transfer and the LFSE. On the other hand, in spite of the 10-fold increase in the absorption of $Pd(1,10-T_218C6)^{2+}$ over that of $Pd(NO_3)_x^{2-x}$, λ_{max} remains nearly unchanged. The agreement of the difference in the ΔH values of the two Pd^{2+} complexes with their spectra confirms that stronger Pd-S bonds exist in $Pd(1,4-T_218C6)_2^{2+}$.

Macrocyclic and Entropic Effects. The relatively high stabilities per ligand bound of the $1,10-T_218C6$ complexes compared to those of the $1,4-T_218C6$ complexes may be a result of the macrocyclic effect of $1,10-T_218C6$ (see Table III). Also, the formation of $1,10-T_218C6$ with either Pd(II) or Hg(II) ion is very entropy favored as compared with the $1,4-T_218C6$ complexes. The ΔS values for the $M(II)/1,10-T_218C6$ systems are much more favorable than those for the $M(II)/1,4-T_218C6$ systems. These entropic differences probably result from the different abilities of the two ligands to effect dehydration of the metal ions and the different degrees of dehydration of the complexed ligands. The increased number of liberated solvent molecules from both metal ion and ligand ($1,10-T_218C6$) accounts for the more favorable ΔS values for these systems. Therefore, it seems reasonable to assign an entropic origin to the macrocyclic effect for these metal ions. The different entropies of formation of the $1,4-T_218C6$ complexes of Pd(II) (square planar) and Hg(II) (tetrahedron) may also be caused by the different degrees of dehydration of the two metal ions.

In conclusion, the relative magnitude of the enthalpy contribution is mainly dependent on the number of S-donor atoms coordinated to the central cations and their orientation with respect to these cations. The magnitude of the entropy contribution is mainly dependent on the dehydration of both the ligand and central cations. The size selectivity for these crown thioether ligands is not critical for the formation of stable complexes of transition-metal and post-transition-metal ions as was found in the complexation of alkali-metal and alkaline-earth-metal ions with crown ethers.

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Supplementary Material Available: Tables of bond lengths, bond angles, anisotropic temperature factors, and atomic coordinates and related temperature factors for both Pd(II) complexes (16 pages). Ordering information is given on any current masthead page.

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Synthesis, Structure, Spectroscopy, and Reactivity of $M(Se_4)_2^{2-}$ Anions, M = Ni, Pd, Zn, Cd, Hg, and Mn

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The $M(Se_4)_2^{2-}$ ions, M = Ni, Pd, Zn, Cd, and Hg, have been synthesized by reaction of the metal xanthate with a polyselenide solution in CH_3CN-DMF. The corresponding $Mn(Se_4)_2^{2-}$ ion was synthesized by reaction of $MnCl_2$ with a polyselenide solution in DMF. The $Pt(Se_4)_2^{2-}$ ion was synthesized in situ by reaction of $Pt(Se_4)_3^{2-}$ with excess BH_4^-. The crystal structures of $[PEtPh_3]_2[Ni(Se_4)_2]$ and of $[PPh_4]_2[Zn(Se_4)_2]$ have been determined. The Ni center in the centrosymmetric $Ni(Se_4)_2^{2-}$ ion is essentially square planar with Ni-Se distances of 2.298 (1) and 2.315 (1) Å. The two independent $Zn(Se_4)_2^{2-}$ ions have approximately tetrahedral Zn centers, but they show significant metrical differences. Zn-Se distances range from 2.450 (5) to 2.493 (6) Å. The MSe_4 rings have the distorted envelope conformation. The ions (except $Mn(Se_4)_2^{2-}$) show two ^{77}Se NMR resonances. These occur for the following M (δ(metal-bound Se), ppm; δ(ring Se), ppm): Ni (820; 748); Pd (893; 758); Pt (727; 642); Zn (127; 598); Cd (62; 608); Hg (76; 594). Trends in these resonance positions are rationalized in terms of the d-electron configurations of the metal. Reaction of the corresponding $M(Se_4)_2^{2-}$ ion with dimethyl acetylenedicarboxylate affords the ions $M(Se_2C_2(COOCH_3)_2)_2^{2-}$ (M = Zn, Ni).

Introduction

The chemistry of soluble transition-metal chalcogenides began more than 100 years ago with the synthesis of the MS_4^{2-} (M = Mo, W) anions[1] and continues to be the subject of intense investigation. The chemistry is rich and presents a variety of structural types,[2] most of which do not have oxide analogues. Although the transition-metal sulfides have been studied extensively,[2] the corresponding selenium and tellurium chemistry is in an embryonic stage.[3] While many of the soluble selenide ions discovered in the last three years do not have sulfide analogues, the $M(Se_4)_2^{2-}$ ions do. These $M(Q_4)_2^{2-}$ ions (Q = S, Se) appear to be especially stable and accessible. Thus, $Ni(S_4)_2^{2-}$,[4,5] $Pd(S_4)_2^{2-}$,[4] $Zn(S_4)_2^{2-}$,[5] and $Hg(S_4)_2^{2-}$[6] are known. While the present work was in progress, new $M(Se_4)_2^{2-}$ ions were reported for M = Zn,[3,7,8] Cd,[7,8] Hg,[7,8] Ni,[8] Pb,[8] and Mn.[9] Here we report a general method of preparation of $M(Se_4)_2^{2-}$ anions, M = Ni, Pd, Zn, Cd, and Hg, a new route to $Mn(Se_4)_2^{2-}$, the in situ synthesis of $Pt(Se_4)_2^{2-}$, their ^{77}Se NMR spectroscopy (except for Mn), selected structural characterization, and the reactivity of $M(Se_4)_2^{2-}$ (M = Ni, Zn) toward dimethyl acetylenedicarboxylate (DMA).

Experimental Section

Syntheses. All the manipulations were carried out under N_2 with the use of standard Schlenk-line techniques. Solvents were distilled and dried. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. UV-vis and IR spectra were recorded on a Perkin-Elmer 330 spectrophotometer and a Perkin-Elmer 283 spectrometer, respectively. ^{77}Se NMR spectra were obtained on a Varian XLA-400 spectrometer with a 10-mm tunable probe and a deuterium lock. All chem-

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(1) (a) Krüss, G. *Liebigs Ann. Chem.* **1884**, *225*, 1-57. (b) Corleis, E. *Liebigs Ann. Chem.* **1886**, *232*, 244-270.

(2) (a) Müller, A.; Jaegermann, W.; Enemark, J. H. *Coord. Chem. Rev.* **1982**, *46*, 245-280. (b) Müller, A.; Diemann, E. *Adv. Inorg. Chem.* **1987**, *31*, 89-122. (c) Coucouvanis, D.; Hadjikyriacou, A.; Draganjac, M.; Kanatzidis, M. G.; Ileperuma, O. *Polyhedron* **1986**, *5*, 349-356. (d) Harmer, M. A.; Halbert, T. R.; Pan, W.-H.; Coyle, C. L.; Cohen, S. A.; Stiefel, E. I. *Polyhedron* **1986**, *5*, 341-347. (e) Fenske, D.; Ohmer, J.; Hachgenei, J.; Merzweiler, K. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1277-1296.

(3) Ansari, M. A.; Ibers, J. A. *Coord. Chem. Rev.* **1990**, *100*, 223-266.

(4) Müller, A.; Krickemeyer, E.; Bögge, H.; Clegg, W.; Sheldrick, G. M. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 1006-1007.

(5) Coucouvanis, D.; Patil, P. R.; Kanatzidis, M. G.; Detering, B.; Baenziger, N. C. *Inorg. Chem.* **1985**, *24*, 24-31.

(6) Müller, A.; Schimanski, J.; Schimanski, U.; Bögge, H. *Z. Naturforsch., B* **1985**, *40B*, 1277-1288.

(7) Adel, J.; Weller, F.; Dehnicke, K. *Z. Naturforsch., B* **1988**, *43B*, 1094-1100.

(8) Banda, R. M. H.; Cusick, J.; Scudder, M. L.; Craig, D. C.; Dance, I. G. *Polyhedron* **1989**, *8*, 1995-1998.

(9) O'Neal, S. C.; Pennington, W. T.; Kolis, J. W. *Inorg. Chem.* **1990**, *29*, 3134.

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ical shifts are referenced to Ph_2Se_2 at δ 460 ppm. The detailed experimental procedures are outlined elsewhere.[10] $M(xan)_2$ (M = Ni, Pd, Zn, Cd, Hg; xan = S_2COEt) were prepared by published methods.[11] Li_2Se was prepared by the reaction of stoichiometric amounts of Li and Se in liquid ammonia, while K_2Se_5 was obtained by stoichiometric reaction of the elements in a sealed, evacuated quartz tube at 450 °C for 72 h. The alkali-metal selenides were characterized by their X-ray powder patterns.

Preparation of $[PEtPh_3]_2[Ni(Se_4)_2]$ (1). The Se_4^{2-} species was generated in situ by stirring a mixture of Li_2Se (93 mg, 1 mmol), black Se (237 mg, 3 mmol), and $PEtPh_3Br$ (371 mg, 1 mmol) in DMF (10 mL). $Ni(xan)_2$ (150 mg, 0.5 mmol) was dissolved in DMF (5 mL) and added to the selenide solution. The resulting green solution turned brown after it was stirred for 1 h. The solution was filtered, and the filtrate was diluted with diethyl ether (20 mL). The solution was kept at room temperature for 2 days to afford black crystals of **1** (320 mg, 50% yield). Anal. Calcd for $C_{40}H_{40}NiP_2Se_8$: C, 37.74; H, 3.17; P, 4.87; Se, 49.62; Ni, 4.61. Found: C, 38.46; H, 3.37; P, 4.47; Se, 46.54;[12] Ni, 4.76. ^{77}Se NMR (DMF, δ): 820, 748.

Preparation of $[PPh_4]_2[Pd(Se_4)_2]$ (2). This compound was prepared in the same manner as **1** except that PPh_4Cl was used in place of $PEtPh_3Br$ (red powder, 430 mg, 60% yield). Anal. Calcd for $C_{48}H_{40}P_2PdSe_8$: C, 40.65; H, 2.85; P, 4.37. Found: C, 39.42; H, 3.13; P, 3.82 ^{77}Se NMR (DMF, δ): 893, 758.

