The bond distances and bond angles with their estimated standard deviations are shown in Figure 3. The three nickel–sulfur distances are unequal and they are all significantly greater than the nickel–sulfur distance, 2.20 Å, that is usually found in low-spin nickel complexes. In high-spin nickel complexes the nickel–sulfur distance lies between 2.4 and 2.6 Å.[6] The Ni–S(2) and the Ni–S(3) distances are well within this range; the Ni–S(1) distance, however, is significantly smaller.

Although in general, the mechanisms of reactions that take place in solution cannot be deduced from structural data, it is reasonable to assume that the pentacoordinated intermediate did exist in solution if it could be isolated in the solid state. Hence it can be speculated that the following mechanism is involved in the formation of the mixed ligand complex. The bidentate ligand, 2,9-dimethyl-1,10-phenanthroline, approaches the planar nickel chelate in an axial direction and coordination of one of the nitrogen atoms disrupts a chelate ring to allow the second nitrogen atom to coordinate in *cis* position. The free sulfur atom, however, does not occupy the sixth coordination position. The reasons for this unexpected behavior will be sought by carrying out further work with a series of substituted 1,10-phenanthrolines and other substituted bidentate ligands such as 2,2′-dipyridyl.

The nickel–nitrogen distances are approximately equal to the nickel–nitrogen distances (2.07 and 2.11 Å) found in the hexacoordinated compound, 2,2′-dipyridylbis(O,O′-dimethyldithiophosphato)nickel(II)[9] and bispyridinebis(O,O′-diethyldithiophosphato)nickel(II).[8] All other interatomic distances in the molecule do not differ significantly from the distances reported for similar molecules. The nickel–sulfur bond lengthening and the chelate ring distortion are similar to those which occur on the addition of an axial ligand to planar metal chelates. The decrease in the S(1)–Ni–S(2) angle and the concomitant increase in the S(1)–P(1)–S(2) angle are of the same order of magnitude as those found when two pyridine molecules were added axially to the planar chelate, bis(O,O′-diethyldithiophosphato)nickel(II).[8] The shortest intermolecular distance observed was 3.39 Å, between C(12) and C(6); all other intermolecular contacts were greater than 3.5 Å. All the atoms in the 2,9-dimethyl-1,10-phenanthroline molecule together with the nickel atom lie in approximately the same plane. The atom C(9) shows a maximum deviation of 0.13 Å from this plane. Unfortunately the accuracy of this structure determination does not warrant any discussion of structural changes in the phenanthroline molecule that may have resulted from coordination to the nickel atom. The high temperature factors and their large standard deviations (which were anticipated from the absence of the high angle reflections in the Weissenbergh photographs) contributed to the low accuracy of this structure determination.

One of the most interesting features in this complex is that although three of the five donor atoms are sulfur atoms, the complex has a magnetic moment of 3.2 BM. The interpretation of the d–d transitions in this compound and related mixed-ligand complexes obtained with other substituted 1,10-phenanthrolines and 2,2′-dipyridyls should be of interest.

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Methylarsaoxanes. Structural Chemistry of Cacodyl Oxide and Arsenosomethane in the Liquid State

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Abstract: Nuclear magnetic resonance data indicate that the oxygen in cacodyl oxide, $(CH_3)_2AsOAs(CH_3)_2$, is in the bridging position and, on dissolution in organic solvents, crystalline arsenosomethane, CH_3AsO, is shown to form a mixture of species in which the tetrameric and trimeric cyclics predominate. Arsenosomethane and cacodyl oxide react immediately in solution or as a neat liquid to give equilibrium mixtures containing compounds of the type $CH_3[As(CH_3)O]_nAs(CH_3)_2$ for $n \geq 2$. The controlling equilibrium constants are reported. Arsenosomethane also reacts with methyldibromoarsine to give compounds of the type $Br[As(CH_3)O]_nAs(CH_3)Br$. However, arsenosomethane does not react with dimethylbromoarsine because the equilibrium for redistribution of bromine and bridging oxygen atoms between the $CH_3As<$ and $(CH_3)_2As-$ is shifted strongly toward the placement of the bromine on the dimethylarsino group.

The methyl-substituted oxides of arsenic are among the oldest organometallic compounds. Cacodyl oxide, $(CH_3)_2AsOAs(CH_3)_2$, was first prepared in 1760 as part of a mixture[2] and its isolation and elemental composition were first demonstrated by Bunsen[3] in

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(2) L. C. Cadet de Gassincourt, *Mem. Math. Phys. Savants Étrangers*, 3, 363 (1760).

