

TABLE I
 DATA ON THE GRAPHITE-BISULFATE COMPOUNDS

Unreacted sample wt, mg	Current, mA	Reacted sample		Unreacted sample wt, mg	Current, mA	Reacted sample	
		H ₂ SO ₄ ·HSO ₄ ⁻ wt in mg	H ₂ SO ₄ :HSO ₄ ⁻ ratio			H ₂ SO ₄ ·HSO ₄ ⁻ wt in mg	H ₂ SO ₄ :HSO ₄ ⁻ 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		Unreacted sample wt, mg	Current, mA	Reacted sample	
		HClO ₄ ·ClO ₄ ⁻ wt in mg	HClO ₄ :ClO ₄ ⁻ ratio			HClO ₄ ·ClO ₄ ⁻ wt in mg	HClO ₄ :ClO ₄ ⁻ ratio
55.6	4	13.7	1.93 ^a	34.4	2	10.4	2.14 ^a
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 ^a

^a 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 HClO₄ 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 H₂SO₄:HSO₄⁻ ratio was determined in two ways.⁴ In one method, the reacted sample was first washed either in pyrophosphoric acid, H₄P₂O₇, or in (CH₃)₂SO₄ followed by CCl₄. This treatment removed the adhering sulfuric acid from the surface of the sample. The sulfate in both the HSO₄⁻ and H₂SO₄ in the sample was then analyzed as BaSO₄. 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 H₂SO₄:HSO₄⁻ 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 H₂SO₄:HSO₄⁻ 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 H₂SO₄:HSO₄⁻ in the bisulfate compounds seems reasonable. The calculated density of each adduct layer is 1.96 g/cm³ 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/cm³, is not too

different from the density of pure sulfuric acid, 1.84 g/cm³. Some preliminary work⁷ on determining the positions of HSO₄⁻ ions and H₂SO₄ molecules in the lattice indicates that a ratio of 2.5 gives sufficient room for all the H₂SO₄ 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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Received July 9, 1970

Few crystalline, well-characterized complexes of niobium(V) are known.¹ 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.² 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.³⁻⁵

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 10⁻³ and 10⁻⁴ M solutions using a fill cell having a cell constant of about 0.4 cm⁻² ml⁻¹ 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 CDCl₃ and CD₃CN as solvents and tetramethylsilane as an internal standard.

Molecular weights were determined using CHCl₃ 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⁻¹ and are from KBr disks (s, strong; w, weak; sh, shoulder). Na(dedtp): 1466, 1441, 1386, 1293 (w), 1158,

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1096, 1021 (s), 921 (s), 905 (sh), 810 (w), 764, 738 (w), 717 (w), 696 (s). $\text{NbCl}(\text{OCH}_3)_2(\text{dedtp})_2$: 1436, 1434, 1381, 1282 (w), 1158, 1095, 1001 (s), 958 (s), 925, 817, 785, 646 (s). $\text{NbCl}(\text{OCH}_2\text{CH}_3)_2(\text{dedtp})_2$: 1470 (w), 1440, 1383, 1290 (w), 1160, 1090, 1003 (s), 960 (s), 920, 810, 790 (s), 645 (s). $\text{NbCl}(\text{OCH}(\text{CH}_3)_2)_2(\text{dedtp})_2$: 1486, 1441, 1391, 1300 (w), 1160, 1119, 1011 (s), 966 (s), 930, 856 (w), 796 (s), 673 (s). $\text{Na}(\text{dchdtp})$: 1463 (sh), 1448 (s), 1370, 1347 (w), 1300 (w), 1258 (w), 1240 (w), 1150 (w), 1037, 1020, 987, 888 (s), 860 (s), 837 (w), 818 (s), 788 (s), 673 (s). $\text{NbCl}(\text{OCH}_3)_2(\text{dchdtp})_2$: 1460 (sh), 1442 (s), 1369 (s), 1331, 1300 (w), 1260 (s), 1240 (w), 1190 (sh), 1150, 1100 (s), 934 (s), 866, 830 (s), 810 (w), 789 (s), 775, 640 (s). $\text{NbCl}(\text{OCH}(\text{CH}_3)_2)_2(\text{dchdtp})_2$: 1460 (sh), 1442 (s), 1370 (s), 1358, 1318, 1258, 1238 (w), 1155, 1126 (s), 991 (s), 960 (sh), 882 (s), 849 (s), 828, 808, 788 (s), 648 (s). $\text{Na}(\text{dmtdtp})$: 1620, 1431 (s), 1306, 1220, 1106 (s), 1010 (s), 911 (w), 760 (s), 711 (s). $\text{NbCl}(\text{OCH}_3)_2(\text{dmtdtp})_2$: 1600, 1450 (s), 1430, 1290 (w), 1170, 1088 (s), 1010 (s), 940 (w), 815 (s), 646.

