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Synthesis and Crystal Structure of $B_{10}H_{10}(C_6H_{11})S(CH_3)_2CNH(t\text{-}C_4H_9)$

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The formation of $1,2\text{-}B_{10}H_{10}C_2H_2$ by the reaction of acetylene with $B_{10}H_{12}(SMe_2)_2$ is believed to involve attack on a reactive monoligand intermediate [i.e., $B_{10}H_{12}(SMe_2)$] by the acetylene.[1] At 80–110 °C the reactive monoligand derivative apparently rearranges to an "unreactive" $B_{10}H_{12}(SMe_2)$ isomer. The unreactive isomer has been isolated and characterized by two groups[2,3] and does not form $1,2\text{-}B_{10}H_{10}C_2H_2$ in the presence of acetylene under the normal conditions. More recently it was reported that $B_{10}H_{12}(SMe_2)_2$ reacted with cyclohexane at 80 °C to form dimethyl sulfide (S–B^5)-9-cyclohexyl-*nido*-decaborane-(11).[4] This compound is a cyclohexyl-substituted derivative of the unreactive $B_{10}H_{12}(SMe_2)$ isomer. The single-crystal X-ray structure of this substituted derivative has been reported.[5] When $B_{10}H_{11}C_6H_{11}(SMe_2)$ was reacted with diethyl sulfide at 90 °C, several products were formed, including the simple exchange product $B_{10}H_{11}C_6H_{11}(SEt_2)$.[4] Treatment of the cyclohexyl derivative with pyridine at room temperature formed $6\text{-}C_6H_{11}\text{-}6,9\text{-}(py)_2B_{10}H_{11}$ in good yield.[5] Finally, when $B_{10}H_{11}C_6H_{11}(SMe_2)$ was reacted with NaH in refluxing THF, $Na_2[2\text{-}C_6H_{11}B_{10}H_9]$ was formed in good yield.[4]

We previously observed a different type of nucleophilic attack on both $B_{10}H_{14}$ and $B_{10}H_{13}^-$ by the strong Lewis base RNC (R = alkyl, phenyl).[6,7] In these reactions, the isocyanide carbon atom was inserted into the boron hydride framework to form one-carbon carborane derivatives. In this paper, we report on the nature of the reaction of $B_{10}H_{11}C_6H_{11}(SMe_2)$ with an alkyl isocyanide.

Results and Discussion

We have attempted to convert $B_{10}H_{12}[CN(t\text{-}C_4H_9)]_2$ to a one-carbon carborane via isocyanide insertion, but there was no reaction even in refluxing monoglyme. The recently reported cyclohexyl-substituted derivative, $B_{10}H_{11}C_6H_{11}S(CH_3)_2$ provides an interesting ten-atom structural variation to previously studied systems which we hoped would shed some light on the isonitrile insertion reaction.[4]

When dimethyl sulfide (S–B^5)-9-cyclohexyl-*nido*-decaborane-(11) was reacted with *tert*-butyl isocyanide in benzene–hexane solvent, the major product isolated had the formula $B_{10}H_{10}(C_6H_{11})S(CH_3)_2CNHC(CH_3)_3$. The carbon and hydrogen elemental analysis was consistent with this formulation, and the low-resolution mass spectrum cut off at m/e 349, which corresponds to the $^{11}B_{10}{}^{12}C_{13}{}^{1}H_{37}{}^{14}N^{32}S^+$ molecular ion. In the ^1H NMR spectrum (220 MHz, $CDCl_3$), a singlet at 1.18 ppm (area 9) is attributable to the *tert*-butyl group; the complex pattern centered at 1.7 ppm is indicative of a saturated cyclohexyl group, and two sharp singlets at 2.65 ppm (area 3) and 2.70 ppm (area 3) are ascribed to the nonequivalent methyl groups of the dimethyl sulfide ligand. The infrared spectrum contained a weak band at 3346 cm^{-1}, which was assigned to the N–H stretching mode.

In order to locate the positions of the dimethyl sulfide, cyclohexyl, and *tert*-butyl groups on the eleven-atom *nido*-monocarborane structure, a single-crystal X-ray diffraction study of the compound was completed. The structure of the molecule and the numbering scheme is presented in Figure 1. Selected interatomic distances are listed in Table I. The eleven-atom nido structure for $B_{10}H_{10}(C_6H_{11})S(CH_3)_2CNHC(CH_3)_3$ is confirmed. In this product of the reaction, the isocyanide carbon has apparently inserted into the open face of the starting material without disturbing the relative positions of either the dimethyl sulfide or cyclohexyl substituents. The numbering system in Figure 1 uses the original numbering of the starting material, dimethyl sulfide (S–B^5)-9-cyclohexyl-decaborane(11) and labels the inserted isocyanide carbon atom as C(9). Since the products of this reaction were obtained in moderate (55%) yield, the existence of a second possible isocyanide insertion isomer (with the carbon atom located in the other possible icosahedral position) cannot be precluded.

