

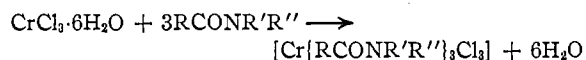
CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF MARYLAND, COLLEGE PARK, MARYLANDChromium(III)-Amide Complex Compounds¹

By CARL L. ROLLINSON AND RUDOLPH C. WHITE

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It has been found that the displacement of water molecules from $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$ by N-substituted amide molecules is quite general. By azeotropic distillation of a benzene solution of $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$ and a substituted amide (A) the reaction can be driven to completion. By means of this procedure, several violet compounds of the type $[\text{CrA}_3\text{Cl}_3]$ and a green compound of the type $[\text{CrA}_4\text{Cl}_2]\text{Cl}$ have been prepared. Evidence has been obtained indicating that the amides coordinate through the oxygen atom. The absorption spectra in the visible region of $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$ in dimethylformamide and dimethylacetamide are compared with those of $[\text{Cr}\{\text{HCON}(\text{CH}_3)_2\}_3\text{Cl}_3]$ and $[\text{Cr}\{\text{CH}_3\text{CON}(\text{CH}_3)_2\}_3\text{Cl}_3]$ and the effect of water on the spectrum of the latter is shown.

In the course of a study involving the synthesis of chromium-amine complex compounds, a dimethylformamide solution of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ was azeotropically dehydrated with benzene. The reaction observed is one of a series that can be represented by the general equation



The reaction occurs with amides in which R is H or an alkyl group such as methyl, and R' and R'' are groups such as methyl, phenyl, etc., or one of these groups and hydrogen.

Some of the amide complex compounds isolated decompose rapidly in contact with atmospheric moisture while others are relatively stable in this respect. They dissolve in water to yield solutions of aquo compounds. Reversal of the reaction by which they are formed is shown by the spectra of the dimethylacetamide-water solutions of $[\text{Cr}\{\text{CH}_3\text{CON}(\text{CH}_3)_2\}_3\text{Cl}_3]$ (Table I; Fig. 3). As the ratio of water to complex compound increases, the absorption maximum appears to approach that of $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$.

Insufficient data are available to establish with certainty the geometrical configuration of the violet triamide compounds. Infrared spectra indicate quite conclusively that the configuration of the green dichlorotetra-(2-pyrrolidinone)-chromium(III) chloride is *trans*.

It is quite probable that the amides coordinate with chromium through the oxygen atom. The infrared spectra of the complex compounds do not differ greatly from those of the corresponding amides except for a shift (40–70 cm^{-1}) of the carbonyl band to lower frequencies, indicating

(1) Abstracted in part from the Ph.D. thesis of R. C. White, University of Maryland, July, 1959.

TABLE I

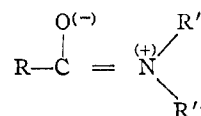
ABSORPTION MAXIMA OF TRIS-(N,N-DIMETHYLACETAMIDE)-TRICHLOROCHROMIUM(III) IN DIMETHYLACETAMIDE AND DIMETHYLACETAMIDE-WATER MIXTURES

Curve, Fig.	Solution	Molarity		Absorption maximum	
		H ₂ O	Cr	H ₂ O/ Cr	λ , μ
1	$[\text{Cr}(\text{dma})_3\text{Cl}_3]$ in dma ^a	0	0.02	0	515 56.3 ^b
...	$[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$ in dma ^c	0.08	.02	4	515 52.3
2	$[\text{Cr}(\text{dma})_3\text{Cl}_3]$ in dma + H ₂ O ^d	1.11	.0196	62	490 45.8
3		2.22	.0192	123	480 42.7
...	$[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3]$ ¹¹	475 ...
4	$[\text{Cr}(\text{dma})_3\text{Cl}_3]$ in dma + H ₂ O ^d	3.33	.0183	135	473 40.5
5		4.44	.0184	247	468 38.5
6	$[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3]$ ¹¹	5.55	.0180	308	460 37.8
7	0180	...	450 27.9

^a dma = dimethylacetamide. ^b From spectrum determined immediately after preparation of solution. ^c From spectra obtained 24 hr. after preparation of solutions.

interaction of the carbonyl group.² Similar results obtained with MgCl_2 ³ and TiCl_4 -dimethylformamide⁴ compounds also have been interpreted as indicating that the carbonyl is the donor group.

