[CONTRIBUTION FROM THE AVERY LABORATORY OF THE UNIVERSITY OF NEBRASKA]

Synthesis and Infrared Study of Some Rhodium Coördination Compounds[1]

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The infrared spectra of five rhodium coördination compounds have been studied. The previously unknown *cis* and *trans* isomers of trichlorotripyridinerhodium(III) have been isolated and characterized. Solubility, color and spectral differences have been utilized to establish the entity of the two isomeric forms.

Introduction

Structural configurations of inorganic coördination compounds have been studied by a number of physical methods. Holtzclaw and Sheetz[3] conducted a polarographic study of a series of *cis*- and *trans*-cobalt complexes. The ultraviolet spectra of *cis* and *trans* isomers of certain compounds in solution were studied by Basolo.[4] Curran, *et al.*,[5] studied the infrared spectra of some metal–amine complexes. Sen[6] has used the infrared spectra of glycine complexes to elucidate their configurations. Merritt and Wiberley[7] used characteristic infrared bands to differentiate between seven pairs of *cis*- and *trans*-cobalt complexes containing amine linkages.

Jorgensen[8,9] has reported recently the ultraviolet spectra for a number of cobalt, rhodium and iridium complexes, samples of which were furnished to him by M. Delepine.

Results and Discussion

Delepine[10] reported that trichlorotripyridinerhodium(III) exists in only one isomeric form. Theoretically, two isomers are possible—(1) the isomer, hereinafter referred to as the "*cis*" isomer, in which all chlorines are *cis* to one another and all pyridines are *cis* to one another, and (2) the isomer, hereinafter referred to as the "*trans*" isomer, in which two chlorines are *trans* to each other and two pyridines are *trans* to each other.

In the present investigation, five compounds were separated from the mixture resulting from the reaction of rhodium(III) chloride and aqueous pyridine. Two of these were established as isomeric forms of trichlorotripyridinerhodium(III). The other three compounds were dichlorotetrapyridinerhodium(III) chloride and two unidentified compounds containing rhodium and nitrogen.

The orange-brown isomer of trichlorotripyridinerhodium(III) is soluble in absolute ethanol, acetone and pyridine, and is slightly soluble in dioxane, whereas the less soluble yellow isomer is only slightly soluble in ethanol, acetone, pyridine and dioxane. Both isomers are soluble in chloroform, dichloromethane and N-dimethylacetamide. The two isomers form red, slightly soluble solvates with chloroform and dichloromethane. Both isomers react with ethanol to form colloidal rhodium, the reaction being more rapid in aqueous ethanol. The yellow isomer is amorphous, whereas the orange-brown isomer exists in crystalline plates.

A sample of the yellow isomer can be obtained relatively free of the orange-brown form by concentrating the mother liquor of a crude mixture of the two isomers. The orange-brown form can be extracted from the crude mixture of the two isomers with hot absolute ethanol or hot acetone. Pyridine separates the two forms but contaminates them by reacting to form dichlorotetrapyridinerhodium(III) chloride. Upon extended refluxing, this reaction yields pure dichlorotetrapyridinerhodium(III) chloride.

Chromatography of the crude mixture gave initial separation into a yellow band and an orange band, but after a few minutes these bands ran together and began to stream rapidly. This behavior is thought to have been caused by formation of chloroform solvates.

The infrared spectra of the two isomers are presented in Table I. The first absorption band that differs for the two forms is the 782 cm.$^{-1}$ band. This band is much more intense in the spectrum of the orange-brown isomer. It may be caused by an absorption in the orange-brown isomer and might not occur in the spectrum of a completely pure sample of the yellow isomer. The spectrum of the orange-brown isomer resembles that for dichlorotetrapyridinerhodium(III) chloride in this region more than does the spectrum of the yellow isomer.

TABLE I

FREQUENCIES, CM.$^{-1}$, OF INFRARED ABSORPTION BANDS FOR THREE PYRIDINE COMPLEXES OF RHODIUM

$[Rhpy_4Cl_2]Cl$	$[Rhpy_3Cl_3]$ (yellow isomer)	$[Rhpy_3Cl_3]$ (orange-brown isomer)
1607s	1608s	1610s
1470s	1455s	1455s
1241w	1240w	1240w
1210s	1213s	1216s
1149m	1155w	1158w
1064s	1067s	1068s
1018m	1018m	1019w
780s	782w	783s
765s	768s	763s
758s	761s	756s
. . .	755sh	. . .
720w	717w	718w
. . .	702s	700sh
. . .	693s	694s
. . .	687s	687s

A second difference between the two spectra is found in the 760 cm.$^{-1}$ region. The 763 cm.$^{-1}$ band

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[1] Abstracted from the M.S. Thesis of James P. Collman, University of Nebraska, June, 1956.

