

preflash apparently resulted in the flashing off of surface intermediates with lower activation energies, revealing the characteristics of those remaining; the formic anhydride was probably flashed off first since it showed the lower activation energy for decomposition, leaving essentially the adsorbed formate. Therefore, the CO₂ "interrupted" spectrum reflected primarily the contribution due to the adsorbed formate. In turn, due to the existence of different binding states for the HCOO(a), the adsorbed formate with the lowest decomposition energy was flashed off first, eventually leaving only the one with the highest decomposition energy. The limiting value of 26.5 kcal/mol represented the highest activation energy required for the decomposition the formate on the alloy. The close agreement between this limiting value and the apparent activation energy measured on the 37% Ni/63% Cu alloy surface further supported that it was a good estimation for the decomposition of the formate on the alloy.

In conclusion, it is interesting to compare these results with the catalytic decomposition of formic acid on the carburized Ni(110) surface studied by McCarty and Madix.²⁶⁻²⁸ In that study, adsorbed formate was found to be the predominant surface intermediate observed, and the CO:CO₂ product ratio was about 0.1, similar to that observed for the 37% Ni/63% Cu alloy surface. The close resemblance of the selectivity and the intermediate involved between these two surfaces suggested that the presence of surface carbide carbon modifies surface reactivity in a fashion similar to alloying with a group 1B element. The results of the present study clearly manifested the importance of clusters in the selectivity and activity for the formic acid decomposition on the Ni/Cu alloy. The present study highlights the fact that the ligand effects can be secondary to the cluster requirement in the surface reactivity of alloys.

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Adducts of Arsenic(III) Halides and Arylarsenic(III) Halides with Thioureas

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A series of arsenic trihalide and arylarsenic dihalide adducts with thioureas have been prepared. New compounds which have been characterized include AsX₃B [X = Cl, Br; B = tmtu (1,1,3,3-tetramethyl-2-thiourea), dmit (1,3-dimethyl-2(3H)-imidazolethione)] and ArAsX₂tmtu [Ar = C₆H₅, 4-CH₃C₆H₄, X = Cl, Br, I; Ar = 4-CH₃OC₆H₄, 4-ClC₆H₄, 4-O₂NC₆H₄, X = Cl]. These adducts are thermally stable at ambient temperature but decompose on exposure to atmospheric moisture at varying rates (Cl ≫ Br; AsX₃B > ArAsX₂tmtu). Adducts were characterized by infrared, Raman, and proton nuclear magnetic resonance spectroscopy. The adducts were found to be molecularly dissociated in solution to varying degrees; the order of acceptor ability toward thioureas is AsBr₃ > AsCl₃; ArAsI₂, ArAsBr₂ > ArAsCl₂. Assignments for solid-state Raman and infrared spectra for the adducts are reported. Trigonal-bipyramidal structures are proposed for the adducts based on vibrational spectra. Secondary bonding leading to the formation of loosely joined dimeric molecules may occur as found by x-ray crystallography for AsCl₃dmit.

The acceptor properties of group 5A trihalides and organic derivatives RMX₂ and R₂MX are well established in the literature.²⁻¹² While the synthesis of numerous adducts has been reported, there have been surprisingly few attempts to determine the structures of these compounds. The overall lack of structural information is due in part to the fact that many of these adducts were made in the early part of this century prior to the advent of modern instrumental techniques.⁴⁻⁸ Structures which are known via single-crystal x-ray analysis

include AsCl₃NMe₃⁹ (Me = methyl), SbCl₃NH₂C₆H₅,¹⁰ SbCl₃(Ph₃AsO)₂² (Ph = phenyl), and Me₂AsCl(tu)₂^{11,12} (tu = thiourea). Vibrational spectra for AsCl₃NMe₃ and SbCl₃NH₂C₆H₅ have been used in conjunction with the above structural studies for spectral interpretation of analogous compounds such as PCl₃NMe₃ and PBr₃NMe₃.¹³ For the most part, however, vibrational data have been used primarily to demonstrate coordination as indicated by shifts in known bands. The lowering of the P=O stretching mode in tri-

Table I. Yields and Solvents for Reactions and Recrystallizations

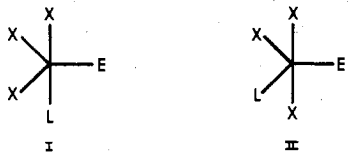
	% yield ^a	Reaction		Recrystallization
		Donor	Acceptor	
AsCl ₃ tmtu	51	CH ₂ Cl ₂	CH ₂ Cl ₂	CH ₂ Cl ₂
AsCl ₃ dmit	56	CHCl ₃	CHCl ₃	CH ₂ Cl ₂
AsBr ₃ tmtu	47	CCl ₄	CCl ₄	CCl ₄ /CH ₃ NO ₂
AsBr ₃ dmit	44	CHCl ₃	CHCl ₃	CH ₃ NO ₂
C ₆ H ₅ AsCl ₂ tmtu	85	CCl ₄	CCl ₄	CHCl ₃ /CCl ₄
4-CH ₃ C ₆ H ₄ AsCl ₂ tmtu	70	CCl ₄	CCl ₄	CHCl ₃ /CCl ₄
4-CH ₃ OC ₆ H ₄ AsCl ₂ tmtu	61	CCl ₄	CH ₂ Cl ₂	CHCl ₃ /CCl ₄
4-ClC ₆ H ₄ AsCl ₂ tmtu	90	CCl ₄	CCl ₄	CHCl ₃
4-O ₂ NC ₆ H ₄ AsCl ₂ tmtu	65	CH ₂ Cl ₂	CH ₂ Cl ₂	CH ₃ CN
C ₆ H ₅ AsBr ₂ tmtu	52	CH ₂ Cl ₂	CCl ₄	CHCl ₃
4-CH ₃ C ₆ H ₄ AsBr ₂ tmtu	90	CH ₂ Cl ₂	CH ₂ Cl ₂	CHCl ₃
C ₆ H ₅ AsI ₂ tmtu	23	CHCl ₃	CHCl ₃	CHCl ₃ /CCl ₄
4-CH ₃ C ₆ H ₄ AsI ₂ tmtu	65	CHCl ₃	CHCl ₃	CHCl ₃

^a Unrecrystallized product.

n-butyl phosphate solutions of AsCl₃ is one example.¹⁴

Adducts of arsenic trichlorides, arylarsenic trichlorides, and most of the phosphorus trihalides are hydrolytically unstable and decompose in atmospheric moisture. Antimony and bismuth trihalide adducts appear to be more stable toward hydrolysis.¹⁵ In addition, several adducts of AsCl₃, PCl₃, and PBr₃ are thermally unstable at room temperature.¹³

For 1:1 adducts of group 5A trihalides a trigonal-bipyramidal (TBP) array of substituents about the central atom may be predicted based on idealized geometry for an AX₃LE¹⁶ system assuming a stereoactive lone pair. Structures I and II show the isomeric possibilities excluding those which have the electron pair in the axial position.¹⁷