This conclusion is consistent with the fact that resonance structures enhance the ability of the oxygen atom to act as an electron-pair donor.⁵ Restricted rotation in N-substituted amides, leading to the planar form



has been demonstrated by nuclear magnetic

(2) R. B. Penland, S. Misushima, C. Curran, and J. V. Quagliano, *J. Am. Chem. Soc.*, **79**, 1575 (1957).

(3) D. Cook, *Can. J. Chem.*, **38**, 2143 (1960).

(4) J. Archambault and R. Rivest, *ibid.*, **36**, 1461 (1958).

(5) A. Weissberger, "Techniques of Organic Chemistry," Vol. IX, Interscience Publishers, New York, N. Y., 1959, p. 523.

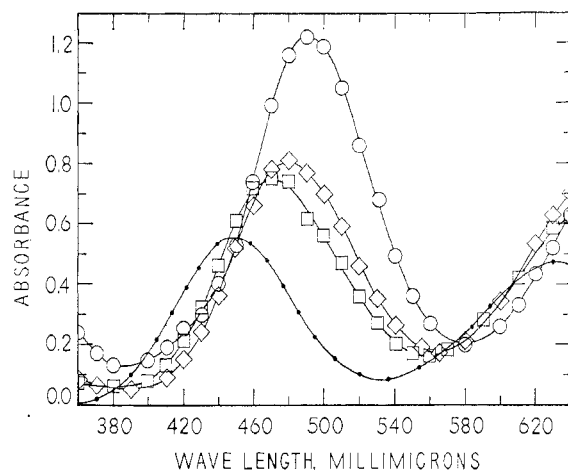


Fig. 1.—Absorption spectra of: $[\text{Cr}\{\text{HCON}(\text{CH}_3)_2\}_3\text{Cl}_3]$ in dimethylformamide, O; $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$ in dimethylformamide, immediately after preparation of solution, □, and after 24 hr., ◇; $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$,¹¹ aqueous solution, ●; all solutions 0.02 M.

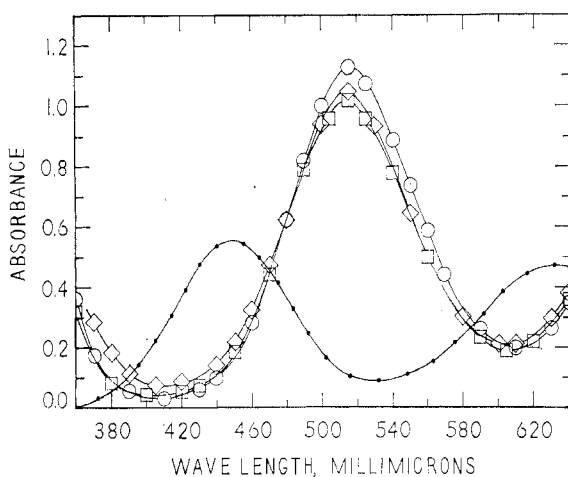


Fig. 2.—Absorption spectra of: $[\text{Cr}\{\text{CH}_3\text{CON}(\text{CH}_3)_2\}_3\text{Cl}_3]$ in dimethylacetamide, O; $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$ in dimethylacetamide, immediately after preparation of solution, □, and after 24 hr., ◇; $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$,¹¹ aqueous solution, ●; all solutions 0.02 M.

resonance measurements.⁶⁻⁸ The contribution of this structure will depend on the nature of R, R', and R''.

