two. The yields obtained by this method are listed in column 3 of Table I.

Method II.—One hundredth mole of the quinone oxime was dissolved in 15 ml. of methyl cellosolve and 1.5 ml. of acetone. To this was added 1.4 g. (0.01 mole) of cuprous oxide (Merck commercial grade) and 4.7 ml. of hydrochloric acid previously diluted with 6 ml. of water. The solution was refluxed for forty-five minutes, and then steam distilled. The quinone was isolated by the procedure described in Method I, and was thus easily obtained in a high state of purity. In the case of thymoquinone dioxime the quantity of the reagents was doubled, and the refluxing time increased to two and one-half hours.

A Modification of Method II.—The conditions described in Method II are too severe for hydrolyzing 3-methylbenzoquinone 1-oxime and 2-methylbenzoquinone-1-oxime, but the following modification of Method II gave fair yields with these oximes. To 1.37 g. (0.01 mole) of the oxime, contained in a glass mortar, was added 2 ml. of acetone and 4.7 ml. of hydrochloric acid. To this mixture was added 1.4 g. (0.01 mole) of cuprous oxide in divided portions with trituration after each addition. The entire mixture was diluted with 20 ml. of water, shaken mechanically for forty-five minutes, and then steam distilled. The quinone was isolated in the usual manner. The yields obtained with this procedure are given in Table I.

TABLE I

RESULTS OBTAINED FROM THE HYDROLYSIS OF THE OXIME

Oxime			Quinone		
	Yield, %	M. p. (uncor.)	Yield Method I, %	Yield Method II, %	M. p., °C. (uncor.)
Benzoquinone-1-					
2-Methyl-	70	135 dec.	Trace (oily)	55[a]	67
3-Methyl	81	157 dec.	Trace	20[a]	67
2,6-Dimethyl-	88	175 dec.	18	78	73
3,5-Dimethyl-	91	172 dec.	26	87	73
2,5-Dimethyl-	90	173 dec.	28	92	125
2,3,6-Trimethyl-	90	172 dec.	7	92	32
2,3,5,6-Tetramethyl-	80	89 dec.	33	66	107
2-Isopropyl-5-methyl-	90	155 dec.	Trace	88	45
2-Methyl-5-isopropyl-	85	162	None	85	45
Thymoquinone dioxime	66	235 dec.	None	80	45
2-Methylnaphthoquinone monoxime	79	165 dec.	45	45	105

[a] These two compounds were hydrolyzed by the Modification of Method II.

Discussion.—Methyl cellosolve was used as a solvent in these reactions because it provided homogeneity and a suitable boiling range of from 97 to 101°. Methyl cellosolve was also tried in the Karrer and Hoffmann method,[5] but in each instance the yield was poorer than with the regular procedure.

Four controlled experiments disclosed that an 85% yield of thymoquinone was obtained from its monoxime by Method II with the use of cuprous oxide and acetone while the same procedure without the acetone gave a 79% yield, and without the cuprous oxide gave a 15% yield, and without either gave only a trace of thymoquinone.

It is evident from the data in Table I that *p*-nitrosophenol $\rightleftharpoons$ quinone monoxime tautomers in which both the nitroso and hydroxyl groups are hindered are more difficult to hydrolyze than those in which only one of these groups is hindered. It appears also that the reaction is slightly favored in those tautomers in which the nitroso group is partially hindered.

The method described here for hydrolyzing quinone oximes has not been applied to *p*-aminophenols, but a similar procedure to Method II using cupric sulfate was found to give an 80% yield of thymoquinone from *p*-aminothymol.

Acknowledgment.—The authors wish to thank Dr. L. I. Smith, of the University of Minnesota, for the samples of 2,3,5-trimethylphenol and 2,3,5,6-tetramethylphenol used in this study.

Summary

A method for hydrolyzing *p*-quinone oximes with the aid of cuprous chloride has been described, and the results obtained with eleven oximes have been given in a tabular form.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POMONA COLLEGE]

Some Glycol Complexes of the Light Transition Metals

BY ROBERT GOMER AND G. N. TYSON, JR.

