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Some Substitution Reactions of Cobalt(III) Complexes in N,N-Dimethylformamide and Mixed Solvents

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Reactions of *trans*-$[Co(en)_2NO_2Cl]^+$ and related Co(III) complexes with thiocyanate have been studied in dimethylformamide (DMF) and DMF-based mixed solvents. The reactions are thiocyanate-independent and the rates in mixed solvents differ very little from those obtained in pure DMF. No effects ascribable to the variation in the nucleophilicity of the solvent molecule were observed. This may be interpreted to indicate a minor role for bond formation in the transition state and a predominantly dissociative mode of reaction.

Introduction

This study was motivated by a desire to obtain some direct kinetic evidence for bimolecular nucleophilic substitution (SN2) into Co(III) complexes of the class $[Co(en)_2AX]$ (en = ethylenediamine) where A is a nonlabile ligand and X is a labile ligand (here Cl^- or Br^-). Acid hydrolysis (aquation) of the complex with A = NO_2 is about the only example for which a generally accepted argument has been made for bimolecular substitution.[1-3] Briefly summarizing this case, the nitro-substituted complex aquates rather fast; the explanation notes that a nitro group is electron withdrawing in carbon compounds and suggests that it withdraws electrons from Co(III), facilitating bond formation with the entering nucleophile. This argument is part of a general mechanistic account of reactions of the complexes $[Co(en)_2AX]$. When A is varied from OH through CNS^- (decreasing electron donating power), the acid hydrolysis rate drops. Continuing through A = NH_3 and NO_2, the rate increases. The change in trend is attributed to a change in mechanism from dissociative (SN1) to bimolecular (SN2).

With the exception of OH^-, none of the entering anions that have been studied appear in the rate law when X is replaced. In a bimolecular mechanism, therefore, water must always be the effective nucleophile. Assuming pre-eminent nucleophilicity for water is perhaps not disturbing when the large concentration advantage of water over the anionic nucleophiles is considered.

The most novel feature of this study was a radically altered competitive position for nucleophiles. The solvent N,N-dimethylformamide (DMF) probably does not form as strong complexes with transition metals and is, therefore, of potentially lower nucleophilicity than water. Moreover, added nucleophiles (other solvents, etc.) were introduced in concentrations near the order of magnitude of the DMF concentration (*i.e.*, *ca.* 10 mole % additive). In these circumstances, a nucleophilicity order might be expected to appear for a bimolecular solvolysis step. Significantly, DMF should not promote dissociative reaction since it has a lower dielectric constant (37) than water and is thought to be a poorer solvent for chloride ions.[4] (However, conductance data show that a number of salts are completely dissociated in DMF, especially KCNS.)

In this report, the thiocyanate-independent replacements of chloride by thiocyanate in *trans*-$[Co(en)_2NO_2Cl]^+$, along with reactions of *trans*-$[Co(en)_2NO_2Br]^+$ and *trans*-$[Co(en)_2Cl_2]^+$, in pure DMF at several temperatures are described and data are given for thiocyanate-independent substitution into *trans*-$[Co(en)_2NO_2Cl]^+$ in the mixed solvents described above. It was not possible to study solvolysis in DMF directly because of the unfavorable equilibrium position.

Experimental

Materials.—The complexes, all well known, were prepared by the methods of Werner[5] with the exception of *trans*-bromonitrobis-(ethylenediamine)-cobalt(III) bromide, which was the gift of Dr. M. L. Tobe. The various salts obtained were converted to perchlorates by precipitation with concentrated perchloric acid from cold aqueous solution. Purity and identity of products was verified by comparison with visible spectra reported in the literature. Simple salts employed were reagent grade, dried but not further purified.

DMF obtained as Eastman "spectro grade" or Fisher "certified reagent" grade gave kinetic results equivalent to those obtained with DMF refluxed over BaO and distilled at reduced pressure. The commercial solvents were used in most experiments. Other solvents were either purchased in similar grades or purified by standard methods[6] with special attention to removal of water. Solids were "analyzed reagent" grades or subjected to conventional recrystallizations.

Reaction Studies.—Substitution rates were determined spectrophotometrically. In all cases except runs above 40°, the procedure was to add a solid sample of complex to a solution (containing potassium thiocyanate and enough potassium perchlorate to maintain ionic strength at 0.1) in a stoppered spectrophotometer cell previously thermostated (±0.10°) in the cell chamber of a Beckman DU spectrophotometer. The optical density at an appropriate wave length was measured at intervals over about 60% reaction. Experimental infinity absorptions were determined after 7 to 8 half-lives. The identity of products

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[1] C. K. Ingold, R. S. Nyholm, and M. L. Tobe, *Nature*, **187**, 477 (1960).

