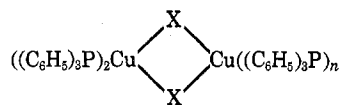


azide ions are nonbridging,<sup>41</sup> the N-N asymmetric stretching frequency differs by about 20 cm<sup>-1</sup> from that of [Cu(N<sub>3</sub>)(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>]<sub>2</sub>.<sup>42</sup> It is interesting to note also that for compounds of the type



$n = 1$  or  $2$  and  $\text{X}^- = \text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ , the 4,4-coordinate complex (*i.e.*,  $n = 2$ ) is relatively rare in the solid state and that attempted isolation usually results

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(42) W. Beck, W. P. Fehlhammer, P. Pöllman, and H. Schächl, *Chem. Ber.*, **102**, 1976 (1969).

in the formation of the 3,4-coordinate complex. When  $\text{X}^- = \text{N}_3^-$  or  $\text{NCS}^-$ , only the 4,4-coordinate complex has been isolated. The dissociation of a triphenylphosphine in the present system in order to explain the solution molecular weight and the constancy of the infrared spectrum in going from the solid to the solution state thus remains as a distinct possibility. The recent work of Muetterties and Alegranti<sup>40</sup> involving temperature-dependent <sup>31</sup>P nmr data on coinage metal-phosphine complexes should prove fruitful in this area.

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## Notes

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### Determination of the H<sub>2</sub>SO<sub>4</sub>:HSO<sub>4</sub><sup>-</sup> and HClO<sub>4</sub>:ClO<sub>4</sub><sup>-</sup> Ratios in Graphite Lamellar Compounds<sup>1</sup>

BY S. ARONSON,\* S. LEMONT, AND J. WEINER

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Graphite reacts with concentrated sulfuric and perchloric acid either by electrolysis or in the presence of oxidizing agents to form layer compounds.<sup>2,3</sup> In these compounds, layers of bisulfate or perchlorate ions are sandwiched between layers of aromatic carbon atoms. In addition to the ions, the corresponding acid molecules are also incorporated into the adduct layers.

The formulas for the most concentrated compounds, in which layers of acid adduct alternate with carbon layers, can be written C<sub>24</sub><sup>+</sup>·HSO<sub>4</sub><sup>-</sup>·xH<sub>2</sub>SO<sub>4</sub> and C<sub>24</sub><sup>+</sup>·ClO<sub>4</sub><sup>-</sup>·yHClO<sub>4</sub>. The next most concentrated compounds, in which two layers of carbon are interposed between nearest-neighbor adduct layers, have the compositions C<sub>48</sub><sup>+</sup>·HSO<sub>4</sub><sup>-</sup>·x'H<sub>2</sub>SO<sub>4</sub> and C<sub>48</sub><sup>+</sup>·ClO<sub>4</sub><sup>-</sup>·y'HClO<sub>4</sub>. Because of the instability of these compounds in air and water, chemical analysis is difficult and values for  $x'$ ,  $y$ , and  $y'$  have not been reported. The value of  $x$  generally consigned to C<sub>24</sub><sup>+</sup>·HSO<sub>4</sub><sup>-</sup>·xH<sub>2</sub>SO<sub>4</sub> is 2.<sup>2-4</sup>

In connection with an electrochemical study of the graphite-bisulfate compounds, it was of interest to determine accurately the H<sub>2</sub>SO<sub>4</sub>:HSO<sub>4</sub><sup>-</sup> ratios in the bisulfate lamellar compounds. A gravimetric method of analysis in which graphite compounds formed by electrolysis were weighed in sulfuric acid was used. The method was extended to the graphite-perchloric acid system.

#### Experimental Section

##### Procedure for the Determination of the H<sub>2</sub>SO<sub>4</sub>:HSO<sub>4</sub><sup>-</sup> Ratio.

(1) This work was supported by a grant from the National Science Foundation.

(2) W. Rudorff, *Advan. Inorg. Chem. Radiochem.*, **1**, 223 (1959).

