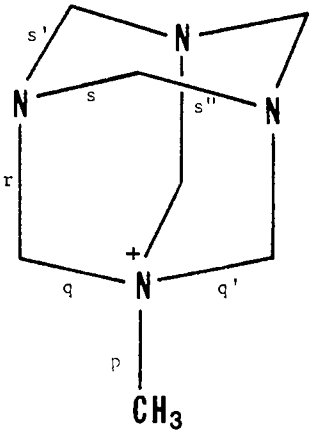

Figure 2. Averaged dimensions of the 1-methyl-1,3,5,7-tetraazaadamantan-1-ium cation, $[(CH_2)_6N_4CH_3]^+$: p, 1.500 (7) Å; q, 1.535 (4) Å; r, 1.430 (5) Å; s, 1.469 (3) Å; pq, 111.3 (3)°; qq', 107.8 (3)°; qr, 110.0 (3)°; rs, 109.8 (3)°; ss', 107.8 (3)°; ss'', 111.7 (3)°.

The cage-type $[(CH_2)_6N_4CH_3]^+$ cation, which forms a salt containing an $I_8{}^{2-}$ anion in an "outstretched letter Z" configuration,[4] undoubtedly plays a similar dominant role in stabilizing the $(H_2O{\cdot}Br^-)_2$ species of opposite charge. This may be considered an extension of the principle of large ions stabilizing large counterions in the solid state.[23] The averaged dimensions of the organic cation (Figure 2) are in good agreement with corresponding values found in $[(CH_2)_6N_4CH_3]_2I_8$[4] and $[(CH_2)_6N_4CH_3]I_3$,[5] and the variation of C-N bond lengths follows the general pattern effected by quaternization of one N atom of the hexamethylenetetramine skeleton.[1]

Acknowledgment. The author acknowledges the useful comments on the results reported in this paper by Professors Jerry Donohue and George A. Sim.

Registry No. 2, 88343-76-4.

Supplementary Material Available: Tables of hydrogen atomic coordinates (Table II), bond lengths and bond angles (Table III), anisotropic thermal parameters (Table IV), and structure factors (Table V) (11 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
University of Cincinnati, Cincinnati, Ohio 45221

Nucleophilicity of Thiolato Sulfur When Coordinated to Ruthenium(II). Kinetics of the Alkylation of (8-Mercaptoquinolinato)bis(2,2'-bipyridine)ruthenium(II) by Iodomethane[1]

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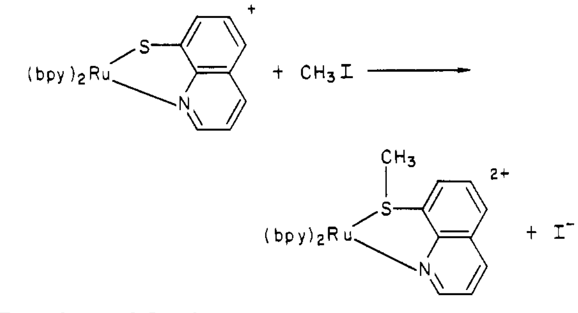
Perhaps the most important aspect of the reactivity of a coordinated thiol is its nucleophilicity.[2,3] The nucleophilicity of thiolate ligands coordinated to cobalt(III) and chromium(III), as measured by CH_3I methylation, is considerable, being approximately the same as that of other two-coordinate sulfur species such as noncoordinated thiols and noncoordinated thioethers.[3] In order to assess more fully the influence of the central metal ion in determining the nucleophilicity of coordinated thiolate, we have investigated the CH_3I methylation of $[(bpy)_2Ru(SC_9H_6H_6N)]^+$ (bpy = 2,2'-bipyridine; $^-SC_9H_6N$ = 8-mercaptoquinolinate), eq 1, and compared these results to those obtained for analogous Co(III),[3] Cr(III),[3] and Ni(II)[4] thiolate complexes.



(1)

Experimental Section

Materials. All materials were reagent grade unless otherwise noted. Triply distilled, charcoal-filtered water, spectral grade DMF (*N*,*N*-dimethylformamide), and methanol were used for kinetic experiments. Spectrophotometric and electrochemical measurements were conducted in spectral grade acetonitrile. Lithium perchlorate was recrystallized from water and dried at 110 °C for 24 h. Tetraethylammonium perchlorate (TEAP) was recrystallized twice from water and dried at 110 °C for 24 h. Iodomethane was distilled and stored over copper wire at −10 °C in the dark. $Ru(bpy)_2Cl_2{\cdot}H_2O$ was prepared by a published procedure.[5] The ligand 8-mercaptoquinoline was obtained from Sigma as the hydrochloride salt.