Methods of Analysis.—Niobium was determined as Nb_2O_5 by dissolving the samples in 5 ml of hot methanol and adding 10 ml of distilled water and 2 ml of concentrated ammonium hydroxide. After this solution had evaporated to 5 ml, 10 ml of distilled water was added and the solid was collected on quantitative filter paper. The residue and filter paper were ignited in porcelain crucibles and the ash was weighed. Halide analyses were done by the Volhard method preceded by fusion of the sample with Na_2O_2 and NaOH . Carbon, hydrogen, and sulfur analyses were performed by Midwest Micro Lab., Inc.

Preparation of Compounds.—The sodium salts of the dialkyl-dithiophosphate ligands were prepared as described by Makens, Vaughn, and Chelberg.⁶

The niobium complexes were prepared by the following two methods. The ligands used were the sodium salts of dimethyl-dithiophosphate (dmtdtp^-), diethyl-dithiophosphate (dedtp^-), and dicyclohexyldithiophosphate (dchdtp^-).

$\text{NbX}(\text{OCH}_3)_2\text{L}_2$.—A 0.056-mol sample of NbX_5 (15 g of NbCl_5 , 28 g of NbBr_5) was weighed out in a 500-ml round-bottom flask in a drybox. Methanol (20 ml) was added. Vigorous evolution of HX gas and a clear, colorless solution resulted. Nitrogen was bubbled through this solution for 1 hr to remove the HX gas. A solution of 0.135 mol of the sodium salt of the ligand in 45 ml of methanol was prepared and added to the previous solution. The resulting solution gradually turned deep purple and a precipitate of NaX formed which was immediately removed by filtration. The clear purple solution was cooled to 0° and purple-pink crystals precipitated in 2–3 hr. The crystals were collected by decanting most of the solvent and then removing the remaining solvent under vacuum. The product was recrystallized from methanol.

$\text{NbX}(\text{OR})_2\text{L}_2$.—Complexes with coordinated alkoxides other than methoxide were prepared from the methoxide derivative by recrystallizing them from the appropriate alcohol. For example, $\text{NbCl}(\text{OCH}(\text{CH}_3)_2)_2(\text{dedtp})_2$ was prepared by recrystallizing $\text{NbCl}(\text{OCH}_3)_2(\text{dedtp})_2$ from dry isopropyl alcohol. The final compounds were obtained as purple-pink crystals by keeping these alcohol solutions at 0° for 2–3 hr.

Tantalum Compounds.—Reaction of solutions of dithiophosphates with alcohol solutions of tantalum pentahalide produced pink solutions. However, no product precipitated from these solutions on standing or cooling. Only sodium halide and oils were obtained when the solvent was removed by evaporation under vacuum.