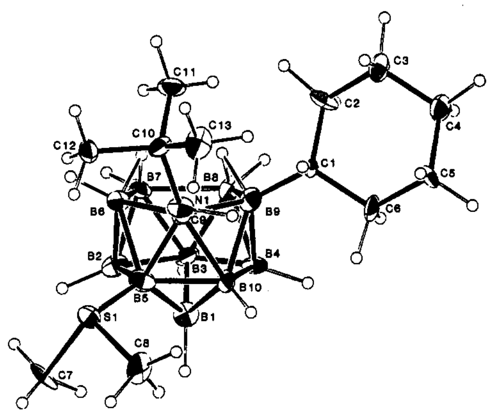

Figure 1. ORTEP view of the $B_{10}H_{10}(C_6H_{11})S(CH_3)_2CNHC(CH_3)_3$ molecule, showing the atom-numbering scheme used in the tables. Hydrogen atoms are represented as open circles.

Table I. Bond Distances (Å) for the $B_{10}H_{10}(C_6H_{11})S(CH_3)_2CNH(t\text{-}C_4H_9)$ Molecule

		distance	
A	B	molecule 1	molecule 2
S(1)	C(7)	1.807 (8)	1.807 (9)
S(1)	C(8)	1.787 (9)	1.782 (9)
S(1)	B(5)	1.884 (9)	1.894 (9)
N(1)	C(9)	1.473 (9)	1.456 (9)
N(1)	C(10)	1.498 (9)	1.504 (9)
C(9)	B(5)	1.702 (11)	1.690 (11)
C(9)	B(6)	1.651 (11)	1.658 (12)
C(9)	B(9)	1.690 (11)	1.696 (11)
C(9)	B(10)	1.724 (11)	1.726 (11)
B(1)	B(2)	1.797 (13)	1.814 (13)
B(1)	B(3)	1.750 (13)	1.762 (13)
B(1)	B(4)	1.782 (13)	1.797 (13)
B(1)	B(5)	1.748 (13)	1.740 (13)
B(1)	B(10)	1.760 (13)	1.762 (13)
B(2)	B(3)	1.777 (13)	1.797 (13)
B(2)	B(5)	1.727 (13)	1.740 (13)
B(2)	B(6)	1.807 (12)	1.787 (13)
B(2)	B(7)	1.773 (13)	1.769 (14)
B(3)	B(4)	1.780 (13)	1.800 (13)
B(3)	B(7)	1.747 (13)	1.745 (13)
B(3)	B(8)	1.736 (13)	1.743 (13)
B(4)	B(8)	1.789 (13)	1.780 (13)
B(4)	B(9)	1.817 (12)	1.817 (12)
B(4)	B(10)	1.749 (13)	1.737 (13)
B(5)	B(6)	1.781 (13)	1.777 (13)
B(5)	B(10)	1.745 (13)	1.728 (13)
B(6)	B(7)	1.874 (13)	1.857 (14)
B(7)	B(8)	1.876 (13)	1.880 (14)
B(8)	B(9)	1.872 (13)	1.884 (13)
B(9)	B(10)	1.817 (13)	1.820 (12)

The cage carbon–nitrogen bond length is 1.473 (9) Å, which is in good agreement with the single C–N bond length of 1.472 Å found in primary and secondary amines.[8] The product from

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Table II. 70.6-MHz ^{11}B NMR Data

compound (solvent)	rel area	δ_B (J_{BH}, Hz)
$B_{10}H_{10}(C_6H_{11})S(CH_3)_2$-$CNHC(CH_3)_3$($CH_2Cl_2$)	1:1:2:1:1:1:1:2	+2.4; −5.6 (151); −9.6; −12.3 (146); −21.6 (146); −26.7 (137); −28.8 (142); −33.7 (146)
$B_{10}H_{11}(C_6H_{11})S(CH_3)_2$·$C{\equiv}NC(CH_3)_3$($CH_2Cl_2$)	1:2:4:1:1:1	+9.5; −5.3 (11); −8.7; −18.9; −39.6 (136.7); −45.1 (142)

the reaction of $B_{10}H_{14}$ with alkyl isocyanides appears to have the zwitterionic structure, $B_{10}H_{12}C^{-}{\leftarrow}N^{+}H_2R$.[6] In the present structure, an amino (NHR) instead of an amine (NH_2R) group is attached to the cage carbon atom. There are two hydrogen atoms located in bridging positions between the boron atoms on the open face.

