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**The synthesis and properties of some zero charged
[Codien X_2Y] complexes ($X, Y = Cl, NO_2, NCS,$
 $OH, OCOR$)**

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Chimica. — *The synthesis and properties of some zero charged [Codien X₂Y] complexes (X, Y = Cl, NO₂, NCS, OH, OCOR) (*)*.
Nota di FEDERICO MASPERO, presentata (**) dal Corrisp. G. SARTORI.

RIASSUNTO. — Si descrive la sintesi di alcuni nuovi complessi della serie, cioè del dinitro-benzoato, ossalato-cloro, malonato-cloro e malonato-idrosso. Questi composti, come anche altri complessi simili già noti, sono caratterizzati sulla base delle loro proprietà spettrali e magnetiche, e del loro comportamento chimico in soluzione acquosa, neutra e acida, e in altri solventi. Si dimostra che alcuni complessi, già noti, hanno in realtà una struttura diversa da quella già descritta.

INTRODUCTION.

Cobalt(III) zero charged complexes of the formula [CodienX₂Y] (dien = diethylenetriamine, X, Y = anionic ligands) have been known for a long time. Crayton and Mattern [1] obtained [Codien(NO₂)₃], [Codien(NO₂)₂Cl] and [Codien Cl₃]. Ablov and Popa [2] have described the synthesis of [Codien(NO₂)₂Br], [Codien(NO₂)₂NCS] and [Codien oxNO₂].

The complexes have been characterized on the basis of their absorption spectra and chemical properties. The *peripheral* position has been assigned to the tridentate chelating agent, after comparing the spectrum of [Codien(NO₂)₃] with those of the two isomers, *peripheral*- and *facial*-[Co(NH₃)₃(NO₂)₃]. The complexes of the type [Codien(NO₂)₂Y] (Y = Cl, Br, NCS) have been characterized as *trans* isomers, with regard to the relative position of the two NO₂ ligands.

In view of further studies of reaction mechanisms, an extension to other terms of the series was needed. In the present paper, we are reporting the synthesis of some carboxylato complexes, i.e. the chloro-malonato, the hydroxo-malonato, the chloro-ossalato and the benzoato-dinitro. We also attempted to elucidate further the structure of other complexes with thiocyanato ligands described by Crayton and Mattern [1], which have not as yet been sufficiently characterized.

RESULTS AND DISCUSSION.

Dinitro complexes.

In order to obtain [Codien(NO₂)₂OCOC₆H₅], the chloro-dinitro complex was made to react with silver benzoate in a suitable solvent. The complex [Codien(NO₂)₂H₂O]Cl was precipitated from a hot, concentrated aqueous solution of the chloro-dinitro complex.

(*) Lavoro eseguito presso il Centro di Chimica dei Composti di Coordinazione del C.N.R., dell'Università di Roma.

(**) Nella seduta del 13 maggio 1967.

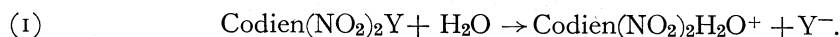
In table I we report some spectral data for the I band of electronic transition for these complexes.

TABLE I.
Spectral data for some [Codien(NO₂)₂Y] complexes.

COMPLEX	$\lambda_{\max}(m\mu)$	$\log \epsilon$	Solvent	Remarks
[Codien(NO ₂) ₂ Cl]	461	—	—	Reflectance on the solid product
»	461	2.37	DMF	—
»	460	2.12	water + satd. NaCl	—
»	442	2.30	water	—
[Codien(NO ₂) ₂ OCOC ₆ H ₅]	451	—	—	Reflectance
»	450	2.58	dioxane	—
»	450	2.41	methanol	—
»	443	2.30	water	—
[Codien(NO ₂) ₂ H ₂ O]Cl	443	—	—	Reflectance
»	443	2.31	water	—

The absorption bands of the complexes in all the solvents used except water, are coincident with the reflectance band on the solid product. Hence, solvolysis reactions probably do not occur in such solutions. In addition, the relative position of the bands is in agreement with the spectrochemical series of the ligands $\nu_{\max}(\text{H}_2\text{O}) > \nu_{\max}(\text{OCOC}_6\text{H}_5) > \nu_{\max}(\text{Cl})$.