Preparation of $[PPh_4]_2[Zn(Se_4)_2]$ (3). A mixture of Li_2Se (186 mg, 2 mmol), black Se (474 mg, 6 mmol), and PPh_4Cl (750 mg, 2 mmol) in CH_3CN (30 mL) and Et_3N (5 mL) was stirred for 1 h. A solution of $Zn(xan)_2$ (305 mg, 1 mmol) in DMF (10 mL) was added to that mixture. The resulting solution was stirred for 1 h and then filtered. The volume of the filtrate was reduced to 20 mL, and 2-propanol (20 mL) was layered on it. Red crystals of **3** were produced in 2 days (655 mg, 48% yield). Anal. Calcd for $C_{48}H_{40}P_2Se_8Zn$: C, 41.90; H, 2.93; P, 4.50; Se, 45.91; Zn, 4.75. Found: C, 43.03; H, 2.87; P, 3.80; Se, 39.70; Zn, 4.13. ^{77}Se NMR (DMF, δ): 598, 127.

Preparation of $[PPh_4]_2[Cd(Se_4)_2]$ (4). This compound was obtained by the procedure adopted for $[PPh_4]_2[Zn(Se_4)_2]$ (23% yield). Anal. Calcd for $C_{48}H_{40}CdP_2Se_8$: C, 40.52; H, 2.83; P, 4.35; Cd, 7.90; Se, 44.39. Found: C, 39.81; H, 2.87; P, 4.14; Cd, 7.28; Se, 46.03. ^{77}Se NMR (DMF, δ): 608, 62.

Preparation of $[NEt_4]_2[Hg(Se_4)_2]$ (5). Compound **5** was prepared in the same manner as **3** except for the substitution of $Hg(xan)_2$ for $Zn(xan)_2$ and NEt_4Cl for PPh_4Cl (49% yield). Anal. Calcd for $C_{16}H_{40}HgN_2Se_8$: C, 17.59; H, 3.69; Hg, 18.36; Se, 57.80. Found: C, 17.47; H, 3.72; Hg, 17.49; Se, 56.14. ^{77}Se NMR (DMF, δ): 594, 76.

Preparation of $[PPh_4]_2[Mn(Se_4)_2]$ (6). $Mn(xan)_2$ was difficult to prepare in pure form so a solution of anhydrous $MnCl_2$ (0.378 g, 3 mmol) in DMF (20 mL) was added to a solution of K_2Se_5 (2.365 g, 5 mmol) and PPh_4Cl (1.5 g, 4 mmol) in DMF (20 mL). The red solution so obtained was stirred for 1 h and then filtered. To the filtrate were added toluene and diethyl ether until nucleation started. After several days at room temperature the solution gave red-brown crystals. The crystals were separated, washed with ether, and dried under vacuum (900 mg, 22% yield). Anal. Calcd for $C_{48}H_{40}MnP_2Se_8$: C, 42.24; H, 2.95; P, 4.54. Found: C, 40.71; H, 3.0; P, 3.38. ^{77}Se NMR (DMF, δ): 720–790, br.

Reactivity of $[PPh_4]_2[Zn(Se_4)_2]$ toward DMA: Synthesis of $[PPh_4]_2[Zn(Se_2C_2(COOCH_3)_2)_2]$ (7). $[PPh_4]_2[Zn(Se_4)_2]$ (138 mg, 0.1 mmol) was dissolved in DMF (10 mL), and DMA (0.5 mL) was added to the solution. This solution was stirred for 0.5 h and then filtered. Toluene was added (20 mL) to the filtrate. Orange crystals of **7** formed overnight at room temperature (92 mg, 69% yield). Anal. Calcd for $C_{60}H_{52}O_8P_2Se_4Zn$: C, 53.69; H, 3.91; P, 4.62; Se, 23.53; Zn, 4.87. Found: C, 53.31; H, 4.02; P, 4.22; Se, 23.27; Zn, 5.22. IR (KBr, cm^{-1}): 1715, 1700, 1680, (ν_{CO}); 1450 ($\nu_{C=C}$). UV-vis (DMF) [λ_{max}, nm (ε, M^{-1} cm^{-1})]: 390 (8400). ^{77}Se NMR (DMF, δ): 180.

Reactivity of $[PEtPh_3]_2[Ni(Se_4)_2]$ toward DMA: Synthesis of $[PEtPh_3]_2[Ni(Se_2C_2(COOCH_3)_2)_2]$ (8). The procedure followed was identical with that for **7** to afford brown crystals (85 mg, 68% yield). Anal. Calcd for $C_{52}H_{52}NiO_8P_2Se_4$: C, 50.31; H, 4.22; P, 4.99; Se, 25.44; Ni, 4.73. Found: C, 49.30; H, 4.20; P, 5.13; Se, 24.20; Ni, 4.34. IR (KBr, cm^{-1}): 1720, 1700, 1680 (ν_{CO}); 1440 ($\nu_{C=C}$). UV-vis (DMF) [λ_{max}, nm (ε, M^{-1} cm^{-1})]: 340 (7400). ^{77}Se NMR (DMF, δ): 540.

Table I. Crystallographic Details

compd	$[PEtPh_3]_2[Ni(Se_4)_2]$	$[PPh_4]_2[Zn(Se_4)_2]^a$
formula	$C_{40}H_{40}NiP_2Se_8$	$C_{48}H_{40}P_2Se_8Zn$
fw	1273	1376
a, Å	11.086 (6)	10.048 (10)
b, Å	14.027 (9)	13.923 (13)
c, Å	13.470 (8)	33.98 (3)
β, deg	92.79 (3)	92.21 (3)
V, Å^3	2092	4750
Z	2	4
d(calcd), g/cm^3	2.309	1.923
space group	C_{2h}^5–$P2_1/n$	C_2^2–$P2_1$
t, °C	−163	−163
λ, Å	0.7093 (Mo Kα$_1$)	0.7093 (Mo Kα$_1$)
μ, cm^{-1}	85.2	67.0
transm coeff	0.177–0.455	0.334–0.750
$R(F_o)$ ($F_o^2 > 3\sigma(F_o^2)$)	0.054	0.085
$R_w(F_o)$ ($F_o^2 > 3\sigma(F_o^2)$)	0.057	0.081

[a] Banda et al.[8] report a room-temperature cell of *a* = 10.159 (5) Å, *b* = 14.020 (4) Å, *c* = 34.26 (1) Å, β = 92.11 (2)°, *Z* = 4, and $P2_1$, but they did not collect data on the compound.

Table II. Positional Parameters and Equivalent Isotropic Thermal Parameters (Å^2) for $[PEtPh_3]_2[Ni(Se_4)_2]$

atom	*x*	*y*	*z*	*B*
Ni	0	0	0	1.08 (2)
Se(1)	−0.159 376 (49)	−0.102 802 (40)	0.015 665 (43)	1.48 (1)
Se(2)	−0.218 269 (53)	−0.162 791 (45)	−0.146 172 (46)	1.94 (1)
Se(3)	−0.042 971 (53)	−0.132 453 (43)	−0.228 180 (43)	1.71 (1)
Se(4)	−0.008 136 (51)	0.023 236 (40)	−0.170 381 (41)	1.46 (1)
P(1)	0.143 81 (12)	−0.355 716 (96)	−0.093 415 (96)	0.99 (3)
C(1)	0.215 47 (46)	−0.466 87 (38)	−0.061 01 (38)	1.2 (1)
C(2)	0.303 74 (51)	−0.471 19 (41)	0.017 26 (41)	1.6 (1)
C(3)	0.361 23 (52)	−0.555 66 (44)	0.040 37 (44)	1.9 (1)
C(4)	0.333 25 (54)	−0.636 86 (42)	−0.014 99 (46)	2.0 (1)
C(5)	0.247 05 (55)	−0.634 76 (42)	−0.093 67 (45)	2.0 (1)
C(6)	0.189 56 (51)	−0.549 01 (41)	−0.115 89 (41)	1.6 (1)
C(7)	0.261 00 (44)	−0.273 06 (36)	−0.120 46 (36)	1.0 (1)
C(8)	0.244 73 (46)	−0.175 84 (37)	−0.105 20 (39)	1.2 (1)
C(9)	0.337 33 (49)	−0.113 32 (37)	−0.123 91 (40)	1.4 (1)
C(10)	0.445 79 (50)	−0.147 64 (41)	−0.157 76 (41)	1.6 (1)
C(11)	0.461 07 (48)	−0.244 23 (41)	−0.173 50 (40)	1.5 (1)
C(12)	0.368 98 (47)	−0.307 26 (38)	−0.155 69 (39)	1.2 (1)
C(13)	0.042 31 (45)	−0.375 34 (35)	−0.198 76 (38)	1.1 (1)
C(14)	−0.076 39 (56)	−0.402 68 (44)	−0.183 83 (45)	2.0 (1)
C(15)	−0.154 71 (52)	−0.422 91 (44)	−0.265 18 (48)	2.1 (1)
C(16)	−0.114 24 (53)	−0.415 09 (42)	−0.359 76 (48)	2.0 (1)
C(17)	0.003 26 (57)	−0.387 27 (42)	−0.376 06 (45)	2.0 (1)
C(18)	0.082 77 (50)	−0.368 16 (39)	−0.295 19 (39)	1.4 (1)
C(19)	0.059 58 (50)	−0.309 28 (42)	0.005 84 (41)	1.6 (1)
C(20)	0.132 43 (60)	−0.286 04 (50)	0.101 26 (43)	2.4 (2)
H1C(2)	0.324	−0.414	0.054	2.5
H1C(3)	0.419	−0.559	0.095	2.9
H1C(4)	0.376	−0.696	0.002	2.9
H1C(5)	0.228	−0.692	−0.132	2.9
H1C(6)	0.130	−0.545	−0.170	2.6
H1C(8)	0.170	−0.153	−0.081	2.2
H1C(9)	0.327	−0.046	−0.115	2.3
H1C(10)	0.511	−0.104	−0.170	2.6
H1C(11)	0.536	−0.268	−0.197	2.4
H1C(12)	0.380	−0.374	−0.168	2.2
H1C(14)	−0.104	−0.409	−0.118	3.0
H1C(15)	−0.237	−0.442	−0.256	3.0
H1C(16)	−0.168	−0.429	−0.416	2.9
H1C(17)	0.030	−0.381	−0.443	3.0
H1C(18)	0.165	−0.350	−0.305	2.4
H1C(19)	0.020	−0.252	−0.017	2.6
H2C(19)	−0.001	−0.355	0.022	2.6
H1C(20)	0.106	−0.323	0.154	3.2
H2C(20)	0.216	−0.299	0.092	3.2
H3C(20)	0.124	−0.220	0.117	3.2

Crystallographic Studies. An initial cell was determined from X-ray photography for $[PEtPh_3]_2[Ni(Se_4)_2]$ and was confirmed from setting angles on a Picker FACS-1 diffractometer. Data collection, structure solution, and refinement were straightforward. Some experimental details are given in Table I.

