is 0.023 M is seen (Table IV) to be in fair agreement with that for [HLig$^-$] = 0.20 M. Note that in the second of these mixtures over 93% of the recovered chromium product is the diligated species.

In sum, the reduction of carboxylato-bound chromium(V) with hydroxylamine resembles the corresponding reduction with hydrazine[3] in that both reactions require preliminary loss of one ligand per Cr(V) and both appear to proceed through a Cr^{V}–N precursor formed with attendant loss of a proton. Significant differences between the two systems arise after the initial act of electron transfer. The 2e oxidation of bound hydrazine yields N_2H_2, which, in either the free or ligated state (we cannot at present say which), undergoes further rapid external oxidation to N_2. In contrast, the Cr^{III}–N^{I} species, arising (in principle) from a 2e transaction in the hydroxylamine system, quickly (perhaps instantaneously) undergoes a second internal 2e transfer, yielding the Cr^{I}(NO) products we observe. The occurrence of this very unexpected net change of 4e, in what approaches a single transfer, may reasonably be attributed, in major part, to the unusally marked mutual stabilization of the NO^+ group and the chromium(I) center by strong metal-to-ligand back-bonding.[24]

Registry No. I, 84622-43-5; II, 84622-44-6; III, 84583-15-3; NH_2OH, 7803-49-8.

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Reactivity of Sulfoxides toward the Tetrachloroplatinate(II) Anion

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The kinetics of the reactions between $[PtCl_4]^{2-}$ and a series of sulfoxides, $(CH_3)_2SO$, $(CH_3)(C_2H_5)SO$, $(C_2H_5)_2SO$, (c-C_4H_8)SO, (2-ClC_2H_4)(CH_3)SO, $(C_6H_5)(CH_3)SO$, (*p*-$CH_3C_6H_4$)(CH_3)SO, (*p*-ClC_6H_4)(CH_3)SO, (*p*-$CH_3OC_6H_4$)(CH_3)SO, (*n*-C_3H_7)(CH_3)SO, and (*n*-C_3H_7)$_2$SO, have been studied in 95:5 vol % methanol/water at 25 °C and μ = 1.0 (LiCl). In all cases the reaction is the simple replacement of one chloride by a sulfoxide. The second-order rate constants are insensitive to the change in inductive effect on changing the substituents but decrease with increasing bulk. An interpretation is proposed in terms of the intimate mechanism of the substitution, and a comparison is made with the behavior of thioethers and amines.

In recent years much has been published to indicate a number of peculiarities in the behavior of sulfoxides in platinum-group chemistry.[3] These ligands are known to bind Pd(II) and Pt(II) through sulfur unless there are steric reasons to prevent this, in which case oxygen bonding is observed.[4] Dimethyl sulfoxide exerts a moderate trans effect[5,6] but is a relatively poor nucleophile,[7] a combination which is also observed for ethene[8] but which is otherwise uncommon. In spite of the moderate trans effect, the product of the reaction between $[PtCl_4]^{2-}$ and $(CH_3)_2SO$ is *cis*-$[Pt(Me_2SO)_2Cl_2]$,[4] although there is evidence for the presence of the trans isomer as a labile intermediate. Two cis sulfoxides exert a considerable labilizing effect on one another[9,10] while the displacement of a single sulfoxide is generally very slow.[11,12] In spite of the inertness of a single coordinated sulfoxide, dimethyl sulfoxide has been used as a solvent for the study of substitution reactions in d^8 systems without any apparent interference from irreversible solvolysis.[13]

In palladium(II) systems the entry of sulfoxides into $PdCl_4^{2-}$ is rapid and reversible and the equilibrium constants have been determined.[14] The second successive equilibrium constant for dimethyl sulfoxide in this system is some 2 orders of magnitude less than the first, and it is another example of the parallel in the behavior of sulfoxides and olefins.

The study of sulfoxides as nucleophiles has been confined until now to the reaction between $[PtCl_n(H_2O)_{4-n}]^{(2-n)-}$ and $(CH_3)_2SO$,[7] and as a part of our investigation of the role of electronic and steric effects on the nucleophilicity of ligands with common donor atom features, we have extended our studies from amines, heterocyclic nitrogen bases, and thioethers to sulfoxides. In this paper we report the kinetics of the reactions

$$[PtCl_4]^{2-} + RR'SO \rightarrow [Pt(RR'SO)Cl_3]^- + Cl^- \quad (1)$$

where RR′SO is one of a series of 11 sulfoxides.

