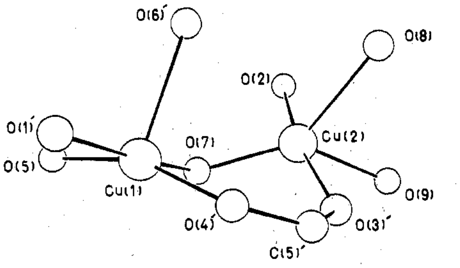

Figure 3. Relative orientations of the Cu(1) and Cu(2) coordination spheres.

quantify but probably leads to reduced spin–spin coupling relative to that of a fully planar system. On the basis of the reported magnetic behavior of $Cu_2(OH)_2^{2+}$ and $Cu_2(OR)_2^{2+}$ structural species,[2,19,20] the alkoxo bridge in the citrate structure might also be expected to result in substantial antiferromagnetism. Furthermore, the reported variation of spin–spin coupling with the bridging angle of $Cu_2(OH)_2^{4+}$ systems indicates that the bent (115°) alkoxo bridge in the citrate structure should allow particularly effective coupling.[2] The observed net magnetic behavior indicates either that the anticipated antiferromagnetic coupling between Cu(1) and Cu(2) within the asymmetric unit is overcome by ferromagnetic coupling along and/or between the chains or that coupling via the alkoxo and syn–syn carboxylate links is unexpectedly small. We believe this latter result is most likely. Strong antiferromagnetic coupling within the dimeric copper(II) carboxylate and $Cu_2(OH)_2^{4+}$ units is associated with a characteristic absorption band at ~380 nm not exhibited by magnetically dilute Cu(II) reference complexes.[19,21] The reflectance spectra of $Cu_2cit\cdot 2H_2O$ at 300 K consist of a broad d–d absorption centered at ~775 nm along with the usual carboxylate → Cu(II) charge-transfer band at ~250 nm. There is no indication of the "extra" absorption band associated with strongly coupled oxygen-bridged Cu(II) dimers. Presumably, coupling via the syn–syn carboxylate bridge has been seriously reduced by the noncoplanarity of this unit (vide supra). Also, it appears that the twist between the coordination spheres of Cu(1) and Cu(2) (Table IV) has reduced the ability of the alkoxo bridge to couple Cu(1) and Cu(2) magnetically.

Finally, the reported magnetic[22] (weak ferromagnetism) and structural[23] studies of the royal blue modification of copper formate support the inference that spin–spin coupling via the anti–syn B and C type bridges is not strongly ferromagnetic. The structure of $Cu(HCO_2)_2$ consists of a three-dimensional array of Cu(II) ions linked primarily by anti–syn formate bridging to all four equatorial positions. An additional apical bond results in five-coordination.

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Registry No. $Cu_2C_6H_4O_7\cdot 2H_2O$, 58846-97-2.

Supplementary Material Available: Listing of structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

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Notes

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Chalocogen Chemistry. 10. Synthesis and Characterization of Triarylphosphine Adducts of Selenium(II) Bromide

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There have recently been reported compounds of the general type $SeBr_2(Z)$ where Z is a two-electron donor. One example is $SeBr_2tmtu$ (Z = tmtu, 1,1,3,3-tetramethyl-2-thiourea),[1] which is prepared either through the reaction of $SeBr_4$ with excess tmtu in CH_2Cl_2 or through reaction of $RSeBr_3$ (R = CH_3, CH_3CH_2) and tmtu. $SeBr_2tmtu$ is a red crystalline solid stable to atmospheric moisture. T-shaped $SeBr_2tmtu$ units loosely joined via halogen bridges exist in the crystal.

Salts containing the $C_6H_5SeBr_2^-$ anion ($Z = C_6H_5^-$)[2] and the $SeCNBr_2^-$ anion ($Z = CN^-$)[3] are also known. The former is prepared through the reaction of a tetraalkylammonium bromide with phenylselenyl bromide, and the latter is prepared through the reaction of bromine with tetraalkylammonium selenocyanates. This work reports our attempts to extend knowledge of selenium(II) chemistry to include triarylphosphines as the two-electron donor, Z.