For $[PPh_4]_2[Zn(Se_4)_2]$ an initial unit cell was determined from 25 reflections automatically centered on an Enraf-Nonius CAD4 diffractometer. The crystal was then transferred to a Picker FACS-1 diffractometer where data collection was carried out. The material crystallizes with 4 formula units in space group $P2_1$ or $P2_1/m$ of the monoclinic

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[10] Wardle, R. W. M.; Bhaduri, S.; Chau, C.-N.; Ibers, J. A. *Inorg. Chem.* **1988**, *27*, 1747–1755.

[11] (a) Hunt, M. R.; Krüger, A. G.; Smith, L.; Winter, G. *Aust. J. Chem.* **1971**, *24*, 53–57. (b) Watt, G. W.; McCormick, B. J. *J. Inorg. Nucl. Chem.* **1965**, *27*, 898–900.

[12] The Se analyses are generally unreliable, even for the Ni and Zn compounds where the purity of the complexes was established beyond doubt from the X-ray analysis.

Table III. Positional Parameters and Isotropic Thermal Parameters ($Å^2$) for $[PPh_4]_2[Zn(Se_4)_2]$

atom	*x*	*y*	*z*	*B*	atom	*x*	*y*	*z*	*B*
Zn(1)	−0.76109 (36)	−0.4453	−0.37594 (12)	2.05 (8)	C(56)	−0.3654 (36)	0.4390 (32)	−0.2839 (12)	3 (1)
Zn(2)	−0.48413 (34)	−0.04779 (38)	−0.12696 (12)	1.88 (8)	C(57)	−0.3618 (26)	0.4284 (23)	−0.32501 (87)	1.4 (6)
Se(1)	−0.92174 (30)	−0.33570 (38)	−0.40915 (10)	1.95 (7)	C(58)	−0.2496 (31)	0.3966 (25)	−0.3423 (10)	3.0 (8)
Se(2)	−0.84086 (33)	−0.37962 (39)	−0.46985 (11)	2.16 (7)	C(59)	−0.1397 (32)	0.3763 (26)	−0.3215 (11)	3.2 (8)
Se(3)	−0.61764 (31)	−0.33313 (39)	−0.46178 (10)	1.87 (7)	C(60)	−0.1374 (30)	0.3865 (25)	−0.2807 (10)	1.9 (8)
Se(4)	−0.54435 (33)	−0.42171 (39)	−0.40677 (11)	2.37 (8)	C(61)	−0.4056 (29)	0.4534 (25)	−0.19459 (97)	2.1 (7)
Se(5)	−0.85513 (32)	−0.60638 (38)	−0.38841 (11)	2.25 (8)	C(62)	−0.4675 (32)	0.5475 (26)	−0.1998 (10)	2.8 (8)
Se(6)	−0.73415 (40)	−0.68605 (43)	−0.33859 (14)	4.4 (1)	C(63)	−0.6083 (36)	0.5554 (30)	−0.1913 (11)	5 (1)
Se(7)	−0.77178 (43)	−0.58440 (47)	−0.28217 (15)	5.5 (1)	C(64)	−0.6732 (31)	0.4784 (26)	−0.1750 (10)	2.6 (8)
Se(8)	−0.69777 (40)	−0.43095 (45)	−0.30503 (13)	4.4 (1)	C(65)	−0.6073 (28)	0.3937 (23)	−0.17167 (92)	1.5 (7)
Se(9)	−0.27342 (31)	−0.07722 (39)	−0.16067 (11)	2.24 (7)	C(66)	−0.4755 (27)	0.3816 (22)	−0.18032 (87)	1.8 (6)
Se(10)	−0.34028 (33)	−0.19645 (39)	−0.20492 (11)	2.54 (8)	C(67)	−0.1417 (28)	0.5490 (23)	−0.20064 (93)	1.7 (7)
Se(11)	−0.56443 (34)	−0.15909 (39)	−0.21677 (11)	2.68 (8)	C(68)	−0.1658 (34)	0.6035 (27)	−0.1685 (11)	3.5 (9)
Se(12)	−0.63810 (31)	−0.17105 (38)	−0.15277 (10)	1.81 (7)	C(69)	−0.0762 (32)	0.6814 (26)	−0.1601 (10)	3.1 (8)
Se(13)	−0.54749 (32)	0.12261 (39)	−0.13546 (11)	2.19 (7)	C(70)	0.0256 (29)	0.6953 (24)	−0.18431 (98)	2.1 (7)
Se(14)	−0.37709 (34)	0.16995 (40)	−0.09144 (11)	2.76 (8)	C(71)	0.0390 (39)	0.6427 (34)	−0.2193 (13)	4 (1)
Se(15)	−0.43986 (33)	0.09116 (40)	−0.03338 (11)	2.63 (8)	C(72)	−0.0453 (30)	0.5771 (25)	−0.22820 (95)	2.0 (7)
Se(16)	−0.45315 (31)	−0.06930 (39)	−0.05436 (11)	2.21 (7)	C(73)	−0.0102 (28)	0.0185 (24)	−0.26969 (95)	1.7 (7)
P(1)	−0.55609 (79)	−0.01964 (70)	−0.43649 (27)	1.4 (2)	C(74)	−0.0003 (33)	−0.0540 (30)	−0.2386 (11)	3.9 (9)
P(2)	−0.11167 (75)	−0.32311 (70)	0.00382 (25)	1.4 (2)	C(75)	0.0917 (31)	−0.0337 (26)	−0.2069 (10)	2.6 (8)
P(3)	−0.24056 (77)	0.44442 (73)	−0.21085 (26)	1.7 (2)	C(76)	0.1722 (37)	0.0448 (32)	−0.2083 (12)	5 (1)
P(4)	−0.13344 (79)	−0.00521 (68)	−0.30767 (26)	1.5 (2)	C(77)	0.1627 (34)	0.1064 (29)	−0.2406 (11)	3.5 (9)
C(1)	−0.5020 (24)	0.1024 (20)	−0.43408 (77)	0.4 (5)	C(78)	0.0773 (31)	0.0905 (25)	−0.26884 (99)	2.6 (7)
C(2)	−0.3644 (31)	0.1225 (27)	−0.4345 (10)	2.9 (8)	C(79)	−0.1783 (34)	−0.1399 (26)	−0.3096 (10)	2.8 (8)
C(3)	−0.3209 (26)	0.2199 (22)	−0.43291 (86)	0.9 (6)	C(80)	−0.3092 (30)	−0.1543 (25)	−0.31232 (97)	2.6 (7)
C(4)	−0.4059 (31)	0.2868 (26)	−0.4319 (10)	2.5 (8)	C(81)	−0.3404 (39)	−0.2489 (33)	−0.3216 (13)	5 (1)
C(5)	−0.5434 (29)	0.2703 (23)	−0.42909 (94)	1.9 (7)	C(82)	−0.2382 (37)	−0.3273 (31)	−0.3217 (11)	5 (1)
C(6)	−0.5933 (28)	0.1775 (25)	−0.43037 (93)	2.0 (7)	C(83)	−0.1087 (38)	−0.2888 (30)	−0.3169 (12)	4 (1)
C(7)	−0.4259 (26)	−0.0966 (22)	−0.44715 (88)	1.7 (6)	C(84)	−0.0779 (29)	−0.1949 (25)	−0.30995 (94)	1.8 (7)
C(8)	−0.3704 (27)	−0.1616 (24)	−0.42033 (91)	1.7 (7)	C(85)	−0.0755 (32)	0.0292 (28)	−0.3547 (11)	2.8 (8)
C(9)	−0.2677 (29)	−0.2183 (25)	−0.43194 (98)	2.3 (7)	C(86)	−0.0371 (32)	0.1183 (27)	−0.3627 (10)	3.0 (8)
C(10)	−0.2069 (28)	−0.2073 (24)	−0.46778 (96)	1.7 (7)	C(87)	0.0121 (27)	0.1425 (22)	−0.39974 (91)	2.1 (7)
C(11)	−0.2605 (28)	−0.1455 (23)	−0.49328 (93)	1.5 (7)	C(88)	0.0167 (26)	0.0762 (23)	−0.43028 (86)	0.9 (6)
C(12)	−0.3681 (27)	−0.0845 (24)	−0.48194 (94)	1.8 (7)	C(89)	−0.0237 (30)	−0.0146 (24)	−0.4212 (10)	2.5 (7)
C(13)	−0.6836 (29)	−0.0301 (24)	−0.47499 (97)	1.6 (7)	C(90)	−0.0655 (28)	−0.0398 (25)	−0.3828 (10)	2.2 (7)
C(14)	−0.6824 (27)	0.0393 (23)	−0.50523 (91)	1.6 (6)	C(91)	−0.2770 (27)	0.0682 (22)	−0.29481 (90)	1.3 (6)
C(15)	−0.7774 (31)	0.0243 (26)	−0.5366 (10)	2.6 (8)	C(92)	−0.3208 (30)	0.0531 (25)	−0.2598 (10)	2.4 (8)
C(16)	−0.8666 (29)	−0.0500 (26)	−0.53605 (98)	2.5 (7)	C(93)	−0.4269 (30)	0.1114 (25)	−0.24657 (96)	2.1 (7)
C(17)	−0.8665 (27)	−0.1098 (23)	−0.50646 (91)	1.5 (6)	C(94)	−0.4736 (37)	0.1831 (33)	−0.2710 (13)	4 (1)
C(18)	−0.7725 (27)	−0.1001 (22)	−0.47505 (89)	1.3 (6)	C(95)	−0.4230 (34)	0.1931 (28)	−0.3081 (11)	3 (1)
C(19)	−0.6146 (28)	−0.0525 (26)	−0.3895 (10)	1.9 (7)	C(96)	−0.3227 (26)	0.1347 (21)	−0.31995 (85)	1.2 (6)
C(20)	−0.6572 (27)	−0.1445 (23)	−0.38113 (93)	1.5 (7)	H1C(2)	−0.301	0.069	−0.436	3.7
C(21)	−0.7072 (30)	−0.1689 (26)	−0.3478 (10)	2.8 (8)	H1C(3)	−0.226	0.236	−0.432	2.1
C(22)	−0.6994 (28)	−0.0981 (24)	−0.31615 (96)	2.0 (7)	H1C(4)	−0.374	0.354	−0.434	3.5
C(23)	−0.6685 (28)	−0.0027 (24)	−0.32151 (97)	1.9 (7)	H1C(5)	−0.605	0.327	−0.427	2.8
C(24)	−0.6221 (32)	0.0228 (27)	−0.3598 (11)	3.0 (8)	H1C(6)	−0.692	0.166	−0.429	3.1
C(25)	−0.2357 (29)	−0.3733 (26)	−0.03166 (95)	2.0 (7)	H1C(8)	−0.401	−0.166	−0.394	2.6
C(26)	−0.2970 (29)	−0.3052 (24)	−0.05831 (96)	1.9 (7)	H1C(9)	−0.239	−0.271	−0.415	3.2
C(27)	−0.3789 (30)	−0.3389 (27)	−0.0858 (10)	2.6 (7)	H1C(10)	−0.127	−0.243	−0.473	2.7
C(28)	−0.4038 (35)	−0.4391 (29)	−0.0910 (11)	4 (1)	H1C(11)	−0.227	−0.141	−0.520	2.7
C(29)	−0.3278 (36)	−0.5105 (28)	−0.0676 (12)	4 (1)	H1C(12)	−0.400	−0.033	−0.499	2.9
C(30)	−0.2411 (34)	−0.4701 (29)	−0.0377 (11)	3.6 (9)	H1C(14)	−0.620	0.095	−0.505	2.4
C(31)	−0.1810 (25)	−0.2197 (21)	0.02647 (83)	0.7 (6)	H1C(15)	−0.783	0.072	−0.558	3.5
C(32)	−0.1445 (29)	−0.1274 (25)	0.01498 (98)	2.1 (7)	H1C(16)	−0.931	−0.057	−0.559	3.2
C(33)	−0.1970 (33)	−0.0459 (28)	0.0320 (11)	3.5 (9)	H1C(17)	−0.933	−0.161	−0.507	2.4
C(34)	−0.2911 (28)	−0.0611 (26)	0.05926 (97)	2.3 (7)	H1C(18)	−0.771	−0.147	−0.453	2.3
C(35)	−0.3344 (28)	−0.1498 (25)	0.06977 (93)	2.3 (7)	H1C(20)	−0.647	−0.195	−0.401	2.6
C(36)	−0.2793 (29)	−0.2286 (24)	0.05219 (98)	2.2 (7)	H1C(21)	−0.750	−0.232	−0.344	3.6
C(37)	0.0374 (26)	−0.2879 (21)	−0.02039 (87)	0.9 (6)	H1C(22)	−0.718	−0.119	−0.290	3.0
C(38)	0.1402 (30)	−0.2393 (24)	0.00091 (99)	2.7 (7)	H1C(23)	−0.681	0.045	−0.301	2.7
C(39)	0.2604 (28)	−0.2201 (23)	−0.01655 (95)	1.9 (7)	H1C(24)	−0.597	0.089	−0.366	4.2
C(40)	0.2775 (27)	−0.2433 (22)	−0.05315 (91)	1.4 (6)	H1C(26)	−0.274	−0.234	−0.057	3.1
C(41)	0.1822 (31)	−0.2967 (24)	−0.0748 (10)	2.2 (8)	H1C(27)	−0.429	−0.295	−0.103	3.5
C(42)	0.0625 (28)	−0.3186 (24)	−0.05806 (94)	2.0 (7)	H1C(28)	−0.472	−0.461	−0.111	5.1
C(43)	−0.0740 (27)	−0.4179 (23)	0.03969 (88)	1.3 (6)	H1C(29)	−0.337	−0.582	−0.072	5.2
C(44)	0.0541 (27)	−0.4390 (22)	0.04814 (86)	1.3 (6)	H1C(30)	−0.180	−0.512	−0.021	4.4
C(45)	0.0817 (29)	−0.5140 (23)	0.07524 (95)	2.1 (7)	H1C(32)	−0.081	−0.122	−0.005	3.3
C(46)	−0.0210 (26)	−0.5600 (23)	0.09413 (84)	1.2 (6)	H1C(33)	−0.172	0.022	0.024	4.7
C(47)	−0.1472 (30)	−0.5396 (25)	0.0862 (10)	2.3 (8)	H1C(34)	−0.329	−0.006	0.072	3.2
C(48)	−0.1774 (30)	−0.4618 (25)	0.05869 (98)	2.6 (7)	H1C(35)	−0.402	−0.158	0.088	3.0
C(49)	−0.1606 (27)	0.3466 (23)	−0.18312 (91)	1.3 (6)	H1C(36)	−0.311	−0.293	0.059	3.2
C(50)	−0.1768 (30)	0.2501 (26)	−0.1953 (10)	2.7 (8)	H1C(38)	0.128	−0.221	0.029	3.3
C(51)	−0.1144 (32)	0.1757 (28)	−0.1727 (11)	3.7 (8)	H1C(39)	0.333	−0.186	−0.003	2.8
C(52)	−0.0337 (33)	0.1986 (26)	−0.1431 (11)	3.4 (8)	H1C(40)	0.356	−0.221	−0.065	2.2
C(53)	−0.0087 (32)	0.2883 (29)	−0.1314 (11)	3.6 (9)	H1C(41)	0.202	−0.317	−0.102	3.5
C(54)	−0.0739 (32)	0.3704 (26)	−0.1543 (11)	3.2 (8)	H1C(42)	−0.009	−0.354	−0.073	3.0
C(55)	−0.2526 (26)	0.4148 (22)	−0.26325 (86)	1.9 (6)	H1C(44)	0.127	−0.403	0.036	2.4

