parameters for the hydrogens, and converged to the residuals of $R(F) = 0.0755$ and $R_w(F) = 0.0740$. A final difference Fourier synthesis was featureless with the largest peak being 0.32 e/Å^3.

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Supplementary Material Available: Atomic coordinates and isotropic temperature factors (Table 1S), anisotropic temperature factors (Table 2S), and selected bond angles (Table 3S) (13 pages); observed and calculated structure factors (Table 4S) (24 pages). Ordering information is given on any current masthead page.

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Interaction of Sulfur Dioxide with Heteropolyanions in Nonpolar Solvents. Evidence for Complex Formation

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It is generally recognized that the structures of heteropolyanions[1] resemble fragments of metal oxide lattices[2] and consequently such polyanions deserve (and are receiving) increased attention with respect to their catalytic activities.[3] We have previously reported that heteropolyanions can easily be transferred into nonpolar solvents like benzene and toluene and that, with appropriate metal-ion-substituted structures under anhydrous conditions, a number of reactions not feasible in aqueous (or polar) solutions can occur.[4] These include substitution, oxidation, and oxygenation reactions, as well as metalloporphyrin-type chemistry. In the course of our studies of the interactions of heteropolyanions with small molecules[4] we have noted reactions of sulfur dioxide with several heteropolytungstate structures.

Experimental Section

Sulfur dioxide (Matheson 99.98%), extra dry nitrogen (99.997%, water content less than 1 ppm), benzene ("Photrex", "Baker analyzed"), and toluene ("Baker analyzed") were used without further purification. Electronic spectra were determined on a Cary 14 or Hewlett-Packard 8451A diode array spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer Model 225 instrument either in KBr disks or in solution with a two-piece Delrin plastic cell (Fisher Scientific Co.) equipped with AgCl windows (0.050 cm path length).

The syntheses of the heteropolyanions were carried out by using previously described procedures: $K_6SiW_{11}O_{39}M(OH_2)$ (M = Mn, Ni, Cu);[5] $K_6SiW_{11}O_{39}Co(OH_2)$;[6] $K_8P_2W_{17}O_{61}Co(OH_2)$;[7] $K_{10}P_2Co_4(OH_2)W_{18}O_{68}$.[8]

Table I. Solution Spectra (nm) of Heteropolyanion–Aquo and Heteropolyanion–SO_2 Complexes in Toluene/0.1 M (tHA)Br

	L = H_2O	L = SO_2
$SiW_{11}O_{39}Co(L)^{6-}$	540, 520, 505	545, 515 (sh),[a] 505 (sh)
$PW_{11}O_{39}Co(L)^{5-}$	565, 540, 524, 495	602 (sh), 570, 540 (sh), 520 (sh), 510 (sh), 493
$P_2W_{17}O_{61}Co(L)^{8-}$	540, 520, 490 (sh)	540 (sh)
$P_2W_{18}O_{68}Co_4(L)_2{}^{10-}$	565, 548 (sh), 515	567, 510
$SiW_{11}O_{39}Cu(L)^{6-}$	*b*	800
$SiW_{11}O_{39}Ni(L)^{6-}$	696, 702 (sh)	698, 718 (sh)

[a] sh = shoulder. [b] In toluene solutions the water immediately dissociates.

Table II. Vibrational Frequencies (cm^{-1}) of the SO_2 Ligand in Heteropolyanion Complexes[a]

compd	S–O asym str	S–O sym str	O–S–O bend
SO_2 (solid)[b]	1330, 1308	1147	521
SO_2 (soln)[c]	1325, 1305	1120	518
$SiW_{11}O_{39}Co(SO_2)^{6-}$	1255	1068	563
$SiW_{11}O_{39}Mn(SO_2)^{6-}$	1259, 1222	1043	569
$SiW_{11}O_{39}Ni(SO_2)^{6-}$	1240	*d*	580
$SiW_{11}O_{39}Cu(SO_2)^{6-}$	1252, 1221	*d*	565
$P_2W_{17}O_{61}Co(SO_2)^{8-}$	1257, 1222	*d*	565
$P_2W_{18}O_{68}Co_4(SO_2)_2{}^{10-}$	1260	1132	565

[a] Conditions: solution spectra in toluene/1 M (tHA)Br; concentration of complexes ca. 0.1 M; cell path length 0.05 cm, AgCl cells. [b] Wiener, R. N.; Nixon, E. R. *J. Chem. Phys.* **1956**, *25*, 1751. [c] In toluene/1 M (tHA)Br. [d] Not observed.