The marked effect of changing R from H to CH_3 is shown by the absorption spectra of the triamide complexes of dimethylformamide and dimethylacetamide (Fig. 1 and 2). Not only is the wave length of the maximum considerably longer for the latter, but also conversion of the tetra-aquo compound to the triamide complex is more

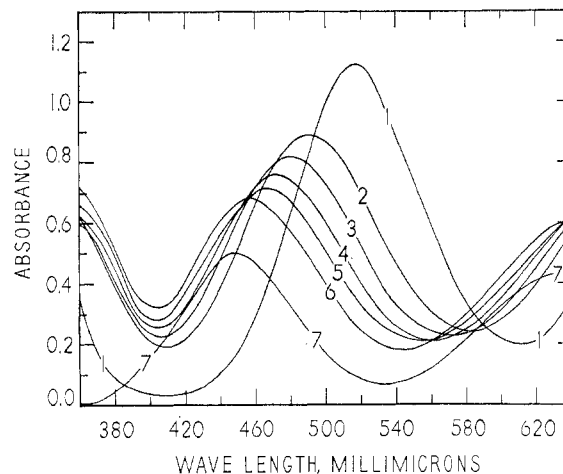


Fig. 3.—Absorption spectra of: $[\text{Cr}\{\text{CH}_3\text{CON}(\text{CH}_3)_2\}_3\text{Cl}_3]$ in dimethylacetamide (0.02 M solution), 1; $[\text{Cr}\{\text{CH}_3\text{CON}(\text{CH}_3)_2\}_3\text{Cl}_3]$ in dimethylacetamide-water mixtures (compositions given in Table I), 2-6; $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$,¹¹ aqueous solution (0.018 M), 7.

nearly complete, and equilibrium is reached more rapidly in dimethylacetamide than in dimethylformamide. Further investigation of the effect of structure of the amide is in progress.

Experimental

Analytical Procedures.—Solutions were prepared for chromium determination by wet-ashing samples with nitric, sulfuric, and perchloric acids, neutralization, and addition of sodium peroxide to ensure complete oxidation of chromium. The solutions, acidified with sulfuric and phosphoric acids, were titrated with ferrous ammonium sulfate solution to the diphenylamine sulfonate end-point. The reliability of the procedure¹ was confirmed by analysis of synthetic samples prepared from N.B.S. $\text{K}_2\text{Cr}_2\text{O}_7$, reagent grade NaCl, and anhydrous ethylenediamine.

Total chloride was determined by potentiometric titration of sample solutions after decomposition of the complex compound. This may be accomplished by adding sodium hydroxide, heating, and dissolving the precipitated chromium hydroxide in HNO_3 ⁹; or by adding ammonium acetate and warming the solution, the acetate ion displacing coordinated chloride.¹⁰

An interesting phenomenon is observed if the complex is not deliberately decomposed prior to the titration. When a sample of a triamide complex is put in water, there is an immediate color change from violet to green as the compound hydrolyzes, but only about two thirds of the chloride is ionic initially; considerable time is required for all the chloride to become ionic. The following data are typical; the figures are for per cent. of total chloride titrated after 3 min., 7 min., 70 min., and 24 hr.:

$[\text{Cr}\{\text{CH}_3\text{CON}(\text{CH}_3)_2\}_3\text{Cl}_3]$	70.8	74.7	86.6	100.0
$[\text{Cr}\{\text{CH}_2(\text{CH}_2)_2\text{CONCH}_2\}_3\text{Cl}_3]$	68.3	70.2	84.8	99.4

It is tempting to speculate as to the significance of these

(6) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

(7) W. D. Phillips, *ibid.*, **23**, 1363 (1955).

(8) A. Berger, A. Loewenstein, and S. Meiboom, *J. Am. Chem. Soc.*, **81**, 62 (1959).

(9) H. G. Murad, M.S. Thesis, University of Maryland, 1957.