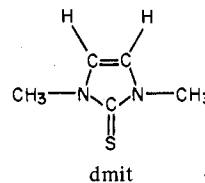
Replacing a halogen with an organic radical (AX₂RLE where R is an organic group) also leads to two isomeric possibilities as shown by III and IV. Again, those possibilities having either the lone pair or the R group in the axial position are unprecedented and normally considered energetically unfavorable.¹⁷



The difference between I and II and between III and IV reduces to whether the ligand (L) occupies an axial or equatorial position in a TBP array. The crystal structures of AsCl₃NMe₃ and SbCl₃NH₂C₆H₅ show these molecules possess structure I which is predicted based on the well-known electronegativity rule.¹⁸ This predicts that the more electronegative substituent will occupy the axial position. No structural data are yet available for an AX₂RLE system which could display structure III or IV. Again, the electronegativity rule provides a basis for prediction. Structure III would be predicted for donors of relatively high electronegativity, whereas structure IV would be expected for donors of low electronegativity.

Because structural data are available primarily for adducts containing highly electronegative or hard¹⁹ donor sites, an investigation of the synthesis and structure of adducts containing soft donors seemed essential for stereochemical understanding. In order to characterize and determine the structure of adducts containing soft donors, a series of

compounds was prepared using 1,1,3,3-tetramethyl-2-thiourea (tmtu) and 1,3-dimethyl-2(3*H*)-imidazolethione (dmit, structure below) as donors in combination with arsenic tri-



halides and arylarsenic dihalides. This paper reports the synthesis, chemical properties, and spectroscopic data for these adducts. The results of a single-crystal x-ray structural determination on one of these, AsCl₃dmit, will be reported separately.

Experimental Section

Due to the moisture sensitivity and toxic nature of some of the compounds involved, all preparations were carried out in polyethylene glovebags under a dry nitrogen atmosphere.

Spectra and Conductivity. Infrared, Raman, and nuclear magnetic resonance spectra²⁰ and conductivity data²¹ were all obtained as previously reported.

Molecular Weights. Molecular weights were obtained cryoscopically in nitrobenzene which had been stored over Linde 4-Å molecular sieves. A slow stream of dry nitrogen was passed over the solution to prevent hydrolysis.

Chemicals. Solvents used in synthesis were purified by distillation and stored over Linde 4-Å molecular sieves. Arsenic trichloride (Baker), arsenic tribromide and chlorodiphenylarsine (Research Organic/Inorganic) and tmtu and benzenearsonic and 4-nitrobenzenearsonic acids (Eastman) were all used as obtained without further purification. Aryldichloroarsines and aryldibromoarsines were prepared from their corresponding arylarsenic acids.²² Arylarsenic acids²³ other than those listed above as well as arsenic triiodide,²⁴ dmit,²⁵ dichlorotriphenylarsorane,²⁶ dibromotriphenylarsorane,²⁶ and arylidiodoarsines²⁷ were all prepared via methods outlined in the literature.

Analytical Section. Halogen analysis was obtained in our laboratory by gravimetry using AgNO₃. Carbon, hydrogen, and nitrogen analyses were obtained from Meade Microanalytical, Atlantic Microlabs, and Schwarzkopf Analytical.

Adduct Synthesis. Adducts were prepared by combining solutions of donor and acceptor in 1:1 molar ratios in suitable solvents. The reaction of AsI₃ with tmtu and dmit yielded inseparable mixtures of products and was not investigated further. Table I lists yields and preferred solvents for preparation and recrystallization. A typical procedure is given below.

Dichloro(tetramethylthiourea)-4-tolyarsenic(III). 4-Tolyldichloroarsine (2.0 g, 8.0 mmol) was dissolved in 20 mL of CCl₄. To this solution was added tmtu (1.1 g, 8.0 mmol) dissolved in 20 mL of CCl₄. The resultant yellow solution was cooled for 24 h at -20 °C. The pale yellow crystals which formed were filtered and dried

Table II. Physical Properties and Analytical Data

	Mp ^a	Appearance ^b	Mol wt ^c		Δ^d, e	% C		% H		% N		% halogen	
			Calcd	Obsd		Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd
AsCl ₃ tmtu	117-119	wh pw	313.56	156 (± 10)	4.3	19.16	19.16	3.86	3.96	8.94	8.93	33.93	33.29
AsCl ₃ dmit	147-150	wh nd	309.48	192 (± 20)	5.3	19.41	19.49	2.61	2.70	9.05	9.00	34.37	34.40
AsBr ₃ tmtu	135-137	ye pw	446.88	288 (± 25)	16.7	13.44	13.54	2.71	2.75	6.27	6.28	53.65	53.65
AsBr ₃ dmit	185-186	ye cr	442.85	317 (± 40)	15.5	13.56	13.48	1.82	1.88	6.33	6.30	54.13	54.10
C ₆ H ₅ AsCl ₂ tmtu	89-91	wh cr	355.16	187 (± 10)	3.1	37.20	36.93	4.82	4.87	7.89	7.73	19.96	20.29
4-CH ₃ C ₆ H ₄ AsCl ₂ tmtu	91-92	wh pw	396.19	167 (± 10)	2.7	39.04	38.91	5.19	5.19	7.59	7.41	19.21	18.87
4-CH ₃ OC ₆ H ₄ AsCl ₂ tmtu	84-85	wh pw	385.19	182 (± 10)	2.6	37.42	37.64	4.79	4.94	7.27	7.20	18.41	18.50
4-ClC ₆ H ₄ AsCl ₂ tmtu	120-121	wh pw	389.61	214 (± 10)	2.3	33.91	33.95	4.14	4.11	7.19	7.06	27.30	27.23
4-O ₂ NC ₆ H ₄ AsCl ₂ tmtu	124-126	amb cr	400.16	187 (± 15)	3.3	33.02	33.27	4.03	4.17	10.50	10.40	17.72	17.23
C ₆ H ₅ AsBr ₂ tmtu	134-135	ye pw	444.07	233 (± 10)	10.1	29.75	30.30	3.86	3.99	6.31	6.39	35.99	36.01
4-CH ₃ C ₆ H ₄ AsBr ₂ tmtu	139-140	ye pw	458.10	260 (± 15)	9.3	31.46	31.30	4.18	4.34	6.12	6.01	34.89	34.76
C ₆ H ₅ AsI ₂ tmtu	119-121	og pw	538.06	171 (± 15)	21.9	24.55	24.60	3.18	3.09	5.21	5.14	47.17	46.80
4-CH ₃ C ₆ H ₄ AsI ₂ tmtu	130-132	og pw	552.09	184 (± 15)	20.9	26.11	26.17	3.47	3.42	5.07	4.93	45.97	45.45

^a °C uncorrected. ^b Key: wh, white; ye, yellow; amb, amber; og, orange; pw, powder; nd, needles; cr, crystals. ^c Cryoscopically determined in nitrobenzene. ^d Nitromethane. ^e Units: cm² equiv⁻¹ Ω⁻¹; ca. 10⁻³ M.

in vacuo. Recrystallization from CHCl₃/CCl₄ yielded a product melting at 91-92 °C.

