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Nucleophilicity of Coordinated Chalcogens As Evaluated in DMF-Water Media

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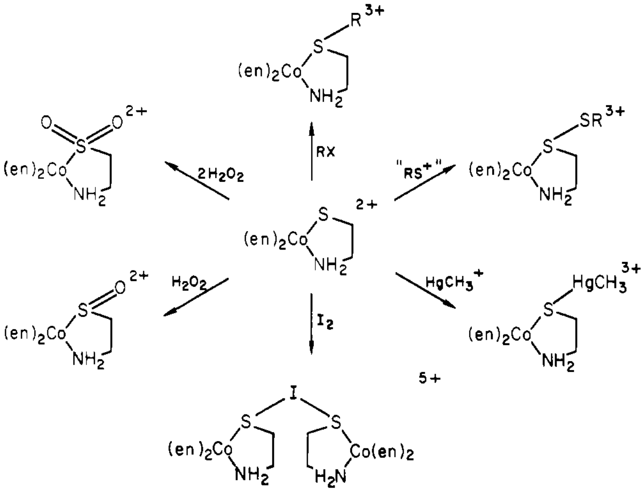
The rates of methylation of some coördinated thiolato, selenolato, and sulfenato complexes of cobalt(III) and chromium(III) by CH_3I have been investigated in DMF-water and methanol-water media. The medium 65% w/w DMF-H_2O ($\mu = 1.00$ *m* maintained with $(H/Li)ClO_4$) proved optimal for these studies, and it is suggested that this may be a useful standard medium for a variety of other kinetic investigations involving reagents of disparate solubilities. The rate law and solvent dependence of the methylation reaction are consistent with a simple S_N2 mechanism, the relative ordering of nucleophilicities toward CH_3I being $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+} < [(en)_2Co(SC_6H_4NH_2)]^{2+} < [(en)_2Cr(SCH_2CH_2NH_2)]^{2+} \approx [(en)_2Co(SCH_2COO)]^{+} \approx [(en)_2Co(SCH_2CH_2NH_2)]^{2+} < [(en)_2Co(SeCH_2CH_2NH_2)]^{2+}$. Coordination to cobalt(III) does not significantly alter the relative nucleophilicities of selenium and sulfur nucleophiles or the relative nucleophilicities of aromatic and aliphatic thiols. A coordinated thiol is about as reactive toward CH_3I as both noncoordinated thiols and noncoordinated thioethers. The 2-equiv oxidation of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ to $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ by H_2O_2 was also studied in 65% w/w DMF-H_2O, and the results were compared to those obtained in purely aqueous media and to the rate of methylation of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$. Nucleophilic attack by coordinated sulfur on either CH_3I or H_2O_2 is viewed as the key mechanistic step which unifies the S_N2 methylation reaction and the atom transfer redox reaction.

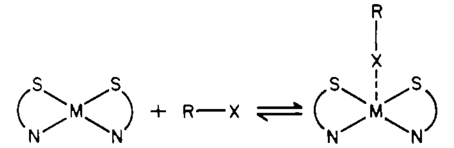
Introduction

The coordinated chalcogen atom of thiolato (or selenolato) complexes retains considerable nucleophilicity relative to the noncoordinated analogue. Just as the nucleophilicity of organic sulfur compounds is central to their chemistry,[1] the nucleophilicity of coordinated sulfur may well be the single most important factor in determining its chemistry and reactivity. With $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ as an example, nucleophilic attack by the coordinated sulfur atom on soft metal centers,[2,3] iodine,[4] H_2O_2,[5,6] *N*-thiophthalimides,[7] and alkyl halides[8] leads to a variety of coordinated sulfur adducts as shown in Scheme I.

Scheme I



Busch[9] and Burke,[10,11] attempted to gauge the nucleophilicity of coordinated thiols by investigating the alkylation of square-planar Ni(II) and Pd(II) thiolato complexes. However, the rates measured in these studies do not reflect the relative nucleophilicities of coordinated thiols since the reactions proceed by a mechanism involving a rapid preequilibrium wherein the halide atom of the alkyl halide weakly coordinates to the metal to form a five-coordinate intermediate (eq 1).



(1)

This serves to polarize the R-X bond and promote alkylation of the coordinated sulfur atom. Thus, the relative reaction rates are determined by the ability of the central metal atom to coordinate the alkyl halide and by the energy required to distort the five-coordinate intermediate into the transition-state geometry, as well as by the nucleophilicity of the coordinated sulfur atom. In order to more directly compare nucleophilicities of coordinated chalcogens, we have monitored the kinetics of the reaction of iodomethane with some thiolato and selenolato complexes of cobalt(III) and chromium(III). With the use of coordinatively *saturated* octahedral complexes rather than coordinatively *unsaturated* square-planar complexes, the possibility of a preequilibrium involving coordination of the alkyl halide to the metal center is precluded. The measured methylation rates are then directly determined by the inherent nucleophilicity of the coordinated chalcogen. These comparative studies, involving coordination complexes which are water soluble and iodomethane which is only sparingly soluble in water, were facilitated by the use of a mixed DMF-water solvent system. So that the effects of using a mixed DMF-water medium, relative to pure water, could be evaluated, the nucleophilic cleavage of H_2O_2 by a thiolato complex was studied in DMF-water; the kinetics of this system in purely aqueous media have previously been well characterized.[12]

