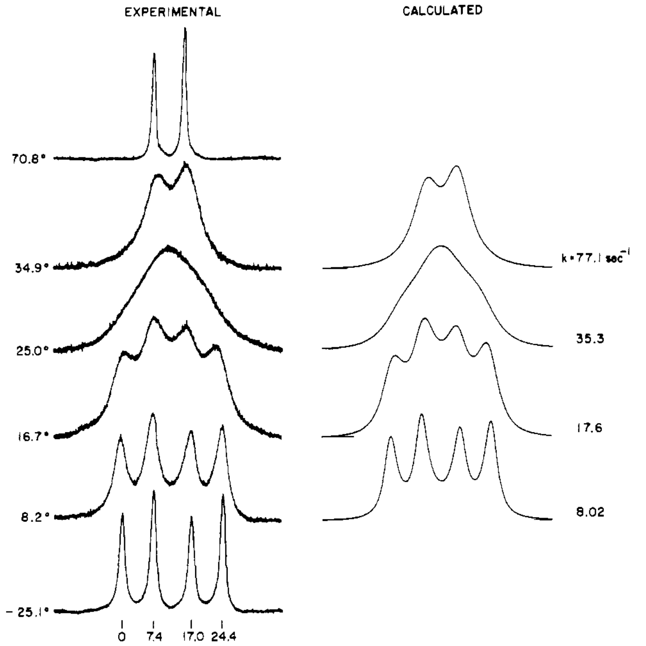

**Figure 8.** Observed and calculated $^1$H NMR line shapes for the isobutyl methylene resonances of MeSC(S)N($i$-Bu)$_2$, 0.60 M in dichloromethane solution, at 60 MHz.

exchanged by C$\overset{\cdots}{-}$N rotation (3.8 and 8.2 Hz). As a check on the values of $k$(C—N) and $k$(C$\overset{\cdots}{-}$N) obtained from the isopropyl methyl region of the spectrum, rate constants for exchange of $S$-methyl groups, $k$(C—N) + $k$(C$\overset{\cdots}{-}$N), were determined from the line shape of the $S$-methyl resonances (Figure 6). The values of $k$(C—N) + $k$(C$\overset{\cdots}{-}$N) (Table VI) are in good agreement with the values obtained by summing the individual rate constants determined from the isopropyl methyl region.

A least-squares plot of log $k$(C—N) vs. $1/T$ for MeSC(S)N($i$-Pr)$_2$ is included in Figure 3, and activation parameters are given in Table IV. The rate of rotation about the C—N bond in the ester, $k = 51$ s$^{-1}$ at −10 °C (for the rotation that converts the trans conformer to the cis conformer), is at the low end, and the activation energy, 12.4 ± 0.6 kcal/mol, is at the high end of the ranges found for the metal complexes (cf. Table IV). These results are consistent with a model in which steric congestion in the diisopropylamino group is relieved by formation of strong metal–sulfur bonds. The only piece of kinetic data for MeSC(S)N($i$-Pr)$_2$ in the literature with which we can compare our results is a value of $\Delta G^{\ddagger} = 13.6 \pm 0.1$ kcal/mol for cis-to-trans conversion at −8 °C in dichlorofluoromethane solution.[19] Our value of $\Delta G^{\ddagger}$ for the C—N rotation that converts the cis to the trans conformer at −8 °C in dichloromethane is 13.34 ± 0.05 kcal/mol.

Since the rate constants for C$\overset{\cdots}{-}$N rotation in MeSC(S)N($i$-Pr)$_2$ are not sufficiently accurate for determination of activation parameters, we studied the C$\overset{\cdots}{-}$N rotation process in the corresponding diisobutyl derivative, MeSC(S)N($i$-Bu)$_2$, where the NMR spectra are not complicated by hindered rotation about the C—N bonds. Rate constants for rotation about the C$\overset{\cdots}{-}$N bond in MeSC(S)N($i$-Bu)$_2$ (Table VI) were determined by comparison of observed and calculated NMR line shapes for the isobutyl methylene proton resonances (Figure 8). Activation parameters are included in Table IV. The activation energy for C$\overset{\cdots}{-}$N rotation in MeSC(S)N($i$-Bu)$_2$, 15.0 ± 0.4 kcal/mol, should be a fairly good estimate[39] of the activation energy for C$\overset{\cdots}{-}$N rotation in MeSC(S)N($i$-Pr)$_2$; rate constants for the two esters are similar ($k$(C$\overset{\cdots}{-}$N) at −10 °C is 1.2 s$^{-1}$ for MeSC(S)N($i$-Bu)$_2$ and ~6 ± 3 s$^{-1}$ for MeSC(S)N($i$-Pr)$_2$). The barrier to rotation about the C$\overset{\cdots}{-}$N partial double bond is 2.6 ± 0.7 kcal/mol higher than the barrier to rotation about the C–N single bonds.

**Acknowledgment.** The support of this research by National Science Foundation Grants GP-30691X and MPS7424297 is gratefully acknowledged. We thank John R. Weir for synthesis of Zr(S$_2$CN($i$-Pr)$_2$)$_4$.