While in general a mixture of 1:1 molar ratios of donor and acceptor yielded a 1:1 adduct, mixing a 1:1 molar ratio of PhAsBr₂ and dmit in CH₂Cl₂ was found to give the 1:2 adduct PhAsBr₂(dmit)₂. This unexpected result was further investigated by Crane.²⁸

Attempts to prepare adducts of chlorodiphenylarsine with tmtu and dmit yielded no isolable products.

Results and Discussion

Table II lists the compounds prepared along with conductivity, molecular weight data, and analytical results. In general, these adducts formed crystalline solids which were stable at ambient temperature. The trichloride adducts were less stable to atmospheric moisture than the tribromide adducts; the former decomposed within 1-2 h while the latter were stable for 4-6 h after exposure to the atmosphere. Arylarsenic dihalide adducts were far more stable toward atmospheric moisture and remained unchanged over periods lasting from several days to weeks.

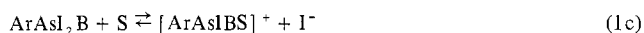
The solubility properties of these compounds were varied. The tmtu arsenic trihalide adducts were generally more soluble than the dmit adducts in polar solvents such as CHCl₃, CH₂Cl₂, CH₃NO₂, C₆H₅NO₂, and CH₃CN. AsBr₃dmit was the least soluble and therefore presented difficulties in data collection. All adducts were completely insoluble in nonpolar solvents such as CCl₄, C₆H₆, and (C₂H₅)₂O. Dihalide adducts were much more soluble than the trihalide adducts in the polar solvents mentioned above. In general, the dichloride adducts were more soluble than the corresponding dibromide adducts, and the diiodide adducts were the least soluble. All of the adducts decomposed in water.

Molecular Weight Data. The cryoscopic determination of molecular weights in nitrobenzene (Table II) indicates that all adducts are dissociated in varying degrees. The trihalide adducts are least dissociated and will be discussed in greater detail below. Arylarsenic dihalide adducts are almost entirely dissociated since observed molecular weights are approximately half that of the calculated value for the combined molecular unit. Molecular weights less than half that of the calculated are observed for arylarsenic diiodide adducts; their results are discussed below.

Conductivity Data. The conductivity data (Table II) show that these compounds are nonelectrolytes in nitromethane. Conductivity and molecular weight data taken together indicate that molecular rather than ionic dissociation is the primary dissociation process.

Conductivity of the adducts increases in going from chloride to iodide; conductivities for trichloride and tribromide adducts are higher than those of the dichloride and dibromide adducts. The relatively high conductivities for the arylarsenic diiodide adducts coupled with low molecular weights suggest that in

addition to molecular dissociation (eq 1a, B = tmtu), solvent (S) displacement of iodide may occur (eq 1b, 1c).



Nuclear Magnetic Resonance Data. As seen in Table III, chemical shifts in CDCl₃ for methyl protons on tmtu and dmit in the adducts do not differ greatly from those in the free ligand. In CDCl₃, the differences in chemical shifts for the *N*-methyl protons of the adducts and the free ligand, $\Delta\delta$ (i.e., $\Delta\delta = \delta_{\text{adduct}} - \delta_{\text{free}}$), are 0.05, 0.08, and 0.08 for AsCl₃tmtu, AsCl₃dmit, and AsBr₃tmtu, respectively. AsBr₃dmit was too insoluble for study in CDCl₃. The $\Delta\delta$'s for dmit adducts in CD₃CN are greater than those observed in CDCl₃. The $\Delta\delta$ for AsCl₃dmit is 0.27 and for AsBr₃dmit it is 0.32. For the corresponding arsenic trihalide tmtu adducts in CD₃CN $\Delta\delta$'s are 0.07 and 0.19, respectively. The $\Delta\delta$'s for the tmtu adducts are much smaller than those observed for SeCl₂tmtu (0.24 in CHCl₃ and 0.34 in CH₂Cl₂)²⁰ and SeBr₂tmtu (0.39 in CH₂Cl₂).²⁰ As discussed below, this may be due in part to the fact that the SeX₂tmtu adducts are entirely associated in solution.

Arylarsenic dihalide tmtu adducts displayed well-separated proton NMR shifts. Integration of the ¹H NMR spectra proved useful in confirming the results from chemical analysis.

It is interesting to note the consistent downfield shift, albeit slight, in progressing from aryl groups with electron-donating substituents such as methyl and methoxy to those with electron-withdrawing groups like chloro and nitro. In CDCl₃, the respective $\Delta\delta$'s for PhAsCl₂tmtu, PhAsBr₂tmtu, and PhAsI₂tmtu are 0.00, 0.05, and 0.03. However, the $\Delta\delta$'s in CD₃CN for the same three adducts are 0.01 for PhAsCl₂tmtu, 0.08 for PhAsBr₂tmtu, and 0.12 for PhAsI₂tmtu. These data indicate that while PhAsCl₂tmtu has the smallest $\Delta\delta$, the relative shifts for PhAsBr₂tmtu and PhAsI₂tmtu are solvent dependent.

Infrared Data and Dissociation Constants. The major feature of interest in solution infrared studies is the N-C-N antisymmetric stretching frequency which occurs at 1505 cm⁻¹ for free tmtu but shifts to higher frequency upon coordination.²⁰ Thus for SeBr₂tmtu this band occurs at 1598 cm⁻¹ in CH₂Cl₂.²⁰

The solution spectra of AsCl₃tmtu and AsBr₃tmtu were recorded in CH₂Cl₂, and both free and coordinated bands were observed for each adduct. For AsCl₃tmtu these bands were at 1505 cm⁻¹ for free tmtu and 1595 cm⁻¹ for coordinated ligand; for AsBr₃tmtu the respective bands were at 1505 and 1598 cm⁻¹. Although an analogous band exists for dmit, its intensity is much lower. This, coupled with the overall lower