Characterization

Analyses, melting points, and yields of the compounds prepared are presented in Table I. The carbon analyses are frequently low. This fact will be discussed later. Molecular weight determinations by osmometry on CHCl_3 solutions of $\text{NbCl}(\text{OCH}_3)_2(\text{dedtp})_2$ and $\text{NbCl}(\text{OCH}_3)_2(\text{dchdtp})_2$ gave values of 498 and 648, respectively, compared to theoretical molecular weights of 558 and 776. These results indicate the compounds are monomeric. The compounds are diamagnetic.

Conductivities.—Conductivities measured in methanol and acetonitrile are presented in Table I. In

(6) R. F. Makens, H. H. Vaughn, and R. R. Chelberg, *Anal. Chem.*, **27**, 1062 (1955).

TABLE I
ANALYSES, MELTING POINTS, YIELDS, AND CONDUCTIVITIES

Compound	Nb(Ta)		Halide		S		C		H		Mp, °C	% yield	Molar conductivities, ^a $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found			CH_3OH	CH_3CN
$\text{Na}(\text{dedtp})$	16.64	16.49	6.35	6.15	30.23	30.23	23.77	23.77	4.80	4.93	186	70	64	120
$\text{NbCl}(\text{OCH}_3)_2(\text{dedtp})_2$	15.41	15.67	13.27	13.95	22.92	22.87	21.66	21.66	4.66	4.67	93–95 dec	70	340	15
$\text{NbBr}(\text{OCH}_3)_2(\text{dedtp})_2$	15.12	15.13	5.77	6.37	20.27	20.27	18.88	18.88	4.35	4.61	71–73 dec	70	350	14
$\text{NbCl}(\text{OCH}(\text{CH}_3)_2)_2(\text{dedtp})_2$	15.78	16.22	6.02	6.48	20.76	20.06	24.60	24.60	5.53	5.34	66–67 dec	50	350	14
$\text{NbCl}(\text{OC}_6\text{H}_5)_2(\text{dedtp})_2$	12.00	12.38	4.58	4.84	23.50	23.50	22.11	22.11	5.14	4.71	92–93	50	58	100
$\text{Na}(\text{dchdtp})$	11.19	11.48	4.27	4.08	17.10	17.10	45.57	48.87	7.01	7.95	168	70	350	17
$\text{NbCl}(\text{OCH}_3)_2(\text{dchdtp})_2$	18.33	18.31	7.00	5.20	16.53	15.68	40.29	39.73	6.46	6.51	156	65	360	15
$\text{NbCl}(\text{OCH}(\text{CH}_3)_2)_2(\text{dchdtp})_2$	18.33	18.31	7.00	5.20	15.47	14.38	43.35	42.56	6.98	7.05	146	50	69	90
$\text{Na}(\text{dmtdtp})$	18.33	18.31	7.00	5.20	35.59	35.59	13.33	13.32	3.36	3.47	153	70	350	15
$\text{NbCl}(\text{OCH}_3)_2(\text{dmtdtp})_2$	18.33	18.31	7.00	5.20	25.31	25.31	14.22	14.22	3.58	3.58	134	70	350	15

^a At a concentration of $1.00 \times 10^{-3} M$.

methanol the compounds gave values which correspond to 3:1 electrolytes. In acetonitrile the dissociation was slight probably because this solvent does not displace alkoxide or halide ions as well as methanol. However the nmr spectra of the compounds in CD_3CN do indicate the presence of some free OCH_3^- which suggests that some displacement by solvent does occur. Conductivity studies in tetrahydrofuran and chloroform indicate that in these solvents there is no dissociation into ions.

Electronic Spectra.—The ultraviolet spectra of the sodium salts of the dithiophosphate ligands are quite similar. In methanol the ligands exhibit a broad absorption beginning at 300 nm which increases to a shoulder or maximum. The measured molar absorptivities at the shoulders are 387 at 251 nm for $\text{Na}(\text{dmdtp})$, 3500 at 224 nm for $\text{Na}(\text{dedtp})$, and 1900 at 226 nm for $\text{Na}(\text{dchdtp})$. The absorbance continues to increase to the cutoff point at 200–210 nm. In methanol, all niobium compounds gave time-stable spectra similar to those of the parent phosphate ligand with molar absorptivities of 780 at 251 nm for $\text{NbCl}(\text{OCH}_3)_2(\text{dmdtp})_2$, 1730 at 225 nm for $\text{NbCl}(\text{OCH}_2\text{CH}_3)_2(\text{dedtp})_2$, and 2000 at 226 nm for $\text{NbCl}(\text{OCH}_3)_2(\text{dchdtp})_2$.