Experimental Section

Due to the moisture sensitivity of the compounds involved, all work was done in polyethylene glovebags under a dry nitrogen atmosphere.

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Spectra. Infrared, Raman, and nuclear magnetic resonance spectra were all obtained as previously reported.[1]

Conductivity. Specific conductivity at 10^{-3} M was measured utilizing a Yellow Springs Instrument Co. Model 31 conductivity bridge equipped with a standard conductance cell ($\theta = 0.2189$ cm^2). Measurements were made in nitrobenzene which had been stored over Linde 4-Å molecular sieves. The specific conductivity of the solvent was negligible.

Molecular Weights. Molecular weights were obtained osmometrically with a Perkin-Elmer Hitachi Model 115 molecular weight apparatus calibrated with five standard benzene solutions of purified diphenylamine (Baker).

Chemicals. Solvents used in synthesis were stored over Linde 4-Å molecular sieves prior to use. Triphenylphosphine (Eastern Chemical Corp.), tri-*m*-tolylphosphine, and tri-*p*-tolylphosphine (Eastman) were used as obtained without further purification. The corresponding triarylphosphine selenides were prepared via the method of Nicpon and Meek.[4] The KSeCN required for this method was prepared in our laboratory by Dr. William Maxwell.

Analyses. Elemental analyses were obtained from Atlantic Microlabs, Inc., and from Schwarzkopf Microanalytical Laboratory.

Dibromo(triphenylphosphine)selenium(II), I. A suspension of 6.8 g (20 mmol) of triphenylphosphine selenide in anhydrous diethyl ether was prepared in a 250-ml three-necked round-bottom flask cooled in an ice bath. The flask was equipped with a constant-pressure dropping funnel and dry nitrogen purge. Bromine (2.9 g, 18 mmol) was dissolved in 70 ml of CH_2Cl_2 and added over a period of 0.5 h to the ether suspension. The resulting yellow precipitate was filtered in a glovebag, washed with anhydrous ether, and dried in vacuo (yield 8.0 g, 88%). Recrystallization from C_6H_6/Et_2O at −20 °C gave a fine yellow powder, mp 88–89 °C dec. Anal. Calcd: C, 43.15; H, 3.02; Br, 32.89. Found: C, 43.41; H, 3.12; Br, 32.15. Molecular weight: calcd; 501.07; found, 482 (±15). $\Lambda = 0.21$ cm^2 equiv^{-1} ohm^{-1} at ca. 10^{-3} M in nitrobenzene.

Dibromo(tri-*m*-tolylphosphine)selenium(II), II. A solution of 5.8 g (15 mmol) of tri-*m*-tolylphosphine selenide was prepared in 50 ml of benzene. In a glovebag, 2.3 g (13 mmol) of Br_2 dissolved in 15 ml methylene chloride was added dropwise to the benzene solution. Dry Et_2O was added and the resultant yellow precipitate was filtered and dried in vacuo (8.0 g, 99%). Recrystallization from $C_6H_6/Et_2O/CHCl_3$ gave lemon yellow plates, mp 112–113 °C dec. Anal. Calcd: C, 46.45; H, 3.90; Br, 29.43. Found: C, 46.22; H, 3.74; Br, 29.55. Molecular weight: calcd, 542.97; found, 517 (±15). $\Lambda = 0.10$ cm^2 equiv^{-1} ohm^{-1} at ca. 10^{-3} M in nitrobenzene.

Dibromo(tri-*p*-tolylphosphine)selenium(II), III. The *p*-tolyl isomer was prepared in a fashion similar to that reported for the *m*-tolyl isomer in approximately 80% yield (mp 90–92 °C dec). Elemental analyses and NMR data showed this compound to be an unstable etherate. Recrystallization from C_6H_6/heptane gave a yellow ether-free powder decomposing at 97–98 °C. Anal. Calcd: C, 46.45; H, 3.90; Br, 29.43; P, 5.70. Found: C, 46.23; H, 4.10; Br, 28.17; P, 5.79. Molecular weight: calcd, 542.97; found, 536 (±15). $\Lambda = 0.0$ at ca. 10^{-3} M in nitrobenzene.