Table III. Proton NMR Spectral Data

Complex ^a	tmtu	dmit	Organic group
Free donors	3.00	3.58	6.67
AsCl ₃ tmtu	2.92	3.41	6.69
	3.05		
	2.99		
AsCl ₃ dmit		3.66	6.36
		3.68	7.05
AsBr ₃ tmtu	3.08		
	3.11		
AsBr ₃ dmit		3.73	7.15 ^b
C ₆ H ₅ AsCl ₂ tmtu	2.93		7.36 mult (3)
	3.00 (12)		7.69 mult (2)
4-CH ₃ C ₆ H ₄ AsCl ₂ tmtu	2.99 (12)		2.34 (3) 7.17 d (2)
			meta ^{c,d}
			7.62 d (2)
			ortho ^c
4-CH ₃ OC ₆ H ₄ AsCl ₂ tmtu	3.00 (12)		3.78 (3) 6.89 d (2)
			meta ^{c,e}
			7.69 d (2)
			ortho ^e
4-ClC ₆ H ₄ AsCl ₂ tmtu	3.03 (12)		7.34 d (2)
			meta ^{c,f}
			7.70 d (2)
			ortho ^c
4-O ₂ NC ₆ H ₄ AsCl ₂ tmtu	3.05 (12)		8.00 d (2)
			meta ^{c,g}
			8.24 d (2)
			ortho ^c
C ₆ H ₅ AsBr ₂ tmtu	3.00		7.35 mult (3)
	3.05 (12)		7.81 mult (2)
4-CH ₃ C ₆ H ₄ AsBr ₂ tmtu	3.07 (12)		2.34 (3) 7.12 d (2)
			meta ^{c,h}
			7.62 d (2)
			ortho ^c
C ₆ H ₅ AsI ₂ tmtu	3.04		7.20 mult (3)
	3.03 (12)		7.79 mult (2)
4-CH ₃ C ₆ H ₄ AsI ₂ tmtu	3.05 (12)		2.37 (3) 7.10 d (2)
			meta ^{c,i}
			7.77 d (2)
			ortho ^c

^a Shifts are in δ units 0.01 ppm vs. internal Me₄Si. Values reported were recorded in CDCl₃. Values in italics were recorded in CD₃CN. Aryl shifts and splitting patterns in CD₃CN are similar to those given for CDCl₃ and thus are not reported. ^b Limited solubility gives uncertainty to value quoted. ^c Relative to arsenic substituent. ^d $J_{\text{ortho-meta}} = 8.5$ Hz. ^e $J_{\text{ortho-meta}} = 8.0$ Hz. ^f $J_{\text{ortho-meta}} = 8.9$ Hz. ^g $J_{\text{ortho-meta}} = 8.9$ Hz. ^h $J_{\text{ortho-meta}} = 8.3$ Hz. ⁱ $J_{\text{ortho-meta}} = 8.4$ Hz.

solubility of dmit adducts in CH₂Cl₂, did not allow obtaining useful solution IR data. For arylarsenic dihalide adducts, the 1500–1600-cm⁻¹ region is occupied by phenyl bands which obscure the N–C–N absorption.

Beer's law was utilized in order to obtain equilibrium constants for AsX₃tmtu adducts. A plot of ln(P/P₀) vs. molar concentration was made for five tmtu solutions of known concentration in CH₂Cl₂. Considering the equilibrium shown in eq 2 and the definition of K_D (eq 3), the amount of free tmtu



$$K_D = [\text{AsX}_3][\text{tmtu}]/[\text{AsX}_3 \cdot \text{tmtu}] \quad (3)$$

arising from dissociation was determined by carrying out a standard baseline analysis²⁹ of the free tmtu peak for an adduct solution of known concentration. Assuming the equilibrium represented by eq 2 is the only equilibrium of significance, it follows that [AsX₃] = [tmtu]. Thus [AsX₃tmtu] may be determined by taking the difference between the analytical concentration of the adduct, T_A, and [tmtu]. The K_D determined for AsCl₃tmtu is (8 ± 3) × 10⁻², and for AsBr₃tmtu it is (1.5 ± 0.3) × 10⁻². As can be seen, AsBr₃tmtu is more associated in CH₂Cl₂ than AsCl₃tmtu.

Another useful parameter is α , the fraction of adduct dissociated. Equation 4 shows how α is related to K_D and T_A.

For AsCl₃tmtu, α is 0.8₄ (±0.1) in CH₂Cl₂; for AsBr₃tmtu, α is 0.67 (±0.03).

$$K_D = \alpha^2 T_A / (1 - \alpha) \quad (4)$$

Another way to calculate α utilizes molecular weight data as shown in eq 5 where W_C is the calculated molecular weight

$$\alpha = (W_C - W_O) / W_O \quad (5)$$

and W_O is the observed. From the molecular weight data in nitrobenzene, the respective α 's for AsCl₃tmtu, AsBr₃tmtu, AsCl₃dmit, and AsBr₃dmit are 1.00 (±0.05), 0.9₆ (±0.1), 0.62 (±0.05), and 0.40 (±0.05). The AsX₃dmit adducts show a greater degree of association in nitrobenzene than the AsX₃tmtu adducts and are substantially associated despite the presence of a coordinating solvent. Assuming volume differences to be insignificant at these concentrations, values for molality from the molecular weight determinations may be directly converted to molar concentrations assuming a density of 1.20 g/mL for nitrobenzene. Values for K_D may be calculated using eq 4 with known α values and molar concentrations obtained as described above. Since α 's approximating 1.0 are calculated for tmtu adducts in nitrobenzene, the K_D's are infinitely large. For AsCl₃dmit ($\alpha = 0.62$) and AsBr₃dmit ($\alpha = 0.40$) the respective K_D's are (9.7 ± 0.4) × 10⁻³ and (1.8

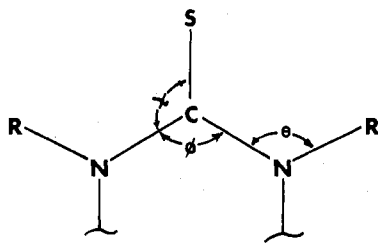


Figure 1. General thiourea skeleton showing angles ϕ , χ , and θ .

$\pm 0.7) \times 10^{-3}$ indicating the substantial association of the dmit adducts in nitrobenzene relative to the tmtu adducts.

The above data indicate that AsBr_3 is a better Lewis acid than AsCl_3 toward thioureas since AsBr_3 adducts are more highly associated, as shown by a smaller dissociation constant in CH_2Cl_2 for AsBr_3tmtu than for AsCl_3tmtu and by lower α values in nitrobenzene for AsBr_3 adducts. This order is opposite to that expected on the basis of an inductive effect, but it is consistent with the HSAB (hard/soft acid/base)¹⁹ approach in explaining relative Lewis acidity and basicity.

Molecular weight data, solution infrared studies, and NMR data indicate that tmtu adducts of SeBr_2 and SeCl_2 are entirely associated in solution, and thus it appears that Se(II) halides are better acceptors than As(III) halides toward thioureas. This can be explained in part by the increased electronegativity of selenium. Although the relative order of Lewis acidity is not known for SeCl_2 and SeBr_2 , from the above information a relative order of acceptor power toward thioureas as deduced from spectroscopic, molecular weight, and NMR data is as follows: SeX_2 ($\text{X} = \text{Cl}, \text{Br}$) $>$ AsBr_3 $>$ AsCl_3 .