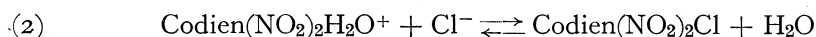
From the data in Table I it can be seen that the spectra of the aqueous solutions are identical with that of the aquo complex, giving evidence of a rapid hydrolysis reaction of the ligand Y (Cl, OCOC₆H₅).



This scheme finds further support in chromatographic experiments with ion exchange paper, carried out on the aqueous solutions of the complexes. In both cases only one spot at the origin was found, showing that only a positively charged complex was present in solution. On the other hand, a solution of [Codien(NO₂)₃] runs with the solvent front, as predicted for an inert, zero charged complex.

If the aqueous solutions are titrated with sodium hydroxide, one equivalent of base is required to neutralize one mole of complex, in agreement with the acidic properties of an aquo complex.

Let us consider now in more detail the behaviour of the chloro complex in aqueous solution. First of all, it should be noted that the spectrum in a solution saturated with NaCl corresponds to the chloro, not to the aquo form. A rapid equilibrium is thus established:



Secondly, consecutive reactions occur when the solutions are sufficiently acidic. In fig. 1 the variation of the spectrum at 45° C in 25 % HCl is shown. The absorption plot at zero time corresponds to the chloro form, as expected from the high concentration of Cl^- ions in solution.

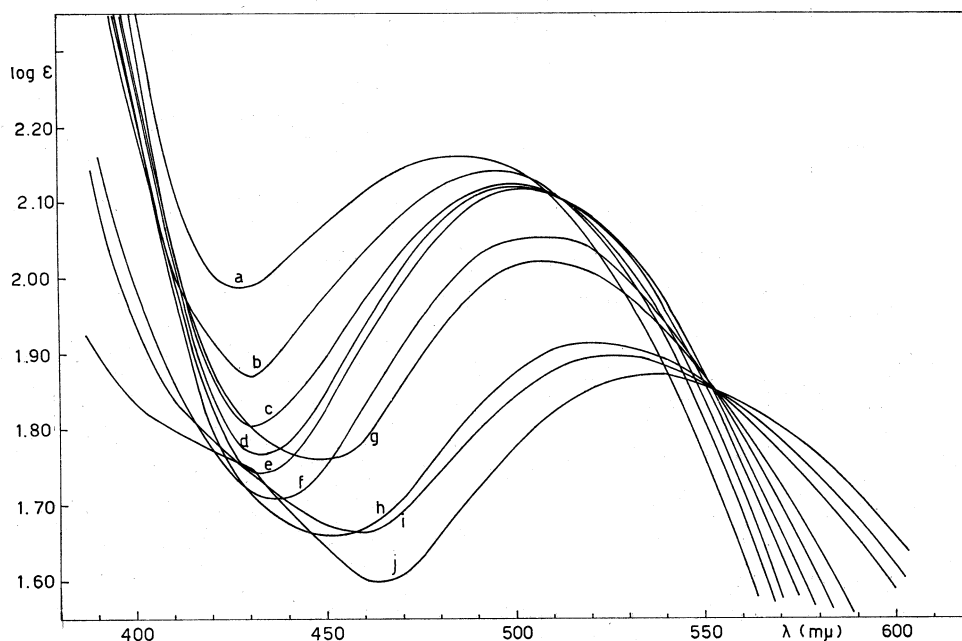
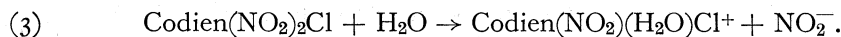


Fig. 1. — Spectrum of $[\text{Codien}(\text{NO}_2)_2\text{Cl}]$ in 25 % HCl at different times ($T = 25^\circ\text{C}$).

(a) 2 hrs.; (b) 4 hrs.; (c) 6 hrs.; (d) 8 hrs.; (e) 10 hrs.; (f) 24 hrs.; (g) 32 hrs.; (h) 72 hrs.; (i) 96 hrs.; (j) 150 hrs.