Experimental Section

Materials. An aqueous solution of Na_2PtCl_4 was obtained by treating the required amount of K_2PtCl_4 in water with excess $NaClO_4$ and filtering off the precipitated $KClO_4$. A known volume (5 cm^3) of this solution was diluted to 100 cm^3 with methanol containing the required amount of LiCl to keep the ionic strength at μ = 1.0. This

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solution was used in the kinetic runs without further change.

$K[Pt(Me_2SO)Cl_3]$ was prepared by adding K_2PtCl_4 (0.199 g) to a solution of *cis*-$[Pt(Me_2SO)_2Cl_2]$ (0.2 g) in water (10 cm^3). The resulting mixture was heated until all of the solid had dissolved, and the yellow solution was filtered and evaporated to small volume under vacuum at room temperature. After a few hours in the desiccator, yellow needles of the product formed. Anal. Calcd for $C_2H_6SOCl_3KPt$: C, 5.74; H, 1.44; Cl, 25.4; S, 7.66. Found: C, 5.71; H, 1.39; Cl, 25.5; S, 7.57. The infrared spectrum agreed with that published.

$(CH_3)_2SO$ was a reagent grade commercial product (Aldrich) and was used without further purification.

$(CH_2)_4SO$, $(C_6H_5)(CH_3)SO$, and $(n\text{-}C_3H_7)_2SO$ were technical grade commercial products and were purified by chromatography on a silica column by eluting with $C_6H_6/CHCl_3$. The purity of the products was checked by thin-layer chromatogrphy, and when necessary, they were redistilled under reduced pressure.

$(p\text{-}CH_3C_6H_4)(CH_3)SO$, $(p\text{-}CH_3OC_6H_4)(CH_3)SO$, $(p\text{-}ClC_6H_4)(CH_3)SO$, and $(n\text{-}C_3H_7)(CH_3)SO$ were prepared by reacting the corresponding thiols with CH_3Br in ethanol in the presence of a small excess of KOH. The thioethers thus formed were oxidized to sulfoxides and purified as indicated below.

$(C_2H_5)_2SO$, $(2\text{-}ClC_2H_4)(CH_3)SO$, and $(C_2H_5)(CH_3)SO$ were obtained by oxidizing the corresponding thioethers (Fluka) with Br_2 in 1:1 CH_3OH/H_2O. After the solutions were evaporated to small volume, they were purified as described above.

Kinetics. The kinetics were followed with a Varian-Cary 219 double-beam spectrophotometer. Each kinetic run was started by mixing known volumes of thermostated solutions of $Na_2PtCl_4 + LiCl$ and the required sulfoxide in 95:5 vol % CH_3OH/H_2O in the thermostated cell of the spectrophotometer, and either the changing spectrum was scanned in the range 260–400 nm from time to time or the changing absorbance at a single wavelength (330 nm) was measured as a function of time. In all cases the concentration of the sulfoxide was large enough to ensure pseudo-first-order conditions. The first-order rate constants, k_{obsd} (Table I) were obtained from a nonlinear regression analysis of A_t vs. time, A_t being the absorbance of the reaction mixture at the wavelength chosen for calculation at time t. The uncertainities in the k_{obsd} values are expressed as $[A_{ii}\sigma^2/(n-3)]^{1/2}$, where A_{ii} is the diagonal element relative to the k_{obsd} resulting from the inverse matrix of the system of linear equations according to the method of Gauss and Newton, σ^2 is the square of the standard deviations, and n is the number of experimental points used in calculating the kinetics.

Results and Discussion

In each of the reactions the initial spectrum (corrected where necessary for the absorbance of the free sulfoxide) agreed with that of the starting material, $[PtCl_4]^{2-}$, and changed to that of the reaction product in a simple first-order fashion, irrespecitve of the wavelength used. Since the spectra did not cross, it was not possible to use the appearance and constancy of isosbestic points as a criterion of a single change. In the case of the reaction with $(CH_3)_2SO$ the final spectrum was identical with that of an authentic sample of $[Pt(Me_2SO)Cl_3]^-$ measured under similar conditions. The products of the other reactions were not independently synthesized and characterized, but the general similarity of the spectral changes indicated that the same type of reaction was being observed. Although the reaction, involving as it does uncharged nucleophiles, would not be expected to exhibit a primary salt effect, excess LiCl was added to suppress the solvolysis and the slow subsequent entry of a second sulfoxide ligand in the way used by Elding.[7] The reaction being followed is therefore represented by (1).