(3) G. R. Hennig, *Progr. Inorg. Chem.*, **1**, 125 (1959).

(4) W. Rudorff and U. Hofmann, *Z. Anorg. Allg. Chem.*, **238**, 1 (1938).

—A schematic diagram of the apparatus used to prepare C<sub>48</sub><sup>+</sup>·HSO<sub>4</sub><sup>-</sup>·x'H<sub>2</sub>SO<sub>4</sub> and C<sub>24</sub><sup>+</sup>·HSO<sub>4</sub><sup>-</sup>·HSO<sub>4</sub><sup>-</sup>·x'H<sub>2</sub>SO<sub>4</sub> is shown in Figure 1. Similar procedures have been used by a number of

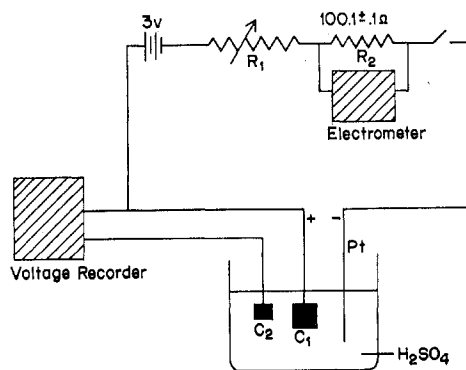


Figure 1.—Schematic of apparatus used for the preparation of graphite layer compounds.

investigators.<sup>2-6</sup> The cathode in the electrolysis was a platinum wire. The anode, C<sub>1</sub>, was a thin piece (about 0.03 cm thick) of annealed (3200°) pyrolytic graphite with a surface area of about 1 cm<sup>2</sup>. This piece was cut from a slab obtained several years ago from the General Electric Metallurgical Products Department, Detroit, Mich. The electrolyte was Baker and Adamson reagent grade concentrated (95.5–96.5 wt %) sulfuric acid obtained from the Allied Chemical Co., Morristown, N. J. The voltage was supplied by two 1.5-V batteries in series. The current was kept constant by manually adjusting the resistance in a resistance box, R<sub>1</sub>. The current was measured using a Keithley 602 electrometer which monitored the voltage across a precision resistor, R<sub>2</sub>, having a resistance of 100.1 ± 0.1 ohms. The voltage drop between the anode, C<sub>1</sub>, and an electrode consisting of another piece of annealed pyrolytic graphite, C<sub>2</sub>, was continuously recorded with a Honeywell Elektronik 19 voltage recorder.

Figure 2 shows data for a typical electrolysis run transcribed from the recorder paper. As bisulfate ions are incorporated into the graphite sample, C<sub>1</sub>, the voltage builds up. The break at 54.5 min is in fairly good agreement with the calculated value of 55.6 min for complete formation of the compound C<sub>48</sub><sup>+</sup>·HSO<sub>4</sub><sup>-</sup>·x'H<sub>2</sub>SO<sub>4</sub> on the assumption that the electrolysis is 100% efficient and that 1 HSO<sub>4</sub><sup>-</sup> ion is present for every 48 carbon atoms. Sample C<sub>1</sub> was weighed three times. It was initially weighed in air as pure graphite. It was weighed in sulfuric acid at the calculated midpoint of the electrolysis (55.6 min) when the for-

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(6) G. R. Hennig, *J. Chem. Phys.*, **19**, 922 (1951).

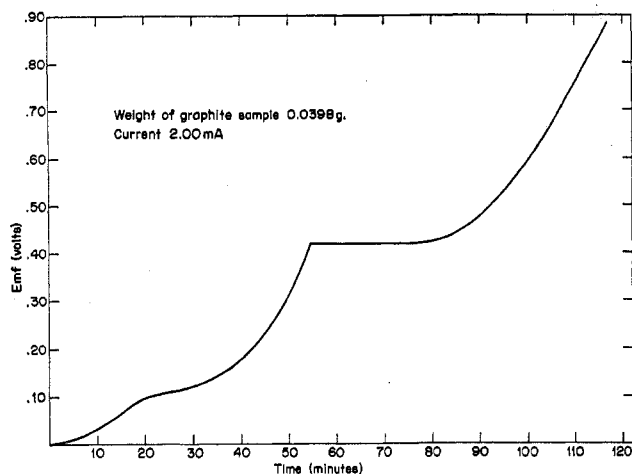
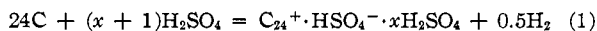


