of 2.33 and 4.0; Bobtelsky and Spiegler[5] explicitly assumed that complexes of the type CoX$_3^-$ did not exist. Conductivity data also gave the latter an indication of a CoX$_2$ complex in water–alcohol mixtures, but it is not possible to say whether this was the CoCl$_2$·4Z or CoCl$_2$·2Z complex. Wormser[3] followed the electrical conductivity changes rather than colors, and the method of continuous variations gave evidence for a trichloro complex. This means only that this complex is much more highly conducting than the other two. Earlier data of Groh and Schmid[20] confirm Wormser's data on the conductivity. Wormser's identification of a spectrum due to a CoCl$^+$ complex is apparently based on a misinterpretation, engendered in part by her recognition of only the CoCl$_3^-$ complex.

Robinson and Brown[2] used a different technique, and concentrated aqueous salt solutions. Their identification of Co(H$_2$O)$_4$Cl$_2$ as the source of blue color is probably due to not properly interpreting the first-formed "rose" solutions with absorption maximum shifted to 525 mμ as due to this entity. A similar rose colored aqueous solution has been recognized by other workers.[21,22] The blue complex dealt with by Robinson and Brown is probably Co(H$_2$O)$_2$Cl$_2$; formation of higher complexes seems unlikely in aqueous solution.

Summary

1. The absorption spectra shown by cobalt chloride dissolved in various solvents are shown to be ascribable to the entities Co(H$_2$O)$_6^{++}$, CoX$_4$Cl$_2$, and CoX$_2$Cl$_2$, with colors, respectively, salmon-pink, rose to magenta, and blue.

2. In a solution containing excess chloride (*e. g.*, as LiCl), the blue forms CoX$_2$Cl$_2$, CoXCl$_3^-$ and CoCl$_4^=$ may be found, their proportions depending on equilibrium between the metal ion, anions and molecular "bases" (electron donors) present. The spectra characteristic of these forms are described.

3. Evidence is given to show that the various blue forms have tetrahedral groupings of electron donors around the metal atom, and suggestions are made for the electron configurations involved.

CHICAGO 80, ILL. RECEIVED APRIL 17, 1950

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[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

Some New Pyridine Compounds of Cobalt(II) Salts

BY LEONARD I. KATZIN, JOHN R. FERRARO AND ELIZABETH GEBERT

The similarity between the hydrates, ammoniates and pyridinates[1] of a number of salts has been observed and commented upon many years ago (*e. g.*, Reitzenstein, 1897,[1a] and literature quoted therein). With particular respect to cobalt(II) chloride, the hexahydrate, dihydrate and monohydrate are known, as well as the corresponding ammoniates and pyridinates.[2] Although the tetrahydrate is usually accepted as stable at room temperature only in the form of mixed crystals with MnCl$_2$,[3] the tetrammoniate[4] and the tetrapyridinate[2] are known. In the case of cobaltous nitrate, the hexahydrate, tetrahydrate,[5,6] trihydrate and dihydrate are recognized; the literature shows only the hexammonia[7,8] and the tetrapyridine[1,9] compounds. Finally, with the perchlorate, the hexahydrate[2] is known, formation of a tetrahydrate is certain,[10] and preparation of the corresponding hexammonia,[2] tetrammonia[2] and tetrapyridine[11] compounds has been reported.

We have confirmed the preparation of the cobalt chloride hexa-, tetra- and dipyridine compounds. In the case of cobalt nitrate, we have prepared all of the pyridine analogs of the hydrates, namely, the hexa-, tetra-, tri- and dipyridinates. In addition, a mixed water–pyridine tetrasolvate, the dihydrate–dipyridinate was prepared. In the case of the perchlorates, the hexapyridinate and tetrapyridinate–dihydrate, a mixed hexasolvate, have been made.

