of structural characteristics in these compounds involving strained coordination.

(5) The various spectroscopic properties of 3 have demonstrated the high-spin configuration of Fe^{2+} ion in a highly distorted octahedral crystal field.

py2SH and related compounds possess antivirial and antifungal activity.[39] Since iron is a necessary nutrient for various microorganisms, the chemistry of the iron complexes of py2SH and related ligands is expected to have other interesting aspects from the unusual structural characteristics discussed in this paper.

Acknowledgment. This research was supported by a Faculty Research Committee Grant at the University of California, Santa Cruz, and by NIH Grant No. GM32690 at the University of Texas, Austin. We are also thankful to Drs. G. Papaefthymiou and R. Frankel of Francis Bitter National Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, MA, for help in acquiring the Mössbauer spectra.

Registry No. $[Et_4N][Fe(SC_5H_4N)_3]$, 102149-44-0.

Supplementary Material Available: Crystal structure data for $(Et_4N)[Fe(SC_5H_4N)_3]$ including thermal parameters of cation and anion (Table S-I), bond distances and angles for the cation (Table S-II), positional parameters for hydrogens (Table S-III), and unweighted least-squares planes of the anion (Table S-IV) (9 pages). Ordering information is given on any current masthead page.

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Disubstituted Tungstosilicates. 1. Synthesis, Stability, and Structure of the Lacunary Precursor Polyanion γ-$SiW_{10}O_{36}^{8-}$

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The polyanion $SiW_{10}O_{36}^{8-}$ was obtained from β_2-$SiW_{11}O_{39}^{8-}$ at pH 9.1 and isolated as K^+ and Rb^+ salts. The structure of $Rb_8SiW_{10}O_{36}\cdot 10H_2O$ (monoclinic, $P2_1/c$; a = 12.426 (3) Å, b = 19.319 (6) Å, c = 19.743 (5) Å, β = 96.33 (3)°; Z = 4) has been determined and refined to final indices R and R_w of 0.070 and 0.073. The polyanion is a γ isomer, and the ^{183}W NMR spectra of aqueous solutions agree with the solid-state structure. They present one exceptionally weak $^2J_{W-W}$ coupling (4.9 Hz) between corner-sharing tungsten atoms. The polyanion gives 1/1 complexes with alkali-metal and alkaline-earth cations, and its stability in solution is strongly dependent on the formation of these complexes.

Introduction

The analogy between heteropoly oxometalates and metal oxides,[1] from structural and reactivity points of view, has recently attracted much attention.[2] In addition, polysubstituted Keggin-structure heteropolyanions of molybdenum and tungsten with Ti^{IV}, V^V, Nb^V, etc., have enough negative surface charges to bind organometallic transition-metal catalysts.[3] Direct syntheses of these substituted polyanions from constitutive elements always lead to mixtures of isomers.[4] In order to develop stereospecific syntheses of trisubstituted 12-heteropoly compounds, we had prepared the A-type trivacant lacunary polyanions α- and β-$X^NW_9O_{34}^{(14-N)-}$ with X^N = Si^{IV}, Ge^{IV}, P^V, and As^V.[5] The reaction of Mo^{VI}, V^V, and Nb^V oxoanions with $SiW_9O_{34}^{10-}$ effectively gives pure α and β forms of $SiW_9Mo_3O_{40}^{4-}$,[5a] $SiW_9V_3O_{40}^{7-}$,[6] and $SiW_9Nb_3O_{40}^{7-}$[3g] polyanions in which the three octahedral molybdenum, vanadium, or niobium atoms are adjacent and share a corner.

Stereospecific syntheses of disubstituted Keggin anions were difficult as there were no bivacant lacunary polyanions available in large amounts until now. The $PW_{10}O_{36}^{7-}$ anion has been described,[7] but experience shows that its preparation is difficult, even in small quantities, as several other polyanions are simultaneously present in the solution. We have studied the conditions of formation of 10-heteropolyanions derived from the Keggin structure and selected the tungstosilicic family because the tungstosilicates are generally more stable than other tungsten heteropolyanions.

Results and Discussion

Formation of the 10-Tungstosilicate. The alkaline hydrolyses of the known tungstosilicates were systematically investigated in order to obtain some information about their specificities and to detect eventual new intermediates. These reactions were studied by polarography, each polyanion being characterized by its oxidation-reduction potentials.[8] The results are summarized in Figure 1.

β-$SiW_{12}O_{40}^{4-}$ only gives β_2-$SiW_{11}O_{39}^{8-}$ at pH 6-8. We have previously shown that, in this polyanion, the lacuna is one of the six equivalent sites adjacent to the tritungstic rotated group of the β structure. Conversely, one can recall that β-$SiW_{12}O_{40}^{4-}$ is

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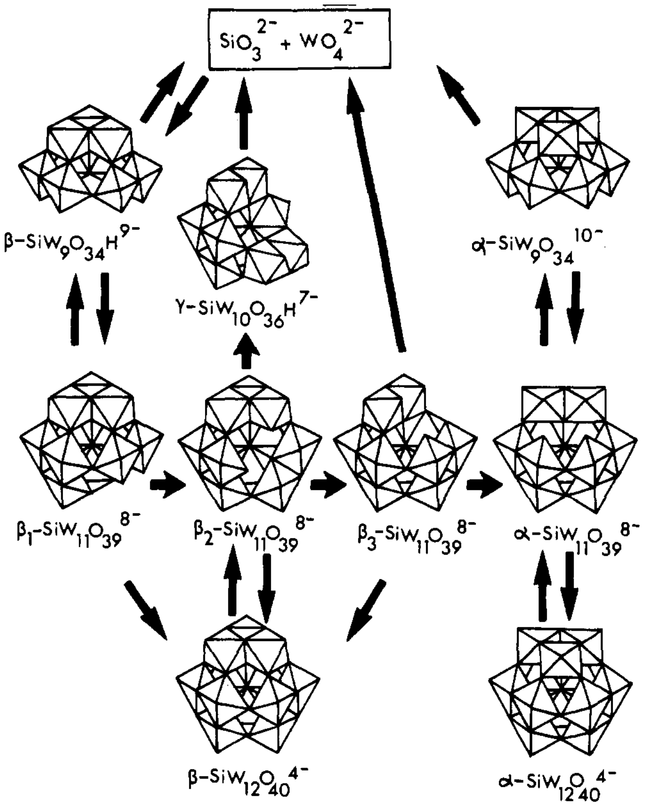

Figure 1. Polyhedral models and relationships between the different known tungstosilicates. This scheme is based partly on structural determination by single-crsytal X-ray diffraction studies and partly on proposed structures. Hydrolysis of the β-$SiW_{12}O_{40}^{4-}$ anion only gives β_2-$SiW_{11}O_{39}^{8-}$ and, then, the γ-$SiW_{10}O_{36}^{8-}$ anion.

the common species obtained by addition of tungsten on β_1-, β_2-, or β_3-$SiW_{11}O_{39}^{8-}$ in acid solution.[8]

In fact, the β_2 isomer is not the thermodynamically stable 11-tungstosilicate since it spontaneously isomerizes into the β_3 and, then, into the α isomer.[8] Thus, the specificity of the hydrolysis of β-$SiW_{12}O_{40}^{4-}$ is due to kinetic control of the reaction.