(8-Mercaptoquinolinato-*N*,*S*)bis(2,2'-bipyridine)ruthenium(II) Salts, $[(bpy)_2Ru(SC_9H_6N)]X$ (X = PF_6, BF_4). To 75 mL of dearerated 50/50 CH_3OH/H_2O containing 3.1 mL of 1 M KOH was added 0.297 g of $HSC_9H_6N{\cdot}HCl$ (1.5 mmol), and the resultant mixture was allowed to stir for ca. 15 min. At this time, 0.522 g of $(bpy)_2RuCl_2{\cdot}H_2O$ (1.0 mmol) was added, and the reaction mixture was refluxed for 2 h. The solution volume was reduced by one-third and the solution cooled to room temperature. Addition of excess solid NH_4PF_6 precipitated the desired complex. Purification was effected by column chromatography on alumina using $CH_3CN/C_6H_5CH_3$ eluents.[5] Reprecipitation from acetone/diethyl ether yielded a black powder that was dried in vacuo. Yield = 81% (based on Ru). Anal. Calcd for $RuC_{29}H_{22}N_5SPF_6$: N, 9.75; S, 4.46; P, 4.31. Found: N, 9.42; S. 4.48; P, 3.90. Visible-UV (CH_3CN) λ_{max}, nm (ϵ, M^{-1} cm^{-1}: 501 (9700), 457 sh (9200), 420 sh (7300), 371 sh (7200), 345 (7800), 331 sh (7600), 293 (45000), 277 sh (31000), 249 (32000), 206 sh (31000). Cyclic voltammetry (0.1 M TEAP in CH_3CN, glassy carbon vs. SSCE) $E_{1/2}$, V: 0.30, −1.49, −1.74.

$[(bpy)_2Ru\text{-}(SC_9H_6N)]BF_4$ was prepared and purified as above but was precipitated with $NaBF_4$. Anal. Calcd for $RuC_{29}H_{22}N_5SBF_4$: Ru, 15.30; N, 10.61; S, 4.85; B, 1.64. Found: Ru, 15.80; N, 11.38; S, 4.84; B, 1.78.

(Methyl 8-quinolinyl thioether-*N*,*S*)bis(2,2'-bipyridine)ruthenium(II) Hexafluorophosphate, $[(bpy)_2Ru(S(CH_3)C_9H_6N)](PF_6)_2$. This complex was prepared by CH_3I methylation of the parent thiolate complex.[6] $[(bpy)_2Ru(SC_9H_6N)]BF_4$ (0.110 g, 0.17 mmol) was dissolved in 10 mL of DMF producing a brown solution to which 1.04 mL of CH_3I (17 mmol) was added. The solution rapidly turned orange and was stirred for 15 min. At this time, 10 mL of H_2O contg. a large excess of NH_4PF_6 was added. To this solution was added 250 mL of diethyl ether, and the mixture was stirred for 30 min. The resulting yellow powder was collected and purified as above. Column chromatography (alumina, $CH_3CN/C_6H_5CH_3$ eluents[5]) showed that only one product was formed. Yield = 76% (based on Ru). Anal. Calcd for $RuC_{30}H_{25}N_5SP_2F_{12}$: N, 7.97; S, 3.65; P, 7.05. Found: N, 7.91; S, 3.86; P, 6.74. Visible-UV (CH_3CN) λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 422

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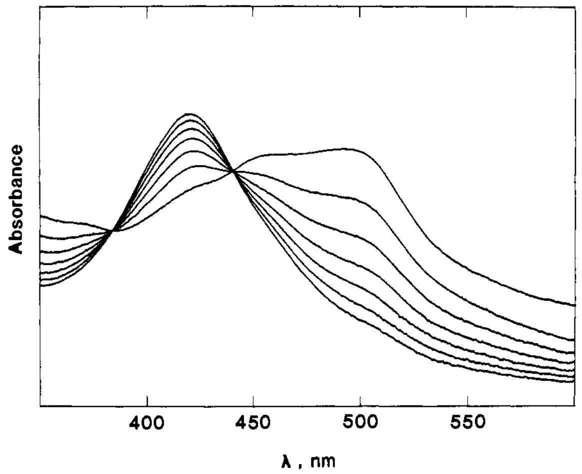

Figure 1. Sequential scans of the visible–UV spectrum during reaction of $[(bpy)_2Ru(SC_9H_6N)]^+$ with CH_3I (conditions: 65.0% w/w DMF/H_2O, 1.00 *m* $LiClO_4$, ambient temperature, $[(bpy)_2Ru(SC_9H_6N)]^+$ = 0.10 mM, $[CH_3I]$ = 0.02 M). The thiolato starting material has a maximum at 501 nm while the thioether product has a maximum at 422 nm.