Plots of k_{obsd} vs. [RR′SO] are generally linear with good correlation coefficients from the weighted linear regression analysis, and the kinetics appear to follow the simple two-term rate law $k_{obsd} = k_1 + k_2[RR'SO]$. The values for the intercept (k_1) are small, and the scatter is generally within the limit of error. There seems to be no significant mass law retardation from the chloride added to prevent solvolysis. The rate constants are summarized in Table II together with the values for $-\sum\sigma^*$ (Taft parameters),[15] which have been shown to be

Table I. First-Order Rate Constants, k_{obsd}, for Reaction 1 in CH_3OH/H_2O (95:5) at 25 °C and μ = 1 M (LiCl)

sulfoxide	10 × [RR′SO], mol dm^{-3}	$10^5 \times k_{obsd}$, s^{-1}
dimethyl sulfoxide	1.04	12.28 ± 0.08
	0.83	10.04 ± 0.01
	0.52	6.40 ± 0.04
	0.31	4.16 ± 0.03
	0.10	1.66 ± 0.01
tetramethylene sulfoxide	2.00	23.7 ± 0.4
	1.60	18.5 ± 0.2
	1.00	13.0 ± 0.1
	0.60	7.69 ± 0.08
	0.40	4.84 ± 0.04
ethyl methyl sulfoxide	4.30	29.4 ± 0.2
	3.40	22.6 ± 0.1
	2.20	15.6 ± 0.1
	1.30	9.43 ± 0.04
	0.90	6.50 ± 0.03
p-methylphenyl methyl sulfoxide	11.78	33.9 ± 0.1
	9.42	27.5 ± 0.4
	6.51	19.6 ± 0.4
	5.89	18.7 ± 0.2
	3.53	11.1 ± 0.1
	1.18	3.64 ± 0.06
p-chlorophenyl methyl sulfoxide	6.64	30.1 ± 0.6
	5.31	24.0 ± 0.2
	3.32	15.0 ± 0.1
	1.99	9.60 ± 0.04
	0.66	3.32 ± 0.03
p-methoxyphenyl methyl sulfoxide	4.60	13.24 ± 0.05
	3.70	10.88 ± 0.05
	2.30	7.26 ± 0.05
	1.40	4.48 ± 0.04
	0.46	3.06 ± 0.04
2-chloroethyl methyl sulfoxide	5.00	34.2 ± 0.2
	4.00	27.3 ± 0.1
	2.50	18.2 ± 0.1
	1.50	11.3 ± 0.1
	1.00	7.74 ± 0.03
diethyl sulfoxide	5.02	7.27 ± 0.08
	4.01	5.99 ± 0.07
	2.51	3.94 ± 0.03
	2.01	3.14 ± 0.02
	1.50	2.65 ± 0.03
phenyl methyl sulfoxide	4.91	13.7 ± 0.1
	2.95	8.92 ± 0.1
	2.46	6.21 ± 0.05
	1.47	3.81 ± 0.03
	1.06	2.85 ± 0.01
	0.85	2.49 ± 0.02
di-*n*-propyl sulfoxide	10.01	5.58 ± 0.02
	8.01	4.30 ± 0.02
	5.00	3.06 ± 0.03
	4.00	2.41 ± 0.04
n-propyl methyl sulfoxide	10.00	38.1 ± 0.2
	8.00	32.4 ± 0.1
	5.00	20.72 ± 0.05
	3.00	13.4 ± 0.1
	2.00	9.51 ± 0.02