At pH $\cong$9 the β_1- and α-$SiW_{11}O_{39}^{8-}$ isomers only give A-β- and A-α-$SiW_9O_{34}^{10-}$, respectively. This reversible reaction corresponds to the loss of two tungstic octahedra linked by a corner. No intermediate was evident when β_3-$SiW_{11}O_{39}^{8-}$ was hydrolyzed at any pH: it decomposes directly into tungstate and silicate.

On the other hand, polarographic waves not assignable to previously known tungstosilicic compounds appeared in the solution of β_2-$SiW_{11}O_{39}^{8-}$ at pH $\cong$9. These waves vanished with time, showing that the transient species is not stable at this pH. A kinetic study allows us to determine the optimal conditions for the preparation of a pure product. Molar weight determination by ultracentrifugation ($M_r \cong 2800$) and analysis of the potassium salt showed that it could be written $K_8SiW_{10}O_{36}\cdot 12H_2O$.

Characterization. The polyanion can be characterized by its IR spectrum and its oxidation–reduction behavior in aqueous solution (Figure 2). The polarogram exhibits two reversible waves of two electrons per ion. The slopes of the $E_{1/2}$–pH plots show that there are simultaneous fixations of two protons according to

$$HSiW^{VI}_{10}O_{36}^{7-} + 2e^- + 2H^+ \rightleftarrows H_3SiW^{VI}_8W^V_2O_{36}^{7-}$$

$$H_3SiW^{VI}_8W^V_2O_{36}^{7-} + 2e^- + 2H^+ \rightleftarrows H_5SiW^{VI}_6W^V_4O_{36}^{7-}$$

Structure of $Rb_8SiW_{10}O_{36}\cdot 10H_2O$. The anion $SiW_{10}O_{36}^{8-}$ can be derived from a Keggin-structure anion by $\pi/3$ rotations of two W_3O_{13} groups and the removal of the two octahedra that become edge shared by these rotations. According to Baker and Figgis,[9] it is a γ polyanion: the compounds formally obtained from the Keggin anion (α) by the rotation of one or two W_3O_{13} groups are respectively referred to as β and γ polyanions. $SiW_{10}O_{36}^{8-}$ is structurally analogous to the $PW_{10}O_{36}^{7-}$ anion previously described.[7] Figure 3 shows the anion and the IUPAC numbering scheme[10] of the W atoms in a polyhedral representation.

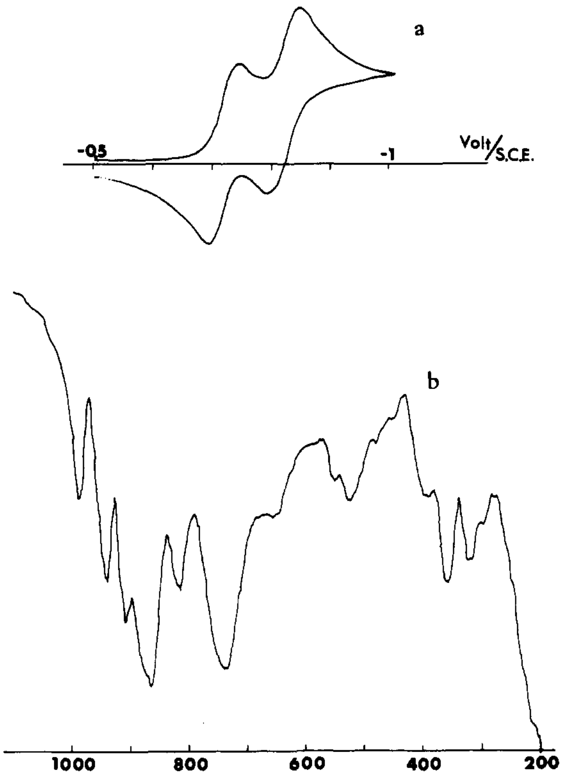

Figure 2. (a) Cyclic voltammetry of γ-decatungstosilicate in acetate buffer. (b) IR spectrum of $Rb_8SiW_{10}O_{36}\cdot 10H_2O$ as a KBr pellet.

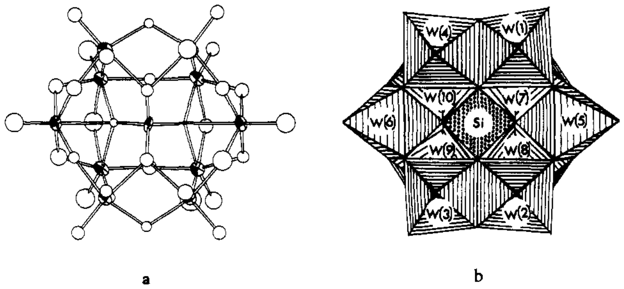

Figure 3. (a) ORTEP plot of the decatungstosilicate anion. All atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of the electron density. Principal ellipses and axes with envelope and octant shading are drawn for tungsten and silicon atoms. (b) Polyhedral model with tungsten numbering.

Designation of oxygen atoms takes into account, by the numbers in parentheses, the W atoms to which they are linked and, by lower case letters, the type of bonding. Oa atoms bridge W atoms and the central Si heteroatom. Ob and Oc oxygens link WO_6 octahedra, respectively, by vertex and by edge. Od atoms are bonded to one W atom. If two Od atoms are linked to the same W, the prime is added when oxygen is not trans to an Oa atom: in fact, it would be an Oc atom in the hypothetical γ-dodecatungstic structure. The atomic coordinates, vibrational parameters, and corresponding standard deviations are reported in Table I. Selected bond lengths and angles are given in Table II.

