even at low temperatures, and its copper(I) complex appears to be polymeric.

Experimental Section

1,1,1-Tris(mercaptomethyl)ethane (I).[11] A mixture of 1,1,1-tris(((tolylsulfonyl)oxy)methyl)ethane[9] (130 g) and KSCN (277 g) in DMF (560 mL) was placed in a 140 °C oil bath and was stirred for 3.75 h. The resulting solution was poured into water (3 L) with stirring. A tan precipitate formed, and after the mixture was allowed to stand at 5 °C for 18 h, the solid was collected and was washed with water, ethanol–ether (1:1), and finally with ether. The air-dried 1,1,1-tris(thiocyanomethyl)ethane (40.7 g, 75%) was sufficiently pure to be used in the reduction step. It may be recrystallized from hot ethanol (1 g/10 mL) to give an off-white solid, mp 118–120 °C. ^{1}H NMR ($CDCl_3$): δ 1.42 (3 H, s), 3.28 (6 H, s). Anal. Calcd for $C_8H_9N_3S_3$: C, 39.5; H, 3.7; N, 17.3; S, 39.5. Found: C, 39.4; H, 3.6; N, 17.2; S, 39.2.

1,1,1-Tris(thiocyanomethyl)ethane (28.4 g) was added in portions over 1.5 h to a stirred ice-cooled mixture of LAH (13.75 g) in dry ether (300 mL) under N_2. The mixture was refluxed for 16 h and then was cooled. The reaction was cautiously quenched by the addition of HCl (6 N, 130 mL) followed by more HCl (12 N, 215 mL). Benzene (200 mL) was then added, and the mixture was stirred for 0.5 h. The organic layer was separated under N_2, and the aqueous phase was extracted with benzene (4 × 200 mL) under N_2. The combined organic extracts were dried ($MgSO_4$) and then the solvent was removed under reduced pressure. The residue was distilled to give 1,1,1-tris(mercaptomethyl)ethane, a pale yellow oil (13.4 g, 68%; bp 70–72 °C (0.2 mm). ^{1}H NMR ($CDCl_3$): δ 1.00 (3 H, s), 1.30 (3 H, t, J = 8.0 Hz), 2.60 (6 H, d, J = 8.0 Hz). Anal. Calcd for $C_5H_{12}S_3$: C, 35.7; H, 7.2; S, 57.1. Found: C, 36.0; H, 7.2; S, 57.4.

***cis,cis*-1,3,5-Trimercaptocyclohexane (II).** A mixture of *cis,cis*-1,3,5-tris((tolylsulfonyl)oxy)cyclohexane[10] (48 g) and KSCN (250 g) in diethylene glycol (200 mL) was heated at 120 °C for 4 h. An amber solution resulted. This was cooled slightly, and water (1250 mL) was added, followed by CH_2Cl_2–ether (1:1; 200 mL). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2–ether (1:1; 6 × 100 mL). The combined organic layers were washed with brine (4 × 100 mL) and then were dried over Na_2SO_4. On removal of the solvents, crude *cis,cis*-1,3,5-trithiocyanocyclohexane remained as a yellow viscous oil (17.7 g), which slowly crystallized. This was used for the reduction step.

The residue from above was dissolved in dry THF (200 mL) and was added dropwise over 2 h to a suspension of LAH (10 g) in dry THF (450 mL) under N_2. After the mixture was stirred at 25 °C for 12 h, the excess of LAH was decomposed by the addition of water (5 mL) followed by 10% aqueous H_2SO_4 (80 mL). The mixture was filtered, and the solid was washed well with THF. The THF was removed under reduced pressure, to the residue were added water (100 mL) and CH_2Cl_2 (250 mL), and the layers were separated. The organic layer was washed with water (100 mL) followed by brine (100 mL) and was then dried (Na_2SO_4); the solvent then was removed under reduced pressure. The residue was distilled to give *cis,cis*-1,3,5-trimercaptocyclohexane as a pale green viscous oil that solidified at 0 °C (5.6 g, 39%; bp 80–82 °C (0.2 mm). ^{1}H NMR ($CDCl_3$): δ 1.0–1.8 (6 H, m), 2.2–3.1 (6 H, m). Anal. Calcd for $C_6H_{12}S_3$: C, 40.0; H, 6.7; S, 53.4. Found: C, 40.2; H, 6.8; S, 53.2.