Table II. Second-Order Rate Constants for Reaction 1 in CH_3OH/H_2O (95:5) at 25 °C and μ = 1 M (LiCl)

sulfoxide	$-\Sigma\sigma^*$	10^5k_2, M^{-1} s^{-1}
dimethyl sulfoxide	0.00	113 ± 1
tetramethylene sulfoxide	−0.18	114 ± 5
ethyl methyl sulfoxide	−0.10	66 ± 1
2-chloroethyl methyl sulfoxide	+0.385	65 ± 1.2
diethyl sulfoxide	−0.20	13.5 ± 0.3
phenyl methyl sulfoxide	+0.60	23.7 ± 1
p-methylphenyl methyl sulfoxide	+0.43	27.9 ± 0.5
p-chlorophenyl methyl sulfoxide	+0.83	44.2 ± 0.7
p-methoxyphenyl methyl sulfoxide	+0.33	25.8 ± 1
n-propyl methyl sulfoxide	−0.115	35.9 ± 0.7
di-*n*-propyl sulfoxide	−0.23	4.9 ± 0.3

Table III. Dependence of the Second-Order Rate Constants upon the Electronic Features of the Entering Nucleophile in Platinum(II) Chemistry

substrate	entering group	leaving group	inductive coeff[a]	ref
$[Pt(bpy)Cl_2]$[g]	am[b]	Cl^-	0.06	21
t-$[Pt(py)_2Cl_2]$	am	Cl^-	0.05	22
$[Pt(L)Cl_2]^-$[c]	am	Cl^-	<0	6, 11, 18
$[Pt(PhMeNN{=}C(CH_3){-}C(CH_3){=}NNMePh)Cl_2]$	am	Cl^-	0.05	23
c-$[Pt(Me_2SO)_2Cl_2]$	am	Me_2SO		17
c-{*meso*-$[Pt(PhS(O)CH_2CH_2S(O)Ph)Cl_2]$}	am	*d*	0.58	9
t-$[Pt(py)_2Cl_2]$	RSR′	Cl^-	1.51	24
$[Pt(bpy)Cl_2]$	RSR′	Cl^-	1.2	16
$[Pt(bpy)(N_3)Cl]$	RSR′	Cl^-	0.45	16
$[Pt(bpy)(NO_2)X]$[e]	RSR′	X^-	2.55	16
$[Pt(dien)Br]^+$[f]	RSR′	Br^-	~0.0	20
$[PtCl_4]^{2-}$	RR′SO	Cl^-	0.0	

[a] The inductive coefficient is the coefficient A or A' in the equations $\log k_2 = A(pK_a)$ + constant or $\log k_2 = A'(-\Sigma\sigma^*)$ + constant for the entry of amines and thioethers, respectively. [b] am = amines having the same form of steric hindrance. [c] L = Me_2S, Me_2SO, PR_3, AsR_3. [d] The reaction corresponds to the opening of the chelate ring. [e] X = NO_2, Cl, N_3. [f] dien = 1,5-diamino-3-azapentane. [g] bpy = 2,2′-bipyridine.

a reliable index of the reactivity of thioethers as nucleophiles toward those Pt(II) substrates where inductive effects are important.[16] Examination of these rate constants shows clearly that with sulfoxides reacting with $[PtCl_4]^{2-}$ the values of k_2 do not appear to be sensitive to the variation in the inductive effects of the substituents of the sulfur but instead respond to steric effects. For example, the rate constants for the entry of $(CH_3)_2SO$ and $(CH_2)_4SO$, which have the same effective bulk but different inductive effects, are virtually identical, and the effect is indicated more strikingly by the similarity of the rate constants for $(C_2H_5)(CH_3)SO$ and $(2\text{-}ClC_2H_4)(CH_3)SO$ and for the para-substituted phenyl methyl sulfoxides (with the exception of $(p\text{-}ClC_6H_4)(CH_3)SO$, whose higher reactivity is discussed below). On the other hand, the marked decrease in reactivity along the sequence $(CH_3)_2SO > (C_2H_5)(CH_3)SO > (C_2H_5)_2SO > (n\text{-}C_3H_7)(CH_3)SO > (n\text{-}C_3H_7)_2SO$ also confirms the important role of steric hindrance in these reactions. Attempts were made to obtain rate constants for the more hindered $(i\text{-}C_3H_7)_2SO$, but the reaction was too slow to be measured ($k_2 < 10^{-5}$ M^{-1} s^{-1}).