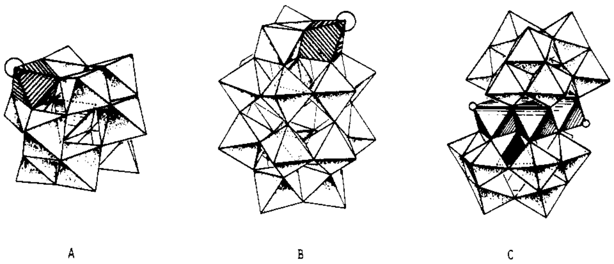

Figure 1. Polyhedral representations of polyanions containing octahedral heteroelements (shaded) examined in this study: (A) Keggin structure, α-$XW_{11}O_{39}M(OH_2)^{m-}$ (X = Si, P; M = Co, Mn, Ni, Cu; m = 5, 6); (B) Dawson structure, α_2-$P_2W_{17}O_{61}Co(OH_2)^{8-}$; (C) $P_2W_{18}O_{68}Co_4(OH_2)_2{}^{10-}$. Circles represent terminal H_2O and the probable site of attachment of SO_2 ligands.

The tetramethylammonium salt of $PW_{11}O_{39}Co(OH_2)^{5-}$ was synthesized from $(Me_4N)_7PW_{11}O_{39}$ and $Co(CH_3COO)_2{\cdot}4H_2O$ by using a modification of Landis' method.[9] The resulting salts were identified by UV–vis and IR spectroscopy.

Reactions of SO_2 with Heteropolytungstates. In a typical experiment, a ca. 0.01 M aqueous solution of the anion was extracted into an equal volume of a benzene or toluene solution containing tetra-*n*-heptylammonium bromide ((tHA)Br) in an amount equivalent to the polyanion's charge.[4b] After the solution had been dried by passage of dry N_2 gas for 1–4 h or by evaporation to dryness and redissolution in dry solvent, gaseous SO_2 was passed through the solution (ca. 0.01 M in the heteropolyanion) for a short time (usually less than 1 min). An almost instantaneous color change occurred for all the complexes except $SiW_{11}O_{39}Mn^{6-}$ (which remained orange-yellow), indicating the reaction of the heteropolyanion with SO_2. The visible spectra of the SO_2–heterpolyanion solutions were recorded (Table I). The solutions were concentrated to ca. 0.1 M polyanion by nitrogen or vacuum-assisted evaporation, and their IR spectra were recorded (Table II).

Results and Discussion

Seven heteropolyanions were examined (see Figure 1). Six contain a single divalent metal ion in place of a tungsten atom in the Keggin or the Dawson structure: α-$SiW_{11}M(OH_2)O_{39}{}^{6-}$

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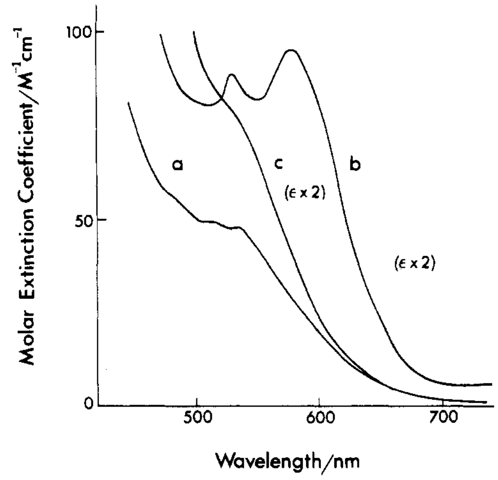

Figure 2. Visible spectra of (a) $P_2W_{17}O_{61}Co(OH_2)^{8-}$, (b) $P_2W_2O_{61}Co^{8-}$, and (c) $P_2W_{17}O_{61}Co(SO_2)^{8-}$ in toluene/(tHA)Br.

(M = Mn, Co, Ni, Cu), α-$PW_{11}Co(OH_2)O_{39}^{5-}$, and α_2-$P_2W_{17}Co(OH_2)O_{61}^{8-}$. We denote these by $SiMOH_2^{6-}$, $PCoOH_2^{5-}$, and $P_2CoOH_2^{8-}$, respectively. The seventh polyanion, $[Co_4(PW_9O_{34})_2(H_2O)_2]^{10-}$, contains two nonadjacent $CoO_5(OH_2)$ octahedra.