Ligand IV. A solution of *cis,cis*-1,3,5-trimercaptocyclohexane (5.6 g) and 2-vinylpyridine (3.3 g) in toluene (100 mL) was refluxed under N_2 for 5 h. The solvent was removed under reduced pressure, the residue, an amber oil, was dissolved in dry THF (75 mL), and the resulting mixture was added dropwise to an ice-cooled solution of sodium (2.14 g) in absolute ethanol (60 mL) and dry THF (50 mL). A solution of methyl iodide (13.2 g) in dry THF (100 mL) was then added dropwise to the cooled solution. The cooling bath was removed, and the solution was stirred at 25 °C for 3 h. Then, the solvents were removed under reduced pressure, and the residue was slurried with benzene (100 mL) and filtered. In order to extract the pyridine-containing compounds, the benzene filtrate was washed with aqueous HCl (2 N, 6 × 40 mL) and then the combined aqueous extracts were washed with benzene (60 mL). Out of the benzene extracts, the permethylated compound of II may be recovered. The combined acidic aqueous layers were basified with solid $NaHCO_3$ and then were extracted with CH_2Cl_2 (4 × 70 mL). These combined CH_2Cl_2 extracts were washed with water (70 mL) and then were dried (Na_2SO_4). After the solvent was removed, the amber oil (7.0 g) was chromatographed on alumina (Brockman activity II). Elution with ethyl acetate–benzene (1:25) yielded *cis,cis*-1-((2-(2-pyridyl)ethyl)thio)-3,5-bis(methylthio)cyclohexane (IV) as a viscous yellow oil (3.2 g, 33%) in the forward fraction; the divinylpyridine compound came off in later fractions. ^{1}H NMR (CD_3CN): δ 0.8–1.6 (3 H, m), 2.16 (6 H, s), 2.0–3.1 (6 H, m), 3.02 (4 H, s), 7.0–7.8 (3 H, m), 8.3–8.5 (1 H, m).

[Cu(IV)]ClO_4. Ligand IV (0.15 g) was dissolved in dry CH_3CN (3 mL), and then solid $[Cu(CH_3CN)_4]ClO_4$ (0.16 g) was added. When all of the solid had dissolved, methanol (10 mL) was added, and the volume was reduced on a steam bath to ~10 mL. The solution was slowly cooled to 25 °C and then was kept at 5 °C for 18 h. The white precipitate was then filtered, washed with methanol containing a few drops of CH_3CN, and vacuum dried, yielding a fine white solid (0.14 g, 59%). ^{1}H NMR (CD_3CN): δ 0.19–1.7 (3 H, m), 2.0–3.1 (6 H, m), 2.16 (6 H, s), 3.12 (4 H, s), 7.2–8.0 (3 H, m), 8.3–8.5 (1 H, m). Anal. Calcd for $[Cu(C_{15}H_{23}NS_3)]ClO_4$: C, 37.8; H, 4.9; N, 2.9; S, 20.2; Cl, 7.4. Found: C, 37.7; H, 4.9; N, 3.2; S, 20.1; Cl, 7.5.

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Registry No. I, 39597-87-0; II, 86101-43-1; IV, 86101-44-2; [Cu(IV)]ClO_4, 86101-46-4; *cis,cis*-1,3,5-tris((tolylsulfonyl)oxy)cyclohexane, 64747-25-7; 2-vinylpyridine, 100-69-6; 1,1,1-tris(thiocyanomethyl)ethane, 2812-68-2; 1,1,1-tris(((tolylsulfonyl)oxy)methyl)ethane, 2387-43-1.

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Second Dissociation Constant of Hydrogen Sulfide

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Published values for the pK_{a2} values of hydrogen sulfide cover a range of almost 8 orders of magnitude.[2] Most of the 22 values quoted by Sillén[3] are larger than K_w. Two contradictory values have been published in an earlier volume of this journal: Stephens[4] selected a value of pK_{a2} = 13.78 ± 1.0 based on calorimetric and thermodynamic reasoning, and Giggenbach[5] derived a value of pK_{a2} = 17.1 ± 0.2 from an UV study that involved reassigned absorption bands. Recent reviews[6] by CODATA[2] and Rao[7] prefer values below pK_w.

In this study we used a Raman spectrometric method[8,9] for in situ identification of the H–S stretch in high-pH solutions and for estimating their concentrations.

Experimental Section

Samples were prepared on a vacuum line in 10-mm diameter Pyrex ampules. The ampules were charged with 1 mL of sodium hydroxide solution prepared by dissolving reagent grade sodium hydroxide pellets in doubly distilled water under nitrogen gas. The sodium hydroxide concentration was determined by weighing and by titration of the solution after the experiments were completed. Sulfide was determined gravimetrically after oxidation and precipitation as barium sulfate. Sodium hydroxide concentrations ranged from 5 to 22 N. Hydrogen sulfide was kept between 0.3 and 0.6 M. All solutions also contained 0.10 M $NaClO_4$ for use as an internal Raman scattering standard.[10] The samples were frozen at 76 K, and a measured amount of hydrogen sulfide gas was condensed in the ampules to yield the desired con-

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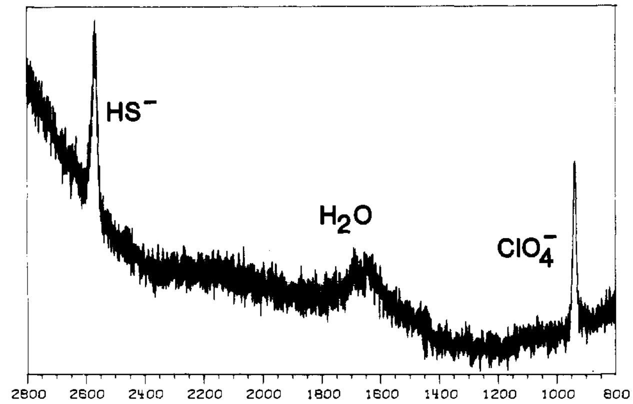

Figure 1. Raman spectrum of 16.9 N NaOH solution containing 0.10 M $NaClO_4$ and 0.6 M H_2S.

centrations. The containers were then sealed in vacuo.