The bond length Si–Oa is shorter if the oxygen atom belongs to a ditungstic group (mean value 1.57 Å) than if its belongs to a tritungstic one (1.68 Å). W–O distances in W_xO_6 octahedra (x = 5–10) are within the usual range for such Keggin-like structures. In W_xO_6 octahedra (x = 1–4), distances between W and Od′ are almost the same as the other W–Od distances and

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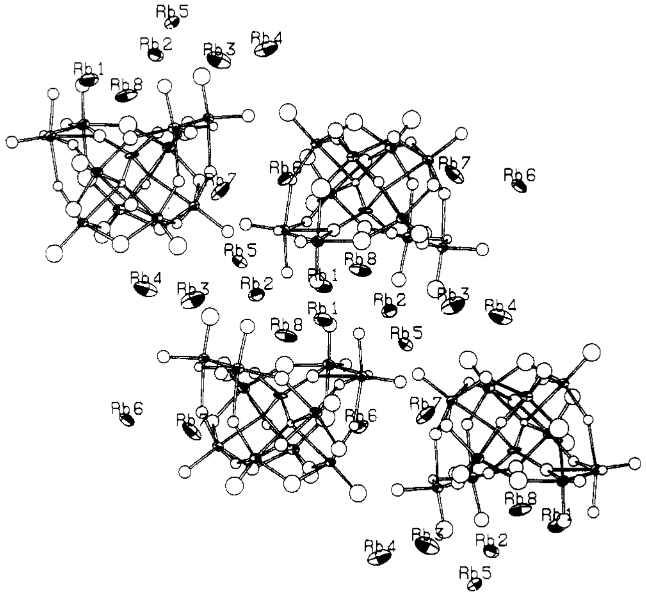

Figure 4. ORTEP drawing of the unit cell. All atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of the electron density. Principal ellipses and axes of Rb, W, and Si atoms are drawn.

correspond to multiple-bonding character. The length of the trans-W–Ob bond is enhanced (mean value 2.19 Å).

The different Rb^+ cations interact with O atoms of two or three different polyoxotungstates and form a network as appears in Figure 4. Two Rb^+ ions can be distinguished: Rb(1) and Rb(2) have a pseudosymmetrical place in front of the aperture of the structure.

The pathway for the formation of the γ-$SiW_{10}O_{36}^{8-}$ anion from the hydrolysis of β_2-$SiW_{11}O_{39}^{8-}$ is worthy of additional considerations. This reaction is rather complex because the β_2–γ structural change implies both the loss of a tungsten and a rearrangement that is formally equivalent to the rotation of a bitungstic group. As has been reported[2] according to "Lipscomb's rule"[11] the β_2 isomer should lead to a stable β-10-tungstosilicate with two adjacent vacancies; actually this β-$SiW_{10}O_{37}^{10-}$ anion has not been evidenced, perhaps because of its relatively high negative charge with respect to that of the γ-10-tungstosilicate.

Stability and Interaction with Alkali-Metal and Alkaline-Earth Cations. The stability of the polyanion in aqueous solution is strongly dependent on the nature of the counterion. Potassium, rubidium, and cesium solutions are stable; in contrast, lithium and sodium solutions, obtained by exchange on cationic resins, slowly transform with formation of mixtures of β-$SiW_{11}O_{39}^{8-}$ anions, identified by their polarograms. This behavior indicates that the $SiW_{10}O_{36}^{8-}$ polyanion is stabilized by the formation of complexes with alkali-metal cations.

The aqueous solution of the acid, obtained by exchange on a Dowex 50W-X2 acid-form resin is stable at least for 1 month. This behavior contrasts with the limited pH zone of stability of the other lacunary polyanions such as $SiW_9O_{34}^{10-}$ and $SiW_{11}O_{39}^{8-}$.

Rapid titrations of $H_8SiW_{10}O_{36}$ aqueous solutions by alkali-metal hydroxides MOH showed seven strong acidities and a weak one. The apparent acidity constant, given by the pH value for half-neutralization, depends on the concentration and the nature of M. This can be interpreted by the occurrence of two simultaneous equilibria:

$$HSiW_{10}O_{36}^{7-} \rightleftarrows SiW_{10}O_{36}^{8-} + H_{aq}^{+} \quad (1)$$

$$SiW_{10}O_{36}^{8-} + M_{aq}^{+} \rightleftarrows MSiW_{10}O_{36}^{7-} \quad (2)$$

Table I. Fractional Atomic Coordinates and Thermal Parameters[a]