In the course of some studies on the complex-forming behavior of the light transition elements, it has been found possible to synthesize and partially characterize by means of magnetic susceptibility measurements the following glycol complexes: $CuSO_4 \cdot 2$ glycol (I), $CuSO_4 \cdot 1$ glycol (II), $NiSO_4 \cdot 4$ glycol (III), $NiSO_4 \cdot 3$ glycol$\cdot 1H_2O$ (IV), $NiSO_4 \cdot 2$ glycol$\cdot 1H_2O$ (V), $CoCl_2 \cdot 3$ glycol (VI), $CoCl_2 \cdot 3$ glycol$\cdot 1H_2O$ (VII), $CoCl_2 \cdot 2$ glycol$\cdot 1H_2O$ (VIII), $FeSO_4 \cdot 1$ glycol$\cdot 2H_2O$ (IX), $FeSO_4 \cdot 3$ glycol (X), $FeSO_4.3$ glycol$\cdot 1H_2O$ (XI), $MnCl_2 \cdot 2$ glycol$\cdot 1H_2O$ (XII). Of these (I), (IV), (V), (VI), (VII), (VIII) have been reported previously by Grün.[1,2] The duplication of some of the syntheses requires rigid adherence to all conditions and these experimental procedures have been given in detail.

Experimental

Synthesis.—In the following syntheses J. T. Baker and Co. C. P. salts were used as the source of the metal ions, and the glycol and pyridine were obtained from Eastman Kodak Company.

(I) is prepared by adding 3.7 g. of $CuSO_4 \cdot 5H_2O$ to 5 g. of glycol on the water-bath. The decanted solution crystallizes after several days of standing in the cold. The

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(1) Grün and Bockisch, *Ber.*, **41**, 3465–3478 (1908).

(2) Grün and Boedecker, *ibid.*, **43**, 1051–1062 (1910).

crystals are pressed between filter paper, washed with cold ether and dried for several days over calcium chloride. When more dilute solutions of copper sulfate in glycol are used the monohydrate of (I) results after some time.

(II) is prepared by adding to a solution of 3.7 g. of $CuSO_4 \cdot 5H_2O$ in 5 g. of glycol enough alcohol till further addition produces no more clouding.

(III) is prepared by dissolving 16 g. of $NiSO_4 \cdot 6H_2O$ in 20 g. of glycol on the water-bath. To the filtered mixture is added 7 cc. of alcohol and 4–5 cc. of ether. The well-mixed solution is placed in the desiccator over sulfuric acid and evacuated till active ebullition of the mixture occurs. The following day solidification is almost complete and the mass is pressed between filter paper, washed with cold abs. alcohol and dried over calcium chloride. If the original mixture is left too long over sulfuric acid a mixture of the quadri and triglycol nickel salts results.

(IV) is prepared by the identical method of Grün.[2]

(V) is prepared by adding absolute alcohol to a solution of 16 g. of $NiSO_4 \cdot 6H_2O$ in 20 g. of glycol till no more clouding is produced on further addition. Approximately 10 cc. of alcohol is required. The green oil, which settles out, crystallizes rapidly. The crystalline powder is washed with 10 ml. of absolute alcohol and dried over calcium chloride.

(VI) is prepared by allowing a solution of 20 g. of $CoCl_2 \cdot 6H_2O$ in 15.7 g. of glycol to solidify over sulfuric acid. The resulting compound is blue and its monohydrate (VII), is red. The mass obtained on solidification may be a mixture of the two forms and can be changed to the dehydrated form only by cautious desiccation over sulfuric acid. The mass must be well broken up mechanically for this purpose. By exposing (VI) to air it is changed completely to (VII) which can be reconverted to (VI) by desiccation.

(VIII) is prepared by letting the same solution used in the preparation of (VI) solidify over phosphorus pentoxide. Here, as in (VI), incipient crystallization will be noted after one or two days, and almost complete solidification will occur after a week. (VIII) is extremely hygroscopic and changes very rapidly to a red dihydrate when exposed to air. The dihydrate continues to pick up water.