[2] Address inquiries concerning this paper to H. F. Holtzclaw, Jr.

[3] H. F. Holtzclaw, Jr., and D. P. Sheetz, THIS JOURNAL, **75**, 3053 (1953).

[4] F. Basolo, *ibid.*, **72**, 4393 (1950).

[5] C. Curran, D. N. Sen, S. Mizushima and J. V. Quagliano, Paper 62, "Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy," March, 1954.

[6] D. N. Sen, Ph.D. Thesis, University of Notre Dame, 1953.

[7] P. E. Merritt and S. E. Wiberley, *J. Phys. Chem.*, **59**, 55 (1955).

[8] C. K. Jorgensen, *Acta Chem. Scand.*, **10**, 500 (1956).

[9] C. K. Jorgensen, *ibid.*, **11**, 151 (1957).

[10] M. Delepine, *Bull. soc. chim. France*, **45**, 235 (1929).

of the orange-brown form is stronger than the 756 cm.$^{-1}$ band found in the spectrum of this compound, whereas the 768 cm.$^{-1}$ band of the yellow isomer is slightly weaker than the next lower band at 761 cm.$^{-1}$. In the spectrum of the yellow isomer, there is an additional shoulder band at 755 cm.$^{-1}$ which is not found or at least is not as pronounced in the spectrum of the orange-brown compound. In this portion of the spectrum the orange-brown isomer again shows greater similarity than the yellow to the dichlorotetrapyridine compound.

A third difference in the spectra of these two compounds is in the 700 cm.$^{-1}$ region, in which three bands occur in each of the two spectra. The center band is the strongest in the spectrum of the yellow isomer, whereas the two lower frequency bands are of about equal intensity and the higher band is much weaker in the spectrum of the orange-brown isomer.

Analyses definitely establish that the two forms have the same stoichiometric composition. Solubility differences, color differences and spectral differences appear to establish conclusively the entity of the two separate forms. Examination of the two spectra indicates that separation of the two forms may not be complete, each probably being contaminated with a small quantity of the other form.

A comparison of the spectra of the three pyridine complexes in Table I shows several similar absorption maxima which are probably due to pyridine groups. The 720 cm.$^{-1}$ band may be due to a rhodium–chlorine vibration, inasmuch as the one infrared absorption band which is shown by rhodium(III) chloride is at a frequency of 720 cm.$^{-1}$.

It is not possible to say conclusively on the basis of present evidence which of the two trichlorotripyridine complexes is *cis* and which is *trans*. However, the greater similarity of the spectrum of the orange-brown form to that of the dichlorotetrapyridine compound provides some evidence that the orange-brown form is the *trans* isomer, inasmuch as it seems reasonable though not certain from the method of preparation that the dichlorotetrapyridine complex is in the *trans* form.

A comparison of the spectrum of potassium oxalate monohydrate with that of *cis*-potassium dichlorodioxalatorhodate(III) monohydrate, shown in Table II, shows striking differences resulting from coördination of the oxalate ion. The presence of the 1700 and 1670 cm.$^{-1}$ bands in the spectrum of the oxalate complex indicates that there are free carbonyl groups present in this compound instead of the delocalized carboxylate ions. This would indicate that the other carbon–oxygen linkages of the two carboxyl ions no longer overlap with the carbonyl groups and that coördination is taking place between one of the oxygens of each carbonyl group and the rhodium(III) ion. The strong band at 1247 cm.$^{-1}$ in the spectrum of the oxalato complex may be caused by a carbon–oxygen single bond absorption.

The frequencies of the infrared absorption bands for dimethylglyoxime and hydrogen dichlorobisdimethylglyoximerhodate(III) are recorded in Table III. Comparison of these spectra indicates that the spectrum of dimethylglyoxime is radically altered by coördination. The absorption maxima at 1597 and 1510 cm.$^{-1}$ in the dimethylglyoxime complexes may be due to carbon–nitrogen double-bond stretching vibrations. It is interesting that these bands do not show up in free dimethylglyoxime.