Values of α approximating 1.0 were found for arylarsenic dihalides based on molecular weight data. These adducts are essentially dissociated in coordinating solvents although some degree of association is indicated by values of $\Delta\delta$ from NMR discussed above. Only $\text{PhAsCl}_2\text{tmtu}$ appears entirely dissociated since chemical shifts in both CDCl_3 and CD_3CN are almost identical with those of the free ligand ($\Delta\delta_{\text{CD}_3\text{CN}} = 0.01$, $\Delta\delta_{\text{CDCl}_3} = 0.00$). Although the relative acceptor power of PhAsBr_2 vs. PhAsI_2 cannot be determined from available data, the larger shifts imply that both are better acceptors than PhAsCl_2 . A direct comparison between the arylarsenic dihalides and the arsenic trihalides cannot be made with regard to relative acceptor power due to the lack of sufficient comparable data. One may expect a decreased acceptor ability of the arylarsenic dihalides relative to the arsenic trihalides due to the increased electron density on arsenic from the replacement of halide by the relatively electropositive aryl group. With the arylarsenic dihalide series, a trend of relative acceptor power toward thioureas appears to be analogous to the trend observed for the trihalides: PhAsI_2 , PhAsBr_2 $>$ PhAsCl_2 . Again this is counter to inductive effects but is consistent with the HSAB¹⁹ approach.

The relative α 's for dmit adducts compared to those for tmtu adducts in nitrobenzene also indicate that dmit is a better donor than tmtu. On the basis of pure inductive effect the opposite would be expected since a methyl group (sp^3) would better stabilize the partially positive nitrogen in a coordinated thiourea. A crystal structure of dmit²⁵ furthermore shows no extra resonance stabilization is attained by the ring. The crystal structure of AsCl_3dmit ³⁰ shows the angles ϕ , χ , and θ (Figure 1) to be 107.8, 126.5, and 125.5°, respectively, while for SeCl_2tmtu ²⁰ the corresponding angles are 121.1, 122.1, and 116.4°. The five-membered ring increases χ and θ thus decreasing the steric interaction of the *N*-methyl groups with the acceptor. This accounts for the greater Lewis basicity of dmit.

Solid-State Spectra. Raman spectroscopic data were collected on the arsenic trihalide and arylarsenic dihalide adducts

in order to obtain information concerning the structure of the adducts. Far-infrared spectra on solids (Nujol mulls) revealed broad and poorly resolved absorption envelopes for the arylarsenic dihalide adducts and to a lesser extent for the arsenic trichloride and arsenic tribromide adducts of tmtu. Such was not the case for the Raman spectra as the low-frequency Raman ligand absorptions were relatively weak while As-X modes were sharp and easily discernible.

Our approach in obtaining structural information is to consider the limiting structures I and II and III and IV in light of the observed and expected As-X frequencies. The discussion first focuses on vibrational spectroscopic studies carried out on molecules containing linear X-M-X groupings ($\text{X} = \text{Cl}, \text{Br}, \text{I}$; $\text{M} = \text{As}, \text{Se}$). Frequencies for X-Se-X groups are included as these are close to the As analogues.

A number of studies have shown that linear X-M-X groups display a characteristic, intense Raman absorption for the symmetric stretching mode. For compounds containing a Cl-As-Cl group this mode is found at the following frequencies [compound]: 260 cm^{-1} [$(\text{CH}_3)_3\text{AsCl}_2$, $(\text{CD}_3)_3\text{AsCl}_2$],^{31,32} 264 cm^{-1} [$(\text{C}_6\text{H}_5\text{CH}_2)_3\text{AsCl}_2$],³³ 265 cm^{-1} [Ph_3AsCl_2].³⁴ The corresponding absorption for compounds containing a Cl-Se-Cl group occurs at 249 cm^{-1} [SeCl_2tmtu]²⁰ and 257 cm^{-1} [SeCNCl_2].³⁷ A linear Br-M-Br group gives rise to a strong Raman absorption in the vicinity of 150-160 cm^{-1} : 154 cm^{-1} [Ph_3AsBr_2],³⁸ 167 cm^{-1} [Me_2SeBr_2],^{38,39} 158 cm^{-1} [SeCNBr_2].³⁷ A symmetric stretching frequency has not been reported for compounds containing a linear I-M-I group, but this mode occurs at 116 cm^{-1} in Me_2TeI_2 ³⁸ and at 114 cm^{-1} in I_3^- .⁴⁰

The antisymmetric stretch for a linear X-M-X group generally is found at higher frequency than the symmetric stretch. This mode occurs at 312 cm^{-1} for $(\text{CH}_3)_3\text{AsCl}_2$ but at 291 cm^{-1} for $(\text{CD}_3)_3\text{AsCl}_2$.³² Such a straightforward assignment has not been the rule; this mode was inexplicably absent for $(\text{C}_6\text{H}_5\text{CH}_2)_3\text{AsCl}_2$ ³³ and was possibly combined with a phenyl mode in Ph_3AsCl_2 .³⁴ Furthermore assignments in the literature for $\nu_{\text{sym}}(\text{Cl-Se-Cl})$ and $\nu_{\text{asym}}(\text{Cl-Te-Cl})$ may be incorrect.⁴¹ By using the assignments for $(\text{CH}_3)_3\text{AsCl}_2$ and $(\text{CD}_3)_3\text{AsCl}_2$ as a guide, "uncoupled" $\nu_{\text{asym}}(\text{Cl-As-Cl})$ may be expected for an arsenic(III) compound to occur below 300 cm^{-1} and above $\nu_{\text{asym}}(\text{Cl-As-Cl})$.

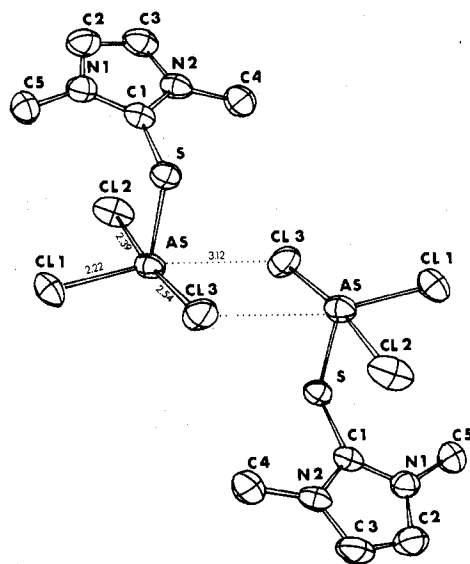
Assignments for ν_{asym} for compounds containing Br-M-Br groups are in agreement.^{20,21,35,38} This mode generally occurs as a strong IR absorption at 170-190 cm^{-1} . An asymmetric stretching frequency has not been reported for a compound containing an I-M-I group; as a rough guide we note this mode occurs at 144 cm^{-1} in Me_2TeI_2 .³⁸