[2] F. Basolo and R. G. Pearson, *Advan. Inorg. Chem. Radiochem.*, **3**, 3 (1961).

[3] M. L. Tobe, *Sci. Progr.*, **48**, 483 (1960).

[4] A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962); (b) D. P. Ames and P. G. Sears, *J. Phys. Chem.*, **59**, 16 (1955).

[5] A. Werner, *Ann.*, **386**, 1 (1912).

[6] H. Weissberger, E. Proskaur, J. Riddick, and E. Toops, "Organic Solvents," Interscience, New York, N. Y., 1955.

was verified by comparing infinity spectra with spectra of synthetic samples. Principal visible absorption maxima and extinction coefficients for some Co(III) complexes in DMF are given in Table I.

TABLE I

ABSORPTION MAXIMA AND EXTINCTION COEFFICIENTS OF SOME Co(III) COMPLEXES IN DMF (400–700 mμ)

Complex	λ_{max}	Molar extinction coeff.
trans-$[Co(en)_2NO_2(SCN)]NO_3$	460	247
trans-$[Co(en)_2NO_2Cl]ClO_4$	489	113
trans-$[Co(en)_2NO_2Br]ClO_4$	500	118
trans-$[Co(en)_2Cl_2]ClO_4$	620	44
trans-$[Co(en)_2(NO_2)_2]NO_3$	434	268

Higher temperature reactions were run in sealed tubes in a thermostated oil bath (±0.1°). Tubes were removed at intervals and the reaction quenched in ice. Spectra of the cooled solution were immediately recorded on a Bausch and Lomb "Spectronic 505" recording spectrophotometer. Samples in these experiments usually were taken for 2 to 3 half-lives.

For each solvent mixture and temperature, kinetic experiments were performed at several thiocyanate concentrations from 0.015 to 0.10 *M*. The initial concentration of the complex was varied from 7×10^{-4} to 2×10^{-3} *M*. All of the kinetic data gave satisfactorily linear plots of the usual log $(A_\infty - A)$ *vs*. time type, from which first-order rate constants were calculated. The constants are reproducible within 5%.

Results

The main body of data from this study concerns the rate of thiocyanate replacement of the chloride of *trans*-$[Co(en)_2NO_2Cl]^+$ in DMF containing 1 *M* (*ca*. 10 mole %) concentrations of added compounds which may variously be regarded as solvents, potential nucleophiles, etc. The results are given in Table II. All the rate constants in the table are expressed as first-order constants. In the experiments summarized in Table II no evidence merges for thiocyanate influence on the rate. Figure 1 shows a typical result. The simple interpretation of thiocyanate-independent substitution is that the slow step of the reaction leads to the formation of an intermediate which then reacts rapidly with thiocyanate. This interpretation implies mass law retardation by chloride. In pure DMF the substitution rate is reduced to 4.6×10^{-5} sec.$^{-1}$ in a solution 0.10 *M* in KCNS and 0.0048 *M* in KCl and further reduced to 4.1×10^{-5} sec.$^{-1}$ where the KCl concentration is raised to 0.0073 *M*. It seems safe to disregard thiocyanate as a participant in the rate-determining step of these reactions.[7] As indicated in the table, the rates vary a little with the nature of the additive. However, several experiments indicate interpretable linear rate *vs*. concentration additive relations are not in general to be found. Therefore, we report first-order constants for a *single* additive concentration.

TABLE II

RATE OF REPLACEMENT OF Cl^- OF *trans*-$[Co(en)_2NO_2Cl]^+$ BY CNS^- IN DMF AT 35°

$[CNS^-] = 0.015$ to 0.10 *M*

Added reagent (1 *M*)	(sec.$^{-1}$) × 10^5
None	5.4 ± 0.3
H_2O	5.9 ± 0.2
Pyridine	4.7 ± 0.1
CH_3OH	5.8 ± 0.1
2-Propanol	5.8 ± 0.1
Urea	5.4 ± 0.2
CH_3COOH	3.6 ± 0.2
Phenol	5.2 ± 0.2