(3) R. Bunsen, *Justus Liebigs Ann. Chem.*, **31**, 175 (1839).

1839. Two decades later (1858), Baeyer[4] prepared arsenosomethane, which has the empirical formula CH_3AsO. Unfortunately, most of the literature on these compounds since the 19th century has been directed toward preparation and biological applications rather than structure and basic chemistry. Because of this, it seemed desirable to apply modern methods of investigation to elucidation of the structural chemistry of these compounds.

Experimental Section

Reagents. Arsenosomethane was prepared by two methods. The first[5] consists of oxidation of arsenomethane with sulfuric acid.[6] After neutralization with sodium carbonate, the oxidized mixture was extracted with benzene with exclusion of air. Slow vacuum evaporation of the benzene gave well-formed crystals of arsenosomethane. The second method[7] is based on the reaction in benzene of methyldibromoarsine with potassium carbonate and a trace of water. The mixture was heated on a water bath until cessation of CO_2 evolution. The liquid phase was removed, the benzene distilled from it, and the resulting residue sublimed at 60° in high vacuum. Except for a small amount of bromine (0.2% Br in the second preparation), there was no detectable difference between the arsenosomethane made by these two methods. The proper melting point and the correct elemental analysis were found for this compound.

Dimethylbromoarsine and methyldibromoarsine were produced by the direct-synthesis method[8] in which methyl bromide is passed over a metallic arsenic–copper mixture. The resulting arsines were separated by distillation. Cacodyl oxide was made by hydrolysis of $(CH_3)_2AsCl$, with a solution of sodium carbonate.[9] The lower phase was removed and carefully distilled to give a product with a boiling point of 151°.

The compounds discussed in this manuscript were handled with great care because of the toxicity of volatile organic–arsenic compounds. Transfers between normally closed receptacles were carried out in a drybag kept in a hood having a good flow of air. The distilling apparatus was also erected in the hood and the nmr measurements were carried out in sealed glass tubes.

Physical Measurements. Hydrogen (^1H) nuclear magnetic resonance (nmr) measurements were made with a Varian A-60 spectrometer equipped with a V-604 variable temperature controller. The reference standard was tetramethylsilane added to the samples and the standard convention of using a negative sign for downfield shifts was employed. The nmr peaks were determined by cutting and weighing and the results were checked in some cases with a Du Pont curve resolver. The mass spectra were obtained with a CEC 21-104 medium-resolution rapid-scan spectrometer, with the solid sample contained in a capillary tube inserted into the vacuum chamber close to the point of ionization. The ionization voltage was set at various values in the range between 4 and 70 eV.

The infrared measurements were carried out on a Beckman IR-4 for the usual region of the spectrum and on an IR-11 for the far-infrared.

Results and Conclusions

Molecular Structures. Although it has generally been supposed that cacodyl oxide has the symmetrical structure $(CH_3)_2As\text{-}O\text{-}As(CH_3)_2$, the unsymmetrical structure, $(CH_3)_2As\text{–}As(O)(CH_3)_2$, is also a possibility. In the temperature range investigated, from 150 to −60°, the nmr spectra of cacodyl oxide showed a single sharp peak at 1.065 ppm for the neat liquid and 1.115 ppm in benzene solution, with the variation in chemical shift with concentration being about ±0.1 ppm—a value commensurate with a single dissolved species. These results support the symmetrical formulation in which the oxygen is in the bridging position. In the mass spectrograph, cacodyl oxide showed a major peak at low ionization voltages which corresponded to the $C_4H_{12}As_2O$ formulation and was the species of highest mass number observed.

Arsenosomethane, CH_3AsO, could have either a bridging oxygen atom or exhibit As–As bonds, with the oxygen in the isolated position. Unfortunately, the nmr chemical shifts of the four resonances observed for this species lie partway between the shift expected for the structure with the oxygen in the bridging position and that having the oxygen in the isolated position. From the results on cacodyl oxide, we tentatively assume that the oxygen is bridging.

The nmr spectra of well-formed crystals of arsenosomethane dissolved in diphenyl ether exhibited four resonances, the relative areas of which were found to vary with both concentration and temperature, as shown in Table I. The same general behavior was observed in a number of different organic solvents: benzene, carbon tetrachloride, chloroform, and naphthalene. Presumably, there is but a single molecular species present in the crystal and this rearranges to give several different species upon dissolution. In view of the fact that the oxygen-bridged cyclic compounds of silicon and phosphorus (such as the siloxanes and the polyphosphate anions) generally show a single nmr peak per molecule, we shall ascribe each of these resonances to a single molecule which is assumed to be cyclic in agreement with the empirical formula of arsenosomethane.