The ready preparation of the stable cobalt chloride tetrapyridinate, and the reported tetraammoniate, are interesting, since one investigator has reported the tetrahydrate to be stable only in the temperature region 48–58°,[12] another has reported its formation at 116°,[13] and deConinck[14]

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(1) To save space, and because the compounds are treated as solvates rather than "complexes," the terms hydrate, ammoniate and pyridinate are used instead of aquo coördination compound, ammine coördination compound and pyridine coördination compound. "Cobalt," without further designation, means cobalt(II).

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describes it as a hydration product of the anhydrous salt, in contrast to a very large number of other investigators who have found no evidence for the existence of such a tetrahydrate.[2] Preliminary results of studies with the salt-water-acetone ternary system[15] which previous experience[6,16] has shown to be the most favorable for revealing hydrates of narrow stability range, indicate that the tetrahydrate does exist at 25°, but with an extremely narrow stability range of partial pressures of water, which would explain some of the conflicting evidence concerning its existence.

A small amount of a blue-colored chloride was once prepared by Reitzenstein,[1] which he tentatively identified as cobalt chloride tripyridine. We have consistently been able to prepare a blue material by treatment of tetrapyridinate with small volumes of benzene. X-Ray investigation, through the kind coöperation of Professor W. H. Zachariasen, showed the pattern of cobalt chloride tetrapyridinate to persist even when the pyridine-cobalt ratio of the solid was less than 3. This means there is no tripyridine compound, and the blue material contains fewer pyridines. Since, while wet with benzene, the blue form at any stage of the depyridination procedure may suddenly transform to a violet color, especially when the pyridine-cobalt ratio approaches 2, it seems to be the unstable blue modification of cobalt chloride dipyridinate.

It has usually been assumed that the blue and violet forms represent *cis* and *trans* planar isomers. A more logical explanation for the direct formation solely of blue dipyridinate, on pyridine removal from the presumedly octahedral tetrapyridinate, is that it is really a tetrahedral molecular group. Furthermore, although X-ray crystallographic evidence has been adduced to support a *trans* planar structure for the violet modification (signficantly, the X-ray pattern of the blue form was found too complicated for analysis),[17] Mellor and Coryell[18] point out that the cobalts here could really be octahedrally coördinated, sharing chlorides with the layers above and below.

Compounds of cobalt chloride and pyridine which are a stable blue are represented in the literature solely by dipyridinium cobalt chloride.[1,19] We have repeated the preparation of this compound and can corroborate its composition. It is presumed[19] to differ from the other pyridine compounds in showing the tetrahedral $CoCl_4^=$ group found crystallographically in Cs_3CoCl_5.[20]

In addition to the above solvates which one might term "normal," as they contain six or less groups per cobalt, we have found an interesting series of solvates of cobalt perchlorate in which solvation numbers are 9.5, 10 and 11.5, and which contain both water and pyridine. The best characterized of these is the hexapyridine-tetrahydrate, which has been obtained in the form of large crystals. Although appearing in smaller crystals, the heptapyridine with 2.5 waters has been obtained in several preparations. It has also been possible to prepare a solid which contains nine pyridines and 2.5 waters per cobalt. This is less stable, and tends to "bleed" pyridine in time.

The literature shows that in the hydrate systems of both the nitrate[21] and the perchlorate[22] salts, at temperatures below −20°, nonahydrates have been reported. A compound of cobaltous nitrate with nine ammonias has been reported,[23] and what may be two different decammonias of the chloride[4,24] are also known. With respect to the perchlorate, a compound taken to be the same hexapyridine-tetrahydrate material we have found is reported,[11] and the identification is probably correct. The relationships of the various water and pyridine groups to the cobalt atom is far from clear, but that solids with such high formal solvation numbers exist seems unmistakable. Whether there is a basic number of 9 or 10, as suggested by the low-temperature hydrates and the high-ammonia chloride, and whether the exact number is constant or is a function of the nature or only the sizes[4,8] of the anions and the molecular bound groups is not certain. The nonahydrates are reported stable only at rather low temperatures, while the ammonia compounds and mixed pyridine-water solvates are stable at room temperatures. Ammonia and pyridine are stronger bases, but also larger groups, than water.