atom	*x/a*	*y/b*	*z/c*	*B*(eq), Å^2
W(1)	0.7974 (2)	0.5825 (1)	0.3686 (1)	1.82 (7)
W(2)	0.9942 (2)	0.3177 (1)	0.3983 (1)	2.05 (7)
W(3)	0.7567 (3)	0.2442 (1)	0.4032 (1)	2.19 (7)
W(4)	0.5614 (2)	0.5119 (1)	0.3761 (1)	1.83 (6)
W(5)	1.0249 (2)	0.4834 (1)	0.3086 (1)	1.83 (6)
W(6)	0.5070 (2)	0.3298 (2)	0.3247 (1)	2.01 (7)
W(7)	0.8191 (2)	0.5137 (1)	0.1902 (1)	1.96 (7)
W(8)	0.9390 (2)	0.3541 (1)	0.2080 (1)	1.92 (7)
W(9)	0.6703 (2)	0.2750 (1)	0.2143 (1)	1.94 (7)
W(10)	0.5510 (2)	0.4352 (1)	0.1990 (1)	2.01 (7)
Si	0.766 (1)	0.408 (1)	0.3263 (8)	1.6 (4)
Rb(1)	0.0000	0.0000	0.0000	5.0 (4)
Rb(2)	0.5851 (8)	0.1422 (5)	0.0229 (4)	3.7 (2)
Rb(3)	0.164 (1)	0.2780 (7)	0.0517 (6)	6.4 (4)
Rb(4)	0.718 (1)	0.3790 (8)	0.0445 (6)	7.9 (5)
Rb(5)	0.8982 (7)	0.1721 (4)	0.1141 (4)	3.3 (2)
Rb(6)	0.6827 (7)	0.0796 (4)	0.2706 (4)	3.3 (2)
Rb(7)	0.1940 (8)	0.2188 (5)	0.2815 (5)	5.0 (3)
Rb(8)	0.2841 (7)	0.4206 (6)	0.4166 (4)	4.1 (2)
atom	***x/a***	***y/b***	***z/c***	***B*(iso), Å^2**
Oa(1-4)	0.732 (4)	0.476 (2)	0.363 (2)	2.4 (9)
Oa(2-3)	0.820 (4)	0.353 (2)	0.377 (2)	1.9 (8)
Oa(5-7-8)	0.859 (3)	0.430 (2)	0.275 (2)	1.1 (7)
Oa(6-9-10)	0.659 (3)	0.371 (2)	0.279 (2)	0.2 (5)
Ob(1-5)	0.938 (3)	0.534 (2)	0.360 (2)	1.8 (8)
Ob(1-7)	0.771 (3)	0.566 (2)	0.262 (2)	1.2 (7)
Ob(2-5)	1.026 (4)	0.410 (3)	0.379 (3)	2.7 (9)
Ob(2-8)	0.968 (3)	0.308 (2)	0.286 (2)	1.8 (8)
Ob(3-6)	0.610 (4)	0.286 (2)	0.383 (2)	2.4 (9)
Ob(3-9)	0.735 (4)	0.240 (2)	0.289 (2)	2.3 (9)
Ob(4-6)	0.525 (5)	0.416 (3)	0.371 (3)	4.1 (13)
Ob(4-10)	0.541 (5)	0.503 (4)	0.265 (4)	5.0 (14)
Ob(7-10)	0.685 (4)	0.468 (3)	0.170 (3)	2.6 (9)
Ob(8-9)	0.798 (3)	0.312 (2)	0.186 (2)	1.7 (7)
Oc(1-4)	0.645 (3)	0.596 (2)	0.360 (2)	1.7 (7)
Oc(2-3)	0.903 (3)	0.233 (2)	0.397 (2)	1.3 (7)
Oc(5-7)	0.959 (4)	0.533 (3)	0.229 (3)	3.3 (10)
Oc(5-8)	1.062 (4)	0.409 (3)	0.246 (3)	2.6 (9)
Oc(6-9)	0.535 (4)	0.264 (3)	0.258 (3)	2.7 (9)
Oc(6-10)	0.445 (3)	0.380 (2)	0.244 (2)	1.6 (8)
Oc(7-8)	0.891 (5)	0.432 (3)	0.151 (3)	4.7 (13)
Oc(9-10)	0.576 (4)	0.348 (3)	0.163 (3)	2.7 (9)
Od(1)	0.827 (4)	0.666 (2)	0.359 (2)	2.2 (8)
Od′(1)	0.818 (3)	0.577 (2)	0.430 (2)	1.9 (8)
Od(2)	1.125 (4)	0.281 (2)	0.398 (2)	2.0 (8)
Od′(2)	0.997 (4)	0.337 (3)	0.485 (2)	2.5 (9)
Od(3)	0.725 (4)	0.159 (2)	0.406 (3)	2.4 (9)
Od′(3)	0.778 (5)	0.259 (3)	0.490 (3)	4.0 (12)
Od(4)	0.432 (4)	0.548 (3)	0.366 (3)	2.4 (9)
Od′(4)	0.593 (4)	0.513 (3)	0.462 (3)	2.8 (9)
Od(5)	1.151 (5)	0.519 (3)	0.336 (3)	4.1 (12)
Od(6)	0.391 (5)	0.295 (3)	0.349 (3)	4.6 (13)
Od(7)	0.816 (5)	0.575 (3)	0.126 (3)	4.7 (13)
Od(8)	1.008 (5)	0.310 (3)	0.154 (3)	3.8 (12)
Od(9)	0.654 (4)	0.204 (2)	0.160 (2)	2.3 (9)
Od(10)	0.455 (4)	0.473 (3)	0.138 (3)	3.3 (10)

[a] Esd's in parentheses refer to the last significant digit.

Attempts to determine the true acidity constant (equilibrium 1) using $(CH_3)_4NOH$ (assuming that there is no complex between the polyanion and the large cation TMA^+) failed. At the high pH values necessary to deprotonate $HSiW_{10}O_{36}^{7-}$ a rapid decomposition of the $SiW_{10}O_{36}^{8-}$ polyanion into silicate and tungstate occurs. We could only obtain an approximate value of 10.5 ± 0.5 for the p*K* of equilibrium 1.

So, the γ-$SiW_{10}O_{36}^{8-}$ polyanion is not stable in aqueous solution, and only the acid $HSiW_{10}O_{36}^{7-}$ and the complexed forms $MSiW_{10}O_{36}^{7-}$ are stable, probably because of the decreasing local charge near the aperture of the structure.

Experiments in the presence of a large excess of the M^{n+} alkali-metal or alkaline-earth cations have been performed in order to quantitatively form the complex $MSiW_{10}O_{36}^{(8-n)-}$. The values of the equilibrium constant of

$$HSiW_{10}O_{36}^{7-} + M_{aq}^{n+} \rightleftarrows MSiW_{10}O_{36}^{(8-n)-} + H_{aq}^{+} \quad (3)$$

are given in Figure 5. K_3 increases with the size of the cations,

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Table II. Selected Geometric Parameters[a]