Table I. Nmr Pattern of Arsenosomethane in Diphenyl Ether

Temp, °C	Concn, wt %	% total CH_3 as peak[a] at (ppm) −1.367	−1.300	−1.285	−1.257
180	10.0	20.3	35.2	40.3	4.1
150	10.0	16.8	38.8	40.9	4.2
120	10.0	11.2	34.9	46.2	7.7
100	10.0	7.0	34.9	49.5	8.5
80	10.0	5.5	32.2	56.7	5.6
60	10.0	3.5	30.4	60.1	6.0
40	10.0	2.9	30.1	62.2	4.1
120	48.0	8.0		92.0	
120	31.8	9.2		91.8	
120	20.1	9.9	31.4	53.1	7.9
120	8.6	14.2	29.5	50.5	5.5
120	4.7	15.9	28.5	49.6	5.8

[a] The reported chemical shifts correspond to 150° and 10% concentrations.

At low ionization voltages, the mass spectra of arsenosomethane exhibited peaks corresponding to the formula $(CH_3AsO)_n$, where n is 2, 3, 4, and 5. Cryoscopic measurements of the molecular weight of arsenosomethane in benzene led to a value of 399. If the resonance at −1.37 ppm in the nmr spectrum of arsenosomethane is tentatively assigned to the $(CH_3AsO)_2$, the second peak at −1.30 ppm to $(CH_3AsO)_3$, the third at −1.29 ppm to $(CH_3AsO)_4$, and the fourth at −1.26 ppm to $(CH_3AsO)_5$, one obtains a molecular weight of 390 at the temperature at which benzene freezes. The fact that the molecular weight calculated from the nmr spectrum is somewhat smaller than the colligative molecular weight is in accord with the idea, resulting from the equilibrium constant calculations given below, that the upfield nmr peak may

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correspond to a mixture of ring and chain molecules averaging somewhat greater than $n = 5$ in the formula $(CH_3AsO)_n$. This interpretation in which the three other resonances are assigned to a series of different cyclic molecules is consistent with the change of the relative areas of the nmr peaks upon dilution.

The equilibria relating the variously sized cyclic molecules to each other can be written in the following form.

$$(j + 1)[(CH_3AsO)_j] \rightleftharpoons j[(CH_3AsO)_{j+1}] \qquad (1)$$

From Table I, we calculate that, for $j = 2$, the equilibrium constant for eq 1, which we shall call $K_{j,j+1}^{00}$, corresponds at 120° to 77.5, with a ΔH for this reaction of 12.0 kcal/mol; and, for $j = 3$, $K_{3,4}^{00} = 4.26$ and $\Delta H = 5.5$ kcal/mol. Attempts to calculate $K_{4,5}^{00}$ from the two downfield nmr peaks led to a numerically ill-defined equilibrium constant, so that the peak farthest downfield probably has too many contributions from structures other than the cyclic pentamer.

$[(CH_3)_2As]_2O$–CH_3AsO Mixtures.[10] Mixtures made by dissolving various proportions of arsenosomethane in cacodyl oxide show more or less broad single-line nmr spectra at room temperature. Upon lowering the temperature, these lines are seen to broaden out and split into a number of resonances. A typical spectrum taken at −30° is shown in Figure 1, where chloroform was used as the solvent in order to achieve this low temperature. Following the rationale that the reaction between cacodyl oxide and arsenosomethane, under the conditions of this study, consists wholly of scrambling of molecular parts due to interchanges at the bridging oxygens, we assume that cacodyl oxide contributes monofunctional terminating groups to straight-chain molecules held together by difunctional groups from the arsenosomethane. Thus, in addition to cyclic compounds of the arsenosomethane composition, there may be straight-chain compounds which formally can be considered as resulting from insertion of CH_3AsO groups into the cacodyl oxide molecule. Following the well-developed procedures which we have reported many times,[10] the assignments of the various peaks in the spectrum of Figure 1 were made from their variation with the ratio of the starting materials and comparison with the spectra of pure arsenosomethane and pure cacodyl oxide.

The relative areas of the various nmr peaks observed in this study are shown in Table II, where the experimental data are compared with theoretical values calculated from the two ring–ring equilibrium constants[10] of the form of eq 1 and a ring–chain equilibrium constant for the tetrameric ring corresponding to the following equation.

$$CH_3(CH_3AsO)_{i-1}As(CH_3)_2 \rightleftharpoons CH_3(CH_3AsO)_{i-5}As(CH_3)_2 + (CH_3AsO)_4 \qquad (2)$$

The equilibrium constant calculated for eq 2 at −30° from the data of Table II is $(K_{mol}{}^0)_4 = 2.0 \pm 0.1$ mol/l.