The first isosbestic point can be detected at $509\text{ m}\mu$ in the curves A—E probably due to the following reaction:



A dichloro-nitro complex could also be present, but it would be expected to absorb at a higher wavelength than that shown by the maximum of curve E, which lies at about $500\text{ m}\mu$.

Successive reactions emerge from curves F—J, but their identification is more ambiguous. On the other hand, at infinite time we obtain a mixture of complex ions whose spectrum depends on the HCl concentration. In fig. 2 the spectra at infinite time of solutions in 50% (a) and 80% (b) HCl,

are applied to these plots, it can be shown (dotted lines) that the same two bands are given. If Tsuchida's methods of gaussian analysis [3] are present in both cases, i.e. at 530 and 610 $m\mu$, and only their relative intensities vary

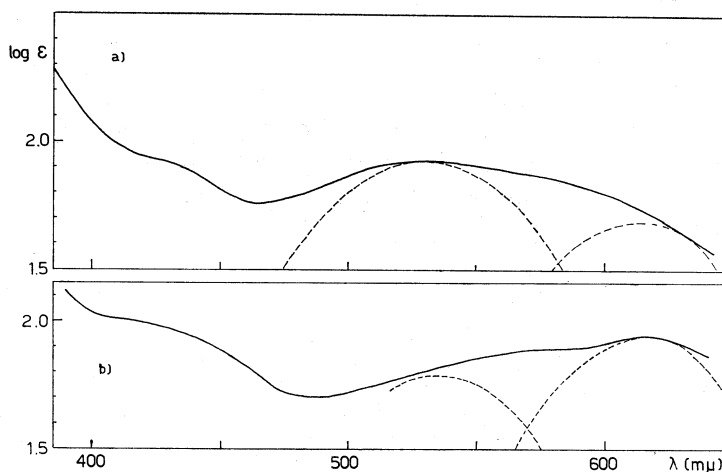
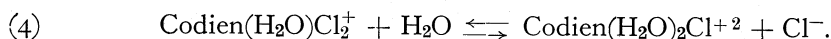


Fig. 2. - Spectrum of $[\text{Codien}(\text{NO}_2)_2\text{Cl}]$.

(a) in 50% HCl after 10 hrs., at 25°C; (b) in 80% HCl after 10 days, at 25°C.

with respect to the HCl concentration. The following equilibrium is believed to be responsible for this behaviour:



The influence of complexes such as $[\text{CodienCl}_3]$ and $[\text{Codien}(\text{H}_2\text{O})_3]^{+3}$ on this equilibrium is considered as negligible, because their spectral properties are known [1].

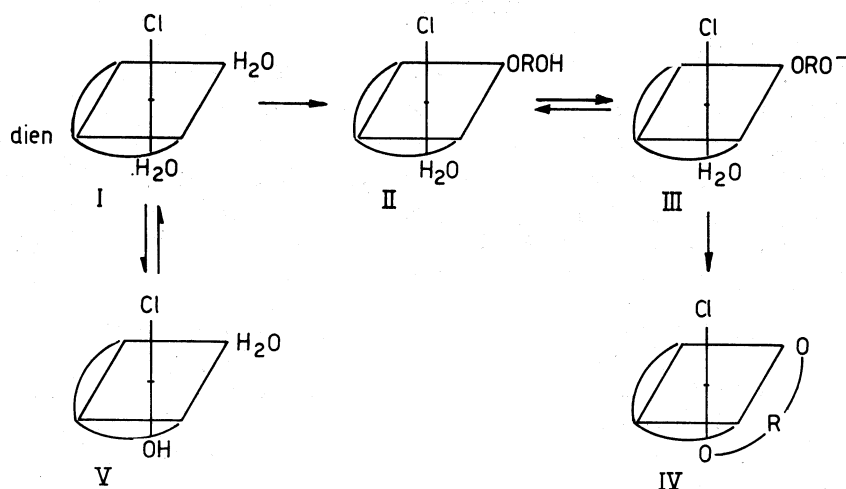
As far as reactions in non-aqueous solutions are concerned, the benzoato-dinitro complex was found to undergo some interesting nucleophilic substitutions in many organic solvents (e.g. methanol, dioxane, nitrobenzene) which will be discussed in a following paper.