atoms	dist, Å	atoms	dist, Å	atoms	dist, Å	atoms	dist, Å	mean value,[b] Å
W(1)–Oa(1-4)	2.21 (5)	W(2)–Oa(2-3)	2.27 (4)	W(3)–Oa(2-3)	2.32 (4)	W(4)–Oa(1-4)	2.27 (5)	2.27
W(1)–Ob(1-5)	2.01 (4)	W(2)–Ob(2-5)	1.88 (5)	W(3)–Ob(3-6)	2.00 (5)	W(4)–Ob(4-6)	1.90 (6)	1.95
W(1)–Ob(1-7)	2.11 (4)	W(2)–Ob(2-8)	2.22 (4)	W(3)–Ob(3-9)	2.25 (5)	W(4)–Ob(4-10)	2.19 (7)	2.19
W(1)–Oc(1-4)	1.90 (4)	W(2)–Oc(2-3)	1.98 (4)	W(3)–Oc(2-3)	1.85 (4)	W(4)–Oc(1-4)	1.97 (4)	1.93
W(1)–Od′(1)	1.79 (4)	W(2)–Od′(2)	1.75 (5)	W(3)–Od′(3)	1.72 (6)	W(4)–Od′(4)	1.70 (5)	1.74
W(1)–Od(1)	1.67 (5)	W(2)–Od(2)	1.77 (4)	W(3)–Od(3)	1.70 (5)	W(4)–Od(4)	1.74 (5)	1.72
W(5)–Oa(5-7-8)	2.34 (4)			W(6)–Oa(6-9-10)	2.32 (3)			2.33
W(5)–Ob(1-5)	1.84 (4)	W(5)–Ob(2-5)	1.99 (5)	W(6)–Ob(3-6)	1.82 (5)	W(6)–Ob(4-6)	1.91 (6)	1.89
W(5)–Oc(5-7)	1.94 (5)	W(5)–Oc(5-8)	1.98 (5)	W(6)–Oc(6-9)	1.90 (5)	W(6)–Oc(6-10)	1.95 (4)	1.94
W(5)–Od(5)	1.74 (6)			W(6)–Od(6)	1.71 (7)			1.72
W(7)–Oa(5-7-8)	2.34 (4)	W(8)–Oa(5-7-8)	2.27 (4)	W(9)–Oa(6-9-10)	2.27 (3)	W(10)–Oa(6-9-10)	2.31 (3)	2.30
W(7)–Ob(1-7)	1.89 (4)	W(8)–Ob(2-8)	1.78 (4)	W(9)–Ob(3-9)	1.73 (5)	W(10)–Ob(4-10)	1.86 (7)	1.82
W(7)–Ob(7-10)	1.89 (5)	W(8)–Ob(8-9)	1.94 (4)	W(9)–Ob(8-9)	1.88 (4)	W(10)–Ob(7-10)	1.92 (5)	1.91
W(7)–Oc(5-7)	1.85 (5)	W(8)–Oc(5-8)	1.94 (5)	W(9)–Oc(6-9)	1.98 (5)	W(10)–Oc(6-10)	1.98 (4)	1.94
W(7)–Oc(7-8)	2.01 (7)	W(8)–Oc(7-8)	1.93 (7)	W(9)–Oc(9-10)	2.03 (5)	W(10)–Oc(9-10)	1.87 (5)	1.96
W(7)–Od(7)	1.74 (7)	W(8)–Od(8)	1.68 (6)	W(9)–Od(9)	1.74 (5)	W(10)–Od(10)	1.75 (5)	1.73
Si–Oa(1-4)	1.59 (5)	Si–Oa(2-3)	1.54 (5)					1.57
Si–Oa(5-7-8)	1.68 (4)	Si–Oa(6-9-10)	1.68 (4)					1.68

atoms	angle, deg	atoms	angle, deg	atoms	angle, deg	atoms	angle, deg	mean value,[b] deg
W(1)–Ob(1-7)–W(7)	143 (3)	W(2)–Ob(2-8)–W(8)	144 (2)	W(3)–Ob(3-9)–W(9)	146 (3)	W(4)–Ob(4-10)–W(10)	138 (3)	143
W(1)–Ob(1-5)–W(5)	149 (2)	W(2)–Ob(2-5)–W(5)	147 (3)	W(3)–Ob(3-6)–W(6)	151 (3)	W(4)–Ob(4-6)–W(6)	153 (4)	150

[a] Esd's in parentheses refer to the last decimal place. [b] Average value of geometric parameters that are equivalent in the idealized C_{2v} symmetry.

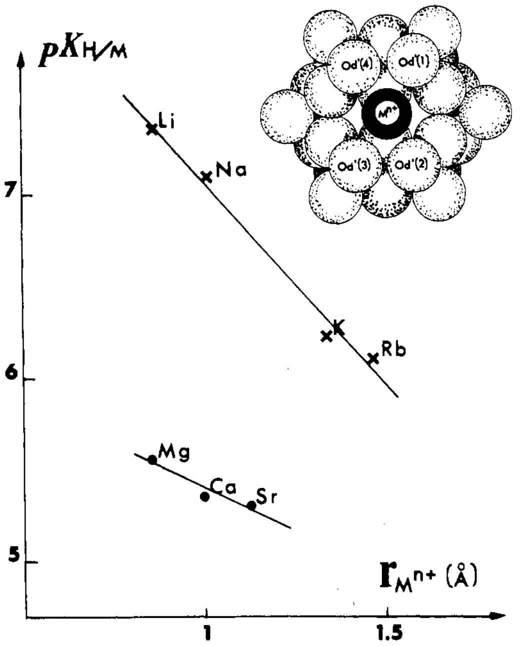

Figure 5. Variation of the H^+/M^+ substitution constant vs. the metallic radii for alkali-metal and alkaline-earth metals. The picture represents a possible space-filling model of the $MSiW_{10}O_{36}^{7-}$ complexes. The spheres represent close-packed oxygen atoms with a radius of 1.4 Å. The M^{n+} radius is that of the K^+ ion.

and a linear variation of pK_3 vs. the cationic radii is observed.

It can be noticed that, in contrast, the stability of the $MSiW_{11}O_{39}^{(8-n)-}$ complexes decreases when the size of the cations M^{n+} increases.[12] This different behavior can be related to the size of the cavity. In $SiW_{11}O_{39}^{8-}$, the size of the cavity is small and a better fit is obtained with small cations such as Li^+. Deformability of the cavity is also an important parameter.[12] In contrast, the aperture of the γ-$SiW_{10}O_{36}^{8-}$ structure is very large, and the larger the cation is, the higher is the stability of the complex. Perhaps a good representation of the $MSiW_{10}O_{36}^{7-}$ complex is that in Figure 5.