CH_3AsBr_2–CH_3AsO Mixtures. Nmr spectra of samples made from various proportions of arsenosomethane dissolved in methyldibromoarsine show a single nmr resonance at room temperature. Resolution of the spectrum into reasonably separated peaks is not achieved until the temperature is lowered to −60°. However, even at this temperature with chloroform as the solvent, the spectra show what is probably viscosity broadening. The spectra at −60° are seen to exhibit three reasonably distinct peaks which have been assigned to neso, CH_3AsBr_2, at −2.73 ppm; end, $Br(CH_3)AsO_{1/2}$–, at −2.17 ppm; and middle groups, $CH_3As(O_{1/2}–)_2$, at −1.59 ppm.

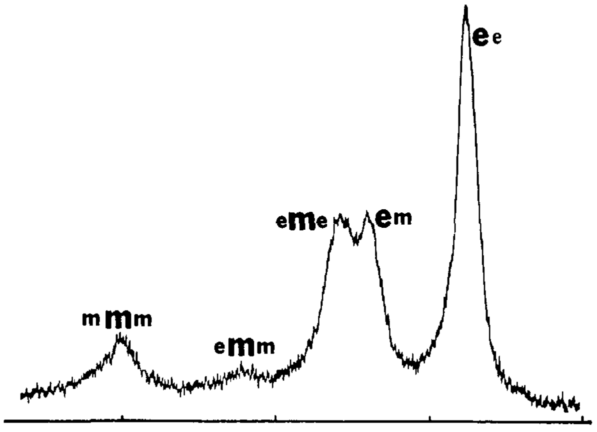

Figure 1. Proton nmr spectrum of a mixture of cacodyl oxide with arsenosomethane at −30°. The large letters correspond to the species exhibiting the methyl group corresponding to the observed peak, as described in footnote *b* of Table II.

Table II. Nmr Peak Areas at −30° for $(CH_3)_3AsO_{1/2}$ End and $(CH_3)_2As(O_{1/2})_2$ Middle Groups in Molecular Mixtures Made from Cacodyl Oxide and Arsenosomethane

	End groups		Middle groups		
R = CH_3/As[a]	**e***e*[b] −1.275[d]	**e***m* −1.338	*e***m***e* −1.360	*e***m***m* −1.422	*m***m***m*[c] −1.505
1.75	45.9	29.1	14.0	7.6	3.4
	46.5[e]	*28.5*	*8.8*	*10.9*	*5.3*
1.56	25.3	30.4	11.0	14.1	19.2
	24.5	*31.5*	*6.9*	*17.8*	*19.3*
1.51	18.8	32.0	2.6	17.2	29.4
	20.2	*30.8*	*6.1*	*18.6*	*24.3*
1.47	16.6	29.9	2.4	18.2	32.9
	17.1	*29.9*	*5.4*	*19.0*	*28.6*
1.28	10.5	18.4	1.9	10.8	58.4
	7.5	*20.5*	*2.8*	*10.0*	*54.2*
1.22	8.1	15.8	1.6	8.4	66.1
	5.0	*17.0*	*1.9*	*13.1*	*62.0*
1.12	3.6	8.5	1.3	6.6	80.0
	2.9	*9.1*	*1.1*	*6.9*	*80.0*

[a] Mole ratio of total methyl groups to total arsenic, a value which ranges from 2 for pure cacodyl oxide to 1 for pure arsenosomethane. [b] End group = e and middle group = m. The boldface letter represents the CH_3As group observed by the nmr and the italics the neighboring group(s). Thus, **e***e* stands for $(C\underline{H}_3)_2AsOAs(C\underline{H}_3)_2$ and *e***m***m* for $(CH_3)_2AsOAs(C\underline{H}_3)OAs(CH_3)O\cdots$, where the observed hydrogens are underlined. [c] The *m***m***m* resonance includes that of the *m***m***m* structure in chain molecules plus the resonances of the arsenosomethane cyclic molecules. [d] Nmr chemical shifts in ppm at −60°. [e] The numbers in italics were computed from the following set of equilibrium constants: $K_{2,3}^{00} = 5 \times 10^4$, $K_{3,4}^{00} = 1 \times 10^2$, $(K_{mol}{}^0)_4 = 2.0$.