The ferrous complexes are prepared as follows: 15 g. of $FeSO_4 \cdot 7H_2O$ is placed on the steam-bath with 20 g. of glycol and 3–5 g. of iron powder. Solution is aided greatly by stirring with a pestle. Metallic iron and undissolved ferrous sulfate are removed by suction filtration. The solution so obtained, (A), is placed over sulfuric acid *in vacuo* to obtain (X), which will appear as the monohydrate (XI), after several days of standing in the cold. The light green crystal cake, so obtained, is pressed between filter paper and dried over sulfuric acid where it soon changes to the dehydrated form (X). (IX) is obtained by adding alcohol to (A) till a dark green oil settles. This oil soon crystallizes and the crystalline mass is filtered off and washed with 10 ml. of alcohol. The compound soon loses water, even in air, and becomes the dihydrate (IX), the color changing from green to light yellow. This change is complete in fifteen or twenty minutes.

(XII) is prepared by dissolving 15 g. of $MnCl_2 \cdot 4H_2O$ in 14 g. of glycol on the water-bath. The filtered solution is placed over sulfuric acid *in vacuo*. After a day incipient crystallization and simultaneous dehydration to a gelatinous mass takes place. The mixture is now diluted with 5–10 ml. of alcohol and kept over sulfuric acid in the cold. After a day or so crystallization is almost complete. The mass is pressed between filter paper and dried for two days over sulfuric acid.

Organic analysis of the compounds precipitated by alcohol, by forming the *p*-nitrobenzoate derivative, indicated that no ethyl alcohol was present.[3]

Analysis was carried out for the metal in each compound by standard methods. The given data represent the average of several analyses and are shown in Table I, together with the color of the respective compounds.

TABLE I

Compound	Metal, % Calcd.	Metal, % Found	Color
I	22.40	22.30	Light blue
II	28.68	28.96	Light blue
III	14.56	14.55	Light green
IV	16.35	16.31	Light green
V	19.77	19.77	Light green
VI	18.65	18.45	Dark blue
VII	17.65	17.66	Pink
VIII	21.67	21.58	Dark blue
IX	22.34	22.37	Light yellow
X	16.52	16.49	Light yellow
XI	15.68	15.51	Yellow green
XII	20.48	20.47	Light rose

Magnetic Measurements.—The results of the magnetic measurements on the solid compounds in powder form by the method of Gouy at 25° are shown in Table II. In the column listing the Bohr magnetons, the calculations have been made assuming complete quenching of the orbital moment. In the conversion of the experimental data into Bohr magnetons a correction has been made for the diamagnetism of the molecule. Not measured magnetically was (VI), because the dehydrated form is too hygroscopic to permit measurement. Also, (XI) and the green form first obtained in the preparation of (IX) could not be measured magnetically, as water is lost too quickly and a change to the yellow forms takes place.

TABLE II

Compound	$\chi_g \times 10^6$	$\chi_m \times 10^6$	Bohr magnetons Exptl.	Bohr magnetons Calcd.	Unpaired electrons present
I	5.67	1636	2.0	1.73	1
II	7.31	1657	2.0	1.73	1
III	12.50	5241	3.6	2.83	2
IV	12.55	4580	3.3	2.83	2
V	16.00	4874	3.4	2.83	2
VII	34.37	11660	5.3	3.88	3
VIII	38.40	10590	5.1	3.88	3
IX	44.70	11290	5.2	4.90	4
X	34.30	11730	5.3	4.90	4
XII	49.10	13300	5.7	5.92	5
XIII	36.15	10550	5.0	3.88	3
XIV	23.30	10640	5.0	3.88	3

Discussion

Analyses and magnetic measurements indicate that the light transition metals undergo complex formation with glycol. The complex salts so obtained are crystalline and, with the exception of the ferrous salts, very hygroscopic. The compounds investigated show good stability for the most part and lose glycol only over strong desiccating agents like phosphorus pentoxide or sulfuric acid. Exceptions are the ferrous glycol complexes and the cobalt pyridine complexes. The former are quite susceptible to oxidation, especially (IX), which is oxidized with great rapidity as soon as the second molecule of water is lost. The ferrous complexes also tend to lose water, rather than take it up. This made it impossible to analyze the green form of (IX) and also made magnetic measurement of (XI) unfeasible.

It is seen that the experimental values for the magnetic moments are well within the range of values commonly found.[4] The assumption of ionic

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[3] Cretcher and Pittinger, THIS JOURNAL, **47**, 2560–2563 (1925).