Experimental Section

Materials. Common laboratory chemicals were of reagent grade unless otherwise noted. Triply distilled, charcoal-filtered water and

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doubly vacuum distilled perchloric acid (70–72%, G. F. Smith) were used in all kinetic experiments. Lithium perchlorate was prepared from Baker "Ultrex" lithium carbonate as previously described.[13] Iodomethane was distilled and stored in the dark at ca. 5 °C over copper wire. Duplicate kinetic experiments showed no significant rate difference when $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ was alkylated with "clear" iodomethane or with photolytically decomposed "yellow" iodomethane. Stock aqueous peroxide solutions, prepared from unstabilized 30% hydrogen peroxide, were standardized within a few hours of use by titration with Ce(IV) to a ferroin endpoint. Methanol was purified by distillation from magnesium methoxide. Reagent grade DMF (*N,N*-dimethylformamide) was used for all reported kinetic experiments; no effort was made to exclude water. In replicate kinetic experiments, there was no significant difference in observed rates using as the reaction medium (1) 65.0% w/w DMF–H_2O prepared from reagent grade DMF, (2) 65.0% w/w DMF–H_2O prepared from DMF which had been purified by slurrying over molecular sieves, slurrying over calcium hydride, and then vacuum distilling with the first and last fractions (each containing at least 30% of the distillate) being discarded, and (3) 63.0% w/w DMF–H_2O prepared with reagent grade DMF but with 1% w/w formic acid, 1% w/w formaldehyde, and 1% w/w dimethylamine added. Sephadex SP-C25 cation-exchange resin (Pharmacia) was converted to the lithium form and stored under triply distilled water at ca. 5 °C.

The recrystallized perchlorate salts of (2-mercaptoethylamine-*N,S*)bis(ethylenediamine)cobalt(III),[6] (2-mercaptoethylamine-*N,S*)bis(ethylenediamine)chromium(III),[12] (*o*-mercaptoaniline-*N,S*)bis(ethylenediamine)cobalt(III),[14] and (mercaptoacetato-*O,S*)bis(ethylenediamine)cobalt(III)[6] were available from previous studies. (2-Selenoethylamine-*N,Se*)bis(ethylenediamine)cobalt(III) perchlorate was prepared by a reported procedure.[15] (2-Sulfenatoethylamine-*N,S*)bis(ethylenediamine)cobalt(III) perchlorate was prepared by a slight modification of the reported synthesis.[6] A 2.0-g sample of $[(en)_2Co(SCH_2CH_2NH_2)](ClO_4)_2$ was dissolved in a minimum amount of water (ca. 25 mL), and a stoichiometric amount (0.4 mL) of 30% H_2O_2 was then added. The solution was brought to pH 1–2 by adding a few drops of 4 M $HClO_4$. When the color of the solution had changed from brown to red-orange, an equal volume of saturated ethanol–$LiClO_4$ was added and the resultant solution was cooled to yield the desired salt in ca. 75% yield.

Equipment. Visible–UV spectra were recorded on a Cary 14 spectrophotometer at ambient temperature. All kinetic experiments were conducted on a Cary 118B recording spectrophotometer serviced by a Haake FK2 constant-temperature bath and equipped with a Hewlett-Packard 5105A thermal printer. Temperature was monitored with a USC Model 581C digital thermometer, which had been calibrated against a NBS-certified mercury thermometer, and was maintained to ±0.1 °C. All computer calculations were performed on the AMDAHL 470/V6-II system located at the University of Cincinnati.

Kinetic Measurements and Calculations. All kinetic experiments but one were conducted in aqueous DMF or aqueous methanol solutions with the ionic strength held constant at 1.00 ± 0.01 *m* with $HClO_4$ or $LiClO_4$ and with a pseudo-first-order excess of CH_3I or H_2O_2. For the methylation experiments, the initial concentration of the various complexes was in the range of 0.4–2.0 mM, and for the oxidation experiments the initial concentration of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ was 0.20 mM. All DMF-water or methanol-water solutions were prepared within a few hours of use. Solutions of most complexes were prepared from the solid salts just prior to each set of kinetic experiments. The metastable complexes $[(en)_2Co(SC_6H_4NH_2)]^{2+}$ [14] and $[(en)_2Co(SeCH_2CH_2NH_2)]^{2+}$ [15] were eluted from a Sephadex SP-C25 column (lithium form) in the dark just prior to kinetic experiments (8 °C; eluant = 0.238 M $LiClO_4$, 0.012 M $HClO_4$). An aliquot of the desired complex solution was then diluted with the proper amounts of DMF, water, and $HClO_4$ to yield a solution that was 65.0% w/w DMF–H_2O, 0.95 *m* in $HClO_4$, and 0.05 *m* in $LiClO_4$. Kinetic experiments performed using the stable complex $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ purified by this method showed no significant difference in k_{obsd} compared to the analogous experiments performed using material not subjected to this column procedure.