Dicarboxylato complexes.

Oxalato and malonato complexes were obtained by a route starting from an aqueous solution of $[\text{CodienCl}_3]$, which probably contained the Co(III) complex mostly as $[\text{Codien}(\text{H}_2\text{O})_2\text{Cl}]^{+2}$. If this solution is made to react with a dicarboxylate buffer, a chloro-dicarboxylato or a hydroxo-dicarboxylato complex is obtained, depending on whether a buffer of the type $\text{HOROH}/\text{HORO}^-$ or $\text{HORO}^-/\text{ORO}^{-2}$ is used. When $\text{R} = \text{OCCH}_2\text{CO}$, both products were obtained in the solid form; when $\text{R} = \text{OCCO}$, only the chloro complex was easily isolated, because of its low solubility.

The features of these synthetic reactions may be easily interpreted based on the assumption that species I (see scheme (5)) can give rise to the chloro

complex on the elimination of two molecules of water:



The equilibrium constant of the system $\text{II} \rightleftharpoons \text{III} + \text{H}^+$ is not known. We can assume, however, that its value is similar to that of the first dissociation constant of HOROH, on the basis of the results obtained by Schwarzenbach et al. [4] for some related systems. Consequently, at a pH value corresponding to the buffer HOROH/HORO⁻, the equilibrium $\text{II} \rightleftharpoons \text{III} + \text{H}^+$ should be sufficiently shifted to the right, so as to give the nucleophile III. On the other hand, at a higher pH, such as that which corresponds to the buffer HORO⁻/ORO⁻², the other equilibrium $\text{I} \rightleftharpoons \text{V} + \text{H}^+$ is probably shifted sufficiently for a hydroxo complex to be obtained.

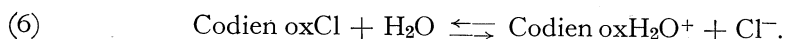
TABLE II.
Spectral data for some [Codien(ORO)Y] complexes.

Complex	λ_{max} (m μ)	log ϵ	Solvent	Remarks
[Codien oxNO ₂] (a)	480	2.24	water	—
[Codien oxCl]	549	—	—	Reflectance on the solid product
»	550	(b)	water + satd. NaCl	—
»	520	2.03	water	—
[Codien malCl]	547	—	—	Reflectance
»	540	(b)	n-propanol	—
»	533	(b)	water	—

(a) from reference [2]; (b) the concentration of these solutions is not accurately known.

In Table II some spectral data for the I band of electronic transition for dicarboxylato complexes are presented, including the already known term [Codien oxNO₂].

The spectrum of the aquo-dicarboxylato complex ions is not known. However, from Table II it is clear that the chloro-oxalato complex readily reacts with water, probably because of the hydrolysis of the chloro ligand. That the oxalato ligand is inert is shown by the fact that the spectrum of an aqueous solution saturated with NaCl is similar to that of reflectance on the solid product. This is probably due to the following equilibrium, which is established rapidly:



In such a case, also for this series the expected trend for the visible bands $\nu_{\max}(\text{NO}_2) > \nu_{\max}(\text{H}_2\text{O}) > \nu_{\max}(\text{Cl})$, is observed.