Figure 2.—Electrolysis of graphite in sulfuric acid.

mation of  $C_{48}^+ \cdot HSO_4^- \cdot x'H_2SO_4$  is complete and at 17 min which is several minutes more than the calculated time, 111.1 min, needed to form  $C_{24}^+ \cdot HSO_4^- \cdot xH_2SO_4$ . The reaction of the graphite sample with sulfuric acid resulted in an increase in the thickness of the sample but did not cause splitting or disintegration.

The electrolytic cell shown in Figure 1 was placed inside the case of an analytical balance. Holes were drilled through the case to accommodate the lead wires. One of the balance pans had been previously removed and the platinum wire attached to sample  $C_1$  could be easily disconnected from the electric circuit and hooked on to the panless side of the balance beam.

The  $H_2SO_4:H_2SO_4^-$  ratio was determined in the following manner. In the case of  $C_{24}^+ \cdot HSO_4^- \cdot xH_2SO_4$ , the electrolysis was allowed to run for a period of time exceeding that required to form the compound. The excess charge passed through the circuit does not alter the composition since  $C_{24}^+ \cdot HSO_4^- \cdot xH_2SO_4$  contains the maximum amount of bisulfate ion. The  $H_2SO_4:H_2SO_4^-$  ratio can be determined on the basis of the reaction



From a consideration of the stoichiometry of the reaction, the value of  $x$  is given by the equation

$$x = \frac{(\text{wt compound})(24)(\text{at. wt C})}{(\text{wt graphite})(\text{mol wt } H_2SO_4)} - \frac{24(\text{at. wt C}) - \text{formula wt } HSO_4^-}{\text{mol wt } H_2SO_4} \quad (2)$$

The term "wt graphite" refers to the weight of the graphite sample used and the term "wt compound" refers to the weight of the reaction product  $C_{24}^+ \cdot HSO_4^- \cdot xH_2SO_4$ . The graphite sample was weighed in air prior to immersion in sulfuric acid. The reaction product was weighed in sulfuric acid to avoid decomposition and reaction with air. The weight of the reaction product in air is equal to the weight in sulfuric acid plus a buoyancy correction. The correction is given by the expression

$$\text{buoyancy correction} = (\text{vol compound})(\text{density } H_2SO_4) = (\text{vol graphite}) \left( \frac{\text{vol compound}}{\text{vol graphite}} \right) (\text{density } H_2SO_4) = (\text{vol graphite}) \left( \frac{7.98}{3.35} \right) (\text{density } H_2SO_4) \quad (3)$$

Graphite expands only along the  $C$  axis upon formation of the layer compounds.<sup>2-4</sup> The ratio of the volume of the compound to the volume of graphite is, therefore, proportional to the ratio of the interlayer distance in the compound to the interlayer distance in graphite. The distance between carbon layers in graphite is 3.35 Å. The distance between carbon layers in  $C_{24}^+ \cdot HSO_4^- \cdot xH_2SO_4$  is 7.98 Å.<sup>2-4</sup> The densities of the graphite and sulfuric acid, respectively, were determined pycnometrically, to be 2.21 and 1.835 g/cm<sup>3</sup>.