The compounds dissolved in acetonitrile exhibited this same region of absorbance except that it began at a longer wavelength (350 nm). The absorbance between 300 and 350 nm however decreased with time. This same behavior was observed in tetrahydrofuran and benzene; however, the decrease in absorbance was slower.

As was noted in the synthesis section, the niobium complexes were isolated from purple solutions as purple to pink crystalline materials. On recrystallization the color faded to a constant pale pink. The two most intensely colored compounds were studied in order to detect the band responsible for the pink color. The compound $\text{NbCl}(\text{OCH}_3)_2(\text{dedtp})_2$ in methanol gave a maximum at 538 nm with an ϵ of 2.0; $\text{NbCl}(\text{OCH}_3)_2(\text{dedtp})_2$ in methanol exhibits a maximum at 518 with an ϵ of 1.7.

Infrared Spectra.—The infrared bands observed in KBr disks containing either salts of ligands or the chloro derivatives of the niobium compounds were listed in the Experimental Section. The bands in the region 600–750 cm^{-1} have been assigned to the P–S stretching mode. The bands present in this region due to the salts of the ligands appear at shorter wavelength than those due to the ligands in the niobium compounds. This suggests that the ligands are bonded to niobium through both sulfur atoms.⁴

Nuclear Magnetic Resonance Spectra.—Spectral data for the isolated compounds are presented in Table II. The spectra of all compounds integrated correctly for the assigned stoichiometry. Comparison of resonance positions for the ligands before and after coordination to niobium was not possible since a solvent which would dissolve sufficient quantities of both was not found.

The nmr data indicate that the two coordinated alkoxide groups in each compound are equivalent as are the four alkoxide groups in the coordinated dithiophosphate ligands. This implies very similar environments or rapid exchange.

The sodium salt of the dimethyldithiophosphate lig-

TABLE II
NMR DATA

Compound	Frequency ^a	Assignment
$\text{Na}(\text{dedtp})^b$	78 t	POCH_2CH_3
	238 o	POCH_2CH_3
	256 o	POCH_2CH_3
$\text{NbCl}(\text{OCH}_3)_2(\text{dedtp})_2$	85 t	POCH_2CH_3
	244 o	POCH_2CH_3
	244	OCH_3
$\text{NbBr}(\text{OCH}_3)_2(\text{dedtp})_2$	85 t	POCH_2CH_3
	254 o	POCH_2CH_3
	244	OCH_3
$\text{NbCl}(\text{OCH}(\text{CH}_3)_2)(\text{dedtp})_2$	74 d (8)	$\text{OCH}(\text{CH}_3)_2$
	84 t	POCH_2CH_3
	254 o	POCH_2CH_3
$\text{NbCl}(\text{OCH}_2\text{CH}_3)_2(\text{dedtp})_2$	282 q	$\text{OCH}(\text{CH}_3)_2$
	66 t	OCH_2CH_3
	85 t	POCH_2CH_3
$\text{Na}(\text{dmdtp})^b$	256 o	POCH_2CH_3
	262 q	OCH_2CH_3
	131 d (14)	Impurity
$\text{NbCl}(\text{OCH}_3)_2(\text{dmdtp})_2$	216 d (14)	POCH_3
	220 d (15)	POCH_3
	243	OCH_3
$\text{Na}(\text{dchdtp})^b$	102 b	$\text{POCH}(\text{CH}_2)_5$
	262 b	$\text{POCH}(\text{CH}_2)_5$
	98 b	$\text{POCH}(\text{CH}_2)_5$
$\text{NbCl}(\text{OCH}_3)_2(\text{dchdtp})_2$	240	OCH_3
	274 b	$\text{POCH}(\text{CH}_2)_5$
	74 d (8)	$\text{OCH}(\text{CH}_3)_2$
$\text{NbCl}(\text{OCH}(\text{CH}_3)_2)(\text{dchdtp})_2$	98 b	$\text{POCH}(\text{CH}_2)_5$
	274 b	$\text{POCH}(\text{CH}_2)_5$
	282 q	$\text{OCH}(\text{CH}_3)_2$