(10) A. Schwebel, Ph.D. Thesis, University of Maryland, 1958.

results with respect to the configuration of the complex, although they may reflect only the rate of aquation of the chloropentaquochromium(III) ion.

Carbon, hydrogen, and nitrogen were determined by microanalysis. We are indebted to Miss J. Swan and Mrs. R. Baylouny for their careful performance of these somewhat difficult determinations.

Synthesis of Chromium-Amide Compounds.—The apparatus used consisted of a flask (250, 500, or 1000 ml.), fitted with a mechanical stirrer and Barrett trap with reflux condenser, heated by a heating mantle. In the smaller scale experiments a 5-ml. Dean-Stark trap graduated to 0.1 ml. was substituted for the Barrett trap.

The usual starting material was reagent grade $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, which is essentially $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$.¹¹ This was purified or purified and dehydrated¹² for some experiments.

Anal. Calcd. for $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$: Cr, 19.52; Cl, 39.9; ratio Cl/Cr, 3.00. Found: Cr, 19.53; Cl, 39.8; Cl/Cr, 2.98. Calcd. for $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$: Cr, 22.57; Cl, 46.2; ratio Cl/Cr, 3.00. Found: Cr, 22.65; Cl, 45.9; Cl/Cr, 2.97.

The reaction mixture (aquo-chromium compound, amide, and benzene) was refluxed and stirred. As the water was removed, the green color changed to violet (except with 2-pyrrolidinone). With $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$, the color of the reaction mixture usually does not change until some water has distilled; if $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$ is used, the color change occurs as soon as the salt is added to the amide-benzene solution with the more strongly coordinating amides.

The cooled reaction mixtures were filtered by suction. The products were washed with anhydrous ether or anhydrous alcohol followed by anhydrous ether. They usually were dried by storage over P_2O_5 in a desiccator.

Tris-(N,N-dimethylformamide)-trichlorochromium-(III).—Numerous samples of this compound, prepared with slight modifications of the procedure, have varied in chromium content from 13.2 to 13.8% and in chloride content from 27.8 to 28.2%. Since no satisfactory solvent for recrystallizing the compound has been found, its purity depends on the use of pure reagents and care in preparation.

As the reaction mixture (10 g. of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, 25 ml. of dimethylformamide, 100 ml. of redistilled benzene) is dehydrated, the distillate is drained from the trap at intervals until 50 ml. of benzene has been removed. After the addition of 125 ml. of benzene, distillation is continued until an additional 75 ml. of benzene has collected, which requires about 1.5 hr. At this point, a small amount of product usually separates.

The cooled reaction mixture should be filtered rapidly to remove adhering solvent as quickly as possible. Subsequent operations also should be conducted as rapidly as possible since the compound is very hygroscopic and decomposes rapidly on exposure to the atmosphere. In a typical experiment the yield was 11.3 g. (79.6%).

Anal. Calcd. for $[\text{Cr}\{\text{HCON}(\text{CH}_3)_2\}_3\text{Cl}_3]$: Cr, 13.8; Cl, 28.2; ratio Cl/Cr, 3.00; C, 28.7; H, 5.61; N, 11.18. Found: Cr, 13.5; Cl, 28.2; ratio Cl/Cr, 3.04; C, 29.5; H, 5.73; N, 11.57.

Tris-(N,N-diphenylformamide)-trichlorochromium-

(III).—To a solution of 13.5 g. of diphenylformamide in 75 ml. of benzene which has been azeotropically dehydrated for an hour is added 4 g. of $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$. As the reaction mixture is dehydrated, most of the chromium salt dissolves and a gray-violet product precipitates. Dehydration is complete in about 2.5 hr. The yield is 8.8 g. (67.5%). The high chloride content of typical preparations (15.0%) may be due to a small amount of unreacted or partially converted starting material; also this is indicated by the green insoluble matter observed when the crude product is recrystallized from 1-nitropropane. The yield on recrystallization (5 g. of crude material, 100 ml. of 1-nitropropane at 100°) is 2.2 g. (44% based on crude product).