Analytical Methods

All preparations were analyzed for water by use of the Karl Fischer reagent; the method used has been described in detail elsewhere.[16] Cobalt was determined by standard electrodeposition procedure. Pyridine was first removed from the solution by evaporation to small volumes. Since quantitative nitrogen recoveries could not be achieved, in part due to characteristics of pyridine (Kjeldahl procedure) and in part due to interference on the part of the cobalt salts (Dumas procedure), they could be used only to substantiate approximately the amount of pyridine present, estimated by difference, from the cobalt and water analyses. We are indebted to Mrs. R. C. Hospelhorn for her work on the nitrogen analyses.

Preparations

All reactions between reagents seem to be instantaneous. Although in the presence of ammonia Co(II) can be oxidized to Co(III), this reaction did not appear with our pyridine preparations. The difference in basicity is probably an important factor.

$CoCl_2 \cdot 6Py$.—One part by weight of cobalt chloride hexahydrate was stirred with 1.1 parts of pyridine dissolved in an equal volume of chloroform, heat being evolved in the

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(15) Katzin and Ferraro, unpublished data.

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reaction. The chloroform layer was separated, and the residual solid was extracted several times with cold chloroform. The pooled extracts were crystallized by evaporation in a draft, to give dark red-violet crystals smelling strongly of pyridine. To avoid decomposition, the crystals were dried only by short sucking on a sintered disk; yield, about 30%. *Anal.* Calcd.: Co, 9.75. Found: Co, 9.00; water, nil.

$CoCl_2\cdot 4Py$.—Procedure as for the hexapyridine, except benzene was used as the solvent. The first benzene extract and two subsequent benzene washes of the solid were discarded (the amount of cobalt salt extracted by the benzene is negligible), and the residual solid then extracted with cold chloroform. The chloroform extracts were let evaporate in a draft. Drying was again only by sucking on a sintered disk. Yield is similar to the preceding preparation. *Anal.* Calcd.: Co, 13.21. Found: Co, 12.54; water, 0.74.

The tetrapyridine compound can also be prepared by subjecting the hexapyridine compound to the action of a mechanical vacuum pump. The crystalline starting material is reduced to a fine red-violet powder in a few hours, and a number of hours further pumping produces no change. The analysis of one such batch showed Co, 13.17, water, 0.28. Prolonged subjection to a stream of flowing dry nitrogen also produced tetrapyridinate (Co, 13.48, water, 0.81).

$CoCl_2\cdot 2Py$.—$CoCl_2\cdot 2Py$ can be obtained from the higher pyridinates by heating with a mixture of *t*-butyl alcohol and ethanol insufficient to dissolve the sample, filtering on a sintered disk, and washing with hot ethanol. As first obtained by this treatment, the solid is blue but after a time it changes suddenly to violet. The dipyridinate can also be obtained by treating the higher pyridinates with successive small volumes of benzene and separating completely from the portions of benzene on a sintered disk. The solid is usually blue for the first few treatments but suddenly at some point shows a transition to violet. The violet material is essentially insoluble in the benzene and is the stable form of $CoCl_2\cdot 2Py$. The blue-violet transition is deferred for longer periods of time, if the benzene is washed out with ethyl ether. Small amounts of water seem to stabilize the blue form; one particularly stable blue solid, prepared by evaporation in air from a benzene solution, showed Co, 18.46; water, 0.63. Another stable blue sample contained 1.1% water.

$(HPy)_2CoCl_4$.—3.2 g. of cobaltous chloride hexahydrate was mixed with 5.9 g. pyridine hydrochloride, both in ethanol solution. The material precipitating out was filtered through a sintered disk, washed with ether, ethanol and ether again. Baby-blue needle crystals were obtained. *Anal.* Calcd.: Co, 16.33; Cl, 39.29. Found: Co, 16.15; Cl, 39.06; water, nil. This material is stable and does not change color; yield was higher than 75%.