Although it is not possible to distinguish between middle groups in rings and in chains, the ring–ring and ring–chain equilibrium constants described above

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(10) For a brief review of equilibrium-controlled chemistry of the general type discussed herein, see J. R. Van Wazer, *Ann. N. Y. Acad. Sci.*, **159**, 5 (1969), or J. R. Van Wazer and K. Moedritzer, *Angew. Chem., Int. Ed. Engl.*, **5**, 341 (1966).

should be applicable to this system of $Br[As(CH_3)O]_n$-$As(CH_3)Br$ linear molecules mixed with $[As(CH_3)O]_j$ cyclics. From an extrapolation of the data of Table I, we roughly estimate that the values of the ring–ring constants at −60° are $K_{2,3}{}^{00} = 3.5 \times 10^6$ and $K_{3,4}{}^{00} = 5 \times 10^2$ mol/l. Furthermore, since the data of Table II correspond to −30°, we shall assume that at −60° the ring–chain constant, which should be independent of the chain-terminating group, is $(K_{mol}{}^0)_4 = 2.1$ mol/l. On this basis, we find that the chain–chain equilibrium constant has the following value at room temperature.

$$K_1 = [\text{chain middles}][\text{neso}]/[\text{ends}]^2 = 8.7 \times 10^{-2} \quad (3)$$

In spite of the fact that methyldibromoarsine reacts immediately with arsenosomethane, it was found that dissolution of arsenosomethane in dimethylbromoarsine led to no reaction, as evidenced by the nmr spectrum. This superficial anomalous behavior could be due either to the absence of a suitable reaction mechanism path or to an unfavorable equilibrium constant. In view of the fast reaction causing line coalescence in mixtures of methyldichloroarsine with arsenosomethane, it would seem most reasonable to assume that the lack of reaction was due to an unfavorable equilibrium situation[11] rather than to kinetic control. In other words, it would appear that when bridging oxygen atoms exchange with bromines between $CH_3As<$ and $(CH_3)_2As-$, there is a strong preference for the oxygen to be on the monomethylarseno and the bromine on the dimethylarseno group.

If this is the case, a mixture of cacodyl oxide with methyldibromoarsine should react rapidly, with significant evolution of heat. When equimolar amounts of these two reagents were combined in a 5-mm tube, heat evolution was noted, and the nmr showed the starting materials to have disappeared completely. The reaction products consisted of a liquid composition exhibiting about the same nmr pattern as obtained from mixing arsenosomethane with methyldibromoarsine plus a white precipitate which, from direct analysis as well as from material-balance calculations, was shown to be arsenosomethane—perhaps a linear polymeric modification. Thus, the exchange of bromine and bridging oxygens between the methyl- and dimethylarsine moieties obeys the same general principles[11,12] as have been described for the exchange of halogens and bridging oxygens between dimethylgermanium and dimethylsilicon. It is interesting to note that in the exchange of chlorine with methoxyl groups between various methyl-substituted silicon moieties,[13–15] there is a strong preference for the halogen to be on the silicon atom having the most methyl groups. This is the same situation as deduced here for the exchange of bromine with bridging oxygen on methyl-substituted arsenic moieties.

Reaction Rates. The four nmr peaks observed for arsenosomethane show no appreciable line broadening at temperatures up to 120°, and no lag was observed in the establishment of the relative peak areas upon preparing the solutions and measuring them promptly. This is interpreted to mean that the mean lifetime for exchange at room temperature among the various cyclic $(CH_3AsO)_n$ molecules lies between 1 and 300 sec. However, studies on mixtures of cacodyl oxide or methyldibromoarsine with arsenosomethane show that the rate of exchange between chains and rings is fast and that the presence of the chains gives a path for rapid exchange of parts between the various cyclic molecules. With an overall mole ratio of $CH_3/As = 1.60$ in mixtures of cacodyl oxide with arsenosomethane, the mean exchange time for the cacodyl oxide is about 0.6 sec at 0° and 1.1 sec at −30°. In a mixture of methyldibromoarsine with arsenosomethane having an overall Br/As mole ratio of 0.74, the mean exchange time for the methyldibromoarsine is 0.5 sec at 0°.

Although crystals of arsenosomethane are stable for long periods of time at room temperature, nmr measurements indicate that in solution, the arsenosomethane undergoes in a matter of months at 25° reactions which appear to be due to exchange of methyl groups.

Acknowledgment. We wish to thank the National Science Foundation for support of the work carried out at Vanderbilt University under Grants No. GP-9525 for this study and 1683 for purchase of the A-60 nmr spectrometer.

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(11) For an example of such a situation, see J. R. Van Wazer and K. Moedritzer, *J. Amer. Chem. Soc.*, **90**, 47 (1968).

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