The methylation reactions were initiated by syringe injection of the requisite volume of CH_3I into a quartz spectrophotometer cell capped with a rubber septum and containing the complex ion solution which had been temperature equilibrated in the thermostated cell block of the spectrophotometer. The oxidation reactions were initiated in a somewhat different manner. Aliquots of a $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ solution in 65.0% w/w DMF–H_2O and requisite amounts of the solvent mixture were added to quartz cells. Reactions were then initiated by rapid addition of aliquots of 0.0100 M H_2O_2 in 65.0% w/w DMF–H_2O.

Kinetics were monitored for more than 99% of the reaction, with the infinite time absorbance readings being obtained after this point. Absorbance changes observed during methylation of complexes with sulfur–nitrogen or selenium–nitrogen chelates were monitored at the characteristic[14,16,17] shoulder in the 560–620-nm region of the spectrum of the starting material. Absorbance changes observed during methylation of $[(en)_2Co(SCH_2COO)]^+$ were monitored at both 499 and 610 nm, there being no significant dependence of k_{obsd} on the monitoring wavelength. The kinetics of oxidation of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ by H_2O_2 were monitored at the 367-nm peak characteristic of the sulfenato product complex.[5]

In one series of experiments, the rate of methylation of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ by CH_3I was determined in 100% methanol, with no ionic strength control.

Values of k_{obsd} (as well as its associated standard deviation $\sigma_{k_{obsd}}$), A_0, and A_∞ which best fit the observed $A_t - t$ data within the first-order rate expression

$$A_t = A_\infty - (A_\infty - A_0)e^{-k_{obsd}t} \qquad (2)$$

were calculated with standard nonlinear least-squares techniques.[18] Values of the second-order rate constant, k_2 (and the associated standard deviation σ_{k_2}), were calculated by linear least-squares analysis of k_{obsd} – [reagent] data or by averaging replicate values of k_{obsd}/[reagent]. In both procedures each value of k_{obsd} was weighted by $(1/\sigma_{k_{obsd}}{}^2)$. All reported errors are standard deviations. Conversions between molality (*m*) and molarity (M) concentration units were made by using experimentally determined densities of the appropriate solutions.

Results

Product Identification. All product complexes are identified by their visible–UV spectra which are characteristic for thioether and sulfenato complexes.[5,8] A most important spectrophotometric characteristic of both types of product complexes is the presence of an intense LTMCT band at ca. 280 nm which confirms that the Co–S bond remains intact during the oxidation or methylation reaction. The spectrum of the selenoether product complex is similar to that of the thioether complex, the LTMCT band occurring at 297 nm.[15] The sulfenato complex is also identified by its characteristic[5] absorption at 367 nm. The reaction of CH_3I with $[(en)_2Cr(SCH_2CH_2NH_2)]^{2+}$ leads to a metastable product which can reasonably be formulated as $[(en)_2Cr(S(CH_3)CH_2CH_2NH_2)]^{3+}$ on the basis of (a) ion-exchange chromatographic analysis of the product mixture, (b) absorbance changes observed during the methylation reaction, (c) the visible–UV spectrum of the metastable product (λ_{max} = 360 and 482 nm), and (d) previously reported chemistry.[19,20]

Solvent Dependence. The effect of varying the DMF–H_2O solvent ratio on the rate of methylation of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ by CH_3I is illustrated in Figure 1. A general increase in reaction rate with increasing DMF–H_2O is observed. The reaction medium 65.0% w/w DMF–H_2O was chosen for these and future studies in order to minimize the dependence of the methylation rate on the DMF concentration

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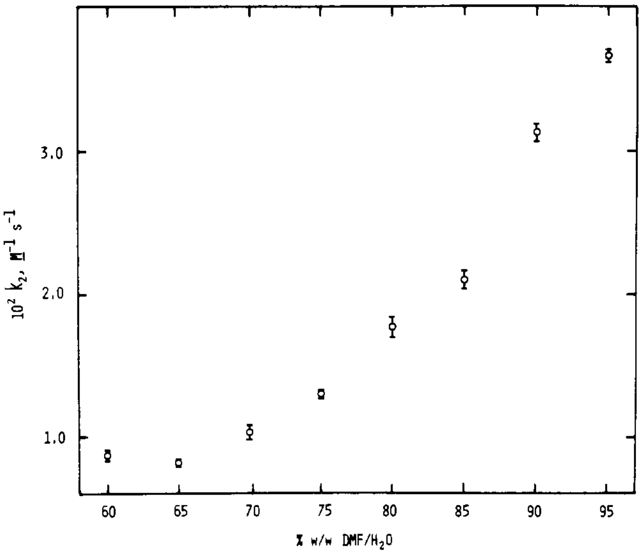

Figure 1. Plot of 10^2k_2 vs. % w/w DMF/H_2O for the reaction of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ with iodomethane.

and to provide good solubility for a variety of potential substrates. The methylation of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ by CH_3I was also monitored in 65.0% w/w CH_3OH-H_2O (25 °C; $\mu = 1.00$ *m* ($HClO_4$)). The rate is considerably slower in the methanol medium; $k_2 = (6.0 \pm 0.3) \times 10^{-4}$ M^{-1} s^{-1} as compared to $(8.2 \pm 0.2) \times 10^{-3}$ M^{-1} s^{-1} in the DMF medium. This same methylation reaction was also monitored in 100% methanol, with no ionic strength control, and k_2 was found to be $(6.8 \pm 1.1) \times 10^{-5}$ M^{-1} s^{-1} (25 °C).