$Co(NO_3)_2\cdot 6Py$.—Thirty grams of cobaltous nitrate was stirred with sufficient pyridine to give a liquid layer, and heated to boiling. The pyridine was decanted, and additional extractions of the residual solid made with boiling chloroform, until the color showed negligible further extraction of cobalt. The chloroform and pyridine extracts were combined, concentrated by evaporation of the hot solutions and left to cool and crystallize in a draft. The resulting dark pink crystals, when partially dry, were filtered on a sintered disk and washed with ether. *Anal.* Calcd.: Co, 8.96. Found: Co, 8.87; water, nil. The solid smelled very strongly of pyridine. The yield was about 30%.

$Co(NO_3)_2\cdot 4Py$.—This could be formed from the hexapyridinate in two ways. One, analogous to the method of formation of the tetrahydrate,[6] consisted of placing the hexapyridinate in a metal sintered-disk crucible and fusing the crystals over a steam-bath. When at equilibrium, the crucible was connected to a water aspirator and the liquid portion sucked through. The residual pink-violet solid analyzed: Co, 12.04; water, 0.61. Calcd.: Co, 11.80. A better preparation was obtained by placing hexapyridinate in a tube connected to a mechanical vacuum pump, warming to 70°, and pumping at this temperature for about five minutes. The pink-violet product analyzed: Co, 11.82, water, 0.41. The tetrapyridinate could also be prepared directly from the hydrate-pyridine reaction mixture, if a preliminary extraction or two with cold chloroform were first used to remove the excess pyridine. The coarsely crystalline material obtained by such procedure was a brick-red when first prepared, and darkened on standing over a period of days to a wine color. A sample prepared in this fashion gave: Co, 12.21; water, 1.22. As these preparations demonstrate, the nitrates are slightly more hygroscopic than the corresponding chlorides.

$Co(NO_3)_2\cdot 3Py$.—29.4 g. of cobaltous nitrate hexahydrate was stirred with 36.8 g. of pyridine and an equal volume of chloroform. All the solid went into a dark red solution, and as it cooled from the heat of reaction, a precipitate formed. The supernatant chloroform solution was evaporated in a draft, and gave large pink crystals. *Anal.* Calcd.: Co, 14.02. Found: Co, 13.87; water, nil. Yield was 30–50%. The tripyridinate could also be prepared by lengthy pumping of the hexapyridine salt under vacuum or by treating the hexapyridinate with small portions of benzene, as with the cobalt chloride dipyridine compound.

$Co(NO_3)_2\cdot 2Py$.—This was prepared by taking a hot chloroform extract of a mixture of 19.5 g. of cobaltous nitrate dihydrate and 17.5 g. of pyridine, and allowing it to evaporate to dryness in a draft. The crystals were orange-salmon in color, when first prepared, but on standing in the desiccator turned to a wine hue. *Anal.* Calcd.: Co, 17.27. Found: Co, 17.17; water, 0.74.

$Co(NO_3)_2\cdot 2H_2O\cdot 2Py$.—The solid left after chloroform extraction in the preparation of the dipyridinate was extracted with chloroform until essentially no further color could be removed. The orange-salmon coarsely crystalline solid was dried with ether. On standing in the desiccator its color became a dark wine. *Anal.* Calcd.: Co, 15.63; water, 9.54. Found: Co, 15.53; water, 8.97. The appearance of this compound explains the phenomenon observed in the reaction of the lower cobalt nitrate hydrates with pyridine, in which complete solution precedes deposition of solid.

$Co(ClO_4)_2\cdot 6Py$.—Cobalt perchlorate hexahydrate was extracted with portions of pyridine in chloroform. Extractions were performed rapidly and the solid discarded as soon as it started to darken. The extracts were filtered, and evaporated to dryness in a draft. Pink needle crystals were obtained. *Anal.* Calcd.: Co, 8.04. Found: Co, 7.98; water, nil. The yield was small.