(5800), 283 (51 000), 253 sh (22 000), 234 (35 000), 204 sh (70 000). Cyclic voltammetry (0.10 M TEAP, glassy carbon vs. SSCE) $E_{1/2}$ V: 1.38, −1.28, −1.48, −1.74.

Equipment. Cyclic voltammetric experiments were conducted with use of a Bioanalytical Systems CV-1B potentiostat and sweep generator served by a Kiethley Instruments Model 178 digital multimeter and a Houston Instruments 100 X-Y recorder. All electrochemical measurements were measured vs. a saturated sodium chloride calomel reference electrode (SSCE).

Visible and UV spectra were recorded on a Cary 210 spectrophotometer. Computer calculations were performed on the Amdahl 470/V7A system located at the University of Cincinnati.

Kinetic Procedures and Calculations. In general, kinetic experiments were conducted as previously described.[3] The reaction medium was either 65.0% w/w aqueous DMF that was also 1.00 ± 0.01 *m* in $LiClO_4$ (where *m* represents molality) or CH_3OH with no ionic strength control. In all cases at least a 20-fold excess of CH_3I was employed, and the initial concentration of the thiolato complex was 0.10 mM.

Kinetics were monitored for more than 99% of the reaction; infinite time absorbance readings were obtained after this time. Absorbance changes during the course of the reactions were monitored at either 419 nm following the increase in the MLCT band for the thioether product (vide infra) or at 501 nm (494 nm in CH_3OH) following the decrease in the thiolato complex ion concentration. Isosbestic points were preserved throughout the reaction (Figure 1).

Values of k_{obsd} and its associated standard deviation $\sigma_{k_{obsd}}$ that best fit the observed OD_t–t data within the first-order rate expression

$$OD_t = OD_\infty - (OD_\infty - OD_0)e^{-k_{obsd}t} \qquad (2)$$

were calculated by using a standard nonlinear least-squares technique.[7] The value of the second-order rate constant, k_2, and its associated standard deviation, σ_{k_2}, were calculated by averaging $k_{obsd}/[CH_3I]$ values, each value of k_{obsd} being weighted by $(1/\sigma_{k_{obsd}}{}^2)$. All reported errors are standard deviations.

Results and Discussion

The thiolate and thioether complexes $[(bpy)_2Ru(SC_9H_6N)]^+$ and $[(bpy)_2Ru(S(CH_3)C_9H_6N)]^{2+}$ are characterized by (1) satisfactory elemental analyses, (2) visible and UV spectra, and (3) electrochemical parameters. Continuous monitoring of the visible–UV spectrum during a reaction (Figure 1) shows that, under conditions used in the kinetic experiments, CH_3I cleanly converts the thiolato starting material to the thioether product, with no detectable intermediate species being produced.

Table I. Derived Second-Order Rate Constants for the Reactions of Selected Thiolate Complexes with CH_3I^a

complex	10^2k_2, $M^{-1}\,s^{-1}$	ref
$(bpy)_2Ru(SC_9H_6N)^+$	15.3	this work
$(en)_2Co(SCH_2CH_2NH_2)^{2+}$	1.11	3
$(en)_2Co(SC_6H_4NH_2)^{2+\,b}$	0.051	3
$(en)_2Cr(SCH_2CH_2NH_2)^{2+\,b}$	0.66	3
$Ni(SC_9H_6N)_2{}^c$	0.010	4

[a] Conditions: 65.0% w/w DMF/H_2O, 25 °C, I = 1.00 *m* $LiClO_4$ unless otherwise noted. [b] I = 1.00 *m* $HClO_4$. [c] In chloroform with no ionic strength control.