Methylation Kinetics. The observed pseudo-first-order rate constants, k_{obsd}, and the derived second-order rate constants, k_2, governing the reaction of CH_3I with various thiolato and selenolato complexes are given in Table I. Values of k_2 are calculated from at least two independent determinations of k_{obsd}. For all applicable data, plots of k_{obsd} vs. $[CH_3I]$ are linear with no significant intercept. The rate laws governing methylation are thus eq 3 and 4. At concentrations of CH_3I

$$-d[\text{complex}]/dt = k_2[\text{complex}][CH_3I] \qquad (3)$$

$$k_{obsd} = k_2[CH_3I] \qquad (4)$$

greater than 0.2 M, the plots of k_{obsd} vs. $[CH_3I]$ for methylation of the selenolato complexes $[(en)_2Co(SeCH_2CH_2NH_2)]^{2+}$ and $[(en)_2Co(SeCH_2COO)]^{+}$ deviate from linearity with an upward curvature. It is unlikely that this reflects a second-order $[CH_3I]$ term in the rate law governing methylation of these complexes; it is much more likely that this nonlinearity results from reaction of CH_3I photolysis or decomposition products with the coordinated selenol. In these selenol systems, the precision of replicate experiments also seems to be adversely affected at high CH_3I concentrations (Table I). The reaction of the sulfenato complex $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ with CH_3I is so slow that spontaneous decomposition[5] of the starting complex significantly interferes with determination of the methylation rate; in light of this difficulty, only an upper limit ($k_2 \leq 1.60 \times 10^{-4}$ M^{-1} s^{-1}, 25 °C, $\mu = 1.00$ *m* ($LiClO_4$), 65% w/w DMF-H_2O) can be obtained for the rate of the methylation reaction.

Table I. Observed Pseudo-First-Order and Derived Second-Order Rate Constants for the Reaction of Some Co(III) and Cr(III) Chalcogen Complexes with Iodomethane[a]

complex	$[CH_3I]$, M	10^3k_{obsd}, s^{-1}	10^3k_2, M^{-1} s^{-1}
$(en)_2Co(SCH_2CH_2NH_2)^{2+}$	0.250	2.11 ± 0.03	8.2 ± 0.2
	0.250	2.01 ± 0.03	
$(en)_2Co(SCH_2CH_2NH_2)^{2+}$ [b]	0.300	3.30 ± 0.06	11.1 ± 0.3
	0.300	3.53 ± 0.15	
$(en)_2Co(SCH_2COO)^{+}$	0.250	2.15 ± 0.02	8.3 ± 0.2
	0.250	1.96 ± 0.02	
	0.250	2.06 ± 0.04	
	0.250	2.01 ± 0.06	
	0.250	2.02 ± 0.04	
	0.250	2.22 ± 0.07	
$(en)_2Cr(SCH_2CH_2NH_2)^{2+}$	0.200	1.33 ± 0.02	6.65 ± 0.01
	0.300	2.00 ± 0.02	
$(en)_2Co(SC_6H_4NH_2)^{2+}$	0.200	0.106 ± 0.001	0.51 ± 0.07
	0.200	0.103 ± 0.004	
	0.250	0.124 ± 0.002	
	0.300	0.167 ± 0.005	
	0.300	0.167 ± 0.004	
	0.400	0.206 ± 0.008	
$(en)_2Co(SeCH_2CH_2NH_2)^{2+}$	0.010	0.47 ± 0.02	25 ± 4
	0.020	0.70 ± 0.03	
	0.040	1.16 ± 0.03	
	0.050	0.85 ± 0.05	
	0.050	1.01 ± 0.02	
	0.060	1.72 ± 0.03	
	0.080	2.61 ± 0.06	
	0.100	2.5 ± 0.2	
	0.100	3.89 ± 0.08	
	0.200	5.0 ± 0.1	
	0.200	6.7 ± 0.3	

[a] Conditions: 65.0% w/w DMF-H_2O; 25 °C, $\mu = 1.00$ *m* ($HClO_4$). [b] $\mu = 1.00$ *m* ($LiClO_4$).

Table II. Observed Pseudo-First-Order and Derived Rate Constants for the Reaction of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ with H_2O_2 as a Function of $[H_2O_2]$ and $[H^+]$ in 65% w/w DMF-H_2O

$[H^+]$, *m*	$[H_2O_2]$, mM	10^3k_{obsd}, s^{-1}	k_2, M^{-1} s^{-1}
1.00	2.00	4.12 ± 0.03	2.13 ± 0.06
	4.00	8.46 ± 0.15	
	5.00	10.3 ± 0.3	
0.10[b]	4.00	1.63 ± 0.09	0.398 ± 0.004
	4.00	1.59 ± 0.03	

[a] Conditions: $\mu = 1.00$ *m*; 25 °C. [b] $\mu = 1.00$ *m* ($LiClO_4$).