**Registry No.** Co(S$_2$CN($i$-Pr)$_2$)$_3$, 24412-36-0; Ni(S$_2$CN($i$-Pr)$_2$)$_2$, 15694-55-0; Zr(S$_2$CN($i$-Pr)$_2$)$_4$, 85883-31-4; Al(S$_2$CN($i$-Pr)$_2$)$_3$, 85883-32-5; In(S$_2$CN($i$-Pr)$_2$)$_3$, 85883-33-6; Na(S$_2$CN($i$-Pr)$_2$), 4092-82-4; MeSC(S)N($i$-Pr)$_2$, 28248-88-6; MeSC(S)N($i$-Bu)$_2$, 70785-27-2.

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(39) Steric crowding may cause a slight increase in the barrier for MeSC(S)N($i$-Pr)$_2$. Activation energies in the range 10–13 kcal/mol have been reported for MeSC(S)NR$_2$ (R = Me or Et).[21,40]

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# Mutual Labilization of Dimethyl Sulfoxide in the Bis(dimethyl sulfoxide)(1,2-diaminoethane)platinum(II) Cation

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*Received October 19, 1982*

The kinetics of the reactions [Pt(en)(Me$_2$SO)(L)]$^{2+}$ + Y$^{n-}$ → [Pt(en)(Me$_2$SO)Y]$^{(2-n)+}$ + L (L = Me$_2$SO, Y$^{n-}$ = NO$_2^-$, N$_3^-$, Cl$^-$, Br$^-$, I$^-$, SCN$^-$, SC(NH$_2$)$_2$ in MeOH at 30 °C; L = H$_2$O, Y$^{n-}$ = Cl$^-$, Br$^-$, I$^-$, SCN$^-$, SC(NH$_2$)$_2$ in H$_2$O at 30 °C) have been studied. In all cases the simple second-order rate law is obeyed. The reactivity of the bis(dimethyl sulfoxide) complex is always greater than that of the aquo–dimethyl sulfoxide complex, and a comparison of the rate constants (corrected to zero ionic strength) for the two systems shows that the substrate where L = Me$_2$SO has a significantly greater nucleophilic discrimination ability than that where L = H$_2$O. A mechanism is suggested for the mutual labilization.

## Introduction

Sulfoxides as ligands offer many problems and apparent contradictions in their various roles in the substitution reactions of platinum(II) and other four-coordinate planar d$^8$ metal complexes. For example, dimethyl sulfoxide can exert a moderately strong trans effect[1] while having a negligible trans influence.[2] It is also a poor nucleophile.[3] In these respects

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0020-1669/83/1322-2006$01.50/0

**Table I.** Analytical, Spectroscopic, and NMR Data for the Starting Complex and the Isolated Reaction Products

| | % C | | % H | | % N | | $\nu_{S=O}$[a]/ cm$^{-1}$ | $\delta(CH_3)$ | $\delta(CH_2–CH_2)$ |
|---|---|---|---|---|---|---|---|---|---|
| | calcd | found | calcd | found | calcd | found | | | |
| $[Pt(en)(Me_2SO)_2](PF_6)_2 \cdot Me_2SO$ | 12.32 | 12.32 | 3.36 | 3.35 | 3.59 | 3.44 | 1150 | 3.60[a] | 2.90[b] |
| $[Pt(en)(Me_2SO)Cl](PF_6)$ | 9.35 | 9.38 | 2.74 | 2.65 | 5.45 | 5.42 | 1110 | 3.55[c] | 2.90[c] |
| $[Pt(en)(Me_2SO)I](PF_6)$ | 7.94 | 8.09 | 2.33 | 2.37 | 4.63 | 4.66 | 1115 | 3.55[c] | 2.80[c] |
| $[Pt(en)(Me_2SO)N_3](PF_6)$ | 9.23 | 9.42 | 2.71 | 2.71 | 13.46 | 13.34 | 1128 | 3.45[c] | 2.85[c] |
| $[Pt(en)(Me_2SO)NO_2](PF_6)$ | 9.16 | 9.20 | 2.69 | 2.72 | 8.01 | 7.81 | 1110 | 3.60[c] | 2.90[c] |

[a] Nujol mulls. [b] In $D_2O$. [c] In $(CD_3)_2CO$.

it resembles ethene. It is perhaps as leaving groups that sulfoxides are at their most enigmatic. The mutual labilizing power of two sulfoxides has long been recognized in preparative chemistry[4] and more recently has been studied kinetically,[5] and it is now clear that, whereas under normal circumstances a single sulfoxide is difficult to remove, the displacement of one of a pair is facile.