Table III (Continued)

atom	x	y	z	B
H1C(45)	0.172	−0.532	0.081	3.2
H1C(46)	0.001	−0.608	0.115	2.2
H1C(47)	−0.215	−0.575	0.099	3.7
H1C(48)	−0.269	−0.439	0.054	3.4
H1C(50)	−0.232	0.237	−0.219	3.5
H1C(51)	−0.130	0.106	−0.180	4.3
H1C(52)	0.007	0.147	−0.128	4.1
H1C(53)	0.051	0.303	−0.108	4.6
H1C(54)	−0.056	0.440	−0.149	4.1
H1C(56)	−0.445	0.468	−0.270	5.8
H1C(57)	−0.444	0.442	−0.341	2.4
H1C(58)	−0.248	0.391	−0.372	3.7
H1C(59)	−0.059	0.353	−0.333	4.1
H1C(60)	−0.054	0.375	−0.264	3.6
H1C(62)	−0.414	0.604	−0.209	3.8
H1C(63)	−0.657	0.616	−0.198	5.4
H1C(64)	−0.765	0.487	−0.166	3.8
H1C(65)	−0.658	0.338	−0.163	2.9
H1C(66)	−0.430	0.318	−0.174	2.3
H1C(68)	−0.241	0.590	−0.151	4.6
H1C(69)	−0.086	0.726	−0.137	3.9
H1C(70)	0.098	0.739	−0.176	3.1
H1C(71)	0.101	0.670	−0.240	6.7
H1C(72)	−0.042	0.544	−0.253	3.1
H1C(74)	−0.055	−0.113	−0.241	4.9
H1C(75)	0.095	−0.074	−0.182	3.7
H1C(76)	0.240	0.061	−0.188	5.8
H1C(77)	0.217	0.165	−0.243	4.6
H1C(78)	0.075	0.132	−0.292	3.3
H1C(80)	−0.375	−0.101	−0.311	3.2
H1C(81)	−0.434	−0.264	−0.325	6.2
H1C(82)	−0.263	−0.393	−0.325	5.3
H1C(83)	−0.034	−0.335	−0.321	5.5
H1C(84)	0.009	−0.165	−0.305	3.0
H1C(86)	−0.037	0.169	−0.342	3.9
H1C(87)	0.041	0.207	−0.405	2.5
H1C(88)	0.046	0.095	−0.456	2.2
H1C(89)	−0.026	−0.062	−0.442	3.3
H1C(90)	−0.088	−0.107	−0.377	3.2
H1C(92)	−0.281	0.001	−0.243	3.5
H1C(93)	−0.468	0.103	−0.220	3.2
H1C(94)	−0.538	0.225	−0.260	6.0
H1C(95)	−0.465	0.244	−0.326	4.7
H1C(96)	−0.284	0.146	−0.346	2.0

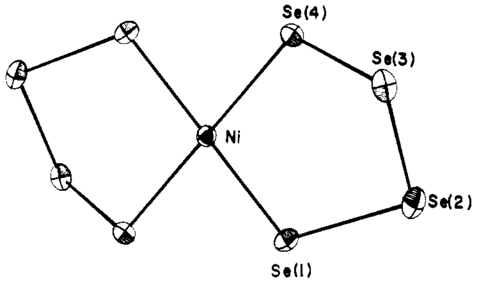

Figure 1. The $Ni(Se_4)_2^{2-}$ ion in $[PEtPh_3]_2[Ni(Se_4)_2]$. The anion has a crystallographically imposed center of symmetry. Here and in Figure 2 the 50% probability ellipsoids are shown.

system. In anticipation of the former group (which is more common), a series of Friedel pairs were collected in addition to the reflections unique in a centrosymmetric monoclinic space group. Examination of the Patterson function confirmed our fears that the space group is $P2_1$ and hence that structure solution involves the determination of two independent formula units. The refinement proceeded smoothly. After the data were corrected for absorption those Friedel pairs showing statistically significant intensities were compared for the two possible directions of the polar axis. Choice of this direction was straightforward: for the particular crystal used that direction resulted in the correct relative magnitudes of the structure amplitudes for 163 out of the 175 Friedel pairs examined. Owing to the number of independent atoms involved and the limited number of data, refinement of this structure was restricted to isotropic motion of the atoms. This is not a serious problem, as the data were collected at −163 °C and anisotropic effects should not be large. Some experimental details are given in Table I.