The process of phase transfer described above results in the transfer of some 20–30 mol of water/mol of heteropolyanion (as shown by Karl Fischer titration). The same quantity of water is transferred if the heteropolyanion is omitted from the original aqueous solution, and since in either case the quantity exceeds the normal solubility of water in benzene or toluene, we conclude that the water is incorporated in reverse micelles formed by the tetraalkylammonium ions. Aspiration of dry N_2 through the solution for 1–2 h results in almost complete removal (to a residual 1–2 mol of H_2O/mol of heteropolyanion) of the "extra" water. The resulting low activity of water in the nonpolar solution favors dissociation of the water molecule coordinated to the "surface" heteroatom of the polyanion, e.g.

$$SiCuOH_2^{6-} \rightleftharpoons SiCu^{6-} + H_2O \qquad (1)$$

The existence of equilibria such as (1) is readily detected visibly (and verified spectroscopically) for the Co, Ni, and Cu species. The ease of dehydration (rate of water loss and magnitude of the equilibrium constant of eq 1) varies with both the metal ion involved and the structure of the polyanion. The anion $SiCuOH_2^{6-}$ is immediately dehydrated upon extraction into "wet" benzene or toluene (λ_{max} 870 → 710 nm). Dehydration of the remaining anions is achieved by aspirating dry N_2 for 1–2 h or, for the more stubborn species ($PCoOH_2^{5-}$, $SiNiOH_2^{6-}$, $SiMnOH_2^{6-}$, $P_2CoOH_2^{8-}$), by stripping the solvent at <30 °C and redissolving in fresh solvent. The Co(II) species have previously been shown to be five-coordinate (square pyramidal) by means of their characteristic ligand field spectra (see ref 4a,b and Figure 2). Modest changes in the spectra of $SiNiOH_2^{6-}$ and $SiMnOH_2^{6-}$ occur in the charge-transfer region and lead to color changes of green to yellow and yellow to orange, respectively. In every case (M = Mn, Co, Ni, Cu), addition of a drop of water to the dehydrated solutions restored the original spectrum.

In Tables I and II are summarized the spectroscopic characteristics of the dehydrated solutions following passage of SO_2 gas for ca. 1–2 min. The electronic spectra are similar, but not identical, to those of the aquo anions and are consistent with the attachment of a ligand in the vacant coordination position. The vibrational spectra show new absorption bands at ca. 1250, 1050, and 560 cm^{-1} that we assign to the asymmetric and symmetric stretching and bending modes, respectively, of coordinated SO_2. With one exception, noted below, the spectra of the SO_2-treated solutions are unaffected by prolonged passage of dry N_2 or by evaporation to dryness and subsequent redissolution. However, addition of a drop of water to all SO_2-treated solutions was sufficient to restore the spectra of the aquo anions immediately.

In the case of $[Co_4(PW_9O_{34})_2]^{10-}$ (from $[Co_4(PW_9O_{34})_2(H_2O)_2]^{10-}$) the spectrum of the SO_2-treated solution could be transformed into that of the anhydrous anion by passage of dry N_2 for ca. 1 h. Subsequent treatment with SO_2 restored the spectrum summarized in Table I, and the cycle of SO_2-off and -on could be repeated. This behavior is consistent with our observation[4b] that pyridine is only weakly coordinated to the same heteropolyanion in benzene and with the apparent inability of the anion to bind ligands in aqueous solution.[10] The heteropolyanion has two nonadjacent Co sites for binding the SO_2, and we tentatively presume that both become occupied since the spectrum did not change after further addition of SO_2.

Heteropolyanion–SO_2 Bonding. The main types of M–SO_2 binding that have been observed in conventional coordination complexes are η^1(S–) planar, η^1(S–) pyramidal, and η^2(S–O).[11] Of all the metal–SO_2 complexes that have been structurally characterized, only a limited number have been shown to adopt the η^2 geometry. There are also only a few reports of O-bonded SO_2 complexes,[12] one of which is a manganese(II) high-spin complex.[12c] For most SO_2 complexes X-ray data are not available and infrared data have been used[11] as indicators of bonding modes—a sometimes risky procedure.

It has been argued that the π-acceptor nature of SO_2 is reflected in the shift of the S–O stretches toward lower frequencies when the SO_2 is coordinated to a metal. In η^2-SO_2 complexes, principally as a result of M → SO_2 π donation, $\Delta\nu$ is much larger than in η^1 structures.[11b] Examination of the data in Table II reveals that the heteropolyanion–SO_2 complexes have shifts for the symmetric and asymmetric S–O stretches that fall well outside the η^2-SO_2 region[11b] and into the region of the S-bonded M–SO_2 complexes. Since O-bonded SO_2 complexes are rare and appear to be characterized by a $\Delta\nu_{as-s}$ value larger than 210 cm^{-1},[12a] we tentatively propose that the heteropolyanion–SO_2 complexes are S-bonded. The lability of the SO_2–$P_2W_{18}Co_4$ complex is also consistent with S attachment.[11c]

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