In an attempt to understand this mutual labilization, we have prepared the complex $[Pt(en)(Me_2SO)_2](PF_6)_2 \cdot Me_2SO$. A single-crystal X-ray diffraction study[6] has confirmed that two of the sulfoxides are bound to the platinum through sulfur while the third is present in the lattice and has no significant interaction with the platinum. Furthermore, there is no evidence in terms of unusually close nonbonding interactions or unusual bond lengths or angles that would suggest any significant bond weakening in the ground state through steric repulsion. In this paper we compare the structure of the complex in solution with that of the crystalline solid, examine the kinetics of the displacement of one of the coordinated dimethyl sulfoxides by a range of nucleophiles in methanolic solution, and compare these with those for the displacement of water from $[Pt(en)(Me_2SO)(H_2O)]^{2+}$ by members of the same group of nucleophiles in aqueous solution.

## Experimental Section

**Reagents. $[Pt(en)(Me_2SO)_2](PF_6)_2 \cdot Me_2SO$.** $[Pt(en)(Me_2SO)Cl]Cl$ (1.794 g, 4.44 mmol), prepared by the method of Romeo et al.,[7] was dissolved in dimethyl sulfoxide (25 cm$^3$) and treated with a filtered solution of anhydrous $AgPF_6$ (2.246 g, 8.88 mmol) in dimethyl sulfoxide (25 cm$^3$). The mixture was stirred in the dark at room temperature for 48 h, and the precipitated AgCl was filtered off. Addition of diethyl ether led to the separation of two layers, and the lighter (ether) layer was discarded. Further diethyl ether was added to the lower layer, and the process was repeated until no more dimethyl sulfoxide could be extracted from the oily residue. This was then placed in a refrigerator and left until it crystallized to a white solid, which was dissolved in methanol and the filtered solution evaporated under reduced pressure until the volume was 20 cm$^3$. Addition of diethyl ether resulted in the formation of white crystals, which were filtered off, washed with ether, and air-dried. They were recrystallized from methanol a second time. Analytical, spectroscopic, and NMR data are reported in Table I.

The complexes $[Pt(en)(Me_2SO)X]PF_6$, (X = Cl, I, $NO_2$, $N_3$) were prepared by adding stoichiometric quantities of solid LiCl, LiI, $NaN_3$, and $NaNO_2$, respectively, to concentrated (ca 0.1 M) methanolic solutions of $[Pt(en)(Me_2SO)_2](PF_6)_2 \cdot Me_2SO$. The iodo and nitro complexes separated out when the reaction mixture was cooled, but the chloro and azido complexes needed to be precipitated by the addition of diethyl ether. The crystals were filtered off, washed with ether, and dried. Analytical and spectroscopic data are collected in Table I. Reagent grade inorganic salts were dried over $P_2O_5$ in a vacuum desiccator and used without further purification.

**Acid Dissociation Constants.** The p$K_a$ of $[Pt(en)(Me_2SO)(H_2O)]^{2+}$ was determined by titrating aged aqueous solutions of weighed samples of $[Pt(en)(Me_2SO)_2](PF_6)_2 \cdot Me_2SO$ ($1-2 \times 10^{-3}$ M) with standard, $CO_2$-free sodium hydroxide solution. All solutions were brought to an ionic strength of 0.1 with $NaClO_4$ and thermostatted at 25 °C. The titration was carried out with a Radiometer automatic titration system consisting of a PHM62 pH meter, a TTT60 titrator, an ABU autoburet, a TTA60 titration assembly, and a REC61 Servograph recorder provided with a REA160 Titrigraph module. The saturated KCl solution in the standard calomel reference electrode was replaced by saturated NaCl to avoid precipitation of $KClO_4$ in the perchlorate medium. The instrument was calibrated with standard buffers at pH 4.01 and 9.00. The p$K_a$ value of the complex was determined from the pH vs. titer data by means of a nonlinear least-squares ACBA computer program.[8]

**Kinetics.** The rates of the reaction of $[Pt(en)(Me_2SO)_2]^{2+}$ in methanol were followed with a standard Durrum D131 stopped-flow spectrophotometer equipped with a photometric log amplifier. Absorbance changes at the appropriate wavelength were displayed on a Gould 054100 storage oscilloscope, and traces were recorded on a Radiometer REC61 potentiometric recorder. The rates of anation of $[Pt(en)(Me_2SO)(H_2O)]^{2+}$ in aqueous solution were studied in a similar way. In order to avoid complications due to the acid dissociation of the solvento complex (the p$K_a$ for $[Pt(en)(Me_2SO)(H_2O)]^{2+}$ is 4.05 ± 0.04 in water at 25 °C, $\mu = 0.1$), all reagent solutions were acidified to $(1-2) \times 10^{-3}$ M with perchloric acid and sufficient $LiClO_4$ was added to bring the ionic strength to 0.1. In all cases, a large excess of the nucleophile salt was used to ensure first-order conditions and to force the reactions to go to completion. The pseudo-first-order rate constants, $k_{obsd}$, were obtained either from the slopes of the plots of $\ln (A_t - A_\infty)$ against time ($A_t$ and $A_\infty$ are the absorbances of the solution at time $t$ and at the end of the reaction, respectively) or from a nonlinear least-squares fit of the experimental data to the expression $A_t = A_\infty + (A_0 - A_\infty) \exp(-k_{obsd}/t)$ with $A_0$ (the absorbance at $t$ = 0), $A_\infty$, and $k_{obsd}$ as parameters to be optimized. Infrared spectra of Nujol mulls of the complexes were measured with a Perkin-Elmer 577 spectrometer, and $^1H$ NMR spectra were recorded on a 60-MHz Perkin-Elmer R24A spectrometer.