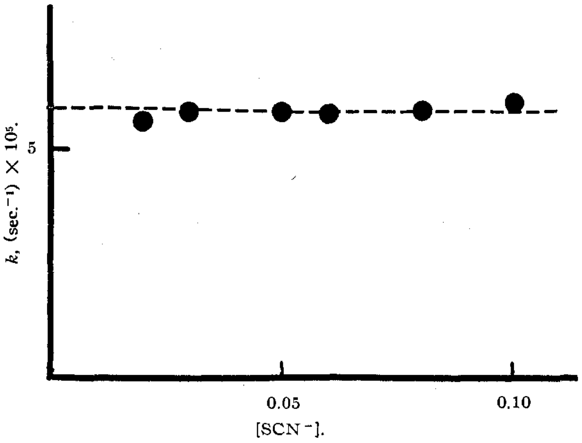

Fig. 1.—First-order rate constants for the reaction of thiocyanate with *trans*-$[Co(en)_2NO_2Cl]$ in DMF containing 1.0 *M* CH_3OH at 35°; $\mu = 0.10$.

The rates of thiocyanate substitution into *trans*-$[Co(en)_2NO_2Cl]^+$, *trans*-$[Co(en)_2NO_2Br]^+$, and *trans*-$[Co(en)_2Cl_2]^+$ in pure DMF were determined at several temperatures. Arrhenius activation energies are collected in Table III. Since it is probable that the slow step of the DMF reaction is mechanistically similar, activation energies and computed 35.0° rates for aqueous acid hydrolysis are included in Table III for comparison. The substitution into *trans*-$[Co(en)_2Cl_2]^+$ yielded the product $[Co(en)_2ClCNS]^+$ which reacted 10 to 100 times more slowly to yield $[Co(en)_2(CNS)_2]^+$, corresponding to a sizable reduction of the substitution rate as the A group is changed from Cl^- to CNS^-; this effect parallels the effect of the same change on aqueous acid hydrolysis rates.

The stereochemical results of the substitutions in DMF reported here are fairly unambiguous. *trans*-Nitro reactants led to the product *trans*-$[Co(en)_2NO_2CNS]^+$. The distribution of the products of substitution into *trans*-$[Co(en)_2Cl_2]^+$ was not determined but the infinity spectrum could plausibly be interpreted as that for a mixture of *cis*- and *trans*-$[Co(en)_2Cl(CNS)]^+$.

Discussion

(1) **The Role of Thiocyanate.**—We would have preferred to study the solvolysis of the *trans*-$[Co(en)_2NO_2X]^+$ ions in DMF and mixed solvents. However, Parker's[4] conclusions that anions are poorly solvated in DMF led to the prediction that the solvolysis equilibrium would be quite unfavorable. This prediction

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[7] In this connection, it is interesting that our rate of thiocyanate substitution into *trans*-$[Co(en)_2Cl_2]^+$ agrees with the low chloride concentration rate of chloride exchange in *trans*-$[Co(en)_2Cl_2]^+$ measured by Tobe and Watts in DMF at 50°. We are indebted to Dr. M. L. Tobe for communicating this result prior to publication.

TABLE III

RATES OF CNS SUBSTITUTION IN DMF, ACID HYDROLYSIS IN WATER, AND ARRHENIUS ACTIVATION ENERGIES

Complex	T, °C.	Solvent	k_1, sec.$^{-1}$	E_a, kcal./mole	Ref.
trans-$[Co(en)_2NO_2Cl]^+$	35.0	DMF (μ = 0.1)	5.4×10^{-5}	23.5 ± 1.0	
	49.4		3.2×10^{-4}		
	55.0		5.2×10^{-4}		
	35.0	H_2O	3.3×10^{-3}	21.5	*a*
trans-$[Co(en)_2NO_2Br]^+$	12.5	DMF (μ = 0.1)	4.5×10^{-5}	20.4 ± 0.5	
	16.8		7.1×10^{-5}		
	24.6		2.8×10^{-4}		
	25.5		2.9×10^{-4}		
	35.0		6.9×10^{-4}		
	35.0	H_2O	1.7×10^{-2}	22	*b*
trans-$[Co(en)_2Cl_2]^+$	35.0	DMF (μ = 0.1)	5.8×10^{-6}	24	
	65.0		2.0×10^{-4}		
	35.0	H_2O	1.2×10^{-4}	24	*a*
trans-$[Co(en)_2ClCNS]^+$	35.0	DMF (μ = 0.1)	$<5 \times 10^{-7}$		

[a] From a table compiled by M. L. Tobe, ref. 3. [b] C. H. Langford and M. L. Tobe, to be published.