ArAsX₂tmtu Adducts. The Raman and IR spectra (Table IV) were studied with reference to idealized structures III and IV. A strong Raman absorption occurred at 240 cm^{-1} ($\text{PhAsCl}_2\text{tmtu}$), 144 cm^{-1} ($\text{PhAsBr}_2\text{tmtu}$), and 103 cm^{-1} ($\text{PhAsI}_2\text{tmtu}$). The *p*-tolyl derivatives showed strong corresponding absorptions at 231, 144, and 101 cm^{-1} , respectively. No higher frequency As-X absorptions were observed. The absence of a high-frequency As-X mode, expected for structure III and observed for "equatorial" or short As-X bond(s) ($\text{AsCl}_3\text{NMe}_3$,¹³ AsX_3tmtu , AsX_3dmit) is taken as evidence favoring structure IV for the RAsX_2tmtu adducts. The strong Raman absorptions are close to those observed previously for linear X-M-X groupings and are assigned accordingly (Table IV). As expected $\nu_{\text{sym}}(\text{X-As-X})$ for the $\text{ArAsX}_2\text{tmtu}$ adducts which contain As(III) is consistently lower than the corresponding mode for compounds containing As(V).

The IR spectra of the arylarsenic dibromide and diiodide tmtu adducts showed relatively discrete, though broad, absorptions in the X-As-X stretching regions. For these

Table IV.³⁶ Solid-State Spectral Data for Arylarsenic Dihalide tmtu Adducts (cm⁻¹)

	PhAsCl ₂ tmtu ^a		p-TolAsCl ₂ tmtu ^a		PhAsBr ₂ tmtu		p-TolAsBr ₂ tmtu		PhAsI ₂ tmtu		p-TolAsI ₂ tmtu	
	Raman ^b	IR	Raman ^c	IR	Raman ^c	IR	Raman ^c	IR	Raman ^c	IR	Raman ^c	
$\nu_{\text{sym}}(\text{X-As-X})$	240 s	147 w, sh	144 s	148 w, sh	144 s	148 w, sh	103 vs	101 vs	103 vs	101 vs	103 vs	101 vs
$\nu_{\text{asym}}(\text{X-As-X})$	260 m	166 s	273 m	165 s	267 m	165 s	139 w, sh	142 s, br	139 w, sh	150 s, br	139 w, sh	144 w
$\nu(\text{As-S})$	275 wm	277 wm	399 w, sh	270 wm	267 m	270 wm	256 m	258 s	256 m	260 m	256 m	263 wm
$\nu(\text{tmtu})$	461 w	396 s	293 w, br	396 s	394 m	396 s	459 m	464 ms	459 m	390 w	459 m	458 vw
$\nu(\text{phenyl})$	295 wm	296 m	488 vw, br	477 m, br	394 m	296 m	396 m	396 m	396 m	390 w	396 m	387 w
	500 vw		353 wm	357 wm	293 w, br		290 s	290 s	290 s		290 s	
			235 w, sh	253 m								
			220 m	239 m								
Other peaks	405 vw, sh	301 m	458 w	411 m	313 vw, br	411 m	320 vw, sh	315 m	320 w	320 w	320 vw, sh	305 vw, br
	320 vw	243 w, sh	391 m	368 m	120 m	368 m	120 w, sh	120 w, sh	120 w, sh	94 w	120 w, sh	236 vw, sh
	219 w, sh	178 s	119 m	310 m	104 m	310 m	104 m	94 w	94 w	94 w	104 m	120 w, sh
	158 w, sh	142 w	91 wm	118 s, br	84 w	118 s, br	84 w	83 m	83 m	83 m	84 w	213 wm
	141 m	124 m										
	115 ms											
	100 s											

^a Infrared spectrum broad and unresolved. ^b 5145 Å. ^c 6471 Å.Figure 2. A perspective view of the structure of the dimeric unit in AsCl₃dmit.

compounds no peaks, weak peaks, or weak shoulders were observed at frequencies corresponding to the symmetric X-As-X modes observed in the Raman spectra (Table IV). However, strong absorptions at 166 cm⁻¹ (PhAsBr₂tmtu), 142 cm⁻¹ (PhAsI₂tmtu), and 150 cm⁻¹ (*p*-tolAsI₂tmtu) were observed and are readily assigned to the antisymmetric X-As-X stretching mode (Table IV). The inverted order of relative intensities for ν_{sym} and ν_{asym} in the IR and Raman spectra of PhAsBr₂tmtu, *p*-TolAsBr₂tmtu, PhAsI₂tmtu, and *p*-TolAsI₂tmtu is expected (but not always observed in the solid state) for a linear X-M-X grouping.

The IR spectra of PhAsCl₂tmtu and *p*-TolAsCl₂tmtu exhibit only broad structureless absorptions from ca. 100 to 300 cm⁻¹. This together with complete dissociation of the adducts in solution provided no data for assignment of $\nu_{\text{asym}}(\text{Cl-As-Cl})$. However, a peak was observed in the Raman spectrum of PhAsCl₂tmtu at 260 cm⁻¹ which, considering relative intensity and position, is assigned to the antisymmetric stretch.

A very strong absorption at 275 cm⁻¹ for [Me₂As(tu)]⁺X⁻tu (X = Cl, Br) and at 303 cm⁻¹ for [Me₂As(tu)]⁺X⁻ was assigned to an As-S stretch.¹² The PhAsX₂tmtu adducts do not display a similarly strong Raman absorption; neither do AsX₃tmtu, AsX₃dmit (vide infra), or previously studied SeX₂tmtu adducts.²⁰ In contrast to the thiourea adducts, the relatively weak As-S and Se-S absorptions for tmtu and dmit adducts make assignment of an As-S mode difficult. An absorption which occurs at 260–270 cm⁻¹ for each of the PhAsX₂tmtu adducts is tentatively assigned to the As-S stretch.

Additional support for structure IV may be inferred from the crystal structure of AsCl₃dmit.²⁵ In contrast to the structure of AsCl₃NMe₃ (structure I) where the AsCl₃ unit is little changed from the free molecule, the AsCl₃ unit undergoes reorganization in the AsCl₃dmit molecule so that the *local* environment around each arsenic is described approximately by structure II (Figure 2).²⁵ By analogy, a similar reorganization to structure IV is expected in proceeding from ArAsX₂ to the corresponding thiourea adduct.