## Results

The cationic complex $[Pt(en)(Me_2SO)_2]^{2+}$ has been briefly described by Farrell,[9] who obtained it, inter alia, by adding 1,2-diaminoethane to the difficult to prepare $[Pt(Me_2SO)_4]^{2+}$ cation. In our preparation, in which the sulfoxide enters last, the crystalline salt $[Pt(en)(Me_2SO)_2](PF_6)_2 \cdot Me_2SO$ retains an extra molecule of dimethyl sulfoxide even after recrystallization from methanol. The infrared spectrum contains characteristic $\nu_{N-H}$ absorptions in the region 3350–3000 cm$^{-1}$ and a strong band at 1600 cm$^{-1}$ assigned to an $NH_2$ bending mode. The noncoordinating $PF_6^-$ anion gives a sharp peak at 565 cm$^{-1}$ and a strong band at 850 cm$^{-1}$ that does not obscure the region of the S–O stretching mode that has been used to distinguish between O and S bonding of this ligand.[10] A sharp peak at 1150 cm$^{-1}$ is assigned to $\nu_{S-O}$ of dimethyl sulfoxide bound to platinum through sulfur, and a similar peak at 1030 cm$^{-1}$ is assigned to $\nu_{S-O}$ of an uncoordinated $Me_2SO$. This peak

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is absent from the spectra of the $[Pt(en)(Me_2SO)X]PF_6$ species, which are otherwise similar to that of the bis(dimethyl sulfoxide) species, with $\nu_{S-O}$ in the region 1110–1140 cm$^{-1}$. A single-crystal X-ray diffraction study of the bis(sulfoxide) complex[6] has shown that the third $Me_2SO$ molecule sits in the crystal lattice at a site well removed from the platinum.

The $^1H$ NMR spectrum of a freshly prepared solution of $[Pt(en)(Me_2SO)_2](PF_6)_2 \cdot Me_2SO$ in $D_2O$ has a peak at $\delta$ 3.60 (12 H) with a $^{195}Pt$ doublet ($J_{^{195}Pt-^1H}$ = 21 Hz). The chemical shift is consistent with that previously reported for S-bonded dimethyl sulfoxide.[11] The peak at $\delta$ 2.9 (4 H) with $^{195}Pt$ satellites ($J_{^{195}Pt-^1H}$ = 42 Hz) is assigned to the methylene protons of the diamine. No signals were observed for the amine protons, suggesting that these have exchanged rapidly with the $D_2O$ solvent. A sharp peak at $\delta$ 2.70 (6 H) is assigned to the protons of the free dimethyl sulfoxide. As the solution aged, the area under the signal at $\delta$ 2.70 increased at the expense of that at $\delta$ 3.60 until eventually the relative areas under the peaks were reversed, i.e., $\delta$ 2.70 (12 H), $\delta$ 3.60 (6 H). A similar change is observed in $CD_3OD$ solution, but much more slowly, and a similar change is observed immediately (i.e., within the time required to record the NMR spectrum) when NaCl is added to the $D_2O$ solution.

It is therefore clear that in aqueous (and methanolic) solution, the complex cation, which is originally $[Pt(en)(Me_2SO)_2]^{2+}$, readily loses one dimethyl sulfoxide to substitution by the solvent or any other nucleophile. The second sulfoxide, however, remains bound to the platinum throughout.

The p$K_a$ of the $[Pt(en)(Me_2SO)(H_2O)]^{2+}$ cation was determined from the pH titration of an aged solution of the bis(sulfoxide) complex in water. The value, 4.05 ± 0.04 in water at 25 °C, $\mu$ = 0.1, is typical of aquo complexes of Pt(II) containing sulfoxide ligands,[12] which appear to be somewhat stronger acids than the corresponding ammine species.

**Kinetics of the Displacement of Dimethyl Sulfoxide from $[Pt(en)(Me_2SO)_2]^{2+}$.** In addition to causing the changes in the $^1H$ NMR spectra reported above, addition of the appropriate nucleophiles to methanolic solutions of the $[Pt(en)(Me_2SO)_2]^{2+}$ cation leads to a rapid change of the near-UV spectrum, the final spectrum being that of the independently characterized $[Pt(en)(Me_2SO)X]^+$ cation. There is no indication of any slower subsequent changes.