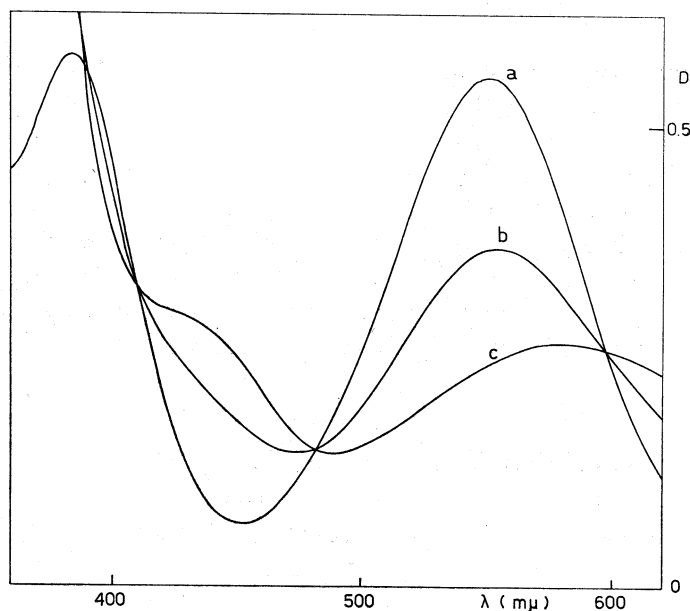


Fig. 3. - Spectrum of [Codien oxCl in conc. HCl] at different times ($T = 25^\circ \text{C}$).

(a) 5'; (b) 2 hrs; (c) 14 hrs.

The malonato complex probably behaves in a similar manner. It is interesting to note that the position of the band relative to [Codien oxCl] practically coincides with that of [Codien malCl]. This is in agreement with the finding that the spectra of oxalato and malonato complexes belonging to other series are also almost identical [5].

Chromatographic experiments with ion exchange paper provide further evidence for scheme (6). For all the complexes, except [Codien oxNO₂], there was only one spot at the origin, while the nitro complex runs with the solvent

front. Alcalimetric titrations of the aqueous solutions give more ambiguous results, both for the chloro-oxalato and for the chloro-malonato complexes, because of the subsequent reactions which occur in a basic solution.

Let us now consider the behaviour of the chloro-oxalato complex in an acid solution. Fig. 3 shows the variation of the spectrum in concentrated HCl at 25° C. At zero time it appears from the spectrum that the chloro-oxalato complex is the predominant species in solution. Four isosbestic points are then defined by the curves, and the final spectrum is similar to that of fig. 2 *b*. If 80 % HCl is used as the solvent, then the final spectrum becomes identical to that in fig. 2 *b*.

These data indicate that the acid-catalyzed hydrolysis of the bidentate oxalato ligand occurs in two consecutive steps, the second of which is much faster than the first. As a result, the intermediate species could not be isolated under the conditions of our experiments. In this respect the acid-catalyzed reaction differs from that with the chloro-dinitro complex, although the same final products are formed in both cases, i.e. a mixture of complex ions $[\text{Codien}(\text{H}_2\text{O})_n\text{Cl}_{3-n}]^{+n}$ ($n = 1, 2, 3$).

Complexes with thiocyanato ligands.

Crayton and Mattern [1] have described the products obtained by oxidizing a mixture of dien and a Co(II) salt under different conditions. A product (I), described as $[\text{Codien}(\text{NCS})_2\text{OH}]$, was obtained from aqueous solutions, while a product (II) described as $[\text{Codien}(\text{NCS})_3]$ was obtained in an alcoholic medium. In what follows, it will be shown that the structures of I and II are different from those suggested by these Authors.

Our attempts to synthesize $[\text{Codien}(\text{NCS})_2\text{Cl}]$, based on the reaction of $[\text{Codien}(\text{NCS})_3]$ with HCl were unsuccessful. The product obtained is a new complex (III) and is practically Cl-free.

The conversion of the product I into the aquo form was also unsuccessful; the complex does not react with acids at all, and presents a rather acidic character in aqueous solution. This might possibly be due to an olato-bridged structure; the presence of a band at $\bar{\nu} = 10,850 \text{ cm}^{-1}$ in its infrared spectrum might also be interpreted as a confirmation of this hypothesis [6].

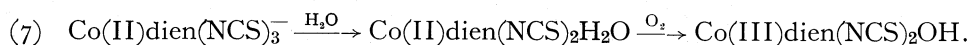
Both products I and II were found to be paramagnetic. This is in contrast with the expected magnetic behaviour of an octahedral strong-field Co(III) complex. The effective moments are 0.8 B.m. for I, and 2.1 B.m. for II. Thus, the latter must be a Co(II) complex, containing one spin electron per Co atom [7]. It is not easy to give accurate analytical data for it, because the complex easily undergoes change. However, the data reported for III clearly show that three NCS ligands must also be present in the former complex. The most probable composition is $[\text{Codien}(\text{NCS})_3]^-$, possibly crystallized as the potassium salt.