AsX₃tmtu and AsX₃dmit Adducts. Before discussing the far-infrared and Raman spectra on the AsX₃(thiourea) adducts, it is appropriate to note again the crystal and molecular structure of AsCl₃dmit.³⁰ This compound is made up of loosely joined dimeric molecules (Figure 2). IR and Raman spectra in the As-Cl stretching region do not reflect the loose dimerization but rather are interpretable with reference to

Table V.³⁶ Solid-State Spectral Data for Arsenic Trihalide tmtu and dmit Adducts (cm⁻¹)

Modes	AsCl ₃ tmtu		AsCl ₃ dmit		AsBr ₃ tmtu		AsBr ₃ dmit	
	IR	Raman ^a	IR	Raman ^b	IR	Raman ^a	IR	Raman ^b
$\nu_{\text{sym}}(\text{X-As-X})$	235 w, br	239 m		245 wm, br	136 w, br	136 m	137 m, br	135 s
$\nu_{\text{asym}}(\text{X-As-X})$	257 s		248 s, br		180 s, vbr		188 m, br	
$\nu(\text{As-X}_{\text{eq}})^c$	354 ms	347 s	350 s	345 m	238 m	236 s	246 w	239 s
$\nu(\text{thiourea})$	465 m	451 w 408 wm		491 m	454 m	448 vw 418 vw		487 m
		397 s 387 wm 331 s	382 m	380 s 308 w	389 s	385 vw 336 m		369 s 303 w
	286 m, br	293 wm 251 w, sh 165 ms		269 wm 184 m 164 m	293 w 247 m	291 w 245 vw, sh 166 w	260 w, sh	260 wm 177 m
Other peaks			324 m 200 s, br 150 w		474 wm	326 w, sh		
	183 m, br 136 m ^d 115 m ^d 85 m	139 s ^d 113 vs ^d		140 m ^d 108 s ^d	117 w, br	170 w, sh 136 m	118 m	102 m
		79 s		84 ms 61 ms	96 w, br	88 w		

^a 5145 Å. ^b 6471 Å. ^c Alternative assignment: IR absorption $\nu_{\text{asym}}(\text{S-As-X}_{\text{eq}})$; Raman absorption $\nu_{\text{sym}}(\text{S-As-X}_{\text{eq}})$. See text.
^d As-Cl bending modes.

structure II, which describes the *local* environment about each arsenic in the dimer. The discussion below concerning the interpretation of the spectra for AsCl₃tmtu and AsCl₃dmit (local structure II) seeks to compare those spectra with that for AsCl₃NMe₃ (structure I).¹³

Two high-frequency modes (primarily equatorial AsCl₂) are expected for structure I together with an additional mode (axial AsCl) whose frequency will depend on the donor strength of the trans base. These three modes appeared at relatively close frequencies for AsCl₃NMe₃ (A', 384 cm⁻¹; A'', 363 cm⁻¹; A''', 356 cm⁻¹).¹³ No distinct assignments could be made with reference to axial and equatorial positions since the modes are mixed. For structure II, one high (A') and two low (A'', A''') frequencies are expected. A characteristic symmetric mode for a linear X-M-X group should be observed.

By assuming a similar basic structural type for AX₃tmtu and AsX₃dmit adducts the ligand vibrations can be systematically assigned as those absorptions which for a given ligand remain approximately constant when X = Cl or Br but change when X is held constant and the ligand is changed. After this process only As-X and As-S absorptions should remain. In this manner it is found that three As-Cl frequencies occur above 200 cm⁻¹ for AsCl₃tmtu (347, 257, and 239 cm⁻¹) and AsCl₃dmit (345, 248, and 245 cm⁻¹) (Table V). These frequencies are in marked contrast to those observed for AsCl₃NMe₃ and reflect the different structures.

The presence of a linear X-As-X group in each adduct as required for structure II is suggested by Raman peaks at 239 (AsCl₃tmtu), 245 (AsCl₃dmit), 136 (AsBr₃tmtu), and 135 cm⁻¹ (AsBr₃dmit). These frequencies are in very close agreement with those observed in the appropriate ArAsX₂tmtu adducts and are assigned as A', $\nu_{\text{sym}}(\text{X-As-X})$. Strong absorptions corresponding to $\nu_{\text{asym}}(\text{X-As-X})$ were observed in the IR spectra of the adducts confirming the presence of a linear X-As-X group (Table V). The remaining higher frequency Raman peaks at 347 (AsCl₃tmtu), 345 (AsCl₃dmit), 236 (AsBr₃tmtu), and 239 cm⁻¹ (AsBr₃dmit) are assigned as A'', $\nu(\text{As-X}_{\text{eq}})$.

Assignment of an As-S stretch is difficult as the mode appears to be relatively weak (vide supra). Alternatively it may be combined with AsCl modes. Thus the IR and Raman absorptions assigned to $\nu(\text{As-X}_{\text{eq}})$ could alternatively be assigned to $\nu_{\text{asym}}(\text{S-As-X}_{\text{eq}})$ and $\nu_{\text{sym}}(\text{S-As-X}_{\text{eq}})$, respectively.

The IR and Raman spectra are in agreement with II for the local environment about As in AsX₃(thiourea) adducts. However, Figure 2 shows that AsCl₃dmit exists as loosely held

dimeric units; it is therefore likely that secondary halogen bridging may be common to all AsX₃ and ArAsX₂ thiourea adducts. Single-crystal structural determinations will be needed to uncover the details of individual structures.

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Registry No. AsCl₃tmtu, 65452-78-0; AsCl₃dmit, 65452-79-1; AsBr₃tmtu, 65452-80-4; AsBr₃dmit, 65483-47-8; C₆H₅AsCl₂tmtu, 65452-81-5; 4-CH₃C₆H₄AsCl₂tmtu, 65452-82-6; 4-CH₃OC₆H₄AsCl₂tmtu, 65452-84-8; 4-ClC₆H₄AsCl₂tmtu, 65452-85-9; 4-O₂NC₆H₄AsCl₂tmtu, 65483-46-7; C₆H₅AsBr₂tmtu, 65452-86-0; 4-CH₃C₆H₄AsBr₂tmtu, 65452-88-2; C₆H₅AsI₂tmtu, 65452-89-3; 4-CH₃C₆H₄AsI₂tmtu, 65452-91-7.

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 (41) A reexamination of the IR spectra of Me_2Se ,³⁸ Me_2SeCl_2 (benzene solution),^{29,39} and Me_2SeBr_2 (benzene solution)³⁹ suggests that the previous assignments²⁰ for ν_{sym} (280 cm^{-1}) and ν_{asym} ($244\text{ vs }244\text{ cm}^{-1}$) for Cl-Se-Cl modes in Me_2SeCl_2 should be reversed. It is now proposed that the coincidence of the C-Se-C deformation, which occurs in Me_2Se at 233 cm^{-1} (Raman) and at 238 cm^{-1} (m, sh) (IR) in Me_2SeBr_2 ,³⁹ with the Cl-Se-Cl mode at 244 cm^{-1} leads to an enhanced intensity for this lower frequency absorption. This resulted in an incorrect assignment to $\nu_{\text{asym}}(\text{ClSeCl})$; it is now assigned to $\nu_{\text{sym}}(\text{ClSeCl}) + \nu_{\text{def}}(\text{CSeC})$. The absorption at 280 cm^{-1} is assigned to $\nu_{\text{asym}}(\text{ClSeCl})$. In the solid state Me_2SeCl_2 exhibits a very broad and structureless absorption envelope in the Se-Cl region. We also note that in contrast to the Raman spectrum of the solid³⁸ the far-IR spectrum of Me_2TeCl_2 in benzene solution is interpretable in a standard fashion, i.e., $\nu_{\text{asym}}(\text{ClTeCl}) > \nu_{\text{sym}}(\text{ClTeCl})$. Absorptions (cm^{-1}) and assignments: 265 (vs) ($\nu_{\text{asym}}(\text{ClTeCl})$), 223 (s) ($\nu_{\text{sym}}(\text{ClTeCl})$), 188 (w) ($\nu_{\text{def}}(\text{CTeC})$), 124 (ms) ($\nu_{\text{def}}(\text{ClTeCl})$); other absorptions are at 87 (wm) and 55 (w, br). Finally, we add that the IR spectrum of Me_2TeBr_2 in benzene confirms previous assignments:³⁸ 190 (s) ($\nu_{\text{asym}}(\text{BrTeBr})$), 166 (w, sh) cm^{-1} ($\nu_{\text{sym}}(\text{BrTeBr})$).