Raman spectra were recorded on a J-Y Ramanor HG-2S double monochromator interfaced with a Nicolet 1280 minicomputer. The 488.0-nm blue line of a Coherent Radiation Model CR-4 0.2-W laser was used for excitation. Spectra were recorded from 50 to 3050 cm^{-1} at a speed of 5 cm^{-1}/s. Signals from four scans were superimposed. The spectra were analyzed by matching the experimental peaks with synthetic Lorenzian curves generated with the Nicolet computer by a procedure described earlier.[8] The spectra were evaluated by comparing the integrated intensity of the HS^- peak at 2570 cm^{-1} with that of the perchlorate peak at 935 cm^{-1}. The concentration of bisulfide was then determined by comparison of the observed intensity ratios of HS^- to ClO_4^- with those of standard solutions plotted on a calibration curve.

Results and Discussion

Figure 1 shows part of the Raman spectrum of a 16.9 N NaOH solution containing 0.5 M H_2S and 0.1 M $NaClO_4$. The 2570 cm^{-1} belongs to the H–S stretch[11] and indicates that the solution still contains appreciable amounts of undissociated HS^-. From the calibration curve,[9] we derived an HS^- concentration of 0.3 ± 0.1 M, equal to about 50% of the total sulfide present. The same data were obtained for a second, independently prepared sample. Spectra were replicated for both samples after several heating cycles, which were used to mix the contents of the tubes. The spectrum recorded for a 8.9 N NaOH solution containing 0.6 M H_2S and 0.1 M $NaClO_4$ showed approximately 0.5 ± 0.1 M HS^-, indicating that virtually all sulfide was in the form of bisulfide. The in situ observation of high concentrations of HS^- in 8.9 N NaOH contradicts any pK_{a2} value lower than K_w.

We agree with Giggenbach[5] that pK_{a2} values lower than 15 by earlier workers[3] were due to oxygen contamination, which is known to convert sulfide rapidly into polysulfide and thiosulfate.[11] Our spectra did not show the characteristic peaks of any of these strong Raman scatterers.[8]

Evaluation of the above data, neglecting solute–solute interactions, leads to the prediction of an equivalence point $K_e' = (3.0 \pm 2.0) \times 10^{-16}$ for our system. This value is subject to several sources of systematic errors. First, at 16.9 N NaOH the solvent to solute ratio is only 3.3. This is insufficient to maintain normal hydration spheres for the sodium ion, and the solutions can no longer be treated as an aqueous system. Furthermore, the effect of the ionic strength on the scattering intensity of HS^- and ClO_4^- is not known at these high concentratios.[10] However, inspection of the signal-to-noise ratio of the perchlorate and bisulfide ions indicates that the scattering intensity does not dramatically alter. Also, deviations will likely cancel, at least partly. We estimate the combined effects to be less than 25%. The error due to carbon dioxide in the sodium hydroxide pellets was eliminated by titration of the solutions after the experiments were finished.

The value of the equivalence point derived from our Raman work is about one-third of that reported by Giggenbach.[5] We believe that this is within the combined range of accuracy of the two methods employed.

To translate our data into pK_{a2} values, we face the same problems as Giggenbach.[5] As indicated, 20 N NaOH does not behave like water. Upon freezing at 76 K, our samples visibly contract, while water samples would expand sufficiently to burst the tubes. We do not wish to speculate at this place about the best procedure for computing pK_{a2} in such a system. We used the correlation

$$K_{a2} = K_w \frac{[S^{2-}]\alpha_w}{[HS^-][OH^-]}\left(\frac{\gamma(S^{2-})}{(\gamma(OH^-))(\gamma(HS^-))}\right) \qquad (1)$$

so that our data can be compared with those of other authors.[5] Our data yield a pK_{a2} value of 17 ± 1.0, the highest value yet reported. This value is consistent with the higher limit reported by the UV method.[5] A review of old literature shows that high pK_{a2} values were already postulated more than 50 years ago by Wasastjerna,[12] who proposed a value of 6×10^{-17}, and by Aumeras,[13] who used the solubility data for cadmium sulfide to derive a value of 3.6×10^{-16}. Both of these values are consistent with our value. Our value is also consistent with the value obtained by Brewer[14] on the basis of a thorough review of current thermodynamic data.

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Registry No. H_2S, 7783-06-4.

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