Complex I contains 1/2 spin electron per Co atom, i.e. it is a mixed Co(II)/Co(III) complex. A simple formula might be $[\text{Codien}(\text{NCS})_2\text{OH}]$

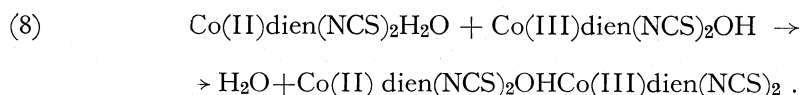
Codien(NCS)₂], which agrees with both the analytical data and the possible olate structure.

If the procedures used to obtain the two complexes are kept in mind, the above findings can explain why product II is always obtained in an anhydrous medium. The same product is also immediately formed in aqueous solution, and is converted to I after air has been bubbled through the mixture for a long time. Presumably, oxidation by air is only possible in the presence of water.

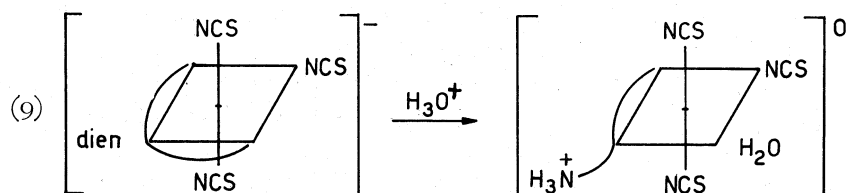
Qualitative tests for free NCS⁻ indicate that a partial hydrolysis of this ligand occurs in aqueous solutions of [Codien (NCS)₃]⁻, prior to the oxidation step:



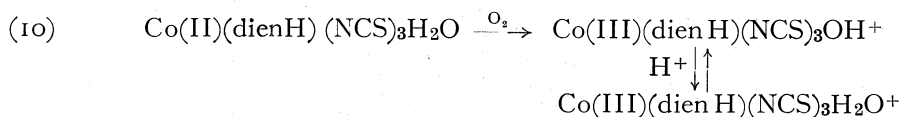
The complete oxidation Co(II) → Co(III) is probably prevented by the precipitation of a slightly soluble olate compound on the elimination of one molecule of water from the as yet unoxidized aquo complex:



On the other hand, one of the two chelation rings probably opens in a highly acid medium, thus forming a trithiocyanato aquo complex:



From here the oxidation may proceed via a hydrogen atom transfer:



Hydrogen chloride can be removed from the hydrochloride by repeated washings, as shown by the analytical data reported for the different fractions of product III.

The last complex is diamagnetic. It is not considered as suitable material for the synthesis of [Co(III)dien(NCS)₂Y] complexes, because dien acts as a bidentate ligand.

EXPERIMENTAL.

Materials.

The diethylenetriamine used, a « technical » grade Fluka product, was fractionally distilled over KOH at a pressure of 1 mm of Hg. The silver salts used in the syntheses were prepared by the general method described by Aprile, Caglioti and Illuminati [8]. All the other chemicals used were reagent grade.

The known complexes were synthesized as indicated by previous Authors: [Codien(NO₂)₃], [Codien(NO₂)₂Cl] and [CodienCl₃] according to Crayton and Mattern [1], [Codien oxNO₂] according to Ablov and Popa [2]. The products prepared by Crayton and Mattern and presented as [Codien(NCS)₃] and [Codien(NCS)₂OH] were also obtained by the method indicated by the Authors.

[Codien(NO₂)₂H₂O]Cl.

This compound was obtained by cooling to room temperature a solution of 1.2 g of [Codien(NO₂)₂Cl] in 70 ml of water at 80°C. Yield 0.4 g. The product was orange-yellow in colour and soluble in water.

[Codien(NO₂)₂OCOC₆H₅].