$Co(ClO_4)_2\cdot 6Py\cdot 4H_2O$.—Forty grams of pyridine was stirred into a solution of 13.5 g. cobaltous perchlorate hexahydrate in 28 g. of water. Heat was evolved. On cooling and stirring of the wine-red solution, fine yellow-orange crystals separated. The mother liquor was decanted and placed in a draft. After two days slow evaporation, a mass of large orange-red crystals of triangular cross-section was obtained. The mother liquor yielded still another crop, this time smaller crystals but still of good size. Analyses of the crystals, dried by suction and gentle wiping, were Co, 7.35; water, 9.41, and Co, 7.39; water, 9.37, respectively. Theory for the formula is Co, 7.32; water, 8.90. The analytical values show a small replacement of pyridine by water, corresponding to the formula $Co(ClO_4)_2\cdot 5.90Py\cdot 4.17H_2O$. The analysis of the first finely crystalline solid separated from the mother liquor indicated that mother liquor had been trapped. To get slower separation of solid, another 13.5-g. portion of hexahydrate was dissolved in a larger portion of liquid, consisting of 56 g. of water and 81 g. of pyridine. Heat was evolved. After two days evaporation, and stirring, an orange-yellow solid separated which, after filtration and washing with ether analyzed: Co, 7.36; water, 8.88.

$Co(ClO_4)_2\cdot 7Py\cdot 2.5H_2O$.—Solid cobalt perchlorate hexahydrate was treated with several portions of hot pyridine, the extracts combined and evaporated to semi-dryness in a draft. The mixture was filtered on a sintered disk and washed several times with ether. The orange-colored crystals gave: Co, 6.82; water, 5.36 (calcd.: Co. 6.88; water, 5.25). Another preparation has been made by stirring 10 g. of the hexahydrate with three times the weight of pyridine, cooling and filtering. Ether was then stirred into the clear red filtrate until solid precipitated. The solid was filtered on a sintered surface, and rinsed with ether. The analysis, Co, 6.96; water, 5.69, corresponds to the formula $Co(ClO_4)_2 \cdot 6.84Py \cdot 2.68H_2O$, and indicates that under the precipitation procedure used water replaced a small portion of the pyridine in the crystals.

$Co(ClO_4)_2 \cdot 9Py \cdot 2.5H_2O$.—Crystalline $Co(ClO_4)_2 \cdot 7Py \cdot 2.5H_2O$ was dissolved in several volumes of pyridine diluted with benzene and additional benzene added to bring the concentration of pyridine down to 50%. Evaporation was allowed to proceed in a draft until a jelly-like mass had formed. More benzene–pyridine mixture (1:1) was added just sufficient to dissolve the solid, and then ether was slowly added until two liquid phases separated, a colorless supernatant and a cobalt-bearing lower phase. After separation, the lower liquid was set aside to evaporate. Solid which formed was separated on a sintered disk, as flaky light-orange crystals. An ether wash darkened their color to a salmon-orange. *Anal.* Calcd.: Co, 5.81; water, 4.44. Found: Co, 5.68; water, 4.55. On standing the crystals "sweated" pyridine. Another preparation in which the starting solid was dissolved in a smaller volume of pyridine–benzene mixture, so that phase separation occurred without the aid of ether, gave crystals which analyzed: Co, 5.76; water, 4.73. When the preparation is attempted by dissolving the starting solid in pyridine (without added benzene) and evaporating, a gelatinous solid slowly separates. Filtering on a sintered disk gives a wet, gummy preparation, which bleeds pyridine on standing. *Anal.* Co, 5.73; water, 5.02. Apparently from the undiluted pyridine the leaf-like crystals formed pack down so as to retain the mother liquor strongly.