[4] Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 114.

or weakly covalent sp^3 bonds in each compound measured seems, therefore, justified, with the possible exception of the cupric complexes, for which there is no magnetic criterion of bond type. However, the formation of essentially ionic complexes throughout the rest of this series makes such a structure for copper at least probable. The large orbital contribution to total moment, which was encountered in all compounds except (XII), is also an indication of the largely ionic character of the bonds.[5]

It is also found that the color change of cobaltous salts from red to blue cannot be explained on the basis of a change in complex structure, since both the red (VII) and the blue (VIII), cobaltous complexes measured are found to be essentially ionic.

Summary

It has been possible to synthesize several glycol complexes of some of the light transition metals and of cupric ion. As far as can be determined from magnetic data all the complexes measured magnetically are essentially ionic. The probability of ionic cupric complexes in the series is increased by the fact that related metal complexes are ionic in form. It has been found that the color change of the cobaltous complexes investigated is independent of geometrical form.

CLAREMONT, CALIF. RECEIVED APRIL 10, 1944

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[5] Russell, Cooper and Vosburgh, THIS JOURNAL, **65**, 1301-1306 (1943).

[CONTRIBUTION NO. 523 FROM THE DEPARTMENTS OF CHEMISTRY AND PHYSICS, UNIVERSITY OF PITTSBURGH]

X-Ray Investigation of Glycerides. I. Diffraction Analyses of Isomeric Monoglycerides[1]

BY L. J. FILER, JR., S. S. SIDHU, B. F. DAUBERT AND H. E. LONGENECKER

The presence of a large number of isomeric glycerides of closely related physical properties complicates the study of the glyceride composition of natural fats. Since the complexity of these glyceride mixtures has militated against the effective separation of individual glyceride components, an alternative and necessary approach to the study of natural fats has been through the synthesis of glycerides of known configuration and their subsequent characterization.

The glycerides which have thus far been obtained by synthesis usually have been characterized by measurements of their refractive indices, determination of solubility data, melting points of their polymorphic forms, and, in a few instances, heats of combustion. For the purpose of providing more complete identification, X-ray diffraction data for pure synthetic glycerides should be made available. The value of the diffraction diagram for further characterization of synthetic compounds has been fully appreciated only recently in the study of natural fats. When complete long and short spacing data, characteristic for each synthetic glyceride, can be obtained from diffraction diagrams, a supplementary means will have been provided for the positive identification of those glycerides isolated from natural sources. From these accumulative data it is entirely probable that single components in simple glyceride mixtures may be correctly identified as to structure and configuration. Furthermore, it is quite possible that the correlation of all data from thermal curves, X-ray diffraction diagrams, measurements and observations of other physical properties will help in the fundamental interpretation of the relationships of these properties and also provide the necessary data for the identification of naturally occurring glycerides. In a recent review, Ferguson and Lutton[2] have already indicated the desirability of such information. "To identify a single glyceride by X-ray alone without known materials for comparison would be difficult even if the number of possible glycerides could be limited to a few. However, the first steps have been taken to make such identification a real possibility, and, combined with multiple melting points, the X-ray method should serve in many instances to give far more certain results than have hitherto been possible."

In 1934 it was recognized clearly by McElroy and King[3] that powder diffraction diagrams could provide independent evidence of the difference in structure between synthetic isomeric mixed triglycerides. Their data[4] clearly indicated that a specific diffraction pattern was associated with a given triglyceride and that isomeric triglycerides were distinguished on the basis of individual patterns. These investigators, however, reported only limited short spacing data on the solvent crystallized (stable form) compounds.

In a study of the thermal and X-ray properties of many glyceride types, Malkin and associates[5] showed the tremendous supplementary importance of diffraction data for characterization of the different polymorphic forms of synthetic glycerides. Unfortunately, their data are insuffi-

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[1] A grant by the Buhl Foundation in support of this investigation is gratefully acknowledged. Presented at the 107th meeting of the American Chemical Society, Cleveland, Ohio, April 2-6, 1944.

[2] Ferguson and Lutton, *Chem. Rev.*, **28**, 379 (1941).

[3] McElroy and King, THIS JOURNAL, **56**, 1191 (1934).

[4] McElroy, Ph.D. Thesis, University of Pittsburgh, 1934, University of Pittsburgh Bulletin, **31**, 263 (1934).

[5] Malkin and Meara, *J. Chem. Soc.*, 1141 (1939); see other papers of the series.