The  $H_2SO_4:H_2SO_4^-$  ratio in  $C_{48}^+ \cdot HSO_4^- \cdot x'H_2SO_4$  was determined in a similar manner. In this case, the electrolysis was stopped at the time calculated to produce the composition

$C_{48}^+ \cdot HSO_4^- \cdot x'H_2SO_4$ . Excess charge passed through the circuit would have produced some  $C_{24}^+ \cdot HSO_4^- \cdot xH_2SO_4$ . Only half of the interlayer spaces available in graphite are occupied by bisulfate ions and  $H_2SO_4$  molecules in  $C_{48}^+ \cdot HSO_4^- \cdot x'H_2SO_4$ . The ratio of the volume of  $C_{48}^+ \cdot HSO_4^- \cdot x'H_2SO_4$  to the volume of graphite is, therefore,  $(7.98 + 3.35)/(3.35 + 3.35)$  where we are now dealing with two adjacent interlayer spaces.

All weight measurements were made at room temperature. The effect of small temperature variations on the buoyancy correction is negligible since the density of sulfuric acid is not strongly temperature dependent. The buoyancy effect on the platinum wire from which the sample was suspended was accounted for by weighing the empty wire immersed in sulfuric acid to the same depth as the loaded wire.

**Procedure for the Determination of the  $HClO_4:ClO_4^-$  Ratio.**—The compound  $C_{24}^+ \cdot ClO_4^- \cdot \gamma HClO_4$  was prepared in the same manner as the bisulfate compounds using the apparatus in Figure 1 with perchloric acid substituted for sulfuric acid. The perchloric acid was reagent grade concentrated (70.6 wt %) acid obtained from J. T. Baker Co., Phillipsburg, N. J. Its density was measured pycnometrically to be 1.664 g/cm<sup>3</sup>. The emf curves obtained during electrolysis were less reproducible from run to run than the curves in sulfuric acid. A curve obtained on one of the samples is shown in Figure 3. A break and plateau in the

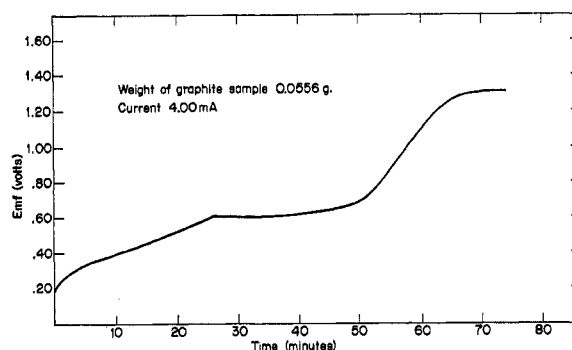


Figure 3.—Electrolysis of graphite in perchloric acid.

vicinity of the midpoint, similar to those produced in sulfuric acid, were always observed. The time at which the plateau occurred was variable, however, occurring between 5 and 20% earlier than the calculated time for complete formation of the  $C_{48}^+ \cdot ClO_4^- \cdot \gamma HClO_4$  compound. Unlike the sulfuric acid system, in which the emf rises steeply in the region of the end point, the emf in this case becomes approximately constant before the calculated end point and eventually begins to decrease.<sup>5</sup> In the electrolysis run shown in Figure 3, the calculated time for the formation of  $C_{24}^+ \cdot ClO_4^- \cdot \gamma HClO_4$  was 77.6 min and the calculated time for the formation of  $C_{48}^+ \cdot ClO_4^- \cdot \gamma HClO_4$  was 38.8 min. Because of the time discrepancy, no weight data were obtained on the  $C_{48}^+ \cdot ClO_4^- \cdot HClO_4$  compound. To obtain data on the  $C_{24}^+ \cdot ClO_4^- \cdot \gamma HClO_4$  compound, the electrolysis was continued until a region of constant voltage was reached. This sometimes occurred before the calculated time for completion of the reaction. The reaction was nevertheless stopped to avoid the possibility of decomposition reactions occurring.<sup>5</sup> The sample was weighed at this time and the  $HClO_4:ClO_4^-$  ratio was determined in the same manner as previously described for the sulfuric acid system. The distance between carbon layers upon incorporation of perchlorate ion is 7.95 Å.<sup>2-4</sup>

## Results and Discussion

The calculated values for the ratios of  $H_2SO_4:H_2SO_4^-$  and  $HClO_4:ClO_4^-$  are shown in Tables I and II, respectively. The results were not significantly dependent on sample weight, sample dimensions, or current density. In the case of the two bisulfate compounds, it is apparent that each bisulfate ion is associated with 2.5 sulfuric acid molecules.