A second crystalline product was isolated, in low yield, from the reaction of $B_{10}H_{11}(C_6H_{11})S(CH_3)_2$ and *tert*-butyl isocyanide. The low-resolution mass spectrum of this minor product also cut off at m/e 349, corresponding to a $^{11}B_{10}{}^{12}C_{13}{}^{1}H_{37}{}^{14}N^{32}S^{+}$ parent ion. The ^{1}H NMR spectrum (see the experimental section) contains signals suggesting the presence of *tert*-butyl, cyclohexyl, and dimethyl sulfide groups in this compound. The infrared spectrum of the minor product contained a strong sharp band at 2252 cm^{-1}, which is attributed to the C≡N– group of the *tert*-butyl isocyanide. The available evidence suggests that this isomeric product is $B_{10}H_{11}(C_6H_{11})S(CH_3)_2$·$C{\equiv}N(t\text{-}C_4H_9)$, an alkyl isocyanide acid–base complex of the starting material, but the relative positions of the three substituents on the decaborane framework have not been determined.

In a previous study we had found that $B_9H_{11}S$, which is isoelectronic with $B_{10}H_{11}(C_6H_{11})(SMe_2)$, formed two different $B_9H_{11}S$·CNR (R = t-C_4H_9) complexes at room temperature.[9] One of these complexes reacted further to form the isocyanide insertion product $B_9H_9SCNH_2R$. The second $B_9H_{11}S$·CNR complex did not undergo further reaction, even in refluxing toluene. The formation of "reactive" and "unreactive" Lewis acid–base complexes with polyhedral boranes may be a common occurrence.

The title compound is a very interesting substituted one-carbon carborane, which can be obtained at present in only moderate yield. Chemistry related to the functional groups in this molecule as well as the synthesis of metallocarborane derivatives is in progress.

Experimental Section

Physical Measurements. Boron (^{11}B) NMR spectra were obtained at 70.6 MHz with a Varian HR-220 spectrometer and were externally referenced to BF_3·$O(C_2H_5)_2$ (positive values downfield). Proton NMR spectra were obtained on either a Varian HR-200 or a Varian T-60A spectrometer and were referenced relative to internal tetramethylsilane (Me_4Si). Infrared spectra were obtained as KBr disks on a Perkin-Elmer 283 spectrometer or a Digilab 15C FTIR spectrometer. Low-resolution mass spectral data were obtained with an Atlas CH-7 spectrometer. Melting points were obtained in sealed, evacuated capillaries and are uncorrected. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY.

Materials. All reactions were performed under an atmosphere of prepurified nitrogen. Benzene (C_6H_6) was dried over calcium hydride. All other commercially available reagents were used as received.

Reaction of Dimethyl Sulfide(S–B^5)-9-cyclohexyldecaborane(11) with *tert*-Butyl Isocyanide. Freshly prepared $B_{10}H_{11}(C_6H_{11})S(CH_3)_2$ (ca. 0.8 g; 3 mmol) was dissolved in a 2:1 benzene–hexane mixture (50 mL), and then, *tert*-butyl isocyanide (0.31 mL; 2.96 mmol) was added via syringe. The reaction mixture was heated with stirring under nitrogen and maintained at reflux temperature for 17 h. After the mixture was cooled to room temperature, a precipitate containing $B_{10}H_{10}(C_6H_{11})S(CH_3)_2C$-$NHC(CH_3)_3$ formed and was removed by filtration through a medium-porosity glass frit. The filtrate was reduced in vacuo to 20 mL, which gave additional $B_{10}H_{10}(C_6H_{11})S(CH_3)_2CNHC(CH_3)_3$ precipitate, which was removed by filtration. The precipitates were combined, yielding crude $B_{10}H_{10}C_6H_{11}S(CH_3)_2CNHC(CH_3)_3$ (0.56 g; 55% based on $B_{10}H_{11}C_6H_{11}S(CH_3)_2$), which was recrystallized from methanol–water, producing white plates (0.29 g; 30%) mp 142–145 °C. The ^{11}B NMR spectral data are given in Table II. The infrared spectrum contained absorptions at 3346 (w), 2913 (s), 2883 (vs), 2530 (vs), 1441 (m), 1419 (m), 1377 (w), 1359 (s, sharp), 1203 (s), 1118 (m), 1005 (w), 977 (m), 953 (m), 875 (w), 610 (m), and 515 (w) cm^{-1}.

Table III. Summary of Crystal Data for $B_{10}H_{10}C_6H_{11}S(CH_3)_2CNHC(CH_3)_3$

fw	347.6
D_x (calcd density)	1.089 g cm^{-3}
Z (formula units/unit cell)	8
cryst size	0.25 × 0.25 × 0.35 mm
a	18.015 (8) Å
b	25.871 (13) Å
c	9.176 (4) Å
β	97.60 (2)°
V	4238.79 Å^3
temp of data collcn	112 K
wavelength of Mo Kα radiation	0.71069 Å
scan range (2θ)	6–40°
scan rate	4°/min
no. of reflcns measd	4382
no. of unique reflcns	3946
no. of reflcns with $F > 2.33\sigma(F)$	3107
space group	$P2_1/a$

Anal. Calcd for $C_{13}H_{37}B_{10}NS$: C, 44.87; H, 10.64. Found (using V_2O_5 as a combustion catalyst): C, 45.23; H, 10.58.