Since this is the first systematic study in platinum(II) chemistry of the effect of varying the substituent on the nucleophilicity of sulfoxides, it is not possible to say whether this is the only pattern that will be found. There is a considerable amount of evidence that shows that two types of behavior can be observed when amines or thioethers act as nucleophiles toward Pt(II), the pattern adopted depending upon the nature of the complex being attached. These reactions are summarized in Table III, where it can be seen that, in one group, the rate constants are insensitive to the variation in the inductive effect of the substituents, while in the other there is a very marked response. The amines and thioethers have been handled differently in the sense that it is easily possible to separate steric and inductive effects in heterocyclic nitrogen bases such as substituted pyridines and diazines by using 4-substituents to vary the inductive effects and methyl substituents in the 2- and 6-positions to vary the steric effects. Furthermore, the inductive effects could be quantified in terms of the proton basicity of the base (pK_a of amH^+ in water at 25 °C). This type of control is lacking for the thioethers (and presumably the sulfoxides), and $-\sum\sigma^*$ for the substituents is used instead as a measure of their inductive effect and the magnitude of the coefficients (slope of the plot of $\log k_2$ vs. $pK_a(amH^+)$ for amines and slope of the plot of $\log k_2$ vs. $(-\sum\sigma^*)$ for thioethers, for systems of comparable steric effect) for the two systems should not be compared.

We have suggested elsewhere[17] that the sensitivity of the rate constant on the inductive effects of the substituents is an indication that the second maximum (bond breaking) in the reaction profile of the A mechanism is the rate-limiting transition state when $k_2 = k_a k_d / k_{-a}$ (where k_a and k_{-a} are the rate constants for the forming and breaking of the bond between the metal and the entering group and k_d is the rate constant for the breaking of the bond with the leaving group). The main contribution from the substituent inductive effect arises from k_{-a} and represents the strength of the metal–ligand bond in the five-coordinate intermediate. When the rate constant is insensitive to these effects, it is assumed that the rate-determining transition state is at the first (bond-making) maximum when $k_2 = k_a$ and the bond between the metal and the entering group is only partially formed. An extreme example of this is to be found in the reactions of $[Pt(PR_3)Cl_3]^-$ with substituted pyridines, where the coefficient is negative (−0.2)[18] and where it has been suggested that biphilicity of the amine through interaction of its empty LUMO of π symmetry with a similar HOMO on Pt(II) enhances the magnitude of k_a.

The lack of response to the inductive effect of the sulfoxide substituents indicates that their reactions with $[PtCl_4]^{2-}$ have the bond-forming maximum as the rate-determining transition state.

The low nucleophilicity of sulfoxides has already been pointed out by Elding,[7] who has also drawn attention to the fact that the combination of low nucleophilicity and high trans effect resembles that of ethene (although the trans effect of the latter is much greater than that of the former). Elding has also ascribed the low nucleophilicity of dimethyl sulfoxide to the polarity of the molecule, in which the sulfur carried a small positive charge. It is possible that the consequence of this is that the initial bond between platinum and this ligand is through the oxygen and that the changeover to Pt–S bonding takes place between the bond-making transition state and the five-coordinate intermediate (this would be required to account for the moderate trans effect).[5,19]

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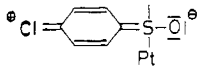
(19) Although there is no supporting evidence, it might be speculated that the trans effect of the sulfoxide arises from an olefinic type of bonding involving the S═O bond in the five-coordinate intermediate. This would also be the intermediate in an intramolecular *O*- to *S*-bonded isomerization. It would be of interest to synthesize and examine the structure of trigonal-bipyramidal complexes of Pt(II) containing sulfoxide in the trigonal plane.

The somewhat greater (twofold) reactivity of 4-chlorophenyl methyl sulfoxide compared to that of the other substituted phenyl methyl sulfoxides might be accounted for by a conjugative displacement of charge that reduces this positive charge on the S and hence increases its nucleophilicity (Elding) or enhances the negative charge on the oxygen and increases its nucleophilicity:



Unfortunately, 4-nitrophenyl methyl sulfoxide is not soluble enough to be used in this study.