Results and Discussion

The addition of bromine to solutions or suspensions of triarylphosphine selenides yielded yellow solids whose elemental analyses indicated the composition Ar_3PSeBr_2. Molecular weight data indicated compounds I–III to be monomeric and undissociated in solution, and specific conductivity data showed them to be nonelectrolytes. Compounds I–III are stable in moist air for approximately 1 h. Solutions are fairly unstable and decompose leaving a deposit of either red or gray selenium. Gray selenium is deposited slowly from solutions of CH_2Cl_2, $CHCl_3$, and CH_3CN. The deposition of gray selenium at room temperature is very unusual; generally the metastable red form is deposited. However, this more common behavior is observed for solutions of I–III in acetone and water in which decomposition is almost instantaneous.

Proton nuclear magnetic resonance spectra of I–III showed little or no difference in chemical shifts relative to the parent selenides. The adducts were too insoluble for ^{31}P NMR study.

Table I. Infrared and Raman Bands for Ar_3PSeBr_2 Adducts (600–90 cm^{-1})

Compd	ν(Br–Se–Br)[a] $\nu_2(A_1)$	ν(Br–Se–Br)[a] $\nu_1(B_1)$	ν(P–Se)[b]	Other bands[b,c]
Ph_3PSeBr_2 (I)	153 w, sh[c]	188 s[c]	526 s	511 s, 497 m, 452 w, 439 mw, 250 s
	157 s, p[d]	182 w, sh, dp[d]		
$(p\text{-tol})_3PSeBr_2$ (II)	155 m[c]	186 s[c]	521 s	577 s, br, 552 m, 541 m, 524 m, 508 m, 493 w, 465 w, 448 mw, 427 mw, 253 m, 245 m, 238 w, 217 w, 91 m
$(m\text{-tol})_3PSeBr_2$ (III)	154 m[c]	190 s[c]	546 s	525 m, 511 m, 479 m, 466 m, 457 m, 424 w, 360 vw, 355 w, 267 w, 248 w, 215 m, 101 m

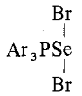
[a] Key: s, strong; m, medium; w, weak; br, broad; sh, shoulder; p, polarized; dp, depolarized; Ph, phenyl; tol, tolyl. [b] Recorded as a Nujol mull between KBr plates on a Perkin-Elmer Model 621 infrared spectrophotometer (600–400 cm^{-1}). [c] Recorded as a Nujol mull between polyethylene plates on a Beckman IR-11 far-infrared spectrophotometer (400–90 cm^{-1}). [d] Recorded as a CH_2Cl_2 solution on a Spex-Ramalog Model 1400 laser-Raman spectrometer using the 5145-Å line of a Carson Model 201 Ar$^+$ laser.

The synthesis of I–III expands our knowledge of the divalent chemistry of selenium and more particularly adds a new example to compounds of the type $SeBr_2(Z)$. It is likely that the structure of I–III is closely related to that of $SeBr_2$tmtu,[1] with the triarylphosphine taking the place of tmtu in the unique position of the "T" which describes the local coordination geometry about selenium. This structure seems reasonable based on the infrared and Raman spectral data presented in Table I, but nothing can be inferred from these data concerning any weak dimerization or other form of oligomerization which may occur in the solid state for I–III as occurs for $SeBr_2$tmtu.