The reactions could be followed by stopped-flow spectrophotometry, but because of the relatively rapid solvolysis of the bis(sulfoxide) complex in water and the time that the reactants have to remain in solution while the stopped-flow experiment is being set up, it was decided to study this reaction in methanol, where solvolysis is very much slower and complications due to the presence of significant quantities of aquo complex, whose reactivity as we shall see is comparable to that of the bis(dimethyl sulfoxide) substrate, could be avoided. Stock solutions of the substrate in methanol, freshly prepared for every batch of kinetic runs, remained unchanged for at least 30 min.

The individual runs, carried out in the presence of at least a 10-fold excess of entering nucleophile, gave good first-order plots, and the rate constants, $k_{obsd}$, obtained for various concentrations $[X^-]$ are collected in Table II. Plots of $k_{obsd}$ vs. $[X^-]$ (or [X] in the case of uncharged nucleophiles) are good straight lines passing through the origin within experimental error. The reaction with iodide was so fast that only one relatively low concentration of iodide was studied. The slopes ($k_2$) and intercepts obtained from a linear least-squares regression analysis are collected in Table III. The value of $k_2$ for iodide is simply $k_{obsd}/[I^-]$.

**Table II.** Pseudo-First-Order Rate Constants, $k_{obsd}$ (s$^{-1}$)

(1) $[Pt(en)(Me_2SO)(H_2O)]^{2+} + Y^{n-} = [Pt(en)(Me_2SO)Y]^{(2-n)+} + H_2O$[a]

| | X | | | | |
|---|---|---|---|---|---|
| $[X^{n-}]$/M | $Cl^-$ | $Br^-$ | $SCN^-$ | $SC(NH_2)_2$ | $I^-$ |
| 0.0010 | | | 1.01 | 0.554 | 6.11 |
| 0.0020 | | | 1.99 | 1.12 | 11.1 |
| 0.0040 | | | 4.74 | 2.54 | 22.6 |
| 0.0050 | 0.148 | 1.00 | | | |
| 0.0080 | | | 9.15 | 4.71 | 44.7 |
| 0.0100 | 0.291 | 2.23 | | | |
| 0.0150 | | | 16.0 | 8.90 | 83.9 |
| 0.0200 | 0.616 | 4.24 | | | |
| 0.0300 | 0.899 | 6.81 | 31.4 | 19.2 | |
| 0.0400 | 1.25 | 9.37 | | | |
| 0.0500 | 1.58 | 11.5 | | | |

(2) $[Pt(en)(Me_2SO)_2]^{2+} + Y^{n-} = [Pt(en)(Me_2SO)Y]^{(2-n)+} + Me_2SO$[b]

| | X | | | | | | |
|---|---|---|---|---|---|---|---|
| $[X^-]$/M | $NO_2^-$ | $N_3^-$ | $Cl^-$ | $Br^-$ | $SCN^-$ | $SC(NH_2)_2$ | $I^-$ |
| 0.00100 | | | | | | | 154 |
| 0.00125 | | | | | | 9.25 | |
| 0.00250 | | | | | 3.40 | 18.9 | |
| 0.00500 | 0.029 | 0.066 | 0.171 | 4.34 | 6.70 | 33.9 | |
| 0.0100 | 0.058 | 0.147 | 0.361 | 8.67 | 13.7 | 67.6 | |
| 0.0200 | 0.113 | 0.283 | 0.745 | 16.2 | 26.1 | 135 | |
| 0.0300 | 0.183 | 0.471 | 1.04 | 25.1 | 38.1 | | |
| 0.0400 | 0.242 | 0.632 | 1.39 | 34.3 | 49.5 | | |
| 0.0500 | 0.305 | 0.778 | 1.75 | | | | |

[a] In water at 30.0 °C with $\mu$ = 0.10 ($NaClO_4$) and pH 2.5–3.0.
[b] In methanol at 30.0 °C with $\mu$ = 0.10 ($LiClO_4$).

**Table III.** Second-Order Rate Constants, $k_2$, at $\mu$ = 0.10 and $k_2^0$ (Extrapolated to $\mu = 0$[a]) for the Reaction

$[Pt(en)(Me_2SO)(L)] + Y^{n-} \rightarrow [Pt(en)(Me_2SO)(Y)]^{(2-n)+} + L$

| L | $X^{n-}$ | $k_2$/M$^{-1}$ s$^{-1}$ | $k_2^0$/ M$^{-1}$ s$^{-1}$ | $k_2^0(L = Me_2SO)/k_2^0(L = H_2O)$ |
|---|---|---|---|---|
| $H_2O$[b] | $Cl^-$ | 31.8 ± 0.2 | 100 | |
| | $Br^-$ | 235 ± 0.6 | 740 | |
| | $SC(NH_2)_2$ | 640 ± 5 | 640 | |
| | $SCN^-$ | 1040 ± 4 | 3300 | |
| | $I^-$ | 5570 ± 4 | 17500 | |
| $Me_2SO$[c] | $NO_2^-$ | 6.2 ± 0.09 | 266 | |
| | $N_3^-$ | 16.0 ± 0.3 | 690 | |
| | $Cl^-$ | 34.7 ± 0.1 | 1500 | 15 |
| | $Br^-$ | 850 ± 9 | 37000 | 50 |
| | $SCN^-$ | 1230 ± 10 | 53000 | 16 |
| | $SC(NH_2)_2$ | 6650 ± 6 | 6650 | 10 |
| | $I^-$ | 154000 | 6700000 | 380 |

[a] See text. [b] In $H_2O$ at 30.0 °C. [c] In MeOH at 30.0 °C.