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Chirality of Oxidized and Reduced Octadecamolybdodiphosphate Anions. Observation of a Pfeiffer Effect

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Recently determined structures of $\text{P}_2\text{Mo}_{18}\text{O}_{62}^{6-}$ and $\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}^{6-}$ show that the molybdate has only D_3 symmetry and is therefore chiral. The infrared spectra of both complexes in the solid state and in acetonitrile solution are reported and they confirm that the chirality of the molybdate is not caused by crystal packing forces. Solutions of the tetrabutylammonium salt of the heteropolymolybdate in acetonitrile in the presence of *l*-brucine sulfate show a significant positive Cotton effect centered at 350 nm ($[\text{M}]_{380} = +1.4 \times 10^3\text{ deg dm}^{-1}\text{ M}^{-1}$). This behavior is attributed to a Pfeiffer effect since analogous measurements with the nonchiral polyanions $\alpha\text{-}$ and $\beta\text{-P}_2\text{W}_{18}\text{O}_{62}^{6-}$, $\alpha\text{-SiMo}_{12}\text{O}_{40}^{4-}$, and $\text{Mo}_6\text{O}_{19}^{2-}$ show only minor amounts of induced optical activity. The heteropoly blue $\text{H}_2\text{P}_2\text{Mo}_2\text{V}_2\text{Mo}_{16}\text{O}_{62}^{6-}$ also exhibits a Pfeiffer effect but of diminished magnitude and no optical activity is associated with the intervalence charge-transfer transitions. An explanation of this behavior and of the apparent nonexistence of odd reduction states of $\text{P}_2\text{Mo}_{18}\text{O}_{62}^{6-}$ is presented.

We recently pointed out¹ that, according to the results of careful x-ray structural analyses,^{2,3} the heteropolyanion $\text{P}_2\text{Mo}_{18}\text{O}_{62}^{6-}$ (" P_2Mo_{18} ") is chiral in a particularly subtle fashion. Although the structure of P_2Mo_{18} is conventionally represented as an assemblage of edge- and corner-sharing MoO_6 octahedra and PO_4 tetrahedra, with an apparent overall point symmetry D_{3h} (see Figure 1a), displacements of molybdenum atoms within their respective MoO_6 octahedra lower the total symmetry to D_3 . The displacements, illustrated in Figure 1b, give rise to loops of Mo-O-Mo bonds that are alternately "short" ($\sim 1.80\text{ \AA}$) and "long" ($\sim 2.05\text{ \AA}$). The chirality of the structure is caused almost entirely by the displacements of the metal atoms since the 62 oxygen atoms, within 0.05 \AA , form a close-packed cluster of D_{3h} symmetry. In contrast to the molybdate, the corresponding "isostructural" tungstate, $\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}^{6-}$ ($\alpha\text{-P}_2\text{W}_{18}$), is virtually nonchiral with all bridging W-O-W bonds of similar length.³ An isomer of the tungstate, $\beta\text{-P}_2\text{W}_{18}$, has a closely related structure and is probably not significantly chiral.⁴

We have investigated the interaction of solutions of a number of related polyanions with *l*-brucine and *d*-cinchonine and have been able to demonstrate a significant Pfeiffer effect with P_2Mo_{18} and its two-electron reduction product. Only trivial amounts of optical activity were induced in nonchiral polyanions.

Experimental Section

Ammonium salts of P_2Mo_{18} ,⁵ $\alpha\text{-P}_2\text{W}_{18}$,⁵ $\beta\text{-P}_2\text{W}_{18}$,⁵ and tetrabutylammonium salts of $\text{Mo}_6\text{O}_{19}^{2-}$ (Mo_6)⁶ and $\alpha\text{-SiMo}_{12}\text{O}_{40}^{4-}$ (SiMo_{12})⁷ were prepared by published methods. Tetrabutylammonium and *l*-brucinium (bru^+) salts were obtained by precipitation from aqueous solution (pH ~ 0) with the corresponding hydrogen sulfates. Anal. Calcd for $[(\text{C}_4\text{H}_9)_4\text{N}]_5\text{HP}_2\text{Mo}_{18}\text{O}_{62}$: C, 24.05; H, 4.58; N, 1.75. Found: C, 23.94; H, 4.81; N, 1.73. Calcd for $(\text{C}_4\text{H}_9)_4\text{N}_5\text{HP}_2\text{Mo}_{18}\text{O}_{62}$: C, 29.02; H, 2.89; N, 2.94. Found: C, 28.48; H, 3.28; N, 2.91. The two-electron blue $\text{H}_2\text{P}_2\text{Mo}_2\text{V}_2\text{Mo}_{16}\text{O}_{62}^{6-}$ was prepared by controlled potential electrolysis⁸ or by chemical reduction with iron(II) sulfate in 1 M sulfuric acid. The tetrabutylammonium salt was isolated as above. Anal. Calcd for $[(\text{C}_4\text{H}_9)_4\text{N}]_3\text{H}_2\text{P}_2\text{Mo}_2\text{V}_2\text{Mo}_{16}\text{O}_{62}$: C, 24.04; H, 4.62; N, 1.75. Found: C, 22.02; H, 4.66; N, 1.62. The UV-visible spectra of the tetrabutylammonium salts in acetonitrile were in close agreement with those reported for aqueous solutions of the corresponding ammonium salts.

Spectroscopic measurements were made on Cary 14, Perkin-Elmer 457, and Jasco ORD/UV-5 instruments.

Results and Discussion

The infrared spectra of P_2Mo_{18} , reduced P_2Mo_{18} , and $\alpha\text{-P}_2\text{W}_{18}$ in the metal-oxygen stretching region are shown in Figure 2. Similar spectra for the oxidized anions have recently been reported by Tsvetkov and Karina.⁹ Although the spectra