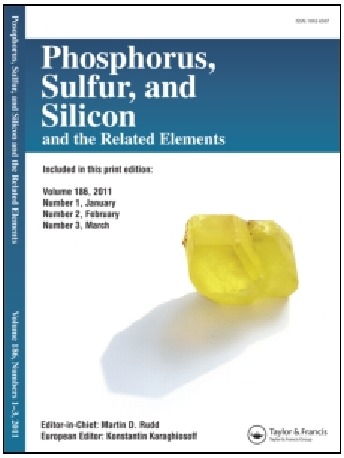

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Phosphor-1,1-Diselenolato Metal Complexes of Group 11 and 12

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Phosphor-1,1-Diselenolato Metal Complexes of Group 11 and 12

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Several copper and silver clusters containing diselenophosphate ligands such as tetranuclear $[Cu\{Se_2P(OR)_2\}]_4$*, hexanuclear* $[Ag\{Se_2P(OR)_2\}]_6$*, octanuclear* $[Cu_8(\mu_8\text{-}Se)\{Se_2P(OR)_2\}_6]$*,* $[Ag_8(\mu_8\text{-}Se)\{Se_2P(OR)_2\}_6]$*,* $[Cu_8(\mu_8\text{-}X)\{Se_2P(OR)_2\}_6](PF_6)$*,* $[Ag_8(\mu_8\text{-}X)\{Se_2P(OR)_2\}_6](PF_6)$*, decanuclear* $[Ag_{10}(\mu_{10}\text{-}Se)\{Se_2P(OR)_2\}_8]$*, undecanuclear* $[Cu_{11}(\mu_9\text{-}Se)(\mu_3\text{-}X)_3\{Se_2P(OR)_2\}_6]$*,* $[Ag_{11}(\mu_9\text{-}Se)(\mu_3\text{-}X)_3\{Se_2P(OR)_2\}_6]$*, and dodecanuclear* $[Cu_{12}(P_2Se_6)\{Se_2P(OR)_2\}_8]$ *have been isolated. All these clusters were well characterized in the solid-state and solution phase by elemental analysis, positive FAB mass spectrometry, multinuclear NMR* (^{1}H, ^{31}P, *and* ^{77}Se)*, and single crystal X-ray diffraction. In addition, tetranuclear zinc clusters* $[Zn_4(\mu_4\text{-}Se)\{Se_2P(OPr)_2\}_6]$*, and* $[Zn_4(\mu_4\text{-}O)\{Se_2P(OR)_2\}_6]$ *(R = Et,* ^{i}Pr*) also are synthesized and characterized. Solution studies of both* $[M\{Se_2P(OEt)_2\}_2]_\infty$ *and* $[M_2\{Se_2P(O^{i}Pr)_2\}_4]$ *(M = Zn, Cd) which display a monomer-dimer equilibrium in solution were performed by VT* ^{31}P *NMR in* CD_2Cl_2*.*

Keywords Copper and silver clusters; diselenophosphate ligand; zinc and cadmium compounds

INTRODUCTION

Under the guidance of Professor John P. Fackler, Jr., I learned the rich metal-sulfur chemistry especially for the 1, 1-dithiolato metal compounds.[1–4] When I started the academic career in spring 1997, a logical thinking was why not going for the metal-selenium chemistry? With this naive idea and a little bit of luck, my choice of selenium donor ligands, diselenophosphates (dsep), turns out very successful toward the coordination chemistry of the metal dialkyl diselenophosphates especially for group 11 and 12 metals. This type of ligand was first made by

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Zingaro et al. in 1968.[2] Over the years the preparation of various dialkyl diselenophosphates and investigations of spectroscopic properties of several main group and transitional metal complexes were reported.[6–9] Powder X-ray patterns of some of the compounds also were included. However, to our surprise the single crystal X-ray diffraction study of the phosphor-1, 1-diselenolato complex of any element never had been reported until the selenide-centered Cu_8 cuboidal cluster, $[Cu_8(\mu_8\text{-}Se)\{Se_2P(O^iPr)_2\}_6]$, was published in 1998 from this group.[10] Later we found this type of ligand is a good selenium atom transfer reagent under acid conditions as evidenced from several structurally characterized selenide-centered metal clusters such as $Ag_8(\mu_8\text{-}Se)\{Se_2P(OR)_2\}_6$[11] $Ag_{10}(\mu_{10}\text{-}Se)\{Se_2P(OR)_2\}_8$,[12] $M_{11}(\mu_9\text{-}Se)(\mu_3\text{-}X)_3\{Se_2P(OR)_2\}_6$ (M = Cu, Ag; X = Br, I),[13,14] and $Zn_4(\mu_4\text{-}Se)\{Se_2P(OPr)_2\}_6$.[15] Besides the unique pattern of ^{31}P NMR spectrum of the ligand in the metal complexes, normally a singlet flanked with a set of satellites, coupled with the ^{77}Se NMR, provides useful information in the structural elucidation prior to the detailed single-crystal X-ray diffraction studies.