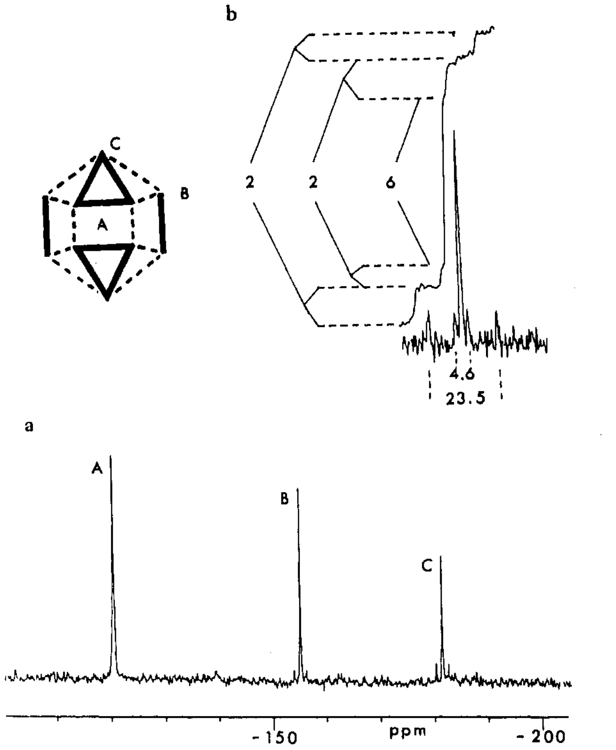

Figure 6. (a) 10.4-MHz ^{183}W NMR spectrum of a 0.13 M solution of $HSiW_{10}O_{36}^{7-}$ as the Li^+ salt in H_2O/D_2O (90/10 v/v) at 297 K (45 000 accumulations of 50° pulses; spectral width 2500 Hz; acquisition time 1.6 s without recycling time; computer size 8K + 8K zerofilling; line broadening 1 Hz; chemical shift reference 2 M Na_2WO_4 in alkaline D_2O). (b) Expanded part for the C line (without exponential multiplication) and its integrated intensity showing that each W(C) atom is strongly coupled with two tungsten (W(B)) atoms and weakly coupled with two tungsten (W(A)) atoms. The schematic plane representation of the anion is adapted from ref 18. Edge and corner junctions are symbolized respectively by solid and dotted lines.

^{183}W NMR Spectrum. The ^{183}W NMR spectra of the protonated or nonprotonated decatungsto anion present three lines with relative intensities of 2:2:1 (Figure 6). Actually the second peak (B) has always a smaller intensity (1.5–1.7) depending on the experimental conditions.[13] In the crystal structure, the 10

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(12) Contant, R. *J. Chem. Res., Synop.* **1984**, 120; *J. Chem. Res., Miniprint* **1984**, 1063–1081.

Table III. Relevant NMR Parameters for the $HSiW_{10}O_{36}^{7-}$ Anion as a Chemical Shift–Coupling Constant Matrix[a,b]

multiplicity	peak designation, assignt	A	B	C
4	A, W(7–10)	−120.5 [2]	*c*	*c*
4	B, W(1–4)	4.9	−155.2 [1.2]	23.8 (15%)
2	C, W(5,6)	4.6 (20%)	23.5 (20%)	−181.5 [1]

[a] By the method in ref 15. [b] Chemical shifts are on the diagonal (ppm/2 M WO_4^{2-}) with line widths (given in Hz) in brackets. The off-diagonal terms are the coupling constants $^2J_{W-W}$ (±0.3 Hz) measured for the satellites of the peak numbered on the same horizontal line. The cumulative integrated intensity of both satellites is reported in parentheses as a percentage of the overall line intensity. [c] Not measurable. Satellites appears as shoulders of the central line.

Table IV. ^{183}W NMR Chemical Shifts of the Decatungstosilicate Anion as a Function of the Protonation and of the Nature of the Alkali-Metal Counterion.

	$HSiW_{10}O_{36}^{7-}$			$MSiW_{10}O_{36}^{7-}$		
M^+	A	B	C	A	B	C
Li^+	−120.5	−155.2	−181.5	−106.9	−147.9	−163.6
Na^+	−118.6	−152.4	−180.0	−102.3	−143.8	−162.8
K^+	−112.6	−144.3	−175.7	−96.4	−137.2	−158.2

tungsten atoms are independent, but in solution, the polyanion adopts the more symmetric conformation (C_{2v}) with three kinds of tungsten atoms (4:4:2 multiplicities).

The high-field C peak of relative intensity 1 unambiguously corresponds to the equivalent W(5) and W(6) atoms.

Assignments of other peaks can be done by observation of $^2J_{W-W}$ coupling constants, which are generally in the range 5–12 Hz for edge-sharing octahedra junctions and 15–30 Hz for corner-sharing octahedra junctions.[14] The spin–spin coupling parameters of $HSiW_{10}O_{36}^{7-}$ are indicated in Table III. Peaks B and C have satellites with the same coupling constant (23.8 ± 0.3, 23.5 ± 0.3 Hz) corresponding to corner-sharing octahedra. The B peak must then be assigned to the four equivalent W(1–4) tungsten atoms and the remaining low-field A peak to the four W(7–10) atoms.

According to this assignment, we will use in the further discussion the following symbolism for equivalent W(*i*) tungsten atoms: W(A) for *i* = 7–10, W(B) for *i* = 1–4, and W(C) for *i* = 5, 6.

The B peak presents a second pair of satellites, with a coupling constant $^2J_{W-W}$ of 4.9 Hz. As is apparent from the structure, edge-junction coupling cannot be observed for the W(B) atom; the 4.9-Hz $^2J_{W-W}$ coupling constant must then be attributed to the corner coupling between W(A) and W(B) atoms.

The C peak exhibits satellites with a low coupling constant ($^2J_{W-W}$ = 4.6 Hz). This value agrees with the edge coupling between W(A) and W(C) atoms (into a trimetallic group).

These nearly equal coupling constants are not measurable for the A peak: satellites appear only as shoulders of the relatively broad A line.

It is worth discussing the unexpectedly low corner coupling between W(A) and W(B) atoms; one can expect a smaller bond coupling when the W–O–W angle is more acute and the W–O bond lengths are longer. The calculated mean values of these parameters obtained from the crystal structure data are indicated in Table II.