The solvent was removed from the filtrate remaining after the second filtration, leaving an off-white residue (0.34 g; 32%). The residue was crystallized from methanol, yielding small white crystals of $B_{10}H_{11}(C_6H_{11})S(CH_3)_2$·$C{\equiv}NC(CH_3)_3$ (12 mg; 1%), mp 144–147 °C. The proton NMR spectrum contained a sharp singlet at δ 1.0 (9 H), a broad multiplet at δ 1.8 (11 H), and two sharp singlets at δ 2.37 (3 H) and δ 2.50 (3 H), respectively. The ^{11}B spectral data are given in Table II. The infrared spectrum included absorptions at 3154 (m), 2983 (w), 2956 (m), 2929 (w), 2903 (w), 2524 (s), 2252 (vs, sharp), 1816 (w), 1793 (m), 1641 (w), 1562 (w), 1469 (s), 1427 (w), 1380 (s), 1247 (m), 1216 (w), and 1095 (s) cm^{-1}.

Crystallography of $B_{10}H_{10}(C_6H_{11})S(CH_3)_2CNH(CH_3)_3$. A summary of crystal data for $B_{10}H_{10}(C_6H_{11})S(CH_3)_2CNH(CH_3)_3$ is given in Table III.

X-ray Data Collection. Crystals were obtained by slow evaporation of a methanol–water solution at room temperature. Initial attempts to grow crystals were unsuccessful, as only microcrystalline samples were obtained. Finally, the crystals grown appeared as diamond shaped plates of various thickness. Initial characterization of the sample indicated the presence of a twin crystal, *mmm* symmetry. Examination under a polarizing microscope indicated that the crystals were well-defined twins, and a suitable sample for the data collection was obtained by cleaving a fragment from a much larger crystal. A crystal of dimensions 0.25 × 0.25 × 0.35 mm was mounted on a previously described goniostat[10] and cooled to 112 K. Lattice parameters were determined from 32 reflections centered by using automated top–bottom/left–right techniques. Intensity data were collected by using θ–2θ scan techniques with a scan speed of 4°/min over a range in 2θ of 2° + dispersion and 10-s stationary background counts at each extreme of the scan. Statistics and Patterson function indicated the proper space group to be the polar $P2_1/a$ (alternate setting of $P2_1/c$, No. 15). An initial data set collected to 2θ = 45° contained less than 30% "observed" data based on the criteria that a reflection is observed if the raw count exceeds twice the background for the count. In spite of the sparsity of data, the structure was readily solved by direct methods (LSAM) and Fourier techniques. Data reduction[10] and full-matrix refinement using isotropic thermal parameters converged to $R(F)$ = 0.1 and $R_w(F)$ = 0.21. Since there appeared to be no disorder present, a second data set was collected with the use of longer background counts and redundant data to 2θ = 40°. The 4382 reflections, including standards, were measured at 112 K over a 2θ range of 6–40°. Of the reflections measured, 3946 were unique and 3107 were considered observed with $F > 2.33\sigma(F)$ and were used in the solution and refinement. The data were reduced as before, and refinement using anisotropic thermal parameters for all non-hydrogen atoms converged to $R(F)$ = 0.099 and $R_w(F)$ = 0.092. A difference Fourier synthesis phased on this refinement located all hydrogen atoms, and these were included in the final full-matrix refinement. The final refinement used anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal

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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.

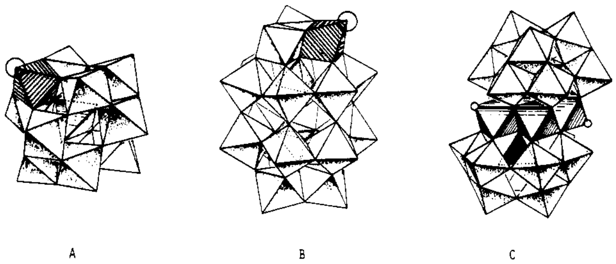

Figure 1. Polyhedral representations of polyanions containing octahedral heteroelements (shaded) examined in this study: (A) Keggin structure, α-$XW_{11}O_{39}M(OH_2)^{m-}$ (X = Si, P; M = Co, Mn, Ni, Cu; m = 5, 6); (B) Dawson structure, α_2-$P_2W_{17}O_{61}Co(OH_2)^{8-}$; (C) $P_2W_{18}O_{68}Co_4(OH_2)_2{}^{10-}$.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