**Kinetics of the Displacement of Water from $[Pt(en)(Me_2SO)(H_2O)]^{2+}$.** Addition of nucleophiles (X or $X^-$) to an acidified aqueous solution of $[Pt(en)(Me_2SO)(H_2O)]^{2+}$ (obtained by allowing an aqueous solution of $[Pt(en)(Me_2SO)_2](PF_6)_2 \cdot Me_2SO$ to come to solvolytic equilibrium) causes the spectrum to change rapidly to one that is identical with that of the independently characterized $[Pt(en)(Me_2SO)X]^{n+}$ ($n$ = 1 or 2) species. Since the leaving group is the same as the solvent, the background exchange of water does not interfere with the observed reactions. When the reaction was carried out in the presence of a sufficient excess of nucleophile to ensure first-order kinetics, good linear semilogarithmic plots were obtained. The first-order rate constants, $k_{obsd}$, are collected in Table II. Plots of $k_{obsd}$ vs. $[X^-]$

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are also good straight lines, passing through the origin. Value for the slopes ($k_2$) and the intercepts, obtained from a linear least-squares regression analysis, are collected in Table III.

## Discussion

The electronic and $^1H$ NMR spectroscopic evidence clearly indicates that the changes that are observed and kinetically analyzed in solution correspond to the reactions

$$[Pt(en)(Me_2SO)_2]^{2+} + X^{n-} \xrightarrow{MeOH} [Pt(en)(Me_2SO)X]^{(2-n)+} + Me_2SO$$

$$[Pt(en)(Me_2SO)(H_2O)]^{2+} + X^{n-} \xrightarrow{H_2O} [Pt(en)(Me_2SO)X]^{(2-n)+} + H_2O$$

The substitution reactions have simple second-order kinetics, the nucleophile-independent, solvolytic pathway playing no significant part under the conditions of the experiment. In the case of the aquo complex, where the leaving group is also the solvent, this is what is expected, but in the case of the bis(dimethyl sulfoxide) complex in methanol no contribution from solvolysis is observed even at the lowest concentration of nucleophile. Attempts to measure $k_1$ by determining the rate of solvolysis in the presence of base led to complications due to deprotonation of the ligand. These are currently the subject of an interesting study that will be reported elsewhere.

The most important fact that emerges from this work is that one sulfoxide in $[Pt(en)(Me_2SO)_2]^{2+}$ has a lability that is comparable to that of water in $[Pt(en)(Me_2SO)(H_2O)]^{2+}$ while the remaining sulfoxide in the common reaction product cannot be displaced under the conditions used. Owing to the experimental difficulties, it was not convenient to study the reaction of the bis(sulfoxido) complex in water nor was it easy to generate the methanolato complex in methanol and so both complexes could not be compared in the same solvent. Comparison of the reactivities therefore can only be semiquantitative at most. Although a change in solvent from methanol to water can lead to considerable change in $k_1$, the rate constant for direct substitution is far less affected. For example, in the reaction *cis*-$[Pt(Me_2SO)(cyclohexylamine)Cl_2]$ + cyclohexylamine → *cis*-$[Pt(Me_2SO)(cyclohexylamine)_2Cl]^+$ + $Cl^-$,[4,13] $k_1$ increases by 2 orders of magnitude while $k_2$ changes by a factor of 2–3. However, in that case, the reagents are uncharged and so there is no primary salt effect whereas in the system we report both reagents are generally charged and such an effect is present. In order to compare the rate constants for anionic and neutral nucleophiles and to take account of the difference of dielectric constant, we have estimated the value at zero ionic strength, using the relationship $\log k_2 = \log k_2^0 + 2z_Az_BA\mu^{1/2}(1 + B\mu^{1/2})^{-1}$, where $z_A$ and $z_B$ are the charges of the substrate and nucleophile and $A$ and $B$ are constants depending, among other things, upon temperature and dielectric constant of the solvent.[14,15] For water at 30 °C, $A = 0.516$ and $B = 0.992$, but for methanol, with a much lower dielectric constant, 32.6, $A = 1.927$ and $B = 1.539$. Values of $k_2^0$ calculated in this way are also included in Table III. Although the above expression is reasonably well behaved at $\mu = 0.1$ in water, it is possible that departures will occur at lower ionic strengths in methanol. In the more extended empirical expression for the mean ion activity coefficient, $\log f_\pm = Az_Az_B\mu^{1/2}(1 + B\mu^{1/2})^{-1} + C\mu$,[15] from which the primary salt effect expression is derived, the correction would be less than that derived from the simpler expression. Unfortunately, $C$ is generally treated as a empirical constant that must be established for the system being studied. In any log–log comparison of rate constants of the sort we shall make below, these problems of changing solvent will not change the relative reactivities when the nucleophiles are of the same charge type, but any discussion of the relative position of thiourea with respect to the other nucleophiles is dangerous until an empirical dependence of $k_2$ upon $\mu$ is established.