Table V. Summary of Crystal and Experimental Data for Rubidium γ-Decatungstosilicate

formula	$Rb_8SiW_{10}O_{36}\cdot 10H_2O$
fw	3307
cryst faces (dist from center, mm)	100, $\bar{1}00$, (0.14); $0\bar{1}1$, $01\bar{1}$ (0.05); 011, $0\bar{1}\bar{1}$ (0.11)
μ, cm^{-1}	315
space group	$P2_1/c$
a, Å	12.426 (3)
b, Å	19.319 (6)
c, Å	19.743 (5)
β, deg	96.33 (3)
V, Å^3	4710
Z	4
density (calcd), g cm^{-3}	4.67
density (obsd), g cm^{-3}	4.78
scan type	θ–2θ
$2\theta_{max}$, deg	48
scan speed, deg s^{-1}	0.02
scan width, deg	0.90 + 0.30 tan θ
std reflecns	3 measd every 2 h; no decay in intens obsd
no. of reflecns	
collected	7290
used in refinement with $I > 3\sigma(I)$	3132
no. of params refined	314
weighting	$3.7697/(\sigma(F)^2 + 0.00839F^2)$
final R $(=\sum\|\|F_o\| - \|F_c\|\|/\|F_o\|)$	0.070
final R_w $(=(\sum w(\|F_o\| - \|F_c\|)^2/\sum wF_o^2)^{1/2})$	0.073

Comparison of the two corner junctions W(A)–O–W(B) and W(B)–O–W(C) shows the following: (i) the bridge angle is more acute for the former (143°) than for the latter (150°); (ii) the W(B)–Ob bond is longer in the W(A)–O–W(B) (2.19 Å) than in the W(B)–O–W(C) (1.95 Å) bridges. The very long W(B)–Ob(A-B) bond is clearly due to the short W(B)–Od′ bond in the trans position. Both variations of the bond angle and W(B)–Ob bond length agree with the decreasing of $^2J_{W-W}$ from the W(B)–W(C) pair (23.7 Hz) to the W(A)–W(B) pair (4.9 Hz).

The chemical shifts of the deprotonated anion in the presence of Li^+, Na^+, and K^+ counterions are shown in Table IV. The whole spectrum depends on the nature of M in the complex $MSiW_{10}O_{36}^{7-}$. This is consistent with a modification of the distribution of the negative charges on all the oxygen atoms of the structure when a M^+ cation substitutes another M'^+ cation.

This work was undertaken with the aim of making a polyanion available in sufficient quantities in order to make disubstituted 12-heteropolyanions, $SiW_{10}Z_2O_{40}^{n-}$. In fact, γ-$SiW_{10}O_{38}^{8-}$ rapidly reacts with molybdenum, vanadium, etc. to form such species.[16]

Experimental Section

Preparation of Compounds. γ-$K_8SiW_{10}O_{36}\cdot 12H_2O$. This compound was prepared by using the potassium salt of the β_2 isomer of 11-tungstosilicate, obtained as previously described.[8] The pH of a solution prepared by dissolution of 30 g of β_2-$K_8SiW_{11}O_{39}$ in 300 mL of distilled water maintained at 25 °C was adjusted to 9.1 by addition of an aqueous solution of 2 mol·L^{-1} K_2CO_3. The pH of the solution was kept to 9.1 for 16 min. The potassium salt of the 10-tungstosilicate was precipitated by addition of 40 g of solid potassium chloride. During the precipitation the pH must be maintained at 9.1 by addition of small amounts of the carbonate solution: the solid was filtered off and air-dried; the number of H_2O groups was determined by thermogravimetric analysis on a Cahn RG electrobalance (sample weight 5–10 mg, heating rate 5 °C·min^{-1}). Yields varied from 50 to 70%. Anal. Calcd: Si, 0.94; W, 61.88; K, 10.53; H_2O, 7.27. Found: Si, 0.92; W, 61.22; K, 10.10; H_2O, 7.56. IR (KBr pellet; cm^{-1}): 989 (m), 941 (s), 905 (s), 865 (vs), 818 (vs), 740 (vs), 655 (sh), 553 (w), 528 (m), 478 (sh), 390 (sh), 360 (s), 328 (sh), 318 (m), 303 (sh).

γ-$Rb_8SiW_{10}O_{36}\cdot 10H_2O$. The rubidium salt was prepared from the potassium salt by precipitation of its solution by RbCl. The salt was reprecipitated three times and, finally, recrystallized from its aqueous solution. No residual potassium was detected by atomic absorption. Anal. Calcd: Si, 0.85; W, 55.61; Rb, 20.68; H_2O, 5.44. Found: Si, 0.91;

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(13) This could reflect a longitudinal relaxation time T_1 significantly longer, for the corresponding W, with respect to the other atoms. Unfortunately the limited concentration of our solutions and the low intrinsic receptivity of the ^{183}W nucleus prevent us from taking T_1 measurements for the decatungstosilicate. However, as indicated by line widths (Table III), the different ^{183}W nuclei certainly experience unequal spin–spin relaxation time T_2.

(14) Domaille, P. J. *J. Am. Chem. Soc.* **1984**, *106*, 7677–7687.

(15) Knoth, W. H.; Domaille, P. J.; Roe, D. C. *Inorg. Chem.* **1983**, *22*, 198–201.

(16) Canny, J.; Tézé, A.; Thouvenot, R.; Hervé, G., manuscripts in preparation.

W, 54.38; Rb, 22.26; H_2O, 5.40. IR (KBr pellet; cm^{-1}): 990 (m), 941 (s), 910 (s), 867 (vs), 816 (s), 738 (vs), 659 (sh), 552 (w), 525 (m), 480 (sh), 450 (sh), 395 (sh), 358 (s), 328 (m), 317 (m), 299 (sh).

Aqueous solution of γ-$H_8SiW_{10}O_{36}$ was obtained by K^+/H^+ exchange on a strongly acidic cation exchanger with sulfonic groups based on styrene-DVB copolymer. A 12-g amount of γ-$K_8SiW_{10}O_{36}$ and 30 mL of water were agitated with 20 mL of a Dowex 50W-X2 resin (H^+ form). The resulting solution was passed through a column containing the same resin (45 cm × 1.2 cm). The effluent was checked by atomic absorption and contained less than 1‰ of the initial potassium.

Physical Measurements. Polarograms were recorded on a Tacussel PRG3 instrument with dropping or stationary mercury electrodes.

Absorption spectra were recorded on Perkin-Elmer 555 (UV) and Perkin-Elmer 283 (IR) spectrophotometers. ^{183}W NMR spectra were obtained at 297 K on a Bruker WM 250 spectrometer operating at 10.4 MHz. The samples were measured in 10 mm o.d. Pyrex tubes either in pure D_2O or in H_2O/D_2O (90/10) mixtures. Chemical shifts are referenced to external 2 M Na_2WO_4 in alkaline D_2O; a negative value means a high-field shift (low frequency) with respect to the reference.