was realized, but thiocyanate substitution appears to permit study of a reaction that is mechanistically equivalent in most important respects to solvolysis. The rate of entry of thiocyanate was independent of the thiocyanate concentration and mass law retardation by chloride was observed; the reaction is presumably a two-step process. The first step may involve dissociation of the complex to a five-coördinate intermediate or it may involve bimolecular reaction of the complex with the solvent.[8] If the first step is dissociative in character, it may lead to a long-lived five-coördinate intermediate which reacts with thiocyanate in the second step or it may lead only to a very short-lived five-coordinate species which picks up a solvent molecule before reacting with thiocyanate in the second step. When the reaction is studied under strictly thiocyanate-independent conditions, rate data are obtained for the first step. The main concern of this discussion is to determine the role of bond formation with solvent molecules in the activation process of the first step.

(2) The Role of Nucleophiles in the First Step.—One sensitive indicator of a major role for bond formation is a correlation of reaction rate with nucleophilicity. If bond formation with an entering group provides the driving force for a reaction, the activation energy and reaction rate should be markedly dependent on the ability of the entering group to form a partial bond with the atom under attack. This expectation is amply documented in the literature of genuine SN2 reactions. One example, perhaps relevant to discussions of Co(III) complexes, is the observation that pyridine attacks 10^4 times faster, and SCN^- 10^6 times faster, than water at Pt(II) centers.[9] In contrast, our results show that the substitution reactions are not detectably thiocyanate-dependent and do not vary appreciably in the presence of large concentrations of neutral nucleophiles of several different types. The variations are even less than might be expected from changes in solvent characteristics. The simplest interpretation is to assume that bond formation is *not* making a major contribution to activation. Of course, the bimolecular interpretation may be saved if DMF is assumed to be the "best nucleophile" in the same way that water is assumed to be the "best nucleophile" in the interpretation of reactions of $[Co(en)_2NO_2X]^+$ in water. Such an assumption is not convincing because the comparable concentrations of solvent and additive prevent large differences in nucleophilicity from being masked by the concentration advantage of the solvent. In fact, the additive in these experiments may well always be present in the immediate solvation shell of the complex, just as is the solvent.

Unfortunately, the present argument for dissociation is based on failure to observe an effect. It must remain somewhat weak in the absence of a wide range of examples. We are, therefore, extending the experiments to the dimethyl sulfoxide solvent system with the view that a "best nucleophile" hypothesis cannot be extended to all solvents.

(3) Electronic Effects of Non-labile Ligands.—We have suggested that a dissociative mechanism is operative in DMF solutions. The original argument for SN2 aquation rests on analysis of the electronic effects of non-labile (A) ligands. Significantly, reactions in DMF respond to changes in the A ligand in much the same way as do aquation reactions. When the A ligand is Cl or NO_2 the reactions are faster than they are when A is SCN. A final decision in favor of dissociative reaction in DMF will seriously undermine the case for SN2 aquation, whether or not reactions in the two solvents can be shown to be mechanistically analogous. In addition, a decision in favor of dissociative reaction will require a new interpretation of the electronic effects of electron withdrawing groups. Haim and Wilmarth[10] claim that reactions of $[Co(CN)_5X]^{n-}$ ($X = H_2O, N_3^-$) where X is replaced proceed by a limiting SN1 mechanism. CN is also an electron withdrawing group. Perhaps a more satisfactory discussion of the role of these ligands would note that they are π-acceptors and investigate the effect of metal to ligand π-bonds

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[8] In this context, "solvent" means any major component of the solvent mixture, either DMF or one of the additives.

[9] H. B. Gray, Ph.D. Thesis, Northwestern University, Evanston, Ill., 1960.

[10] A. Haim and W. K. Wilmarth, *Inorg. Chem.*, **1**, 573, 583 (1962).

on the stability of the five-coördinate species. It is interesting that a five-coördinate complex $Co(NO)[S_2CN(CH_3)_2]_2$[11] is known which is isoelectronic (around the Co atom) with the five-coördinate intermediate required in the substitution reactions of $[Co(en)_2NO_2X]^+$.

Acknowledgment.—We are grateful to the Research Corporation for a Cotrell Grant in support of this work and to Mr. Robert Leibowitz and Mr. Edward Packel for assistance with several experiments.