The visible spectrum of $[(bpy)_2Ru(SC_9H_6N)]^+$ exhibits a number of transitions that are likely due to various MLCT bands (Ru 4d to π^* orbitals on bpy and $^-SC_9H_6N$ while the UV spectra for both the thiolate and thioether complex ions are dominated by intraligand $\pi \rightarrow \pi^*$ transitions. For the $[(bpy)_2Ru(S(CH_3)C_9H_6N)]^{2+}$ complex, a single visible maximum, assigned to a Ru 4d → bpy π^* MLCT band, is observed. These band assignments are consistent with those proposed for similar complexes.[5]

The cyclic voltammograms for the thiolate and thioether complexes show reversible Ru(II)/Ru(III) waves at positive potentials and a series of reversible ligand reduction waves at negative potentials. Separations between anodic and cathodic peak potentials vary from 70 to 90 mV. Although greater than the ideal Nernstian value of 59 mV, such separations are often observed for similar complexes[5,8] due to solution resistance.[8] Plots of peak current vs. the square root of the scan rate are linear indicating diffusion-controlled redox processes. Ratios of cathodic to anodic peak currents for the Ru(II)/Ru(III) wave are 1.00 and 0.97 for the thiolate and thioether complexes, respectively.

The potentials of the Ru(II)/Ru(III) couples show that the thioether Ru(II) complex is considerably (ca. 1 V) more difficult to oxidize than is the thiolate Ru(II) complex. This is as expected on the basis of the higher formal charge on the thioether complex. A third reduction wave is observed for the thioether complex, and this is most likely due to the reduction of the thioether ligand. The negative formal charge of the thiolate ligand apparently prohibits its reduction within the potential range of these experiments. In addition, there is a large, irreversible wave for the thiolate complex at ca. 1.3 V that may represent oxidation of the coordinated sulfur atom.

For the methylation of $[(bpy)_2Ru(SC_9H_6N)]^+$, plots of $\ln(OD_t - OD_\infty)$ vs. *t* are linear for more than 4 half-lives, the resulting slopes being independent of the monitoring wavelength at a constant $[CH_3I]$. Likewise, a plot of observed pseudo-first-order rate constants, k_{obsd}, vs. $[CH_3I]$ is linear with no significant intercept term over the $[CH_3I]$ range of 0.075–0.350 M. Thus

$$-d(\ln\,[\text{thiolato complex}])/dt = k_{obsd} = k_2[CH_3I] \qquad (3)$$

The simple bimolecular rate law of eq 2 is identical with the rate law observed for the analogous methylations of thiolato Co(III) and thiolato Cr(III) complexes.[3] This rate law is consistent with a S_N2 mechanism wherein the coordinated sulfur atom functions as a nucleophile and displaces iodide from CH_3I.[3]

Values of k_{obsd} and the corresponding derived values of the second-order rate parameter, k_2, in 65% w/w DMF/H_2O and in CH_3OH are given in Tables A and B.[9] In the aqueous DMF medium, the average value of k_2 is 0.153 ± 0.004 $M^{-1}\,s^{-1}$ (25 °C I = 1.00 *m*), while in methanol k_2 = 0.0143 ± 0.0003 $M^{-1}\,s^{-1}$ (25 °C, no added electrolyte). The larger value

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(9) Supplementary material.

Table II. Nucleophilic Reactivity Parameters for Selected Sulfur Nucleophiles[a]

nucleophile	n_{CH_3I}	ref
$^-SC_6H_5$	9.92	11
^-SH	8	11
$(bpy)_2Ru(SC_9H_6N)^+$	8.04	this work
$S(CH_3)_2$	5.54	11
HSC_6H_5	5.70	11
$(en)_2Co(SCH_2CH_2NH_2)^{2+}$	5.7	3
$S(CH_2C_6H_5)_2$	4.84	11

[a] $n_{CH_3I} = \log (k_{nuc}/k_{CH_3OH})$.[11] Conditions: 25 °C, CH_3OH, no ionic strength control.

of k_2 in DMF/H_2O is entirely consistent with previous observations,[3] and the well-established ability of DMF to stabilize the large transition states associtaed with S_N2 reactions.[10]