TABLE II

FREQUENCIES, CM.$^{-1}$, OF INFRARED ABSORPTION BANDS FOR POTASSIUM OXALATE MONOHYDRATE AND *cis*-POTASSIUM DICHLORODIOXALATORHODATE(III) MONOHYDRATE

$[K_2(C_2O_4)\cdot H_2O]$	*cis*-$K_3[Rh(C_2O_4)_2Cl_2]\cdot H_2O$
....	3540m
....	3440m
3200s	.....
....	1700s
....	.....
....	1670s,b
....	1654s,b
1625s,b	.....
1413m	1402s
1315s,b	.....
....	1247s
....	895m
....	813s
....	805sh
778s	.....
717m	718m

TABLE III

FREQUENCIES, CM.$^{-1}$, OF INFRARED ABSORPTION BANDS FOR DIMETHYLGLYOXIME AND HYDROGEN DICHLOROBISDIMETHYLGLYOXIMERHODATE(III)

Dimethylglyoxime	$H[Rh(DMG)_2Cl_2]$
3200s,b	3280w,b
....	1597m
....	1510m
....	1400sh
1368s	1337m
....	1218s,b
....	1187m,b
1145s	1120w,b
....	1102s
....	1070s
1028w	1000m
980s	....
902s	965w,b
....	835w,b
745m,b	....
705s	716s

Experimental

A. Analysis.—All analyses for rhodium were made by weighing as metallic rhodium after decomposition to the metal, upon heating the sample to red heat for three hours. The metal, so obtained, suffered no weight change upon heating five hours in a hydrogen atmosphere or upon washing with aqua regia.

Carbon-hydrogen analyses were performed by the Micro-Tech Laboratories, Skokie, Illinois.

B. Preparation of Compounds. 1. ***trans*-Hydrogen Dichlorobisdimethylglyoximerhodate(III).**—This compound was prepared according to the method of Dwyer[11]; yield 58%. *Anal.* Calcd.: Rh, 25.41. Found: Rh, 25.57.

2. ***cis*-Potassium Dichlorodioxalatorhodate(III) Monohydrate.**—This compound was prepared by a modification of the procedure of Delepine.[12]

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(11) F. P. Dwyer, *J. Proc. Roy. Soc. N. S. Wales*, **78**, 266 (1946).

(12) M. Delepine, *Anales real soc. espan. fis. y quim.* (*Madrid*), **27**, 485 (1929).

Two grams of rhodium(III) chloride (0.00955 mole), 3.54 g. of potassium oxalate monohydrate (0.0191 mole) and 21.6 g. of water were combined and refluxed for one-half hour, during which the solution changed from ruby-red to orange-red. The solution was then concentrated to a weight of 15 g. and allowed to stand in a closed container for two days, whereupon a yellow-orange precipitate appeared. The solution was cooled in an ice-bath, and the precipitate collected by suction filtration. In a similar manner, three more crystal crops were collected. Seven days after the initiation of the reaction, the precipitation had almost ceased. The total yield was 0.475 g. (10%). The different crystal fractions had about the same golden yellow color. Each crop was recrystallized from an ethanol–water solution and dried in a vacuum desiccator at 0.005 mm. for 48 hours. *Anal.* Calcd.: C, 9.84; H, 0.41. Found: C, 9.63; H, 0.46.

3. **Dichlorotetrapyridinerhodium(III) Chloride.**—This compound was prepared by a modification of the method of Joergensen.[13] A mixture of 0.397 g. of rhodium(III) chloride (0.0018 mole), 2 g. of pyridine (0.025 mole) and 50 ml. of 95% ethanol was refluxed for 47 hours. The golden solution was evaporated to 15 ml. over a steam-bath, then covered and allowed to cool overnight. The golden needles which separated were collected on a filter disc. Upon further evaporation of the mother liquor under reduced pressure, two more crystal batches were collected. The final 5 ml. of mother liquor was discarded. The crystals were washed with cold, absolute ethanol, and the different batches were combined. The yield was 0.74 g. (68%, calculated on the basis of the tetrahydrate). *Anal.* Calcd. for $[\mathrm{Rhpy_4Cl_2}]\mathrm{Cl{\cdot}4H_2O}$: Rh, 17.22. Calcd. for $[\mathrm{Rhpy_4Cl_2}]\mathrm{Cl{\cdot}5H_2O}$: Rh, 16.99. Found: Rh, 17.07. (Delepine[12] reports a hexahydrate; Joergensen reports the salt as anhydrous.)