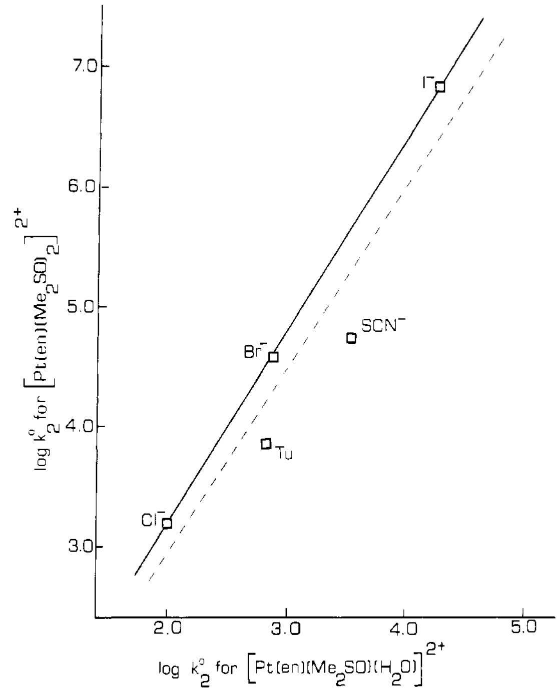

**Figure 1.** Plot of $\log k_2^0$ for the reaction of $[Pt(en)(Me_2SO)_2]^{2+}$ with $Y^{n-}$ against $\log k_2^0$ for the reaction of $[Pt(en)(Me_2SO)(H_2O)]^{2+}$ with the same nucleophile: (—) best line for $X^-$ = $Cl^-$, $Br^-$, and $I^-$ only, slope 1.63 ± 0.01; (---) best least-squares fit with equal weighting for all points, slope 1.56 ± 0.30.

A closer examination of the way in which the reactivity changes with the nature of the nucleophile indicates that the displacement of water and of dimethyl sulfoxide have very little in common. Indications of this emerge from a comparison of the reactivities of $[Pt(dien)(Me_2SO)]^{2+}$ and $[Pt(dien)(H_2O)]^{2+}$ with nucleophiles.[16] There, a plot of $\log k_2^0$ for the $Me_2SO$ complex against $\log k_2^0$ for the aquo complex gave a reasonably good straight line of slope 1.15 ± 0.06, indicating a somewhat greater measure of nucleophilic discrimination in the case of the sulfoxide complex. However, the reactivity of the aquo complex was some three orders of magnitude larger than that of the sulfoxide species. A similar plot of $\log k_2^0$ for $[Pt(en)(Me_2SO)_2]^{2+}$ against $\log k_2^0$ for $[Pt(en)(Me_2SO)(H_2O)]^{2+}$ (Figure 1) shows the three halide ions on a straight line (slope 1.63 ± 0.01) with $SCN^-$ and $SC(NH_2)_2$ displaced from it. The effect can also be seen in the steady increase in the ratio $k_2^0(L = Me_2SO)/k_2^0(L = H_2O)$ as the nucleophilicity of $Y^-$ increases (Table III). The question of the neutral thiourea has already been discussed, but the deviation of thiocyanate cannot be accounted for by salt effects. The slope of the least-squares-fit straight line for all data points is 1.56 ± 0.30. Thus the bis(sulfoxide) complex possesses a significantly greater nucleophilic discrimination ability relative to that of the aquo–sulfoxido species and it can be concluded that, in the rate-determining transition state, the sulfoxide leaving group must still be firmly bound to the metal in order to make its influence so strongly felt. The equivalent transition state for the aquo–sulfoxido complex is far more open with respect to the bond with the leaving group. These results suggest that

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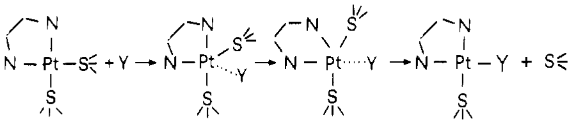
(14) Espenson, J. "Chemical Kinetics and Reaction Mechanisms"; McGraw-Hill: New York, 1981; p 172.

(15) Robinson, R. A.; Stokes, R. H. "Electrolyte Solutions", 2nd ed.; Butterworth: London, 1959; p 231.