Anal. Calcd. for $[\text{Cr}\{\text{HCON}(\text{C}_6\text{H}_5)_2\}_3\text{Cl}_3]$: Cr, 6.94; Cl 14.2; ratio Cl/Cr, 3.00; C, 62.5; H, 4.43. Found: Cr, 6.74; Cl, 13.9; ratio Cl/Cr, 3.03; C, 59.8; H, 5.81.

Tris-(N,N-dimethylacetamide)-trichlorochromium-(III).—Dehydration of the reaction mixture ($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, 20 g.; dimethylacetamide, 50 ml.; benzene, 150 ml.) is complete in about 2.5 hr. Well-defined reddish-violet crystals separate even from the boiling solution. The product may be air-dried for about 15 min. and then dried at 80° for several hours, or dried over P_2O_5 . In a typical experiment, the yield was 25.6 g. (81.5%).

Anal. Calcd. for $[\text{Cr}\{\text{CH}_3\text{CON}(\text{CH}_3)_2\}_3\text{Cl}_3]$: Cr, 12.4; Cl, 25.3; ratio Cl/Cr, 3.00; C, 34.3; H, 6.48; N, 10.01. Found: Cr, 12.4; Cl, 25.3; ratio Cl/Cr, 2.99; C, 33.9; H, 6.35; N, 9.08.

A very pure granular product can be obtained by using a reaction mixture consisting of $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$ (9.22 g.), benzene (350 ml.), and a tenfold excess of dimethylacetamide (104.5 g.). The yield is about 18.2 g. (77%).

Anal. Calcd. for $[\text{Cr}\{\text{CH}_3\text{CON}(\text{CH}_3)_2\}_3\text{Cl}_3]$: Cr, 12.4; Cl, 25.3; ratio Cl/Cr, 3.00; C, 34.3; H, 6.48; N, 10.01. Found: Cr, 12.3; Cl, 25.3; ratio Cl/Cr, 3.01; C, 34.2; H, 6.38; N, 10.99.

Less pure products obtained with other amide-benzene ratios were recrystallized from 1-nitropropane in 80–90% yield with considerable increase in purity. However, if the synthesis is performed as described with pure reagents the product obtained is sufficiently pure without recrystallization. This compound is much less sensitive to moisture and is easier to prepare in pure form than the analogous dimethylformamide compound.

Tris-(N,N-diethylacetamide)-trichlorochromium(III).—When reaction mixtures of $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$, benzene, and N,N-diethylformamide are dehydrated, the usual color change from green to violet occurs, and it is not difficult to remove all the water. Negative results were obtained in attempts to isolate a solid compound by the usual procedures of varying the concentrations of reagents, removing excess solvent, etc.

Addition of dimethyl sulfoxide to the reaction mixture causes precipitation of a small amount of gray-violet solid, apparently the impure triamide complex compound. This is unstable and decomposes even in a desiccator over P_2O_5 .

Anal. Calcd. for $[\text{Cr}\{\text{CH}_3\text{CON}(\text{C}_2\text{H}_5)_2\}_3\text{Cl}_3]$: Cr, 10.3; Cl, 21.2; ratio Cl/Cr, 3.00. Found: Cr, 11.3; Cl, 22.9; ratio Cl/Cr, 2.99.

Tris-(N-methyl-2-pyrrolidinone)-trichlorochromium-(III).—The color of the reaction mixture ($[\text{Cr}(\text{H}_2\text{O})_4$ -

(11) P. J. Elving and B. Zemel, *J. Am. Chem. Soc.*, **79**, 1281 (1957).

Cl₂]Cl, 9.22 g.; N-methyl-2-pyrrolidinone, 24 g.; benzene, 125 ml.) turns from green to violet even before heating is started. Dehydration is complete in about 1.5 hr., during which about 50 ml. of benzene distills and is withdrawn. The yield is 11.3 g. (62%).