Additional details on data collection and refinement for both structures are given in Table SI.[13] Tables II and III contain final positional parameters and equivalent isotropic thermal parameters for the Ni and Zn structures, respectively. Table SII[13] contains information on the anisotropic thermal parameters for the Ni structure. Tables SIII[13] and SIV[13] contain structure amplitudes for the two structures.

A preliminary examination of a crystal of $[PPh_4]_2[Mn(Se_4)_2]$ on a CAD4 diffractometer led to cell constants of a = 10.15 (1) Å, b = 13.99 (1) Å, c = 34.21 (3) Å, and β = 92.14 (6)° (−120 °C) and to the systematic absence $0k0$, k odd. The compound is thus isostructural with the Zn complex. Since structure solution and refinement entails, once again, the determination of the positions of two independent formula units, no further work was carried out. Subsequently, the compound was prepared and its structure determined independently.[9]

Results and Discussion

Synthesis. Although $M(S_4)_2^{2-}$ ions (M = Ni,[4,5] Pd,[4] Zn,[5] Hg[6]) are known, very recently some $M(Se_4)_2^{2-}$ ions have been prepared. Indeed there are now more $M(Se_4)_2^{2-}$ ions known than $M(S_4)_2^{2-}$ ions. Adel et al.[7] prepared $M(Se_4)_2^{2-}$ (M = Zn, Cd, Hg) by the reaction of $[Na(15\text{-crown-}5)]_2[Se_4]$ with $M(O_2CCH_3)_2$ in CH_3CN. Banda et al.[8] prepared M = Zn, Cd, Hg, Ni, and Pb ions by the reaction of Se, Na, and MCl_2 in DMF. O'Neal et al.[9] have prepared $Mn(Se_4)_2^{2-}$ by decarbonylation of $Mn_2(CO)_{10}$ with K_2Se_3 in DMF. We find that reaction of $M(S_2COEt)_2$, M = Ni, Pd, Zn, Cd, and Hg, with Se_4^{2-} in the presence of a quaternary phosphonium or ammonium ion in CH_3CN–DMF proceeds smoothly at room temperature to produce $M(Se_4)_2^{2-}$ ions in high yield. Under our reaction conditions, ethyl xanthate is a good leaving group:

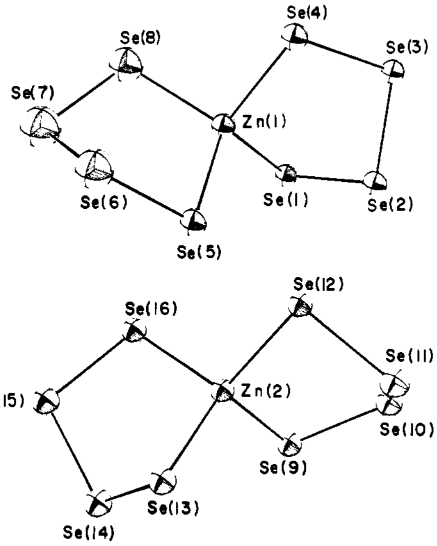

Figure 2. The $Zn(Se_4)_2^{2-}$ ions in $[PPh_4]_2[Zn(Se_4)_2]$.

$$M(S_2COEt)_2 + 2Se_4^{2-} \rightarrow M(Se_4)_2^{2-} + 2S_2COEt^-$$

$$M = Ni, Pd, Zn, Cd, Hg;\ A = N, P;\ R = Et, Ph$$

Presumably this strategy can be applied to other metal ions too. For $Mn(Se_4)_2^{2-}$, $MnCl_2$ turns out to be a more convenient starting material than $Mn(xan)_2$.

Structures. In $[PEtPh_3]_2[Ni(Se_4)_2]$ the anion (Figure 1) has a crystallographically imposed center of symmetry. Some metrical details are provided in Table IV. The Ni atom is nearly square-planar and is bound to two Se_4^{2-} ligands. The $NiSe_4$ ring has a distorted envelope conformation, as is apparent from the torsion angles of Table IV and from the fact that the best least-squares plane through the ring has the following deviations (Å): Ni, 0; Se(1), −0.150 (1); Se(2), −0.247 (1); Se(3), 0.647

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(13) Supplementary material.

Table IV. Selected Bond Distances (Å), Bond Angles (deg), and Torsion Angles (deg) for the $Ni(Se_4)_2^{2-}$ ion in $[PEtPh_3]_2[Ni(Se_4)_2]$

Ni–Se(1)	2.298 (1)	Se(2)–Se(3)	2.321 (1)
Ni–Se(4)	2.315 (1)	Se(3)–Se(4)	2.344 (1)
Se(1)–Se(2)	2.398 (1)		
Se(1)–Ni–Se(4)	100.73 (2)	Se(1)–Se(2)–Se(3)	99.85 (3)
Ni–Se(1)–Se(2)	108.26 (3)	Se(2)–Se(3)–Se(4)	98.10 (3)
Ni–Se(4)–Se(3)	101.30 (3)		
Se(4)–Ni–Se(1)–Se(2)	13.84 (3)		
Ni–Se(1)–Se(2)–Se(3)	20.29 (4)		
Se(1)–Se(2)–Se(3)–Se(4)	−45.29 (3)		
Se(2)–Se(3)–Se(4)–Ni	56.77 (3)		
Se(3)–Se(4)–Ni–Se(1)	−42.93 (3)		

(1); Se(4), −0.560 (1). In $[PPh_4]_2[Ni(Se_4)_2]$[8] it is interesting that both of the independent $NiSe_4$ rings have the half-chair conformation. The Ni–Se distances found here of 2.298 (1) and 2.315 (1) Å appear to be slightly but significantly different (difference = 0.017 (2) Å).[14] They may be compared with a mean Ni–Se distance of 2.297 (7) Å in the PPh_4^+ salt[8] and the mean Ni–Se distance of 2.300 (2) Å in the $NiSe_2$ three-membered ring in the $(WSe_4)Ni(Se_2)^{2-}$ anion.[15] The Se–Ni–Se angle of 100.73 (2)° may be compared with that of 102.0 (4)° in the PPh_4^+ salt[8] and to the S–Ni–S angles of 99.1 (1)[4] or 105.5 (2)°[5] in $[NEt_4]_2[Ni(S_4)_2]$.

The two independent $Zn(Se_4)_2^{2-}$ anions in $[PPh_4]_2[Zn(Se_4)_2]$ are shown in Figure 2, and selected metrical data are given in Table V. Both anions have an approximately tetrahedral Zn center, but the two anions differ in some surprising ways. In particular, the bond angles at Zn(2) are significantly less obtuse than those at Zn(1). All four $ZnSe_4$ rings are best described as having the distorted envelope conformation. The existence of two independent, differently distorted anions in the unit cell presumably arises from the effects of packing forces on these rather flexible anions. It is interesting that the analogous Cd[8] and Mn[9] salts are isostructural with the Zn salt and also contain two independent anions in the cell. While in a different space group, the corresponding Hg salt[8] also crystallizes with two independent anions in the cell. On the other hand, in $[Na(15\text{-crown-}5)]_2[Zn(Se_4)_2]$[7] there is only one independent $Zn(Se_4)_2^{2-}$ anion in the cell. The Zn–Se distances of 2.485 (3) and 2.446 (3) Å found there may be compared with the range 2.450 (5)–2.493 (6) Å found in Table V.

Spectroscopy. The $M(Se_4)_2^{2-}$ anions discussed here show no characteristic stretching vibrations in the 400–250-cm^{-1} region of the IR spectrum and show no characteristic absorptions in the UV-vis region. However, ^{77}Se NMR spectroscopy offers a straightforward and informative means of characterization for these anions in solution.

While MSe_4 rings generally have four crystallographically independent Se atoms in the solid state, for any $M(Se_4)_2^{2-}$ anion in solution one expects only two resonances in the ^{77}Se NMR spectrum, one arising from the Se atoms bound to the central metal atom ("metal bound") and the other from the Se atoms in the ring ("ring").[16] All the $M(Se_4)_2^{2-}$ complexes reported here (except for M = Mn, which is paramagnetic) display the expected two-line spectrum (see Table VI). The assignment of the metal-bound and ring resonances depends upon observation of satellites from an NMR-active central metal or from expected analogies within a triad.

In the $MQ(Se_4)_2^{2-}$ anions (M = Mo, W; Q = O, S Se)[17,18] the metal-bound resonances for M = W show satellites arising from coupling to ^{183}W (spin = $^1/_2$; natural abundance = 14.3%), and for both Mo and W these resonances shift more with variation of the terminal Q atom than do the ring resonances.[17] For these W(IV) and Mo(IV) (d^2) systems the metal-bound resonances occur downfield of the ring resonances.

Within the Ni triad only Pt has an NMR-active nucleus (spin = $^1/_2$; ^{195}Pt, natural abundance = 33.8%). The reaction of $Pt(Se_4)_3^{2-}$[19,20] with excess BH_4^- affords in situ the $Pt(Se_4)_2^{2-}$ species as judged by its clean, two-line ^{77}Se NMR spectrum (δ 727 and 642 ppm). The resonance at 727 ppm shows coupling to ^{195}Pt and thus is the metal-bound resonance. By analogy we assign the downfield resonances in the related Ni and Pd complexes as metal bound (Table VI).

Within the zinc triad, both Cd and Hg have NMR-active nuclei (spin = $^1/_2$; ^{111}Cd, ^{113}Cd, and ^{199}Hg, natural abundance = 12.26%, 12.75%, and 16.84%). The observation of satellites from these nuclei allows definite assignment of metal-bound resonances in these M(II) (d^{10}) species. Surprisingly, the metal-bound resonances occur upfield of the ring resonances, opposite to the trend in the Mo and W and Ni-triad complexes. The ^{77}Se NMR resonances of the $Zn(Se_4)_2^{2-}$ anion are assigned by analogy to those of $Cd(Se_4)_2^{2-}$ and $Hg(Se_4)_2^{2-}$ (see Table VI).

