulae) by MA or FA. The structure of the high charge complexes of MA and FA are identical. The low charge complexes differ in the unsaturated ligand.

Citraconic, itaconic, aconitic, and cinnamic acids did not give organochromium species. Itaconic acid does not react at all, and cinnamic acid reacts slowly without accumulation of any organochromium intermediate. If we speculate that the first step in the formation of the σ Cr^{III}–C bond is the formation of incipient μ-bond, we could perhaps attribute the lack of reactivity of itaconic to poor acceptor properties and the low reactivity of cinnamic to poor donor properties. Methylmaleic (citraconic) and aconitic on the other hand are reduced either by a path not involving metal to carbon bond formation or through highly labile organochromium species *e.g* for steric reasons (CH_3 and CH_2COOH at the double bond).

On looking now more closely at the electronic spectrum of Fig, 4, we first note the dramatic decrease on the absorptivity of the complex in the uv region, compared to the free unsaturated acid. This decrease is of course consistent with the partial destruction of the conjugation and/or planarity implied by structure *9*.

The weak $^4A_{2g} \rightarrow {}^4T_{2g}$ absorptions (Figs. 4, 8 and 9) are centered around 530 nm, whereas the corresponding absorptions of ordinary Cr(III) complexes have maxima above 570 nm. This large hypsochromic shift is consistent with the strong field carbon-bound ligand. The $^4A_{2g} \rightarrow {}^4T_1$ transition at *ca.* 410 nm does not show an analogous shift. The absorptivity at this wavelength increases by as much as an order of magnitude or even more, but the position of λ_{max} is hardly affected. As is seen in the figures the increased absorptivity is to a large extent due to the tail of the strong absorption in the near uv.

The separation between the first states having the same spin multiplicity corresponds to just 10 Dq [10]. In a strong field organochromium compound it is therefore expected this transition to be shifted to shorter wavelengths, as is indeed observed. The energy separation on the other hand between the ground level ($^4A_2$) and the second quartet ($^4T_1$) is approximately equal to 10 Dq + 12B, where B is the Racah electrostatic parameter. In the organometallic complexes Dq is larger than in the corresponding ordinary complexes. Since the observed energies of the $^4A_{2g} \rightarrow {}^4T_1$ transition are approximately equal, it follows that B is smaller in the organometallic species. This decrease in the electrostatic interaction parameter has been related to orbital expansion resulting in an increase of the interelectronic distances [11] and to covalency [12], which is also related to orbital expansion. The Cr^{III}–carbon bond is indeed expected to have a large covalent character.

The bands at 325 and 287.5 nm of the 3-PA compound can both be assigned to ligand-to-metal charge transfer. The first from an orbital polarized towards the ring system, similar to that of pyridinemethylchromium(III) [3b, 13]. The second (287.5 nm) can be assigned to transitions from a chain-centered orbital and it should therefore have its analogues in the maleic and fumaric acid complexes (at ~280 nm). The absorptivity of the 3-PA complex in this region is significantly higher than the corresponding absorptivities of the maleic and fumaric acid complexes. This may be due to an overlapping transition at 280 nm of the free acid. The charge transfer bands of the organochromium compounds prepared by Cohen and Meyerstein [3g, h] have λ_{max} in the range $256 < \lambda_{max} < 310$ nm.

Acknowledgments

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