The sensitivity of the nucleophilicity of the sulfoxides to the bulk of the substituents is quite considerable and greater than the effect already noticed in the case of the reaction between $[Pt(dien)Br]^+$ and thioethers.[20] This is shown by comparing the sequence of *n*-alkyl sulfoxides. Although the order of reactivity is the same, if the rate constant for $(CH_3)_2S$ is taken as 100, the thioether sequence is $(CH_3)_2S = 100 > (CH_3)(C_2H_5)S = 83 > (C_2H_5)_2S = 53 > (n\text{-}C_4H_9)S = 33$ whereas in the sulfoxide sequence the rate constants are $(CH_3)_2SO = 100 > (CH_3)(C_2H_5)_2SO = 58 > (C_2H_5)_2SO = 12 > (n\text{-}C_3H_7)_2SO = 4$. This is even more strongly indicated by the fact that rate constants could be measured for $(i\text{-}C_3H_7)_2S$ and $(s\text{-}C_4H_9)_2S$ whereas the reaction of $(i\text{-}C_3H_7)_2SO$ was too slow to be measured. Of course, these refer to two different substrates, with different charges and steric properties of the ligands cis to the leaving groups (which are the major contributions to steric hindrance from the complex), but until now we have been unable to find a common substrate for both studies. Reactions of $[PtCl_4]^{2-}$ with thioethers are complicated by subsequent reactions, and the sulfoxides will not react with the cationic dien species under kinetically useful conditions.

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Registry No. $PtCl_4^{2-}$, 13965-91-8; MeEtSO, 1669-98-3; Et_2SO, 70-29-1; $(2\text{-}ClC_2H_4)MeSO$, 5331-57-7; PhMeSO, 1193-82-4; $(p\text{-}MeC_6H_4)MeSO$, 934-72-5; $(p\text{-}ClC_6H_4)MeSO$, 934-73-6; $(p\text{-}MeOC_6H_4)MeSO$, 3517-99-5; MePrSO, 14094-08-7; Pr_2SO, 4253-91-2; Cl, 22537-15-1; $(CH_3)_2SO$, 67-68-5; thiophane 1-oxide, 1600-44-8.

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Solubility and Equilibrium Constants of Uranyl(2+) in Phosphate Solutions

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Precipitation studies of uranyl(2+) in phosphate solutions, performed at 298.15 K and various ionic strengths ($I = (3 \times 10^{-4})–(4 \times 10^{-2})$ mol dm^{-3}), complete the present knowledge of uranyl(2+) hydrogen phosphate tetrahydrate and uranyl(2+) phosphate octahydrate solubility and uranyl phosphate complex formation, composition, and stability. The concentrations of uranyl, phosphate, and hydrogen ions have been determined in solution equilibrated with the solid phase. From experimental data the values for equilibrium constants of soluble complexes are obtained and corrected to $I = 0$. The following values of homogeneous and heterogeneous equilibria in the uranyl–phosphate system at $I = 0$ have been determined: $\log [a(UO_2H_2PO_4^+)\ a(H^+)\ a^{-1}(UO_2^{2+})\ a^{-1}(H_3PO_4)] = 1.50 \pm 0.05$; $\log [a(UO_2H_3PO_4^{2+})\ a^{-1}(UO_2^{2+})\ a^{-1}(H_3PO_4)] = 1.30 \pm 0.10$; $\log [a(UO_2(H_2PO_4)_2^0)\ a^2(H^+)\ a^{-1}(UO_2^{2+})\ a^{-2}(H_3PO_4)] = 1.30 \pm 0.05$; $\log [a(UO_2(H_3PO_4)(H_2PO_4)_2^0)\ a^2(H^+)\ a^{-1}(UO_2^{2+})\ a^{-3}(H_3PO_4)] = 2.30 \pm 0.05$; $\log [a(UO_2^{2+})\ a(HPO_4^{2-})] = -12.33 \pm 0.06$; $\log [a^3(UO_2^{2+})\ a^2(PO_4^{3-})] = -49.00 \pm 0.80$.

Introduction

The formation of insoluble and slightly soluble uranyl(2+) phosphates is important in the technology of uranium production, especially for low-grade uranium phosphate ores and in fuel reprocessing.[1-3] Previously published papers reported the precipitation conditions,[4] dissolution,[5] composition,[6,7] and stability ranges[8] of the solid phases.

Apart from the general interest in the interaction between uranyl cations and phosphate anions, there is an important practical application of these data in the recovery of uranium from acid phosphate solutions.[9] Many of the authors[10-16] investigated the formation of uranyl phosphato complexes, and they are in disagreement, both in the composition of the complexes and in their stability constants. The values of the solubility products of uranyl(2+) hydrogen phosphate and uranyl(2+) phosphate have also been determined by different authors,[17-21] and they vary with the stability constants of the complexes used in the calculations.

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