The infrared spectra of I–III (Table I) were of interest in establishing the P–Se stretching frequencies of I–III relative to the parent phosphine selenide. A decrease of about 30 cm^{-1} in the P–Se stretching frequencies is observed upon oxidation of the triarylphosphine selenides. This parallels a similar decrease in the Se–C mode for selenocyanate upon oxidative addition of chlorine or bromine.[3]

Two characteristic stretching modes are observed for T-shaped molecules containing a linear Br–Se–Br group.[1,5,6] The antisymmetric Br–Se–Br $\nu_1(B_1)$ mode generally occurs at the higher frequency and is attributed to the strong ir absorptions observed for I–III between 180 and 190 cm^{-1} (Table I). The symmetric mode $\nu_2(A_1)$ is observed as a medium ir absorption around 150 cm^{-1} (Table I). In comparison, the symmetric and antisymmetric modes occur at 150 and 184 cm^{-1}, respectively, for $SeBr_2$tmtu. A solution Raman spectrum of I further supported the assignments given in Table I with a weak depolarized absorption at 182 cm^{-1} and a strong polarized absorption at 157 cm^{-1}.

The ir and Raman spectra provide evidence for the presence of a linear Br–Se–Br group; thus a structure analogous to that of $SeBr_2$tmtu is proposed for I–III as shown in I. This structure stands in contrast to the charge-transfer complexes of Ar_3PSe with iodine and interhalogens prepared by Zingaro and co-workers.[7]



$$\begin{array}{c} Br \\ | \\ Ar_3PSe \\ | \\ Br \end{array}$$

I

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Registry No. I, 58602-32-7; II, 58602-33-8; III, 58602-34-9; triphenylphosphine selenide, 3878-44-2; tri-*m*-tolylphosphine selenide, 10061-85-5.

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Entropy-Controlled Formation of Metal Complexes with Hindered Ligands. The System Zinc(II)-1,3,5-*cis*,*cis*-Triaminocyclohexane

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Reactions in aqueous solution between linear multidentate amine ligands and metal ions have been thoroughly studied from the thermodynamic point of view.[1] The flexibility of the ligand and its ability to assume the preferred geometry of the metal ion both depend on the length of the aliphatic chain joining the nitrogen atoms. The pronounced stability in solution of metal complexes with linear polyamines is due to either a favorable enthalpy term, $\Delta H°$, or a favorable entropy term, $\Delta S°$. In practice, as far as the enthalpy term $\Delta H°$ is concerned, the endothermic effect of partial dehydration both of the metal ion and of the ligand is more than compensated by the exothermic effect of metal–nitrogen coordinate bond formation.[2] The strength of the coordinate bonds and hence the exothermicity of the reaction depend on the ability of the ligand to arrange its donor atoms at the corners of the coordination polyhedron in a stress-free configuration. The entropy contribution $\Delta S°$ is usually positive (10–20 cal K^{-1} mol^{-1}) since the formation of the complex in solution leads to the release of water molecules of solvation and the resulting increase in translational entropy more than compensates for the loss of librational entropy by the ligand due to its increased rigidity on coordination (for a 1 M standard state). In the reactions of metal ions with linear polyamines the entropy change $\Delta S°$ contributes about 20–30% to the free energy change $\Delta G°$.

In this work we report the thermodynamic functions $\Delta H°$ and $\Delta S°$ for the reactions of the hydrogen and zinc(II) ions at 25 °C in 0.1 M KCl with the ligand 1,3,5-*cis*,*cis*-triaminocyclohexane (tach). tach has three primary amine groups at the corners of an equilateral triangle of side 2.5 Å,[3] and when it coordinates, it is forced to occupy the corners of one face of the coordination polyhedron. Since the nitrogen atoms are separated by propylenic chains, the metal complex formed contains six-membered chelate rings.

The equilibrium constants for the protonation of tach and for its interaction with the Zn^{II} ion have already been determined by means of pH titrations.[4] We have measured the enthalpy changes associated with these reactions and the corresponding values of $\Delta S°$ have been calculated using the values of $\Delta G°$ and $\Delta H°$.