A possible explanation for the reversal of the relative positions of the metal-bound and ring resonances on going from Mo and W and the Ni triad to the Zn triad can be made on the basis of electron density of the Se_4^{2-} ring and the central metal. For the uncomplexed Se_4^{2-} anion the Lewis dot structure gives formal charges of −1 for the terminal Se atoms (which would be metal bound were there a metal present) and of 0 for the ring Se atoms. Shielding arguments then predict that the terminal Se atoms, with greater electron density, should resonate upfield of the ring Se atoms. If one then considers just the d electrons of the metal, Zn, Cd, and Hg are all d^{10} metals and cannot accept electron density from the Se_4^{2-} ligands. The Se_4 rings in these anions thus retain most of the electron density of the Se_4^{2-} anion, and consequently, each anion should display the metal-bound resonance upfield of the ring resonance. In the Ni triad the metals are d^8 and somewhat poorer in electron density. Electron donation from the Se_4^{2-} ligands to the metal apparently is sufficiently great to reverse the trend seen for the Zn triad so that the metal-bound resonances occur downfield of the ring resonances. Of course, the Mo and W anions have electron-poor d^2 metals, and so these show the same trend as the Ni triad.

Structural data for Se_4-containing salts,[21-23] organic compounds,[24] and inorganic complexes,[7,9,10,17,25] provide possible support for the inferred differences in electron donation from Se_4^{2-} ligands to various metals. In Table VII we tabulate average distances in a number of these compounds. Unfortunately, owing to individual and significant differences within the Se_4 rings in many cases and in some instances to the inherent inaccuracies of the structure determinations, firm conclusions cannot be reached from the data of Table VII concerning possible differences in the two

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(14) The reliability of the estimated standard deviations in both the Ni and Zn structures may be judged from the averaging of the phenyl C–C distances. In the Ni structure the 18 distances, which range from 1.374 (8) to 1.404 (7) Å, average 1.389 (8) Å; in the Zn structure the 96 distances, which range from 1.27 (4) to 1.52 (4) average 1.38 (5) Å. Since the standard deviations as estimated from the inverse matrix agree well with those estimated for a single observation from the values averaged, we believe the standard deviations are reliable.

(15) Ansari, M. A.; Chau, C.-N.; Mahler, C. H.; Ibers, J. A. *Inorg. Chem.* **1989**, *28*, 650–654.

(16) The MSe_4 five-membered ring adopts either an envelope or half-chair conformation in the solid state, and interconversions among these conformations probably account for the observed spectra from the $M(Se_4)_2^{2-}$ species in solution at room temperature. In the $MQ(Se_4)_2^{2-}$ system, this fluxional behavior was not stopped to −60 °C (see ref 17). The noninterconversion of such species as $(Se_2)W_2Se_4(Se_4)^{2-}$ and $(Se_3)W_2Se_4(Se_3)^{2-}$ in solution (see ref 10) seems to rule out a dissociative exchange mechanism as the cause of the observed fluxional behavior.

(17) Wardle, R. W. M.; Mahler, C. H.; Chau, C.-N.; Ibers, J. A. *Inorg. Chem.* **1988**, *27*, 2790–2795.

(18) O'Neal, S. C.; Kolis, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 1971–1973.

(19) Reaction of $Pt(xan)_2$ with polyselenide solution affords $Pt(Se_4)_3^{2-}$, rather than $Pt(Se_4)_2^{2-}$. See: Ansari, M. A.; Ibers, J. A. *Inorg. Chem.* **1989**, *28*, 4068–4069.

(20) Ansari, M. A.; Ibers, J. A. Unpublished results.

(21) Brese, N. E.; Randall, C. R.; Ibers, J. A. *Inorg. Chem.* **1988**, *27*, 940–943.

(22) König, T.; Eisenmann, B.; Schäfer, H. *Z. Anorg. Allg. Chem.* **1983**, *498*, 99–104.

(23) König, T.; Eisenmann, B.; Schäfer, H. *Z. Naturforsch., B* **1982**, *37B*, 1245–1249.

(24) Foss, O.; Janickis, V. *J. Chem. Soc., Chem. Commun.* **1977**, 833–834.

(25) Ginsberg, A. P.; Osborne, J. H.; Sprinkle, C. R. *Inorg. Chem.* **1983**, *22*, 1781–1790.

Table V. Selected Metrical Data for the $Zn(Se_4)_2^{2-}$ Anions in $[PPh_4]_2[Zn(Se_4)_2]$

Bond Distance (Å)			
Zn(1)–Se(1)	2.463 (5)	Zn(2)–Se(9)	2.480 (5)
Zn(1)–Se(4)	2.475 (5)	Zn(2)–Se(12)	2.450 (5)
Zn(1)–Se(5)	2.464 (5)	Zn(2)–Se(13)	2.471 (5)
Zn(1)–Se(8)	2.477 (6)	Zn(2)–Se(16)	2.493 (6)
Se(1)–Se(2)	2.328 (5)	Se(9)–Se(10)	2.322 (6)
Se(3)–Se(4)	2.335 (5)	Se(11)–Se(12)	2.330 (6)
Se(5)–Se(6)	2.327 (6)	Se(13)–Se(14)	2.325 (5)
Se(7)–Se(8)	2.401 (7)	Se(15)–Se(16)	2.347 (6)
Se(2)–Se(3)	2.341 (5)	Se(10)–Se(11)	2.332 (5)
Se(6)–Se(7)	2.424 (7)	Se(14)–Se(15)	2.364 (6)
Bond Angle (deg)			
Se(1)–Zn(1)–Se(4)	107.2 (2)	Se(9)–Zn(2)–Se(12)	104.9 (2)
Se(5)–Zn(1)–Se(8)	108.9 (2)	Se(13)–Zn(2)–Se(16)	104.7 (2)
Zn(1)–Se(1)–Se(2)	89.9 (2)	Zn(2)–Se(9)–Se(10)	100.7 (2)
Zn(1)–Se(4)–Se(3)	98.8 (2)	Zn(2)–Se(12)–Se(11)	93.7 (2)
Zn(1)–Se(5)–Se(6)	97.0 (2)	Zn(2)–Se(13)–Se(14)	91.0 (2)
Zn(1)–Se(8)–Se(7)	99.9 (2)	Zn(2)–Se(16)–Se(15)	100.9 (2)
Se(1)–Se(2)–Se(3)	100.9 (2)	Se(9)–Se(10)–Se(11)	101.9 (2)
Se(2)–Se(3)–Se(4)	102.7 (2)	Se(10)–Se(11)–Se(12)	99.3 (2)
Se(5)–Se(6)–Se(7)	101.8 (2)	Se(13)–Se(14)–Se(15)	101.1 (2)
Se(6)–Se(7)–Se(8)	101.8 (2)	Se(14)–Se(15)–Se(16)	101.7 (2)
Torsion Angle (deg)			
Se(4)–Zn(1)–Se(1)–Se(2)	44.4 (2)		
Zn(1)–Se(1)–Se(2)–Se(3)	−60.1 (2)		
Se(1)–Se(2)–Se(3)–Se(4)	58.4 (2)		
Se(2)–Se(3)–Se(4)–Zn(1)	−24.7 (2)		
Se(3)–Se(4)–Zn(1)–Se(1)	−12.9 (2)		
Se(8)–Zn(1)–Se(5)–Se(6)	−29.6 (2)		
Zn(1)–Se(5)–Se(6)–Se(7)	50.2 (2)		
Se(5)–Se(6)–Se(7)–Se(8)	−55.6 (2)		
Se(6)–Se(7)–Se(8)–Zn(1)	32.9 (2)		
Se(7)–Se(8)–Zn(1)–Se(5)	−2.6 (2)		
Se(12)–Zn(2)–Se(9)–Se(10)	6.3 (2)		
Zn(2)–Se(9)–Se(10)–Se(11)	30.1 (2)		
Se(9)–Se(10)–Se(11)–Se(12)	−59.3 (2)		
Se(10)–Se(11)–Se(12)–Zn(2)	58.9 (2)		
Se(11)–Se(12)–Zn(2)–Se(9)	−39.5 (2)		
Se(16)–Zn(2)–Se(13)–Se(14)	46.3 (2)		
Zn(2)–Se(13)–Se(14)–Se(15)	−61.3 (2)		
Se(13)–Se(14)–Se(15)–Se(16)	56.1 (2)		
Se(14)–Se(15)–Se(16)–Zn(2)	−21.8 (2)		
Se(15)–Se(16)–Zn(2)–Se(13)	−15.6 (2)		

Deviations from Least-Squares Plane (Å)

plane 1: Zn(1), −0.040 (2); Se(1), 0.757 (5); Se(2), −0.388 (5); Se(3), 0.635 (5); Se(4), 0.231 (5)
plane 2: Zn(1), 0.123 (4); Se(5), −0.295 (3); Se(6), 0.595 (4); Se(7), −0.522 (4); Se(8), 0.047 (4)
plane 3: Zn(2), −0.223 (5); Se(9), −0.047 (5); Se(10), 0.456 (5); Se(11), −0.619 (5); Se(12), 0.472 (5)
plane 4: Zn(2), 0.308 (3), Se(13), −0.516 (3); Se(14), 0.665 (3); Se(15), −0.335 (3); Se(16), −0.007 (3)

Interplanar Angle (deg)

1 and 2, 95.4; 3 and 4, 99.9

different sets of Se–Se distances, external (a) and internal (b). But it appears that the internal distance is longer than the external distance in the uncomplexed anion and perhaps in the organic tetraselanes, while the reverse may be true on complexation to a metal with the possibility that differences are greatest in the d^2 systems.

Such an alternation was first observed for the S–S distances in Cp_2MS_4 (M = Mo,[26] W[27]), and it has been proposed that this alternation arises from metal(d-π)–sulfur(d-π) orbital overlap. In essence if the metal-bound S atoms give electrons to the metal, they have less density left to bind to the ring S atoms, and hence the external bonds are lengthened. This is also seen in the present Se anions, so that both the reversal in metal-bound and ring resonances and perhaps the greatest change in external vs internal distances occur for those metals best able to accept electron density from the Se_4^{2-} ligands.