^a Frequency of line or center of multiplet in hertz at 60 MHz. Tetramethylsilane (TMS) was the internal standard: t, triplet; o, octet; q, quartet; b, broadened resonance. All triplets and quartets showed a splitting of 7 Hz. The octets were composed of a quartet with a splitting of 7 Hz in which each resonance was split into a doublet with a splitting of 8 Hz. The splittings in the doublets are presented in parentheses.

^b Solvent is CD_3CN ; CDCl_3 was used for other compounds.

and shows a doublet (7-Hz splitting) centered at 131 Hz which appears to be due to an impurity. Integration of the nmr spectra of various samples of this ligand always indicated at least a 25% impurity. It is interesting to note that the spectrum of the dmdtp niobium compound does not show any evidence of the impurity. This suggests that the metal atom is selective in the preparative reaction.

Reactions of the Niobium Compounds.—The reaction between $\text{NbCl}(\text{OCH}_3)_2(\text{dedtp})_2$ and CH_3OH in CDCl_3 was studied using nmr spectra. A solution of the niobium complex was prepared and its spectrum was observed. Methanol was then added to the solution such that the mole ratio of CH_3OH to Nb varied from 1:1 to 10:1 and the nmr spectra of the resulting solutions were recorded. The resonances of the diethyldithiophosphate ligands remained unchanged throughout the study. The integrated intensity of the sharp resonance which corresponds to coordinated OCH_3 had dropped to half its original value (in pure CDCl_3) at a 1:1 methanol:Nb ratio. Its integrated intensity then remained constant until the CH_3OH :Nb ratio became greater than 5. At higher CH_3OH concentrations the resonance disappeared. In the solutions containing methanol a broad resonance appeared between that of coordinated OCH_3 (244 Hz) and the position of the methyl protons of CH_3OH when observed alone in CDCl_3 (204 Hz). No resonance was present at 204 Hz. The position of this broad resonance was found to be a function of the concentration of added methanol, shifting toward 204 Hz as the concentration of methanol was

increased. This behavior indicates that the coordinated OCH_3 groups exchange with CH_3OH molecules in solution. At $\text{CH}_3\text{OH}:\text{Nb}$ ratios of 1:1–5:1 only one OCH_3 is involved in exchange. At larger mole ratios exchange of both coordinated OCH_3 groups occurs. This stepwise behavior in the exchange of coordinated OCH_3 suggests one methoxide group is more easily exchanged than the other.

In a similar study benzyl alcohol was treated with $\text{NbCl}(\text{OCH}_3)_2(\text{dedtp})_2$ in chloroform. The nmr spectrum of the solutions indicated that there was a rapid reaction (complete in less than 1 min) in which coordinated methoxide groups were displaced by the benzyl alcohol.