Table I lists values of k_2 for the reaction of a variety of thiolato complexes with CH_3I. The square-planar Ni(II) complex may constitute a special case since it can coordinate CH_3I in a preequilibrium step that is denied to the octahedral Co(III), Cr(III), and Ru(II) complexes, but it is nevertheless included in Table I since the corresponding k_2 value does not seem discordant with the other k_2 entries. As noted previously,[3] varying the metal ion center from Co(III) to Cr(III) does not significantly affect the reactivity of the coordinated thiolate, and coordinated arenethiolates are less nucleophilic than coordinated alkanethiolates. However, the Ru(II) entry in Table I shows that varying the metal center from Co(III) to Ru(II) markedly enhances the nucleophilicity of a coordinated thiolate; when arenethiolates are compared, k_2 for $[(bpy)_2Ru(SC_9H_6N)]^+$ is ca. 300 times larger than that of $[(en)_2Co(SC_6H_4NH_2)]^{2+}$. This large rate difference is not due to the different formal charges on the complexes since $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ and $[(en)_2Co(SCH_2COO)]^+$ react at essentially the same rate.[3] Rather, this difference in reactivities undoubtedly resides in the greater π-back-bonding tendency of Ru(II); π-back-bonding from Ru(II) to sulfur places greater electron density on the coordinated thiolate and thus makes it a more efficient nucleophile. The efficacy of this π-back-bonding enhancement of nucleophilicity can be appreciated from the data of Table II, which compares values of the nucleophilic reactivity parameter, n_{CH_3I},[11] for a variety of sulfur nucleophiles. On this logarithmic scale it is seen that the positively charged Ru(II) complex is much more nucleophilic than are noncorrdinated thiols and thioethers and is about as nucleophilic as HS^-. Presumably, an anionic thiolato Ru(II) complex would be even more nucleophilic than HS^-.

π-Back-bonding from Ru(II) to nitrogen- and sulfur-containing ligands has often been invoked to explain the increased thermodynamic affinities of these ligands for protons[12-14] and the *reduced* susceptibility of these ligands toward attacks *by* nucleophiles.[15],[16] In this work, π-back-bonding to a sulfur-containing ligand is seen to *enhance* it reactivity *as* a nucleophile. This result may be important in understanding the reactivity patterns of a variety of metal-sulfur systems, including the iron-sulfur cores in ferredoxins and related iron sulfur proteins. E.g., the nucleophilicity of a sulfur ligand in a $Fe_4S_4(SR)_4^{n-}$ core could be controlled by the degree of reduction of the iron atoms, the more highly reduced cores functioning as more efficient nucleophiles.

Acknowledgment. Financial support by National Science Foundation Grant No. CHE79-26497 is gratefully acknowledged. We also thank Dr. B. P. Sullivan and Prof. T. J. Meyer (The University of North Carolina, Chapel Hill, NC) for helpful discussions concerning synthesis of ruthenium thiolate complexes.

Registry No. $[(bpy)_2Ru(SC_9H_6N)]^+$, 88476-04-4; $[(bpy)_2Ru(SC_9H_6N)]PF_6$, 88476-05-5; $[(bpy)_2Ru(SC_9H_6N)]BF_4$, 88476-06-6; $[(bpy)_2Ru(S(CH_3)C_9H_6N)](PF_6)_2$, 88476-08-8; thiooxine, 491-33-8; iodomethane, 74-88-4.

Supplementary Material Available: Tables A and B listing the k_{obsd}–$[CH_3I]$ data (2 pages). Ordering information is given on any current masthead page.

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γ-Ray-Induced Linkage Isomerization of Tetrahedral Thiocyanato Complexes of Iron(II)

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Received March 7, 1983

It is well-known that the thiocyanate ion forms either thiocyanato (M–SCN) or isothiocyanato (M–NCS) metal complexes depending on the nature of the metal and this preference may be modified by other ligands being present or by the complex being in the solid state or in solution.[1-6] Many iron thiocyanate complexes have been reported, and most of them appear to be N bonded.[1,2,7-11] Several examples of linkage isomerization in iron thiocyanate complexes have been reported.[1,2] Both linkage isomers of $[(C_5H_5)Fe(CO)_2NCS]$ have been isolated by column chromatography.[12] in addition, the linkage isomerization of $[Fe(CN)_5NCS]^{3-}$ has been observed in solution,[13,14] and high-pressure-induced linkage isomerization has been reported to have been observed for $Fe(NCS)_3{\cdot}6H_2O$ and $K_3[Fe(NCS)_6]$.[2] So far γ-ray-induced thiocyanate linkage isomerization in a metal complex has not been found.

In the course of a Mössbauer investigation of the aftereffects of ^{57}Co-labeled $M_2[Co(NCS)_4]$ ($M = K^+, Et_4N^+, Me_4N^+$),[15] we have reported that two kinds of iron(II) species were observed on the basis of the emission Mössbauer spectra, which

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