Anal. Calcd. for [Cr{CH₂(CH₂)₂CONCH₃}₃Cl₃]: Cr, 11.4; Cl, 23.3; ratio Cl/Cr, 3.00; C, 39.5; H, 5.97; N, 9.22. Found: Cr, 11.3; Cl, 23.2; ratio Cl/Cr, 3.02; C, 39.8; H, 6.15; N, 9.22.

This compound is quite stable and non-hygroscopic. It can be left exposed to the atmosphere for several hours without decomposition while [Cr{HCON(CH₃)₂}₃Cl₃] hydrolyzes and decomposes in a short time.

Tris-(ε-caprolactam)-trichlorochromium(III).—Dehydration of the reaction mixture (9.22 g. of [Cr(H₂O)₄Cl₂]Cl, 20 g. of ε-caprolactam, 135 ml. of C₆H₆) is complete in about 1 hr. and 20 min. At this point, 75 ml. of benzene is distilled and removed through the trap. About 13.8 g. of product is obtained (69.5% yield).

Anal. Calcd. for [Cr{CH₂(CH₂)₄CONH}Cl₃]: Cr, 10.5; Cl, 21.4; ratio Cl/Cr, 3.00. Found: Cr, 10.4; Cl, 21.1; ratio Cl/Cr, 2.99.

The product apparently is contaminated with a little ε-caprolactam, which is not very soluble in benzene at room temperature. When 5 g. of the crude material is recrystallized from 100 ml. of boiling benzene, 3.5–4.0 g. dissolves, and the yield of purified product is 2.2 g. (55–63%).

Anal. Calcd. for [Cr{CH₂(CH₂)₄CONH}Cl₃]: Cr, 10.5; Cl, 21.4; ratio Cl/Cr, 3.00; C, 43.4; H, 6.68; N, 8.44. Found: Cr, 10.5; Cl, 21.4; ratio Cl/Cr, 3.00; C, 43.5; H, 6.69; N, 8.40.

The crystals obtained in this synthesis are light violet with a silvery sheen. Of the compounds isolated in this investigation, this is outstanding in the ease with which it can be prepared and purified and in stability. Its solubility in benzene, acetone, and dioxane contrasts markedly with the behavior of the other triamide compounds. It is insoluble in water; it hydrolyzes with formation of a solution of aquo compounds only after a considerable period of heating. The reaction is slow because the crystals are not easily wetted. If an acetone solution of the compound is poured in water, hydrolysis occurs rapidly.

trans-Dichlorotetra-(2-pyrrolidinone)-chromium(III) Chloride.—The green reaction mixture (CrCl₃·6H₂O, 10 g.; 2-pyrrolidinone, 27 g.; benzene, 125 ml.), which is dehydrated completely in about 1.5 hr., does not turn violet, but becomes somewhat darker. The product (pale green crystals) starts to precipitate when dehydration is nearly complete.

Anal. Calcd. for [Cr{CH₂(CH₂)₂CONH}Cl₂]Cl: Cr, 10.4; total Cl, 21.3; ratio Cl/Cr, 3.00; ionic Cl, 7.10; C, 38.5; H, 5.66; N, 11.23. Found: Cr, 10.2; total Cl, 20.9; ratio Cl/Cr, 2.99; ionic Cl,^{10,12} 7.86; C, 38.7; H, 5.69; N, 11.47.

In a variant of the procedure the reaction mixture consists of 9.22 g. of [Cr(H₂O)₄Cl₂]Cl, 136.2 g. of 2-pyrrolidinone (a tenfold excess), and 350 ml. of benzene. The

yield is 14.5–15.5 g. (72.6–77.6%).

Anal. Calcd. for [Cr{CH₂(CH₂)₂CINH}Cl₂]Cl: Cr, 10.4; Cl, 21.3; ratio Cl/Cr, 3.00. Found: Cr, 10.3; Cl, 21.2; ratio Cl/Cr, 3.04.