A very characteristic reaction of all the new compounds is their decomposition which occurs with the loss of a coordinated alkoxide group (probably as the alcohol). On standing the crystalline pale purple compounds turn yellow-green. This occurs in the air, in a drybox, or under vacuum. For some compounds appreciable change occurs in 1 day; for others the reaction is slower. The same color change occurs rapidly when the compounds are dissolved in solvents such as acetone, chloroform, or benzene. Ultimately yellow-green solids precipitate from these solutions. The purple color can be restored by dissolving the yellow-green compounds in an alcohol or in some cases simply by exposing these materials to alcohol vapors. The compounds can be stored in the presence of the vapors of the appropriate alcohol. If an nmr spectrum is taken of the yellow compound obtained by placing a sample of $\text{NbCl}(\text{OCH}_3)_2(\text{dedtp})_2$ under vacuum for several days, one observes a spectrum similar to that of the parent niobium compound, containing, however, only one OCH_3 group. The spectrum after restoring the purple-pink color in methanol is identical with that of the $\text{NbCl}(\text{OCH}_3)_2(\text{dedtp})_2$ compound with two OCH_3 groups. The loss of alkoxide accounts for the low carbon analyses reported earlier, since appreciable decomposition of the ethanol and 2-propanol derivatives would be expected during their trip to the analyst.

We are uncertain as to what happens during this decomposition. The analyses, molecular weights, diamagnetism, and nmr spectra are consistent with our formulation of the pale purple compounds. The conversion to a yellow-green material presumably is a hydrolysis or condensation reaction. This is consistent with the limited solubility of the yellow-green materials, which on extended standing become insoluble.

Summary

The results discussed in this paper indicate that the compounds we have prepared are monomers with the stoichiometry $\text{NbX}(\text{OR})_2(\text{S}_2\text{P}(\text{OR}')_2)_2$. Since the dithiophosphate ligands seem to be coordinated as bidentate ligands, the compounds probably contain niobium coordinated to seven donor atoms. The compounds give stable highly conducting solutions in methanol. It seems probable that these solutions contain solvated $\text{Nb}(\text{S}_2\text{P}(\text{OR})_2)_2^{3+}$ cations. Exchange of the coordinated alkoxide groups is readily achieved by recrystallization from the desired alcohol. The compounds slowly decompose in the solid state and in solvents such as CHCl_3 and CH_3CN with the formation of less soluble substances and the loss of one coordinated alkoxide.

In many cases the compounds can be regenerated by exposure to the vapors of the appropriate alcohol.

Acknowledgment.—Mrs. Dot H. Fricks and Mrs. M. K. C. Bechtel contributed significantly to the preparation and characterization of the compounds reported. This research was sponsored by the Air Force Office of Scientific Research, United States Air Force, under Grant AFOSR-68-1355. D. C. P. was an NSF Graduate trainee, 1966–1970.

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Magnetic Properties of Some Polynuclear Hydroxy-Bridged Iron(III) Sulfate Complexes

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Received July 29, 1970

Our recent studies of the extraction of iron(III) from aqueous sulfate solutions with high molecular weight primary² or secondary amines³ have yielded compounds of stoichiometry $(\text{R}(\text{R}')\text{NH}_3)_2\text{FeOH}(\text{SO}_4)_2$ and $(\text{R}_2\text{NH}_2)_2\text{FeOH}(\text{SO}_4)_2$ where R is 3,5,5-trimethylhexyl and R' is *n*-dodecyl. The compounds obtained with the primary amines were crystallized from ethanol solution with 1 mol of ethanol attached. All of these compounds had magnetic moments in the region of 3.6 BM, and preliminary studies suggested hydroxy bridging of dimeric or trimeric aggregates.

In order to obtain a more detailed knowledge of the degree of aggregation and possibly the mode of bridging in the primary amine complexes, we have carried out magnetic susceptibility studies over the temperature range 80–300°K and have fitted the results to various theoretical models. Measurements have also been made on the known⁴ hydroxy-bridged compound $\text{Fe}(\text{OH})\text{SO}_4$ for comparison. This latter hydrolyzed species is suggested to be the one extracted from aqueous solution by the amine sulfate salts.^{2,3}

Although significant advances have been made recently through magnetic,^{5–7} spectroscopic,^{8–10} and X-ray studies^{11–14} toward an understanding of oxygen

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