After drying the compound in a vacuum desiccator for 48 hours at 0.005 mm., it was again analyzed. *Anal.* Calcd. for $[\mathrm{Rhpy_4Cl_2}]\mathrm{Cl}$: Rh, 19.58. Found: Rh, 19.93, 19.22.

4. **Two Isomeric Forms of Trichlorotripyridinerhodium(III).**—The preparation of the compound, prior to separation into the two isomers, was made according to a modification of the method reported by Delepine.[10] A mixture of 5 g. of rhodium(III) chloride (0.024 mole), 11.39 g. of pyridine (0.144 mole) and 57 g. of water was stirred at room temperature, whereupon an oily, red mass separated. This mixture was heated on a steam-bath until all the red mass had been converted to an orange, crystalline material. These orange crystals of crude *cis*- and *trans*-trichlorotripyridinerhodium(III) were filtered, air dried and saved for later extraction of the orange-brown isomer; yield 42%.

The mother liquor was heated for 30 minutes on the steam-bath. Yellow plates (0.68 g.) formed which were filtered off while the solution was hot. These plates are thought to be dichlorotetrapyridinerhodium(III) chloride tetrahydrate, which Delepine[10] reports as having been isolated from a similar reaction mixture.

Upon cooling, the mother liquor yielded some red-orange crystals of unknown composition. This substance was collected by filtration and dried at 110° for 12 hours. *Anal.* Rh, 25.4.

The mother liquor was evaporated to 15 ml. Five ml. of cold water was added and the solution allowed to stand in a closed container for 24 hours. The yellow, amorphous powder which precipitated was collected on a filter and washed with cold water. The wash water and mother liquor were combined and heated for one-half hour on the steam-bath. More yellow substance precipitated and was collected. This process was repeated several times, during which the mother liquor changed from dark red to lighter red-orange. The weight of the combined precipitates of the yellow isomeric form, after drying, was 0.8 g. *Anal.* Calcd. for $[\mathrm{Rhpy_3Cl_3}]$: Rh, 23.05; C, 40.31; H, 3.36. Found: Rh, 23.60, 23.40; C, 40.14; H, 3.55.

The crude, orange mass which had been collected from the original solution was found to contain at least three species—(1) an unknown amorphous pink substance, (2) the yellow isomer of trichlorotripyridinerhodium(III) and (3) the orange-brown isomer of the same compound. This crude material (5.5 g.) was boiled for five minutes with a mixture of 110 ml. of chloroform and 18 ml. of absolute ethanol. Upon filtration of the resulting bright red liquid, a pink, amorphous precipitate (0.47 g.) of unknown composition remained on the filter. *Anal.* Rh, 29.8.

Evaporation of the red filtrate to dryness produced bright red crystals of the chloroform solvate, $[\mathrm{Rhpy_3Cl_3}]\mathrm{{\cdot}2CHCl_3}$, reported by Delepine.[10] Upon prolonged exposure to room air, the red crystals lost chloroform and turned to an orange mixture of the orange-brown and the yellow isomeric forms. *Anal.* Calcd. for $[\mathrm{Rhpy_3Cl_3}]$: Rh, 23.05. Found: Rh, 23.32, 23.27.

A small amount of this mixture was recrystallized by dissolving in N-dimethylacetamide and adding water to reprecipitate. The recrystallized mixture was extracted with 10 ml. of hot, absolute ethanol. The ethanol solution was filtered and quickly evaporated under reduced pressure. (If this is not done rapidly, some of the compound is reduced to metallic rhodium by the ethanol.) The crystals obtained from this filtrate were predominantly the orange-brown form. The infrared spectrum indicates that the compound may contain a small quantity of the yellow form. *Anal.* Calcd.: Rh, 23.05; C, 40.31; H, 3.36. Found: Rh, 23.28; C, 40.08; H, 3.73.

Acetone also may be used to effect a separation of the yellow and orange-brown isomers from the orange mixture. Extraction of the mixture with hot acetone yielded an orange-brown form. *Anal.* Calcd.: Rh, 23.05. Found: Rh, 23.37.

C. **Spectra.**—Infrared spectra were determined in the frequency range 4000–650 cm.$^{-1}$ with a Perkin–Elmer Model 21 recording spectrophotometer, using sodium chloride optics. Compounds were examined as solids in Nujol mulls. Infrared intensity abbreviations used in Tables I, II and III are: s, strong; m, medium; w, weak; b, broad; sh, shoulder.

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[13] S. M. Joergensen, *J. prakt. Chem.*, **27**, 478 (1883).