Equimolecular quantities of [Codien(NO₂)₂Cl] (1.5 g) and of AgOCOC₆H₅ (1.2 g) were mixed in a mortar and suspended in 200 ml. of N,N'-dimethyl formamide. The mixture was kept at room temperature, with constant stirring, for 90 days, until a sample of the filtered solution gave a negative result to the qualitative test of Lassaigne for chlorine. The solution was filtered and the solvent was distilled under reduced pressure (2 mm Hg). The dry residue was washed with dimethylformamide and then with methanol. Yield 0.85 g. (Found: C, 35.1; H, 5.1; N, 17.9; Calc. for [Codien(NO₂)₂OCOC₆H₅]: C, 35.2; H, 4.8; N, 18.7 %).

The product can be obtained in a very pure state by dissolving it in nitrobenzene and reprecipitating by the addition of petroleum ether in large amounts. The yield, however, is extremely low. The complex is light yellow, not very soluble in water, soluble in a large variety of organic solvents (e.g. DMF, ethanol, propanol, nitrobenzene, dioxane).

[Codien oxCl].

a) [Codien oxNO₂] (0.3 g) was pounded in a mortar with 1 ml of conc. HCl, and the mixture was left standing at room temperature. After 48 hours the violet product was filtered off, eliminating the red crystals, which were a visible impurity, by washing with water.

b) [CodienCl₃] (0.5 g) was dissolved in 250 ml of water by shaking the mixture at room temperature for 90'. To this was added a solution of oxalic acid (0.5 g) partially neutralized with 1N NaOH (4 ml) in 50 ml of water. After evaporation to 100 ml of the solvent on a steam-bath, the precipitate was filtered off and washed with water until the washings had no more violet colouring. Yield 0.45 g. The product was violet, crystalline, not very soluble in water. (Found: C, 25.2; H, 4.6; Cl, 11.0; Calc. for [CodienC₂O₄Cl]: C, 25.2; H, 4.6; Cl, 12.4 %).

[Codien malCl].

[CodienCl₃] (0.7 g) were shaken in 200 ml of water at room temperature for 90'. A solution of malonic acid (0.8 g) in 50 ml of water, partially neutralized with 1N NaOH (5 ml), was added to the clear solution. The violet-red solution was evaporated to dryness. The violet residue was dissolved in 1 l of boiling propanol, and the filtered solution was evapo-

rated on a steam bath to 500 ml. The crystalline powder was filtered off and washed with propanol and ether, keeping the solid free from direct contact with moisture. Crystalline powder, violet in colour, extremely hygroscopic; alters rapidly on contact with water; soluble in a variety of organic solvents (e.g. methanol, ethanol, propanol). (Found: C, 27.8; H, 5.5; Cl, 10.5; Calc. for [Codien(OCOCH₂CO₂)Cl]: C, 28.0; H, 5.0; Cl, 11.8 %).

[Codien malOH].

To [CodienCl₃] (2.5 g) dissolved in 300 ml of water a solution of malonic acid (1.9 g) in 300 ml of water, partially neutralized with 1N NaOH (28 ml), was added. The red solution was evaporated to dryness on a steam bath. The residue was recrystallized from 500 ml of absolute alcohol, keeping the solution free from moisture. Yield 0.2g. Pink powder, extremely hygroscopic. (Found: C, 30.6; H, 5.4; Cl, 0.2; Calc. for [Codien(OCOCH₂CO₂)OH]: C, 29.9; H, 5.7; Cl, 0 %).

Description of the attempted syntheses of other complexes.

a) [Codien(NCS)₂H₂O]ClO₄: [Codien(NCS)₂OH] (2.8 g) was dissolved in 1 l of water acidified with HClO₄. Conc. HClO₄ (2 ml) was added to the solution while shaking. After filtration and cooling, a product was precipitated which was filtered off, and washed with water, alcohol and ether. Pink crystalline powder, slightly soluble in water, with the same chemical and physico-chemical properties as the starting material. (Found: C, 24.6; H, 4.4; Cl, 0.2; Calc. for [Codien(NCS)₂H₂O]ClO₄: C, 17.7; H, 3.8; Cl, 8.8; Calc. for [Codien(NCS)₂OH]: C, 23.8; H, 4.6; Cl, 0 %).