Table VI. ^{77}Se NMR Resonances in $M(Se_4)_2^{2-}$ Anions[a]

M	d	δ(Se) metal bound	δ(Se) ring
Ni	d^8	820	748
Pd	d^8	893	758
Pt	d^8	727 (384)[b]	642
Zn	d^{10}	127	598
Cd	d^{10}	62 (255)[c]	608
Hg	d^{10}	76 (1265)[d]	594

[a] Room-temperature, DMF solvent, $\delta(Me_2Se) = 0$. [b] ^{195}Pt $^1J_{Pt-Se}$ satellites (in Hz). [c] $^1J_{Cd-Se}$ satellites (either ^{111}Cd or ^{113}Cd). [d] ^{199}Hg $^1J_{Hg-Se}$ satellites.

Another interesting trend in ^{77}Se NMR resonances can be seen in Table VIII, where the resonances are compared for isoelectronic anions within a triad. Empirically one finds that resonances of those anions containing second-row metals are shifted more than their first- or third-row-metal counterparts, with the shift being downfield for the Mo and Ni triads and upfield for the Zn triad. Electron density arguments can again be invoked here. The lowest unoccupied orbitals on Se are the 5s and 4d electron shells, and these are the orbitals that are being filled in second-row transition metals. One expects that the orbital overlap of Se with second-row transition metals is better than that with either first- (4s, 3d) or third-row (6s, 5d) metals. As long as there are d-electron vacancies then, the Se atoms donate electron density to the metal and are deshielded with concomitant shift downfield of the resonance. The greatest downfield shift in a triad should occur for the second-row metal. When no such donation of electron density from selenium to the metal is possible, as in the d^{10} anions of the Zn triad, decreased shielding of the second-row metal does not occur. In fact, Cd, with the best overlap in this simple picture, is shielded relative to both Zn and Hg.

Structural data provide further support for these overlap arguments. The average metal–selenium distance in $[PPh_4]_2[Zn(Se_4)_2]$ (2.471 (13) Å) is much longer than that in $[PEtPh_3]_2[Ni(Se_4)_2]$ (2.307 (12) Å). This 0.16 (2)-Å difference is approximately 3 times that expected on the basis of radii[28] for four-coordinate Ni(II) (0.55 Å) and Zn(II) (0.60 Å). The ability of d^8 Ni(II) to accept electron density from the Se_4^{2-} ligand seems a likely cause for its much shorter M–Se bond length.

The influence of overlap can also be seen in the absolute difference between the metal-bound and ring resonances, which is greatest for the second-row metals (ignoring trends in ordering). Thus, the metal-bound and ring resonances for $MoQ(Se_4)_2^{2-}$ (Q = Se, S, O) are 760, 726, and 566 ppm apart compared with those of 710, 680, and 548 ppm apart for the $WQ(Se_4)_2^{2-}$ resonances;[17] the $Ni(Se_4)_2^{2-}$, $Pd(Se_4)_2^{2-}$, and $Pt(Se_4)_2^{2-}$ resonances are 72, 135, and 85 ppm apart, respectively; the $Zn(Se_4)_2^{2-}$, $Cd(Se_4)_2^{2-}$, and $Hg(Se_4)_2^{2-}$ resonances are 471, 546, and 518 ppm apart, respectively. Since second-row metals have the greatest absolute shift and the metal affects the metal-bound resonance more than the ring resonance, this observation is consistent with the influence of d-electron density on Se chemical shifts.

A more general example of this influence can be seen by comparing metal-bound Se resonances within a row as a function of d-electron count, e.g. $MoSe_4^{2-}$ (1643 ppm, d^0), $MoSe(Se_4)_2^{2-}$ (1163 ppm, d^2),[17] $Pd(Se_4)_2^{2-}$ (748 ppm, d^8), and $Cd(Se_4)_2^{2-}$ (62 ppm, d^{10}). As the number of d electrons on the central metal increases, there is thus a shift upfield.

Reaction of $Ni(Se_4)_2^{2-}$ and $Zn(Se_4)_2^{2-}$ with dimethyl acetylenedicarboxylate is clean and facile. Their single-line ^{77}Se NMR spectra indicate formation of the diselenene products $M(Se_2C_2(COOCH_3)_2)_2^{2-}$. These ions result conceptually from insertion of the acetylene across the external Se–Se bonds of the Se_4^{2-} ligands. The complexes also show characteristic strong absorbances, probably from charge transfer, in their electronic (UV–vis)

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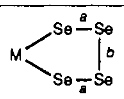
(26) Block, H. D.; Allmann, R. *Cryst. Struct. Commun.* **1975**, *4*, 53–56.
(27) Davis, B. R.; Bernal, I.; Köpf, H. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 921–922.
(28) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751–767.

Table VII. Average Distances (Å) in Various Compounds with $\mathrm{Se_4}$ Moieties[a]



compd	M–Se	*a*	*b*	*b* − *a*
$\mathrm{[PPN]_2[Se_4]}$[b]		2.312 (3)[n]	2.397 (4)	0.085 (5)
$\mathrm{[Ba(222crypt)][Se_4]}$[c]		2.325 (5)	2.344 (5)	0.019 (7)
$\mathrm{[Ba(en)_4][Se_4]}$[d]		2.329 (3)	2.342 (4)	0.013 (5)
$\mathrm{(NC_4H_8O)_2(Se_4)}$[e]	1.836 (6) (Se–N)	2.336 (2)	2.356 (2)	0.020 (3)
$\mathrm{(NC_5H_{10})_2(Se_4)}$[e]	1.832 (6) (Se–N)	2.327 (2)	2.347 (2)	0.020 (3)
$\mathrm{[NEt_4]_2[MoO(Se_4)_2]}$[f]	2.492 (24)	2.41 (3)	2.304 (2)	−0.11 (3)
$\mathrm{[PPh_4]_2[MoSe(Se_4)_2]}$[g]	2.473 (30)	2.42 (4)	2.30 (1)	−0.13 (4)
$\mathrm{[AsPh_4]_2[WS(Se_4)_2]}$[f]	2.472 (25)	2.47 (7)	2.301 (2)	−0.17 (7)
$\mathrm{[PPh_4]_2[(Se_2)W_2Se_4(Se_4)]}$[h]	2.494 (23)	2.321 (9)	2.282 (7)	−0.039 (11)
$\mathrm{[(dmpe)_2Ir(Se_4)]Cl}$[i]	2.546 (4)	2.33 (3)	2.28 (4)	−0.04 (4)
$\mathrm{[Na(15\text{-}crown\text{-}5)]_2[Zn(Se_4)_2]}$[j]	2.466 (28)	2.330 (9)	2.326 (9)	−0.01 (9)
$\mathrm{[Na(15\text{-}crown\text{-}5)]_2[Cd(Se_4)_2]}$[j]	2.642 (14)	2.34 (1)	2.33 (1)	−0.01 (2)
$\mathrm{[Na(15\text{-}crown\text{-}5)]_2[Hg(Se_4)_2]}$[j]	2.646 (22)	2.325 (10)	2.33 (1)	0.01 (2)
$\mathrm{[PPh_4]_2[Mn(Se_4)_2]}$[k]	2.544 (13)	2.311 (10)	2.32 (2)	0.01 (2)
$\mathrm{[PPh_4]_2[Zn(Se_4)_2]}$[l]	2.471 (13)	2.34 (3)	2.36 (4)	0.02 (5)
$\mathrm{[PEtPh_3]_2[Ni(Se_4)_2]}$[l]	2.307 (12)	2.37 (4)	2.321 (1)	−0.05 (4)
$\mathrm{[PPh_4]_2[Pt(Se_4)_3]}$[m]	2.485 (5)	2.339 (2)	2.327 (8)	−0.012 (8)

[a] Abbreviations used: PPN = bis(triphenylphosphine)nitrogen(1+); 2,2,2crypt = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8,8,8]hexacosane; en = ethylenediamine; $\mathrm{NC_4H_8O}$ = morpholino; $\mathrm{NC_5H_{10}}$ = piperidino; dmpe = bis(dimethylphosphino)ethane. [b] Reference 21. [c] Reference 22. [c] Reference 23. [e] Reference 24. [f] Reference 17. [g] Reference 18. [h] Reference 10. [i] Reference 25. [j] Reference 7. [k] Reference 9. [l] This work. [m] Reference 20. [n] The number in parentheses is the estimated standard deviation of a single observation. This number is sometimes large owing to deviations (often statistically significant) among the values averaged.

Table VIII. ^{77}Se NMR Resonances (ppm) for Isostructural Complexes within the Same Triad[a]

	d^0				d^8			d^{10}	
	t				t	b		m	r
$\mathrm{MoSe_4^{2-}}$ [b]	1643			$\mathrm{Ni(WSe_4)_2^{2-}}$ [e]	1628	994	$\mathrm{Zn(Se_4)_2^{2-}}$ [f]	127	598
$\mathrm{WSe_4^{2-}}$ [b]	1235			$\mathrm{Pd(WSe_4)_2^{2-}}$ [e]	1673	1135	$\mathrm{Cd(Se_4)_2^{2-}}$ [f]	62	608
	d^2			$\mathrm{Pt(WSe_4)_2^{2-}}$ [e]	1627	949	$\mathrm{Hg(Se_4)_2^{2-}}$ [f]	76	594
	t	m	r		m	r		s	
$\mathrm{MoSe(Se_4)_2^{2-}}$ [b]	2357	1163	402	$\mathrm{Ni(Se_4)_2^{2-}}$ [f]	820	748	ZnSe[g]	−1622	
$\mathrm{WSe(Se_4)_2^{2-}}$ [b]	1787	1034	324	$\mathrm{Pd(Se_4)_2^{2-}}$ [f]	893	758	CdSe[g]	−1743	
$\mathrm{MoS(Se_4)_2^{2-}}$ [b]		1122	396	$\mathrm{Pt(Se_4)_2^{2-}}$ [h]	727	642	HgSe[g]	−1365	
$\mathrm{WS(Se_4)_2^{2-}}$ [b]		993	313						
$\mathrm{MoO(Se_4)_2^{2-}}$ [b]		946	380						
$\mathrm{WO(Se_4)_2^{2-}}$ [b]		828	280						
$\mathrm{Mo(Se_2C_2R_2)_3^{2-}}$ [c]		990							
$\mathrm{W(Se_2C_2R_2)_3^{2-}}$ [d]		840							

[a] Abbreviations: t = terminal, m = metal bound, r = ring, b = bridging, and s = solid state. [b] Reference 17. [c] Reference 29. [d] Reference 30. [e] References 3 and 15. [f] This work. [g] Reference 31. [h] Reference 20.

spectra. Comparison of the ^{77}Se NMR resonances from diselenene Se atoms with those of metal-bound Se atoms in their precursor complexes shows an upfield shift on reaction with DMA for those complexes with d electron vacancies but a downfield shift for d^{10} Zn, i.e. $\mathrm{MoSe(Se_4)_2^{2-}}$ to $\mathrm{Mo(Se_2C_2R_2)_3^{2-}}$ (1163 to 990 ppm),[29] $\mathrm{WSe(Se_4)_2^{2-}}$ to $\mathrm{W(Se_2C_2R_2)_3^{2-}}$ (1034 to 840 ppm),[30] $\mathrm{Ni(Se_4)_2^{2-}}$ to $\mathrm{Ni(Se_2C_2R_2)_2^{2-}}$ (820 to 540 ppm), but $\mathrm{Zn(Se_4)_2^{2-}}$ to $\mathrm{Zn(Se_2C_2R_2)_2^{2-}}$ (127 to 180 ppm) (R = $\mathrm{COOCH_3}$). Since the electron-withdrawing methoxy-carboxylic acid groups should deshield the diselenene Se center relative to the $\mathrm{Se_4}$ ring Se center, the downfield shift seen for Zn is the one expected. The upfield shift seen for Mo, W, and Ni cannot arise from the diselenene ligand, since it is the same in each complex. Perhaps the diselenene ligand, which can be viewed as somewhat delocalized,[31] is a poorer donor of electrons to those metals that can accept them than is the $\mathrm{Se_4^{2-}}$ ligand.