(11) P. R. H. Alderman, P. G. Owston, and J. M. Rowe, *J. Chem. Soc.*, 668 (1962).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TENNESSEE, KNOXVILLE, TENNESSEE, AND THE DIVISION OF SCIENCE AND MATHEMATICS, HARPUR COLLEGE, BINGHAMTON, NEW YORK

Amides as Ligands. I. Metallic Complexes of N,N-Dimethylacetamide[1]

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The preparation of 26 metallic complexes of 14 different metals of N,N-dimethylacetamide (DMA) is reported. The complexes have been characterized by their melting points, infrared spectra in the 2–15 μ region, electrical conductance in DMA, and magnetic moments. The infrared spectra suggest that coördination through the oxygen of DMA is occurring for all the metals investigated. In most instances, the complexes contain fewer moles of DMA than the maximum coordination number of the metal, indicating coördination by halide ion and/or water.

Introduction

The fact that amides can act as donor molecules is illustrated by the complexes of urea, thiourea, and dithioöxamide which have been known for many years and by the recent studies on dimethylformamide (DMF). A patent[4] recently has described the preparation of complexes of metal halide salts (atomic numbers 26–29) with variously substituted amides. Addition compounds of DMF have been described by several authors. Moeller and Galasyn[5] have prepared complexes of several rare earth metal iodides of the composition $LnI_3 \cdot 8DMF$ (Ln represents a rare earth metal ion). Moeller, Galasyn, and Xavier[6] also have isolated rare earth metal acetates with DMF of solvation. Ehrlich and Siebert[7] report the isolation of the following titanium chloride compounds: $TiCl_2 \cdot 2DMF$, $TiCl_3 \cdot 2DMF$, and $TiCl_4 \cdot 2DMF$. Archambault and Rivert[8] also report the preparation of $TiCl_4 \cdot 2DMF$ as well as $TiCl_4 \cdot 2HCONH_2$.

On the basis of spectral data, Dunn and Buffagni[9] have postulated the existence in DMA and DMF of $MCl_{4-n}X_n$ species where X is DMA or DMF. These workers also report the isolation of complexes of the types $MCl_2(DMF)_2$ and $[M(DMF)_6](ClO_4)_2$ for M = Mn, Co, and Ni.

Recently, Rollinson and White[10] have reported the preparation of a number of chromium(III) complexes of various amides.

We report the preparation and partial characterization of 26 crystalline DMA complexes representing 14 different metals. The new compounds, perchlorates, nitrates, and halides, are listed in Table I, along with their respective compositions, melting points, colors, and perturbed carbonyl stretching frequencies.

Experimental and Results

All materials were of at least reagent grade. The N,N-dimethylacetamide was obtained from Eastman Kodak and was used in the preparations without further purification. The N,N-dimethylacetamide used in the conductance studies was purified as described by Schmulbach and Drago.[11]

Preparation of Complexes. (1) **General.**—Unless indicated elsewhere in the text, all complexes of N,N-dimethylacetamide reported here were prepared as follows. To an excess of DMA (b.p. 165.5°) was added the appropriate metal salt (hydrated or anhydrous according to availability). In most instances a very viscous solution resulted. Crystallization of the complex was accomplished either by removal of the excess DMA under vacuum (0.5 mm. for 48–60 hr.) or by the addition of anhydrous ether. In a number of cases the substances thus obtained were oily in appearance. By repeatedly washing with ether, the pure complexes finally were obtained. The fact that a large number of the compounds contain water indicates that water probably is more strongly coördinated than is DMA. All complexes were dried at room temperature under vacuum over P_4O_{10}. Analytical data for the new compounds are summarized in Table II.

(2) **Chromium Complexes.**—(a) $Cr(ClO_4)_3 \cdot 6DMA \cdot H_2O$ was prepared by adding DMA to a concentrated aqueous solution of $Cr(ClO_4)_3$ which was prepared by treating excess $Cr(OH)_3$ with 71% $HClO_4$. Upon concentrating the solution containing DMA at room temperature under vacuum a green crystalline material separated. The crystalline material was washed with ether and dried under vacuum. (b) $CrCl_3 \cdot 3DMA$ was prepared

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(2) National Science Foundation Research Participant at The University of Tennessee, 1961.

(3) National Science Foundation Undergraduate Research Participant at The University of Tennessee, 1960–1961.

(4) British Patent 774,956, May 15, 1957.

(5) T. Moeller and V. Galasyn, *J. Inorg. and Nucl. Chem.*, **12**, 259 (1960).

(6) T. Moeller, V. Galasyn, and J. Xavier, *ibid.*, **15**, 259 (1960).

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(8) J. Archambault and R. Rivert, *Can. J. Chem.*, **36**, 1461 (1958).

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(11) C. D. Schmulbach and R. S. Drago, *J. Am. Chem. Soc.*, **82**, 4484 (1960).