The perchloric acid results are less conclusive because in some of the runs the emf plateau was reached and the electrolysis was stopped before the calculated total

TABLE I  
 DATA ON THE GRAPHITE-BISULFATE COMPOUNDS

Unreacted sample wt, mg	Current, mA	Reacted sample wt in H <sub>2</sub> SO <sub>4</sub> , mg	H <sub>2</sub> SO <sub>4</sub> : HSO <sub>4</sub> <sup>-</sup> ratio	Unreacted sample wt, mg	Current, mA	Reacted sample wt in H <sub>2</sub> SO <sub>4</sub> , mg	H <sub>2</sub> SO <sub>4</sub> : HSO <sub>4</sub> <sup>-</sup> ratio
$C_{24}^+ \cdot HSO_4^- \cdot xH_2SO_4$							
74.4	4	16.0	2.56	31.9	2	6.8	2.55
50.6	4	10.8	2.56	29.2	2	7.0	2.63
40.5	4	8.4	2.52	25.5	2	4.1	2.37
39.8	2	8.0	2.49				
$C_{48}^+ \cdot HSO_4^- \cdot x'H_2SO_4$							
74.4	4	13.8	2.52	39.1	3	7.3	2.53
50.6	4	9.3	2.51	31.9	2	5.6	2.46
39.8	2	7.5	2.51				

 TABLE II  
 DATA ON  $C_{24}^+ \cdot ClO_4^- \cdot yHClO_4$ 

Unreacted sample wt, mg	Current, mA	Reacted sample wt in HClO <sub>4</sub> , mg	HClO <sub>4</sub> : ClO <sub>4</sub> <sup>-</sup> ratio	Unreacted sample wt, mg	Current, mA	Reacted sample wt in HClO <sub>4</sub> , mg	HClO <sub>4</sub> : ClO <sub>4</sub> <sup>-</sup> ratio
55.6	4	13.7	1.93 <sup>a</sup>	34.4	2	10.4	2.14 <sup>a</sup>
38.5	2	10.8	2.07	33.0	2	6.6	1.85
36.0	2	9.5	2.01	33.0	2	8.2	1.99 <sup>a</sup>

<sup>a</sup> Electrolysis was stopped before calculated end point. Complete formation of  $C_{24}^+ \cdot ClO_4^- \cdot yHClO_4$  was assumed.

reaction time. If we assume complete formation of  $C_{24}^+ \cdot ClO_4^- \cdot yHClO_4$  in each case, the data consistently give a value of two HClO<sub>4</sub> molecules per perchlorate ion as is shown in Table II. The early completion of some of the runs may indicate that a small fraction of the intercalation occurs with the aid of perchloric acid as an oxidizing agent rather than through electrolysis.

The only compound in which the number of acid molecules per ion has been previously determined is  $C_{24}^+ \cdot HSO_4^- \cdot xH_2SO_4$ . The H<sub>2</sub>SO<sub>4</sub>:HSO<sub>4</sub><sup>-</sup> ratio was determined in two ways.<sup>4</sup> In one method, the reacted sample was first washed either in pyrophosphoric acid, H<sub>4</sub>P<sub>2</sub>O<sub>7</sub>, or in (CH<sub>3</sub>)<sub>2</sub>SO<sub>4</sub> followed by CCl<sub>4</sub>. This treatment removed the adhering sulfuric acid from the surface of the sample. The sulfate in both the HSO<sub>4</sub><sup>-</sup> and H<sub>2</sub>SO<sub>4</sub> in the sample was then analyzed as BaSO<sub>4</sub>. The second method involved a pycnometric determination. The unreacted graphite was oxidized in a pycnometer. The change in volume upon oxidation was calculated using the ratio of the distances between adjacent carbon planes in the reacted and unreacted lattice, 7.98/3.35. The H<sub>2</sub>SO<sub>4</sub>:HSO<sub>4</sub><sup>-</sup> ratios obtained by the analytical technique and by the pycnometric technique were 2.0 and 2.4, respectively.