Relatively little theoretical work seems to have been done on ^{77}Se NMR spectroscopy. Koch, Lutz, and Nolle[32] showed that the main contribution to chemical shifts arises from the number of valence electrons about the selenium atoms (a theory originally proposed by Willig and Sapoval for ^{125}Te[33]). While the theory is applicable in the strictest sense only to rather symmetric, solid-state binary main-group chalcogenides MQ (M = Zn, Cd, Hg, Sn, Pb; Q = Se, Te), the results are still consistent with our observations, since the ability of the metal to accept electrons affects the Se valence electron count. Kidd has proposed the three

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(29) Mahler, C. H.; Ansari, M. A.; Ibers, J. A. Unpublished results.
(30) Ansari, M. A.; Mahler, C. H.; Ibers, J. A. *Inorg. Chem.* **1989**, *28*, 2669–2674.
(31) Davison, A.; Shawl, E. T. *Inorg. Chem.* **1970**, *9*, 1820–1825.
(32) Koch, W.; Lutz, O.; Nolle, A. *Z. Physik A* **1978**, *289*, 17–20.
(33) Willig, A.; Sapoval, B. *J. Phys., Lett.* **1977**, *38*, L57–L60.

factors that most affect shielding and thus chemical shift are oxidation state, coordination symmetry, and ligand substitution.[34] Since our comparisons are among atoms of the same oxidation state (-1 for metal bound; 0 for ring; -2 for "terminal" or "bridging") and the coordination symmetry of these Se atoms is low, the largest contribution may arise from ligand substitution. Although it is a reversal of customary coordination chemistry to regard metals as ligands, for the ^{77}Se NMR chemical shifts it is the effect of metals as ligands that seems to have the greatest contribution.

Note Added in Proof. New syntheses and some crystal structures have been reported for $[PPh_4]_2[M(Se_4)_2]$, M = Mn,[35] Pd,[36] and Pt.[36] Huang et al.[37] have synthesized and determined the crystal structure of $[PPh_4]_3[Sn(Se_4)_3]$, whose synthesis and structure were reported earlier.[38] Huang et al.[37] also provide ^{77}Se NMR data for $M(Se_4)_2^{2-}$ species, M = Zn, Cd, Hg, and Ni. The resonances they report are about 10 ppm downfield from those reported here. Their assignment of resonances to ring and metal-bound Se centers in M = Zn, Cd, and Hg is opposite to our assignment reported here. They report no coupling data.

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Supplementary Material Available: Additional crystallographic details (Table SI) and anisotropic thermal parameters for the Ni structure (Table SII) (2 pages); observed and calculated structure amplitudes (×10) for the Ni (Table SIII) and Zn (Table SIV) structures (51 pages). Ordering information is given on any current masthead page.

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(34) Kidd, R. G. In *The Multinuclear Approach to NMR Spectroscopy*; Lambert, J. B., Riddell, F. G., Eds.; NATO ASI Series C, No. 103; D. Reidel: Dordrecht, The Netherlands, 1983; pp 329-341.

(35) Kräuter, G.; Ha-Eierdanz, M.-L.; Müller, U.; Dehnicke, K. *Z. Naturforsch. B* **1990**, *45*, 695-700.

(36) Kräuter, G.; Dehnicke, K.; Fenske, D. *Chem.-Ztg.* **1990**, *114*, 7-9.

(37) Huang, S.-P.; Dhingra, S.; Kanatzidis, M. G. *Polyhedron* **1990**, *9*, 1389-1395.

(38) Banda, R. M. H.; Cusick, J.; Scudder, M. L.; Craig, D. C.; Dance, I. G. *Polyhedron* **1989**, *8*, 1999-2001.

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Ring Expansion and Equilibration in Organophosphazenes and the Relationship to Polymerization

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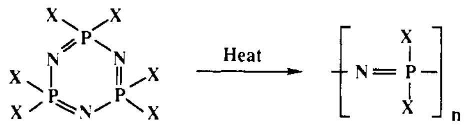
A series of cyclic trimeric phosphazenes that bear both halogen and organic side groups have been found to undergo ring expansion–equilibration reactions at elevated temperatures. Compounds $N_3P_3F_5CMe_3$, $N_3P_3F_5Ph$, *non-gem*-$N_3P_3F_4(CMe_3)_2$, $N_3P_3F_4Ph_2$, $N_3P_3Cl_4Me_2$, $N_3P_3Cl_4Et_2$, $N_3P_3Cl_3Me_3$, and $N_3P_3Cl_3Et_3$ yield cyclic tetramers, pentamers, hexamers, and, in some cases, heptamers, octamers, and nonamers when heated. The cyclic tetramers $(NPClMe)_4$ and $(NPClEt)_4$ also equilibrate to a range of cyclic species that range from trimer to hexamer. Several of these equilibrations also lead to the formation of high polymers. The results are discussed in terms of possible mechanisms for ring–ring equilibration and polymerization.

It is known that certain cyclophosphazenes such as $(NPF_2)_3$ or $(NPCl_2)_3$ (**1**) polymerize to high polymers (**2**) when heated at temperatures between 250 and 350 °C (Scheme I). This is the starting point for the synthesis of a wide range of stable and useful organophosphazene high polymers.[1-7] On the other hand, cyclophosphazenes such as $(NPMe_2)_3$, $(NPPh_2)_3$, or $[NP(OCH_2CF_3)_2]_3$ (**3**)[8-11] undergo thermal ring-expansion reactions but do not give high polymers (Scheme II). This is a mechanistic anomaly that has an important bearing on attempts to synthesize new classes of phosphazene high polymers.

In the present work, we have selected a number of cyclophosphazenes that occupy an intermediate position: they contain both halogeno and organic side groups. When heated they can yield both small-molecule ring expansion products *and* high polymers. Seemingly minor changes within these structures can tip the balance in favor of either of the two extremes. By studying such systems, we hoped to understand the relationship between side group structure in polyphosphazenes and their ability to polymerize.

Scheme I



1 2

X = F or Cl n ~ 15,000

The compounds studied are shown as **7–16**. These were synthesized by methods described previously.[10,12-16] The high polymers obtained from these cyclophosphazenes have been described in another paper.[17] Here we discuss the macromolecules only with respect to their coexistence with the ring–ring equilibration products. Thus, the focus of this paper is on the small-molecule reaction products and on the relationship between the mechanisms of ring–ring equilibration and polymerization. This topic is of practical importance for three reasons. First, it is related to the choice of monomers for conversion to high polymers. Second, it provides information that may allow an understanding of the high-temperature thermal stabilities of phosphazene high

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(1) Allcock, H. R.; Kugel, R. L. *J. Am. Chem. Soc.* **1965**, *87*, 4216.

(2) Allcock, H. R.; Kugel, R. L.; Valan, K. J. *Inorg. Chem.* **1966**, *5*, 1709.

(3) Allcock, H. R.; Kugel, R. L. *Inorg. Chem.* **1966**, *5*, 1716.

(4) Allcock, H. R. *ACS Symp. Ser.* **1988**, *No. 360*, 250.

(5) Tate, D. P. *J. Polym. Sci., Polym. Symp.* **1974**, *48*, 33.

(6) Singler, R. E.; Hagnauer, G. L.; Sicka, R. W. *ACS Symp. Ser.* **1974**, 33.

(7) Penton, H. R. *ACS Symp. Ser.* **1988**, *No. 360*, 277.

(8) Allcock, H. R.; Patterson, D. B. *Inorg. Chem.* **1977**, *16*, 197.

(9) Herring, D. L. *Chem. Ind.* (*London*) **1960**, 717.

(10) Allcock, H. R.; Moore, G. Y. *Macromolecules* **1975**, *8*, 377.

(11) Allcock, H. R.; Schmutz, J. L.; Kosydar, K. M. *Macromolecules* **1978**, *11*, 179.

(12) Allcock, H. R.; Desorcie, J. L.; Wagner, L. J. *Inorg. Chem.* **1985**, *24*, 333.

(13) Allcock, H. R.; Harris, P. J.; Connolly, M. S. *Inorg. Chem.* **1981**, *20*, 11.

(14) Allcock, H. R.; Desorcie, J. L.; Rutt, J. S. *Organometallics* **1988**, *7*, 612.

(15) Allen, C. W.; Ramachandran, K. *J. Am. Chem. Soc.* **1982**, *104*, 2396.

(16) Allen, C. W.; Moeller, T. *Inorg. Chem.* **1968**, *11*, 2177.

(17) Allcock, H. R.; McDonnell, G. S.; Desorcie, J. L. *Macromolecules*, in press.

(18) It was recognized that a potential error in the analysis was the possible equilibration of chloro- or fluorophosphazene small molecules in the mass spectrometer. However, no evidence was found for equilibration when pure trimers or tetramers, **7–16**, were injected into the instrument as controls.

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