$Co(ClO_4)_2 \cdot 6Py \cdot 2H_2O$ (?).—When crystals of the 9-pyridine-$2.5H_2O$ compound that have bled pyridine were thoroughly dried by pressing between sheets of filter paper, the residual orange-pink colored solid showed Co, 7.74; water, 4.75. This corresponds to a formula $Co(ClO_4)_2 \cdot 5.91Py \cdot 2.01H_2O$. This may be fortuitous approximation to the hexapyridine–dihydrate formula, although the analogous $Co(NO_3)_2 \cdot 6NH_3 \cdot 2H_2O$ has been reported.[2]

$Co(ClO_4)_2 \cdot 4Py \cdot 2H_2O$.—Crystalline $Co(ClO_4)_2 \cdot 7Py \cdot 2.5H_2O$ was washed twice with chloroform, which partially dissolves the starting material and changes its appearance. The remaining orange-pink solid analyzed: Co, 9.62; water, 6.25. After the initial wash, the figures had been essentially the same. Theory for $Co(ClO_4)_2 \cdot 4Py \cdot 2H_2O$: Co, 9.66; water, 5.90. The product was then washed a number of times with alternate portions of chloroform and ether–absolute alcohol, and the light-pink solid showed Co, 10.00; water, 5.97. It therefore seems certain that the compound is as formulated, that the water is not present only because of mechanical entrapment and that the deviation of the analyses from theory is probably due to replacement of part of the pyridine by water in the reagents.

Summary

1. Preparations of pyridinates and mixed pyridinate–hydrates of cobalt chloride, nitrate and perchlorate are described, and the relationships to the hydrates and ammoniates are discussed.

2. New compounds reported, or questionable compounds confirmed, include the hexa-, tetra-, tri- and dipyridinate, and the dihydrate–dipyridinate of cobaltous nitrate; hexa- and tetrapyridinate, and the tetrapyridine–dihydrate of cobaltous perchlorate, and crystalline cobaltous perchlorates containing, respectively, six pyridines–four water; seven pyridines–2.5 water; nine pyridines–2.5 water; and a possible six pyridine–two water solvate.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF ILLINOIS INSTITUTE OF TECHNOLOGY]

Kinetics of the Reaction of Lithium Borohydride in Aqueous Acid Solution[1,2]

BY MARTIN KILPATRICK AND C. DANA MCKINNEY, JR.

During a study of the kinetics of fast reactions evolving gases, some data were obtained on the relatively slow reaction between lithium borohydride and acidified water. As pointed out by Schlesinger,[3] when lithium borohydride is dissolved in water only a portion of the available gas is liberated and the solution becomes strongly alkaline. In acid solution the reaction is qualitatively much faster, and Davis, Mason and Stegeman[4] in their study of the heat of formation give the equation for the reaction as

$$LiBH_4 + HCl + 3H_2O \longrightarrow LiCl + H_3BO_3 + 4H_2 \quad (1)$$

Preliminary experiments with an apparatus similar to that used earlier[5] but equipped with a magnetic stirrer indicated that in some cases the volume change of the gas on adding lithium borohydride to water was negative. This effect was attributed to reaction with oxygen and was eliminated by carrying out experiments in an atmosphere of nitrogen. Upon adding lithium borohydride to a solution three normal in acid, the sudden surge of gas last two or three seconds. This is followed by a low increase in volume of gas. This was interpreted to mean that the first reaction produces diborane

$$LiBH_4 + HCl \longrightarrow LiCl + {}^1/_2B_2H_6 + H_2 \quad (2)$$

and the second is the slower hydrolysis of the diborane

$${}^1/_2B_2H_6 + 3H_2O \longrightarrow H_3BO_3 + 3H_2 \quad (3)$$

with the over-all reaction corresponding to equation (1).

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(1) Based upon a part of the thesis submitted by C. Dana McKinney, Jr. to the Graduate School of Illinois Institute of Technology in June, 1950, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) This research was sponsored by the Office of Naval Research.

(3) Schlesinger and Brown, THIS JOURNAL, **62**, 3429 (1940).

(4) Davis, Mason and Stegeman, *ibid.*, **71**, 2775 (1949).

(5) Kilpatrick, *ibid.*, **48**, 2091 (1926).