(16) Romeo, R.; Cusumano, M. *Inorg. Chim. Acta* **1981**, *49*, 167.

the high lability of the bis(sulfoxide) complex is due, in part at least, to stabilization of five-coordination relative to that of reagents and products together with a parallel lowering of the energies of the two transition states. The contribution made by the sulfoxide to this stabilization is thought to be due to its ability to act as a $\pi$-acceptor. This, however, is not enough to explain the peculiar mutual destabilization of a pair of cis sulfoxides. In the classical trigonal-bipyramidal intermediate, the originally cis ligands occupy axial positions and cannot contribute to the $\pi$ interactions and so we would like to suggest that the usual intermediate undergoes a twist that places both sulfoxides in equatorial positions and that this twist occurs early in the bond making stage



otherwise the high lability could not be explained. Any steric effects which would be exacerbated by the increase of coordination number would be reduced again if both sulfoxides were in the trigonal plane, and this might serve as the driving force to the more $\pi$-bonded configuration. The idea of pseudorotation when the incoming group is still loosely bound can account for catalyzed isomerization[17] or substitution without retention of configuration. However, it must be more complicated than the Berry twist.

The extent to which classical steric effects contribute to the mutual labilization is not clear. There is no indication of any strong mutual repulsion between the two sulfoxides in the four-coordinate substrate.[6] Bond lengths and angles are not abnormal; the slightly enlarged S–Pt–S angle (93.8°) is probably due to the small bite of the chelate opposite it (N–Pt–N = 80.9°) since it is not observed in the other *cis*-bis(dimethyl sulfoxide) complexes whose structures have been determined, *cis*-$[Pt(Me_2SO)_2Cl_2]$[2] and *cis*-$[Pt(Me_2SO)_2(C_6H_5)_2]$,[18] the increase in the Pt–S bond length in the latter being ascribed to the trans influence of the phenyl group. In any case, steric acceleration of an A mechanism with a tight transition state seems paradoxical. If the ground state is destabilized by crowding, the associative transition state will be even more destabilized and the reactivity will be reduced (classical steric hindrance). However, if, as suggested above, some of this strain is relieved by an intramolecular twist that places both sulfoxides in equatorial positions, the steric hindrance can be used to facilitate the associative process.

**Acknowledgment.** The authors gratefully acknowledge the financial assistance of the Ministry of Education and of the Italian CNR.

**Registry No.** $[Pt(en)(Me_2SO)_2](PF_6)_2$, 85664-82-0; $[Pt(en)(Me_2SO)(H_2O)]^{2+}$, 51542-85-9; $Me_2SO$, 67-68-5; $NO_2^-$, 14797-65-0; $N_3^-$, 14343-69-2; Cl, 22537-15-1; Br, 10097-32-2; I, 14362-44-8; $SCN^-$, 302-04-5; $SC(NH_2)_2$, 62-56-6.

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(18) Bardi, R.; Del Pra, A.; Piazzesi, A. M.; Trozzi, M. *Cryst. Struct. Commun.* **1981**, *10*, 301.

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# Electrochemistry of Macrobicyclic (Hexaamine)cobalt(III) Complexes. Metal-Centered and Substituent Reductions[1]

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*Received October 26, 1982*

The electrochemistry of a wide range of macrobicyclic hexaamine ("cage") and polyamine complexes of cobalt(III) is reported. All of the substituted $[Co(sar)]^{3+}$ and $[Co(absar)]^{3+}$ cage complexes exhibit chemically reversible Co(III)/Co(II) couples (sar = sarcophagene = 3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane, absar = 3,6,10,13,15,18-hexaazabicyclo[6.6.5]nonadecane). The Co(II) oxidation state for these complexes is substitutionally inert and undergoes irreversible reduction at very negative potentials in nonaqueous solvents ($\lesssim$-2 V). Quasi-reversible behavior is apparent with all the complexes under study in both aqueous ($ClO_4^-$ and $CF_3SO_3^-$ media) and nonaqueous (acetone and acetonitrile, $CF_3SO_3^-$ media) solvents. However, in aqueous perchlorate media, at a mercury interface, these reductions are complicated by adsorption processes. The potential of the Co(III)/Co(II) couple is markedly dependent on the nature of substituents on the cage ligand and varies by ~0.6 V for the apically substituted $[Co(sar)]^{3+/2+}$ series. Other factors that influence the potential are preferred cavity size of the cage ligand and outer-sphere medium effects. For each series of structurally similar ligands with constant medium and electrode, the heterogeneous rate constants are the same within experimental error. In addition to the metal-centered electrochemistry, many of the complexes exhibit redox processes of electroactive organic substituents. These processes are utilized in selected electroorganic syntheses of new cage complexes. The pH dependence of the Co(III)/Co(II) couple is a useful probe to the acidity of various functional groups, and some applications in determining $pK_a$ values are described.

## Introduction

Several syntheses of macropolycyclic molecules, commonly called cryptands, have been described.[4] These ligands can form inclusion complexes with cations, anions, and small molecules, denoted as cryptates. Recently, syntheses of a range of macrobicyclic (hexaamine)cobalt(III) complexes of the 20-membered [6.6.6]icosane structure (I) have been developed, based on organic syntheses with the inert $[Co(en)_3]^{3+}$ ion as a template (en = 1,2-ethanediamine).[5-10] In keeping with the

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(1) Reported in part at the COMO-9 Conference of the Royal Australian Chemical Institute, The University of New South Wales, February, 1980.

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