Table I. Thermodynamic Functions for the Reactions of *cis*,*cis*-1,3,5-Triaminocyclohexane with Hydrogen and Zinc(II) Ions at 25 °C in 0.1 M KCl

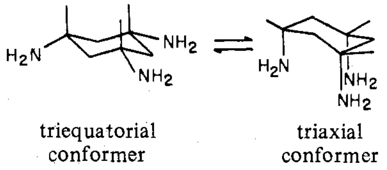
	$\Delta G°$,[a] kcal mol^{-1}	$\Delta H°$, kcal mol^{-1}	$\Delta S°$, cal K^{-1} mol^{-1}
$L + H^+ \rightleftarrows LH^+$	−13.86	−12.44 ± 0.20	4.7 ± 0.7
$LH^+ + H^+ \rightleftarrows LH_2{}^{2+}$	−11.81	−11.69 ± 0.25	0.4 ± 0.8
$LH_2{}^+ + H^+ \rightleftarrows LH_3{}^{3+}$	−9.78	−11.02 ± 0.29	−4.2 ± 1.0
$Zn^{2+} + L \rightleftarrows ZnL^{2+}$	−9.41	−0.05 ± 0.64	31.0 ± 2.1
$ZnL^{2+} + OH^- \rightleftarrows ZnLOH^+$	−7.98	−4.15 ± 0.76	13.0 ± 2.5

[a] Calculated from the log *K* values reported in ref 4.

The complex Zn(tach)$^{2+}$ is less stable by nearly 2 log units than the corresponding complexes with linear triamines of general formula *m*,*n*-tri[5] [*m*,*n*-tri = $NH_2(CH_2)_mNH(CH_2)_nNH_2$]. The most appropriate comparison is with 3,3-tri[6] since this ligand like tach forms six-membered chelate rings on complexation. Our calorimetric study shows that the enthalpy contribution is nil and that the stability in solution is due exclusively to an extremely favorable entropy change, viz., +30 cal K^{-1} mol^{-1} (Table I).

The stereochemistry of zinc complexes in aqueous solution is somewhat uncertain. The thermodynamic data relative to the formation in aqueous solution of complexes with polyamines have been variously interpreted in terms of tetrahedral,[7] pentacoordinate,[8] and, in a few cases, octahedral stereochemistry.[5] From molecular models it is seen that, compared with linear ligands, tach has great difficulty in occupying the corners of the coordination polyhedron. This may well lead to weaker coordinate bonds and hence to a less marked heat change.

Another important point is that the free ligand tach exists as the triequatorial conformer.[3] For coordination to a metal it is necessary that the ligand assume the triaxial conformation (see eq 1): the interconversion from the triequatorial to the triaxial conformer is endothermic and leads to a heat loss by the ligand. It is somewhat difficult to establish the relative importance of these two negative contributions to the enthalpy change. In the gas phase the heat of the triequatorial–triaxial interconversion has been estimated to be 11 kcal mol^{-1}.[3] In aqueous solution solvent interactions probably stabilize the triaxial species more because of its appreciably larger dipole moment and thus reduce considerably the interconversion energy. Thus, if we neglect the endothermic effects due to steric strain in the ligand and if we put the net energy change due to metal–ligand interaction equal to that ($\Delta H°$(Zn(3,3-tri)$^{2+}$) = 5.5 kcal mol^{-1}) for the homologous ligand 3,3-tri, which like tach forms six-membered chelate rings, we arrive at a value of 5.5 kcal mol^{-1} for the conformational interconversion of tach. This energy should be considered as the limiting value for the conversion of tach in aqueous solution.



(1)

The rigidity of this ligand explains the large entropy contribution which alone accounts for the stability of Zn(tach)$^{2+}$. In fact coordination leads to no loss of freedom because the ligand is already nearly completely rigid. Since the entropy contribution to the triequatorial–triaxial interconversion can be considered small, the loss of librational entropy by the ligand is very small and this accounts for the fact that $\Delta S°$ for the entire reaction has an appreciable positive value. Such a favorable entropy change should be found whenever a rigid ligand forms complexes. A typical case is