Structure Determination. Preliminary oscillation and Weissenberg photographs showed a monoclinic lattice, and systematic absences indicated the space group $P2_1/c$. The intensities were collected at room temperature on a Philips PW 1100 four-circle diffractometer (Mo Kα radiation, graphite monochromator and scintillation counter) in the θ–2θ scan mode up to $2\theta_{max} = 48°$ (background measurement in fixed position before and after every scan for a time equal to half of the scan time). The intensities were corrected for the Lorentz and polarization factors and absorption ($\mu = 315\ cm^{-1}$). The cell constants were determined from a least-squares fit of 25 reflections. Crystal data are given in Table V.

Solution and Refinement of the Structure. The 10 tungsten atoms of the asymmetric unit were located by using direct methods (MULTAN). The rubidium, silicon, and anionic oxygen atoms were located from alternate Fourier synthesis and full-matrix least-squares refinements. Refinements to convergences with isotropic thermal parameters for the oxygen atoms and anisotropic thermal parameters for the others gave $R = 0.070$ and $R_w = 0.073$.

As often occurs in structural determination of heteropolyanions, all cations were not found. Half of the rubidium atoms are missing. Water molecules were not located.

Calculations were carried out on the Gould UTX 32 computer of the university with SHELX programs.[17]

Registry No. $K_8SiW_{10}O_{36}$, 102073-48-3; $K_8SiW_{11}O_{39}$, 37300-95-1; $Rb_8SiW_{10}O_{36}$, 102073-49-4; $H_8SiW_{10}O_{36}$, 102073-50-7; $LiSiW_{10}O_{36}{}^{7-}$, 102073-51-8; $NaSiW_{10}O_{36}{}^{7-}$, 102073-52-9; $KSiW_{10}O_{36}{}^{7-}$, 102073-53-0; $RbSiW_{10}O_{36}{}^{7-}$, 102073-54-1; $MgSiW_{10}O_{36}{}^{6-}$, 102073-55-2; $CaSiW_{10}O_{36}{}^{6-}$, 102073-56-3; $SnSiW_{10}O_{36}{}^{6-}$, 102073-57-4.

Supplementary Material Available: A listing of anisotropic thermal parameters of W, Si, and Rb atoms (1 page). Ordering information is given on any current masthead page.

(17) Sheldrick, G. M. "SHELX 76, Program for Crystal Structure Determination"; University of Cambridge: Cambridge, England, 1976.
(18) Pope, M. T.; Scully, T. F. *Inorg. Chem.* **1975**, *14*, 953–954.

Contribution from the Department of Chemistry, The University of Calgary, Calgary, Alberta, Canada T2N 1N4,
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Synthesis and Electronic Structure of the $R_2NCS_2N_3$ Ring: X-ray Crystal Structure of the Bicyclic Compound *i*-$Pr_2NCS_3N_5$ and Preparation of $R_2NCS_2N_3 \cdot C_7H_8$ (R = Me, Et, *i*-Pr), $Et_2NCS_2N_2{}^+Cl^-$, and Salts of the $(R_2NCN)(NSCl)(NS)^+$ Cation

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and Milan Trsic*[‡]

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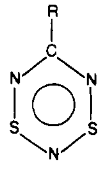
The crystal and molecular structures of *i*-$Pr_2NCS_3N_5$ have been determined by X-ray crystallography. The crystals are triclinic and belong to the space group $P\bar{1}$, with $a = 5.648$ (1) Å, $b = 9.162$ (2) Å, $c = 13.432$ (2) Å, $\alpha = 69.52$ (1)°, $\beta = 79.58$ (2)°, $\gamma = 76.66$ (2)°, $V = 629.7$ (5) Å^3, and $Z = 2$. The final R and R_w values were 0.042 and 0.040, respectively. The molecule is bicyclic and consists of an –N=S=N– bridge (d(S–N) = 1.539 (3) Å) weakly bonded (d(S–N) = 1.748 (3) Å) to the sulfur atoms of a six-membered *i*-$Pr_2NCS_2N_3$ ring. The thermolysis and photolysis of this bicyclic compound and the reduction of $(RCN)(NSCl)_2$ (R = Me_2N, Et_2N, *i*-Pr_2N) have been investigated as possible routes to the six-membered rings, RCS_2N_3. The reduction of $(R_2NCN)(NSCl)_2$ (R = Et, *i*-Pr) with $(Me_3Si)_2Hg$ in diethyl ether at –78 °C produced dark purple solids that react with norbornadiene to give the adducts $R_2NCS_2N_3 \cdot C_7H_8$. In contrast, the reaction of $(Et_2NCN)(NSCl)_2$ with sodium azide in acetonitrile at 23 °C caused ring contraction to give $Et_2NCS_2N_2{}^+Cl^-$ (λ_{max} 530 nm). The purple color of this product is attributed to the HOMO ($n\pi$) → LUMO (π^*) transition on the basis of ab initio level HFS–SCF MO calculations for $RCS_2N_2{}^+$ (R = H, NH_2). Similar calculations for the six-membered ring RCS_2N_3 (R = NH_2) indicate that the heterocyclic ring is an eight-π-electron system but reveal a quasi-degeneracy for the HOMO and LUMO (both π^* orbitals). A single determinant ground-state representation could not be obtained for the planar rings RCS_2N_3 (R = H, CH_3, Cl). The compounds $(RCN)(NSCl)_2$ react with the halide ion acceptors BCl_3, $SbCl_5$, and $SnCl_4$ to give salts of the monocation $(RCN)(NSCl)(NS)^+$, whereas treatment of 1,5-$(Me_2NCN)_2(NSCl)_2$ with $SbCl_5$ yields the dication $(Me_2NCN)_2(SN_2)^{2+}$.

Introduction

In the context of our studies of π-electron-rich S–N heterocycles,[1] ring system **1** represents an interesting target molecule since it is expected to be an eight-π-electron system on the basis of simple electron-counting rules[1a] (cf. **2**).[2] The trifluoromethyl derivative (**1**, R = CF_3) was described by Mews et al. in 1984, but the characterization is based only on mass spectroscopic evidence.[3] White this work was in progress,[4] Oakley et al. reported the preparation of **1** (R = Ph) as an air-stable buff-colored solid, "presumably not monomeric".[5]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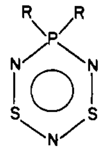
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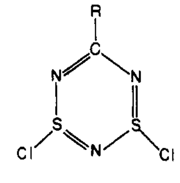
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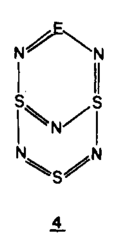
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