The authors preferred the results of the analytical method for reasons that are not stated. It is possible that they intuitively expected an integral value for the H<sub>2</sub>SO<sub>4</sub>:HSO<sub>4</sub><sup>-</sup> ratio. The agreement of their pycnometric data with our values indicates, however, that their pycnometric method was reliable. The low value obtained by the analytical method probably resulted from a loss of internal sulfate during washing.

A ratio of 2.5 for H<sub>2</sub>SO<sub>4</sub>:HSO<sub>4</sub><sup>-</sup> in the bisulfate compounds seems reasonable. The calculated density of each adduct layer is 1.96 g/cm<sup>3</sup> using the value of 4.63 Å for the height of the layer. The value of 4.63 Å is obtained by subtracting the distance between carbon layers in graphite, 3.35 Å, from the distance between filled carbon layers in the bisulfate compounds, 7.98 Å. The density of the adduct layers, 1.96 g/cm<sup>3</sup>, is not too

different from the density of pure sulfuric acid, 1.84 g/cm<sup>3</sup>. Some preliminary work<sup>7</sup> on determining the positions of HSO<sub>4</sub><sup>-</sup> ions and H<sub>2</sub>SO<sub>4</sub> molecules in the lattice indicates that a ratio of 2.5 gives sufficient room for all the H<sub>2</sub>SO<sub>4</sub> molecules and results in a large amount of hydrogen bonding. A possible reason for the lower ratio, 2.0, in the case of the perchlorate compound, is that less hydrogen bonding is possible because of the presence of fewer hydrogen atoms.

(7) S. Aronson and C. Frishberg, unpublished data.

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## Synthesis and Characterization of Dialkyldithiophosphate Complexes of Niobium (V)

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Few crystalline, well-characterized complexes of niobium(V) are known.<sup>1</sup> Compounds of this element are typically unstable in solution and react with water. The work reported here represents some of our efforts to prepare well-characterized, relatively stable complexes of this element.

We have previously reported the preparation of relatively stable niobium(V) complexes containing *N,N*-dialkyldithiocarbamate ligands.<sup>2</sup> Since the dialkyldithiophosphate anions are like dithiocarbamates with respect to charge, the presence of two sulfur donor atoms, and geometry, it was thought that they might also yield stable niobium compounds. Metal complexes of dithiophosphate ligands have been reported for a variety of metals.<sup>3-5</sup>

### Experimental Section

**Reagents.**—Niobium pentahalides were obtained from Alfa Inorganics, Inc. Reagent grade phosphorus pentasulfide was used in the preparation of the ligands. All solvents used were reagent grade and were dried over molecular sieves.

**Physical Measurements.**—Magnetic susceptibilities were measured at room temperature (25°) by the Gouy method. Conductivities were measured on 10<sup>-3</sup> and 10<sup>-4</sup> M solutions using a fill cell having a cell constant of about 0.4 cm<sup>-2</sup> ml<sup>-1</sup> and an Industrial Instruments, Inc., Model RC1B conductivity bridge.

Ultraviolet spectra were recorded on a Cary 14 spectrophotometer. Infrared spectra were recorded in KBr wafers and KBr solution cells using a Perkin-Elmer Model 257 grating spectrophotometer. Nmr spectra were recorded on a Varian T-60 spectrometer using CDCl<sub>3</sub> and CD<sub>3</sub>CN as solvents and tetramethylsilane as an internal standard.

Molecular weights were determined using CHCl<sub>3</sub> solutions in a Mechrolab Inc. vapor pressure osmometer, Model 301A.

**Infrared Spectral Data.**—The positions of the infrared bands for the ligands and compounds prepared follow. All data are reported in cm<sup>-1</sup> and are from KBr disks (s, strong; w, weak; sh, shoulder). Na(dedtp): 1466, 1441, 1386, 1293 (w), 1158,

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