Oxidation Kinetics. Observed specific rates and derived second-order rate parameters for the reaction of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ with H_2O_2 in 65.0% w/w DMF-H_2O as a function of $[H_2O_2]$ and $[H^+]$ are given in Table II. All data are adequately described by the rate law

$$k_{obsd} = (a + b[H^+])[H_2O_2] \qquad (5)$$

which is generally observed for reactions of H_2O_2 with nucleophiles[21] and which specifically was observed for the reaction of H_2O_2 with $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ in aqueous $HClO_4$ media.[12] The data of Table II lead to the derived rate parameters $a = 0.213 \pm 0.007$ M^{-1} s^{-1} and $b = 1.80 \pm 0.01$ M^{-2} s^{-1}.

Discussion

Iodomethane was chosen as a standard electrophilic substrate for this investigation into the nucleophilicity of coordinated chalcogens both because of its uncomplicated chemical structure and because of the large body of data available concerning its reaction with a variety of nucleophiles.[22] However, iodomethane is only slightly soluble in water, the solvent of choice for detailed kinetic studies, and nonaqueous solvents are required to achieve iodomethane concentrations that yield reasonably rapid reaction rates. Concomitantly, the water soluble cationic complexes of interest to this investigation are insoluble in most nonaqueous solvents. This incompatibility in reagent solubilities is a problem commonly encountered in

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designing kinetic studies, and we have attempted to provide a general solution by developing a mixed-solvent system which (1) will afford good solubility to a wide variety of reagents, (2) will be suitable for detailed kinetic investigations, and (3) will be experimentally accessible without untoward syntheses or purification procedures. After evaluation of both mixed methanol–water and mixed DMF–water systems, we have chosen 65% w/w DMF–H_2O ($\mu = 1.00$ *m* maintained with $(H/Li)ClO_4$) as the optimal reaction medium for our specific investigation and suggest that this may be a useful standard medium for a variety of kinetic investigations involving reagents of disparate solubilities.

Solvent Dependence. The data of Figure 1 show that the rate of methylation of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ is relatively insensitive to solvent composition over the range 60%–70% w/w DMF–H_2O ($\mu = 1.00$ *m* $(HClO_4)$), and therefore 65% is the composition at which the effects of any small errors in solvent preparation would be minimized. Since all the complexes of interest to this study, CH_3I, H_2O_2, and a variety of other organic and inorganic reagents, are soluble in 65% w/w DMF–H_2O, we chose this medium for our studies. The medium is readily prepared from reagent grade DMF and distilled water, and obviously, the DMF does not have to be anhydrous. In our kinetic system, the common impurities in DMF (formic acid, formaldehyde, dimethylamine) have no effect when added in large amounts (1%); however, the effect of these impurities would have to be evaluated for each new chemical system to be studied in DMF–water. While medium effects[23] might have been expected to be significantly larger in 65% w/w DMF–H_2O than in pure water, the data of Table I show that this is not the case. Varying the supporting electrolyte from 1.00 *m* $HClO_4$ to 1.00 *m* $LiClO_4$ (with $[H^+] < 0.001$ M) changes 10^3k_2 only from 8.2 to 11.1 $M^{-1}\ s^{-1}$. If all of this change is ascribed to a medium effect (which possibly overestimates the effect since there may be a real rate retardation in $HClO_4$ due to protonation of the coordinated thiol[24]), evaluation within Newton's[23] treatment (eq 6) leads

$$k_2 = k'_2 e^{-\alpha[H^+]} \qquad (6)$$

to a Harned correction term (α) of ca. 0.3 M^{-1}. While H^+/Li^+ α values in purely aqueous media are more usually ca. 0.1 M^{-1},[25,26] values as large as 0.3 M^{-1} have been observed.[27,28]

Further evidence that kinetic results obtained in 65% w/w DMF–H_2O are generally comparable to those obtained in purely aqueous media comes from our brief study of the H_2O_2 oxidation of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ to $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ in DMF–water (Table II). This system was previously studied in detail in aqueous media.[12] The same rate law (eq 5) holds for both media, *a* representing nucleophilic attack by the coordinated sulfur atom on H_2O_2 and *b* representing nucleophilic attack on $H_3O_2^+$. The values of the *b* parameters in the two media are essentially identical (25 °C, $\mu = 1.00$ *m*): 1.83 ± 0.01 $M^{-2}\ s^{-1}$ in pure water and 1.80 ± 0.01 $M^{-2}\ s^{-1}$ in 65% w/w DMF–H_2O. However, the values of the *a* parameters are different, although not remarkably so: 1.18 ± 0.01 $M^{-1}\ s^{-1}$ in pure water and 0.213 ± 0.007 $M^{-1}\ s^{-1}$ in 65% w/w DMF–H_2O. With use of the previously noted[12] correlation of b/a values with nucleophile charge type in DMF–water ($b/a = 9\ M^{-1}$), $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ behaves more like an uncharged nucleophile than it does in pure water ($b/a = 1.5\ M^{-1}$). This observation could reflect the lower dielectric constant of the DMF–water medium which would be manifested in increased ion pairing between perchlorate and $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$; increased ion pairing would reduce the effective cationic charge of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ in its reaction with H_2O_2.