b) [Codien(NCS)₂Cl]: [Codien(NCS)₃] (20 g) was pounded in a mortar with conc. HCl (200 ml). After standing at room temperature for three hours, the red product was filtered off and washed with water. This procedure was repeated twice more. Finally, the washing was continued until no more acid was present in the washing water. Yield 1.4 g. Pink powder, slightly soluble in water and in methanol. (Found for the first fraction: Cl, 3.5; for the second: Cl, 2.8; for the final: Cl, 1.8; S, 25.3; Calc. for [Codien(NCS)₂Cl]: Cl, 11.3; S, 20.4 %).

Analyses.

The elementary microanalyses were performed by Prof. A. Bernhardt, Mülheim/R.

Spectrophotometric measurements.

A Beckman DU spectrophotometer was used for determining the visible and u.v. spectra of the complexes. To determine the variations in absorption for a particular wavelength as a function of time, a Beckman DB spectrophotometer connected to a Sargent SRL recorder was used.

A quartz cell was used for absorption measurements. MgO was used as a reference substance for the reflection spectra.

The sample of the solid malonato chloro complex used to determine the reflection spectrum was prepared in a dry-box, and kept covered with a slide.

A Beckman IR 7 spectrophotometer was used for the infrared spectra.

Acid-base titrations.

The aquo complexes existing in aqueous solutions were potentiometrically titrated as acids with 0.01N NaOH, using a saturated calomel electrode and a glass electrode, connected to a Radiometer M 22 pH-meter.

Magnetic susceptibilities.

The magnetic susceptibility of the complexes was measured at room temperature using a Gouy balance. $\text{HgCo}(\text{NCS})_4$ was used as the calibrating agent. Three different field strengths were used to take in account ferromagnetism. The connections for diamagnetism due to the organic part of the complexes were calculated using Pascal's constants quoted by Figgis and Lewis [7]. The magnetic moment was calculated from the following equation:

$$\mu_{\text{eff}} = 2.84 \sqrt{\chi_{\text{corr}}^{\text{M}} \cdot T}$$

Chromatographic experiments.

A drop of a 0.01 M solution of the complex was placed on a strip of ion exchange Dowex X-1 50 paper. Distilled water, barely acidified with HClO_4 ($\text{pH} = 4-5$), was used as the eluent. To bring out the spots on the chromatogram, the process suggested by Carunchio, Grassini and Ortaggi [9] was followed.

Reactivity.

The variations in the spectrum of the solutions were directly measured in the cell compartment of the spectrophotometer which was kept at a constant temperature by means of an ultrathermostat. Alternatively, the solution was placed in a flask which was immersed in a thermostated bath, and at determined time intervals samples were taken and used for the absorption measurements.

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REFERENCES.

- [1] P. H. CRAYTON and J. A. MATTERN, « J. Inorg. Nucl. Chem. », **13**, 248 (1960).
- [2] A. V. ABLOV and E. V. POPA, « Russian J. Inorg. Chem. », **18-2**, 161 (1963).
- [3] Y. SHIMURA and R. TSUCHIDA, « Bul. Chem. Soc. Japan », **29-3**, 311 (1956).
- [4] G. SCHWARZENBACH, R. GUT and G. ANDEREGG, « Helv. Chem. Acta », **37-4**, 937 (1954).
- [5] S. M. GRAWFORD, « Spectrochim. Acta », **18**, 965 (1962).
- [6] K. NAKAMOTO, *Infrared spectra of inorganic and coordination compounds*, J. Wiley, New York (1963).
- [7] B. N. FIGGIS and J. LEWIS, in: *Modern Coordination Chemistry*, ed. J. Lewis and R. G. Wilkins, Interscience, New York (1960).
- [8] F. APRILE, V. CAGLIOTI and G. ILLUMINATI, « J. Inorg. Nucl. Chem. », **21**, 300 (1962).
- [9] V. CARUNCHIO, G. GRASSINI-STRAZZA and G. ORTAGGI, « J. Inorg. Nucl. Chem. », **27**, 841, (1965).