This compound is quite stable and non-hygroscopic. It is soluble in water but cannot be recrystallized from it because of rapid hydrolysis. It also is soluble in 2-pyrrolidinone but attempts to recrystallize it from this solvent have not been successful.

The only structural difference between 2-pyrrolidinone and ε-caprolactam, which forms a triamide compound, is the smaller ring size of the former. If it is significant that both are N-monosubstituted, it might be expected that both would behave differently from the N,N-disubstituted cyclic amide, N-methyl-2-pyrrolidinone, but one does, and the other does not. Conceivably there is an equilibrium among several chromium complex compounds in the amide solution, the relative coordinating tendency of the amide determining the predominant species; or if such an equilibrium exists, the least soluble compound would crystallize.

Tests with Other Amides.—Many variants of the synthetic procedure described have been tried in unsuccessful attempts to obtain solid identifiable compounds from several other amides, although in some cases there was evidence that coordination occurs. Reaction mixtures containing diethylformamide remained green until all solvent was removed by vacuum distillation, which resulted in formation of a red-violet viscous material. With dibutylacetamide, the reaction mixtures turned red almost immediately and were easily dehydrated; vacuum distillation resulted in formation of viscous products that could not be recrystallized. Somewhat similar results were obtained with diphenylacetamide, although the aquo-chromium compound did not dissolve completely. A red-violet viscous oil was obtained with N-phenylacetamide (acetanilide). The characteristic color change occurs with N-vinyl-2-pyrrolidinone; dark viscous products were obtained by vacuum distillation of the reaction mixtures.

With N-phenylformamide (formanilide) the reaction mixtures remain green even after complete dehydration and vacuum distillation, nor does the aquo-chromium compound ever dissolve completely. No identifiable compound could be obtained from the dark green viscous products.

The aquo complex is not soluble in a mixture of benzene and N-(p-hydroxyphenyl)-acetamide. Coordination apparently does not occur since attempts to dehydrate the reaction mixtures were not successful. Similar results were obtained with formamide and acetamide.

Spectra of Triamide-Chromium Complex Compounds in the Visible Region.—The amides used as solvents and blanks were Eastman "white label" products, azeotropically dried with benzene and distilled through a 61-cm. column. The boiling points of the fractions used were: dimethylformamide, 152.5–153.5°; dimethylacetamide, 163–164°. In the preparation of solutions and determination of spectra, numerous precautions were observed to minimize exposure of the hygroscopic solutions to atmospheric moisture. The data were obtained with a Spectronic 20 spectrophotometer equipped with a Roto-Cell and dual cell of 1-cm. light path. Data for the curves of [Cr(H₂O)₄Cl₂]Cl in water were computed from Elving and Zemel's results.¹¹

(12) A. Nilubol, M.S. Thesis, University of Maryland, 1955.

The spectrum of $[\text{Cr}\{\text{CH}_3\text{CON}(\text{CH}_3)_2\}_3\text{Cl}_3]$ was determined immediately after preparation of the solution and again, in the regions of maximum and minima, after 24 hr. Except for an increase in the short wave length minimum, little change had occurred. Since the solution of $[\text{Cr}\{\text{HCON}(\text{CH}_3)_2\}_3\text{Cl}_3]$ had turned green, an indication of hydrolysis, its spectrum was not redetermined.

The spectra of dimethylformamide and dimethylacetamide solutions of $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$ (0.02 *M* solutions) were obtained by the procedure described immediately after preparation of the solutions and again after 24 hr. The difference in absorption spectra of aqueous and dimethylformamide solutions of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ also was observed by Pflaum and Popov.¹³ The results of the present investigation confirm their conclusion that the effect is attributable to displacement of water molecules by amide molecules.