Table III. Nucleophilicity Constants for the Reaction of Chalcogen Nucleophiles with Iodomethane[a]

nucleophile	n_{CH_3I}	nucleophile	n_{CH_3I}
$(C_6H_5CH_2)_2S$	4.84	C_6H_5SH	5.70
$(C_6H_5CH_2)_2Se$	5.23	$C_6H_5S^-$	9.92
$(CH_3)_2S$	5.54	$C_6H_5Se^-$	~10.7
$(CH_3)_2Se$	6.32	$[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ [b]	5.7

[a] Data from ref 22 unless otherwise noted. Conditions: 25 °C; 100% methanol; no ionic strength control. [b] This work. Value calculated as outlined in ref 22.

The lower dielectric constant of DMF relative to that of water (at 25 °C, $\epsilon_{DMF} = 36.7$, $\epsilon_{H_2O} = 78.5$[29]) is also reflected in the observation that the rate of methylation of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ by CH_3I increases as does the DMF–H_2O ratio of the reaction medium (Figure 1). This is consistent with the generalizations of Hughes and Ingold[30] for S_N2 reactions, i.e., reactions wherein the reactants have ***higher*** charge density than the transition state will proceed more rapidly as the solvent polarity decreases; here, the transition state has the same charge as the reactants, but this charge is distributed among a greater number of atoms, and solvent polarity decreases with increasing amounts of DMF–H_2O. This dependence of rate on solvent polarity is opposite to that observed[11] for the methylation of bis(8-mercaptoquinoline)nickel(II) by CH_3I, since in this reaction the neutral reactants have *lower* charge density than does the transition state.

Implicit in the above discussion is the assumption that methylation of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ by CH_3I proceeds via nucleophilic attack on the coordinated sulfur atom on CH_3I. This is entirely consistent with the well-established nucleophilic character of chalcogen compounds, the chemistry of CH_3I, the observed rate law governing methylation (eq 3), and the above noted effect of solvent polarity on reaction rate (Figure 1). In addition, it is well-known that dipolar aprotic solvents such as DMF are much better than protic solvents such as methanol in solvating the large transition states of S_N2 reactions.[29] Therefore, nucleophilic substitution reactions in general proceed more rapidly in DMF media than in methanol media, and consistent with this generalization the reaction of CH_3I with $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ is over 1 order of magnitude faster in 65% w/w DMF–H_2O than in 65% w/w CH_3OH–H_2O: $10^4k_2 = 82 \pm 2$ and $6.0 \pm 0.3\ M^{-1}\ s^{-1}$, 25 °C, $\mu = 1.00$ *m* $(HClO_4)$.

Relative Nucleophilicities. The data of Table I show that the relative ordering of nucleophilicities of various chalcogen-containing complexes of Co(III) and Cr(III) toward CH_3I is $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+} < [(en)_2Co(SC_6H_4NH_2)]^{2+} < [(en)_2Cr(SCH_2CH_2NH_2)]^{2+} \approx [(en)_2Co(SCH_2COO)]^+ \approx [(en)_2Co(SCH_2CH_2NH_2)]^{2+} < [(en)_2Co(SeCH_2CH_2NH_2)]^{2+}$. For a constant Co(III) center, this corresponds to a relative ligand ordering of sulfenic acid < aromatic thiol < aliphatic thiol < aliphatic selenol.

That the selenato complex is more reactive toward CH_3I than the corresponding thiolato complex is hardly surprising, selenium being more nucleophilic than sulfur because of its greater polarizability. Pearson and co-workers[22] have, through application of the Swain–Scott relationship,[31] determined the

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Table IV. Selected Second-Order Rate Constants for the Reactions of Aromatic and Aliphatic Thiolate Compounds with Various Electrophilic Substrates

	k_2, M^{-1} s^{-1}					
thiol	PNPA[a,b]	PNTPA[a,b]	PNPF[a,c]	PNTPF[a,c]	ethylene oxide[d]	CH_3I
$CH_3CH_2CH_2SH$	2.97×10	5.45×10^2				
CH_3CH_2SH	2.05×10	5.00×10^2			7.05×10^{-2}	
$HOCH_2CH_2SH$	1.21×10	3.30×10^2	2.92×10^4	1.95×10^5	4.10×10^{-2}	
C_6H_5SH	3.57×10^{-1}	3.60×10	3.84×10^2	2.72×10^4	2.11×10^{-2}	
$(en)_2Co(SCH_2CH_2NH_2)^{2+}$[e]						8.2×10^{-3}
$(en)_2Co(SC_6H_4NH_2)^{2+}$[e]						5.1×10^{-4}
$Ni_2(CH_3N(CH_2CH_2S)_2)_2$[f]						4.2×10^{-3}
Ni(8-mercaptoquinoline)[g]						2.1×10^{-4}

[a] PNPA = *p*-nitrophenyl acetate; PNTPA = *p*-nitrothiophenyl acetate; PNPF = *p*-nitrophenyl formate; PNTPF = *p*-nitrothiophenyl formate. [b] Reference 32. [c] Reference 33. [d] Reference 34. [e] This work. [f] Reference 9. [g] Reference 10a.

relative nucleophilicity constants, n_{CH_3I}, for a variety of nucleophiles. As seen from the data of Table III, for each of the three Se/S pairs studied by Pearson, the selenium reagent is more nucleophilic than the sulfur analogue, the ratios of specific rate constants k_{Se}/k_S being 2.4, 5.9, and 6.5. This ratio is 3.0 for the single Se/S pair of coordinated ligands of Table I, and therefore coordination to cobalt(III) does not appear to alter significantly the relative reactivities of selenium and sulfur nucleophiles.