The curves for the dimethylacetamide-water solutions of $[\text{Cr}\{\text{CH}_3\text{CON}(\text{CH}_3)_2\}_3\text{Cl}_3]$ (Fig. 3) were plotted from data taken 24 hr. after preparation of the solutions; the blank in each case was dimethylacetamide containing the same amount of water as the solution. Composition of the solutions is shown in Table I, which also shows some features of the spectra in comparison with those of $[\text{Cr}(\text{H}_2\text{O})_6\text{Cl}_3]$ and $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$.

Infrared Spectra.—The infrared spectra of five chromium-amide compounds were determined with Nujol mulls; spectra of the corresponding amides were determined with thin films. The spectra obtained for dimethylformamide and dimethylacetamide were in good agreement

with those previously reported.¹⁴ We are indebted to Mr. W. Fearheller of this Department for obtaining these spectra.

Coördination of the amide caused no great change in its spectrum except for a considerable shift of the carbonyl band. This is split into two bands in the triamide compounds. The single peak observed for the carbonyl band in the 2-pyrrolidinone complex is in accord with the highly symmetrical structure of the *trans* isomer.¹⁵

In the following the pertinent data are given in the order: $\bar{\nu}$ (cm^{-1}) of the carbonyl band of the amide; $\bar{\nu}$ of the carbonyl band of the amide in the complex compound; shift (wave numbers) of strong band due to coördination (*s* indicates the strong absorption band): tris-(*N,N*-dimethylformamide)-trichlorochromium(III): 1670 *s*; 1665, 1630 *s*; 40; tris-(*N,N*-dimethylacetamide)-trichlorochromium(III): 1655 *s*; 1620, 1585 *s*; 70; tris-(*N*-methyl-2-pyrrolidinone)-trichlorochromium(III): 1685 *s*; 1660, 1615 *s*; 70; tris-(ϵ -caprolactam)-trichlorochromium(III): 1670 *s*; 1660, 1615 *s*; 55; *trans*-dichlorotetra-(2-pyrrolidinone)-chromium(III) chloride: 1690 *s*; 1620 *s*; 70.

Acknowledgment.—The authors are indebted to the Mutual Chemical Division, Allied Chemical and Dye Corporation, for financial assistance which facilitated this investigation; and to Prof. Ellis Lippincott of this Department for assistance in obtaining and interpreting the infrared spectra.

(14) Sadtler Standard Spectra.

(15) J. P. Faust and J. V. Quagliano, *J. Am. Chem. Soc.*, **76**, 5346 (1954).

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CONTRIBUTION FROM WM. A. NOYES LABORATORY,
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Spectrochemical Studies of Dimethyl Sulfoxide, Tetramethylene Sulfoxide, and Pyridine *N*-Oxide as Ligands with Nickel(II), Chromium(III), and Cobalt(II)

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A comparison of the values of the crystal field parameter, Dq , for octahedral complexes of Ni(II) and Co(II) with water, dimethyl sulfoxide, tetramethylene sulfoxide, and pyridine *N*-oxide produces the spectrochemical series: $\text{H}_2\text{O} > \text{C}_6\text{H}_5\text{NO} > \text{DMSO} \sim \text{TMSO}$. Toward Cr(III) a different series is obtained: $\text{H}_2\text{O} > \text{DMSO} \sim \text{TMSO} > \text{C}_6\text{H}_5\text{NO}$. The larger Dq values for the sulfoxides toward Cr(III), compared to pyridine *N*-oxide, are attributed to the greater polarizability of the S-O bond. The decrease of the P-F term splittings for the complexes, compared to the gaseous ion values, has been interpreted to indicate some covalency in the metal ion-ligand bond. This interaction produces the nephelauxetic series: $\text{DMSO} \sim \text{TMSO} > \text{H}_2\text{O} > \text{C}_6\text{H}_5\text{NO}$.

Introduction

Recently, we have discussed the preparation and properties of coördination complexes of di-

methyl sulfoxide with first row transition metal halides.^{3,4} The current interest in this area is indicated by the appearance of several other

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