Literature data compiled in Table IV show that noncoordinated aliphatic thiols are more nucleophilic than noncoordinated aromatic thiols by factors ranging from 2 to 83. Consistent with this, Burke and Brink[10a] found the aliphatic thiolato ligand of $Ni_2(CH_3N(CH_2CH_2S)_2)_2$ to react with CH_3I about 20 times faster than the aromatic thiolato ligand of the 8-mercaptoquinoline analogue $Ni(SC_9H_6N)_2$; as mentioned earlier, this rate difference may not directly reflect the nucleophilicity of the coordinated sulfur. However, our results using octahedral complexes also show that a coordinated aliphatic thiol is a better nucleophile than the analogous coordinated aromatic thiol, the ratio of rate constants being 16 for the pair of complexes $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ and $[(en)_2Co(SC_6H_4NH_2)]^{2+}$. The reduced nucleophilicity of an aromatic thiolato ligand presumably results from two factors. (1) A coordinated aromatic thiol is a weaker Brønsted base than a coordinated aliphatic thiol, as evidenced by the fact that $[(en)_2Co(SC_6H_4NH_2)]^{2+}$ cannot be protonated even in 12 M HCl whereas $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ is 50% protonated in 6 M HCl.[24] (2) The sulfur atom of an aromatic thiolato ligand is bonded to a secondary carbon atom and is thus more sterically restricted than the sulfur atom of a primary aliphatic thiolato ligand. Even secondary steric constraints such as this are known to be important in determining the nucleophilicity of coordinated thiols; e.g., the rate of H_2O_2 oxidation of $[(en)_2Co(SC(CH_3)_2COO)]^+$ is a factor of 5 slower than the rate of oxidation of $[(en)_2Co(SCH_2COO)]^+$.[12] Thus, coordination to cobalt(III) does not appear to significantly affect the relative reactivities of thiols, aliphatic thiols being about 10 times better nucleophiles than aromatic thiols regardless of coordination.

The sulfur atom of $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ is much less nucleophilic than the sulfur atom of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ since the oxygen atom of the sulfenato complex increases the steric requirements of the sulfur atom and concomitantly decreases the electron density available on the sulfur atom. This decrease in nucleophilicity of coordinated sulfur upon increasing the coordination number of sulfur from 2 to 3 has previously been noted in the reaction of H_2O_2 with $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ and $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$; the rate constant for oxidation of two-coordinate sulfur is approximately 3500 times greater than that for oxidation of three-coordinate sulfur.[5,12] Similarly, the data of Table III show that for noncoordinated ligands one-coordinate sulfur is 4–5 orders of magnitude more nucleophilic than is two-coordinate sulfur. The two-coordinate sulfur atom of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ is approximately as nucleophilic as the two-coordinate sulfur atoms of noncoordinated thioethers or thiols (Table III), indicating that the nucleophilicity of two-coordinate sulfur is relatively independent of the nature of the groups bonded to sulfur.

The nucleophilicity of a coordinated thiolato sulfur atom toward CH_3I is not significantly dependent upon whether the thiol is $HSCH_2COOH$ or $HSCH_2CH_2NH_2$ or upon whether the thiol is coordinated to cobalt(III) or chromium(III). Both of these results are consistent with observations previously reported on the nucleophilicity of coordinated thiolato sulfur toward H_2O_2[12] and reflect the fact that nucleophilic attack by coordinated sulfur does not involve significant distortion of the primary coordination sphere of the metal. In a related system, the uptake rates of carbon dioxide by $[(NH_3)_5MOH]^{2+}$, where M = Co, Rh, and Ir, are also essentially independent of the central metal, reflecting the absence of metal–ligand bond breaking or bond making in the transition state.[35,36] On the other hand, when the metal–sulfur bond undergoes significant distortion in the transition state, as, for example, in the 1-equivalent oxidation of $[(en)_2M(SCH_2COO)]^+$ where M = Co and Cr, the observed rate is very sensitive to the nature of the central metal.[37]

Unifying View. The previous discussion has highlighted some of the detailed similarities between the methylation of coordinated thiols by CH_3I and the oxidation of coordinated thiols by H_2O_2. From the large amount of data available on the reaction of H_2O_2 and CH_3I with nucleophiles,[21,22] and especially from the conclusions concerning H_2O_2 oxidation of coordinated thiols in aqueous media,[12] it is clear that both the methylation and the oxidation reactions proceed through nucleophilic attack by the coordinated chalcogen. Thus, the formal S_N2 substitution process involving CH_3I is fundamentally the same process as the formal oxidation reaction involving H_2O_2, the only distinction between the two being how the formal oxidation states are assigned in the final products—the formal oxidation state of the coordinated sulfur does not change in the CH_3I reaction since carbon is less electronegative than sulfur but does change in the H_2O_2 reaction since oxygen is more electronegative than sulfur. This view, unifying S_N2 reactions with atom-transfer redox reactions, is similar to that proposed by Hurst and co-workers[38]

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to explain the various reactions of chlorine(I) through the common intermediate H_2OCl_2.

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Registry No. $(en)_2Co(SCH_2CH_2NH_2)^{2+}$, 42901-32-6; $(en)_2Co(SCH_2COO)^+$, 42901-31-5; $(en)_2Cr(SCH_2CH_2NH_2)^{2+}$, 48131-66-4; $(en)_2Co(SeCH_2CH_2NH_2)^{2+}$, 58866-01-6; CH_3I, 74-88-4; H_2O_2, 7722-84-1; $(en)_2Co(S(O)CH_2CH_2NH_2)$, 68645-75-0.

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Reaction Kinetics of the Intermediate Produced in the Laser Pulse Photolysis of Tungsten Hexacarbonyl in Fluid Solution

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Laser pulse photolysis at 353 nm of tungsten hexacarbonyl in room-temperature methylcyclohexane produces an intermediate, proposed to be $W(CO)_5S$, S denoting solvent, with an absorption maximum at 425 nm and ϵ_{max} 7.5×10^3 M^{-1} cm^{-1}. In the presence of added L = 4-acetylpyridine, the intermediate reacts completely to form $W(CO)_5L$ as the final product. The rate of disappearance of the intermediate is pseudo first order, with k_{app} linear in L at low concentration but approaching a limiting value at higher concentrations. The proposed mechanism is one of reversible dissociation of $W(CO)_5S$ to $W(CO)_5$ and S with rate constants k_1 and k_{-1}, followed by scavenging of the $W(CO)_5$ by L, with rate constant k_2. At 20 °C $k_1 = 1.9 \times 10^6$ s^{-1} and $k_2/k_{-1} \simeq 270$; the corresponding activation quantities are $E_1^* = 3.9$ kcal mol^{-1} and $E_{-1}^* - E_2^* = 2.6$ kcal mol^{-1}. The nature of the primary photolysis step is discussed.

Introduction

The photochemical behavior of organometallic complexes is of importance to the production of catalytically active compounds and to the advancement of synthetic organometallic chemistry.[1] In particular, intermediates produced in the photolysis of group 6 hexacarbonyls have been the subject of an increasing number of investigations. The primary photoreaction appears to be one of efficient CO dissociation:[2-4]

$$M(CO)_6 \xrightarrow{h\nu} M(CO)_5 + CO \ (M = Cr, Mo, W) \quad (1)$$

In the presence of coordinating ligand L, the substitution product $M(CO)_5L$ is formed with near unitary quantum efficiency.[2] It is the structure, the solvation, and the reaction kinetics of the $M(CO)_5$ species that has been of much interest.

In a classical study, Stolz, Dobson, and Sheline[5,6] found the infrared absorption spectrum of $M(CO)_5$ produced in isopentane/methylcyclohexane glasses at 77 K to be consistent with a C_{4v} square-pyramidal structure but with isomerization to a D_{3h} trigonal-bipyramidal structure on thawing of the glass. Extensive investigations by Turner and co-workers[7-9] further supported the presence of a C_{4v} intermediate in low-temperature matrices and one able to undergo thermal reaction with the photoproduced or added CO. A suggestion[10] that $M(CO)_5$ could be weakly coordinating to even poor donors was substantiated by evidence for $M(CO)_5N_2$ in N_2 or Ar/N_2 matrices at 20 K[8] and, more specifically, for weak bonding between $Cr(CO)_5$ and rare gas or hydrocarbon in the corresponding matrices.[9,11]

$M(CO)_5$ intermediates have also been examined in room-temperature fluid solution by means of conventional flash photolysis and pulse-radiolysis techniques.[12-17] Kelly et al.[14] reported that on flash photolysis of $Cr(CO)_6$ in cyclohexane, an intermediate was produced with an absorption maximum at 503 nm, thought to be $Cr(CO)_5$, and highly reactive toward solvent impurities. However, more recent work suggests that the intermediate may have been $Cr(CO)_5S$, S denoting solvent. The intermediate produced in perfluorocarbon solvents was found to combine with CO, N_2, and cyclohexane with rate constants at about the diffusion limit,[16] so that in cyclohexane as solvent the immediately produced species should be the solvent coordinated one. There is thus some gathering of evidence that the first observed intermediate both in fluid solution and in low-temperature matrices is not $M(Co)_5$ but $M(CO)_5S$, although the M–S bond may be a weak one.

We report in this paper the observation of an intermediate following photolysis of $W(CO)_6$ in methylcyclohexane solvent at room temperature and on the kinetics of its subsequent reaction with 4-acetylpyridine. The experiment is one of monitoring absorbance changes, following pulsed-laser photolyses.

Experimental Section

Materials. Tungsten hexacarbonyl (Strem Chemicals) was purified by sublimation. The ligand 4-acetylpyridine (Aldrich) was used without further purification. Solvents used were obtained from MCB Manufacturing Chemists and were OmniSolv grade. The methyl-

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