COPPER AND SILVER CLUSTERS CONTAINING DISELENOPHOSPHATE LIGANDS

There is a tendency for the cluster formation between the reactions of the group 11 metals with 1,1-dithiolato ligands. Notable examples are $[Cu\{S_2P(OR)_2\}]_4$[16] and $[Ag\{S_2P(OR)_2\}]_6$.[2,3] The next question is whether the cluster formation also is general for 1,1-diselenonato ligands. Thus under strictly stoichiometric ratio, the tertanuclear cluster, $[Cu\{Se_2P(OR)_2\}]_4$, was isolated[15] and its structure is shown in Figure 1.

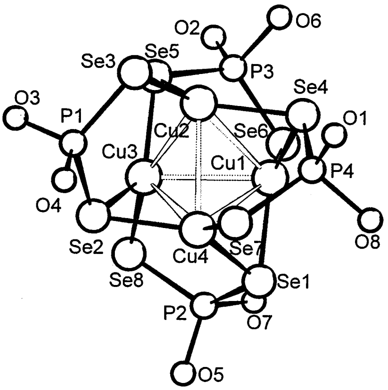
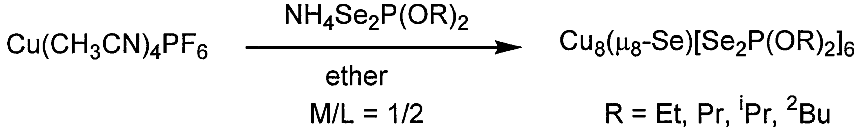


FIGURE 1 The drawing of $[Cu\{Se_2P(O^iPr)_2\}]_4$ with the isopropyl groups omitted for clarity.

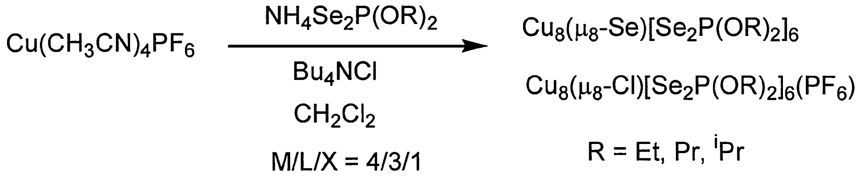
Four copper atoms occupy the vertices of the tetrahedron with each triangular face of the tetrahedron capped by a dsep ligand in a trimetallic, triconnective coordination pattern.[17] By increasing the molar ratio of ligands to metals, an octanuclear copper cluster encapsulated with a selenide anion was obtained.[10] The novelty of this cluster consists of an octacoordinate-bridging selenido ligand in a cubic geometry and each square face of the cube is further capped by a dsep ligand in a tetrametallic, tetraconnective bridging mode. Molecular orbital calculations at the B3LYP level of density functional theory suggest that Cu-μ_8-Se interactions are not very strong and a half bond can be formally assigned to each Cu-μ_8-Se bond.[18] All four clusters shown in Scheme 1 have been well characterized by multinuclear NMR (^{77}Se, ^{1}H, ^{31}P), FAB mass spectroscopy, and single crystal X-ray diffraction. They are iso-structural but crystallize in three different space groups.



$$Cu(CH_3CN)_4PF_6 \xrightarrow[\substack{\text{ether}\\ M/L = 1/2}]{NH_4Se_2P(OR)_2} Cu_8(\mu_8\text{-Se})[Se_2P(OR)_2]_6 \quad R = Et, Pr, {}^iPr, {}^2Bu$$

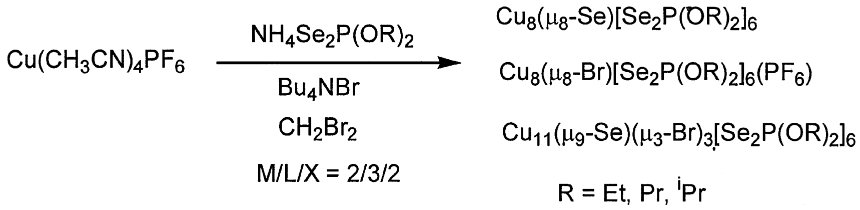
SCHEME 1

When the above reactions were carried out in the presence of halides such as bromide and iodide, new types of clusters were uncovered and the cluster nuclearity was increased from eight to eleven.[13] The addition of chloride ions to the reaction produces the chloride-centered Cu_8 cubic clusters (Scheme 2).[19] The X-ray structure consists of discrete cationic cluster in which eight copper ions are linked by six diselenophosphate ligands and a central μ_8-Cl ion. Like the selenide-centered cube, each copper atom of the cube is coordinated by three selenium atoms with a strong interaction to the central chloride ion. The observed Cu—Cl distances lie in the range 2.649 Å to 2.878 Å. In the presence of bromide ion, two new clusters besides the selenide-centered Cu_8 cube were isolated (Scheme 3).[13] One contains the bromo-centered Cu_8 cube which is iso-structural with the chloride-centered Cu_8 cubic cluster, the other



$$Cu(CH_3CN)_4PF_6 \xrightarrow[\substack{Bu_4NCl\\ CH_2Cl_2\\ M/L/X = 4/3/1}]{NH_4Se_2P(OR)_2} \begin{array}{c} Cu_8(\mu_8\text{-Se})[Se_2P(OR)_2]_6 \\ Cu_8(\mu_8\text{-Cl})[Se_2P(OR)_2]_6(PF_6) \\ R = Et, Pr, {}^iPr \end{array}$$

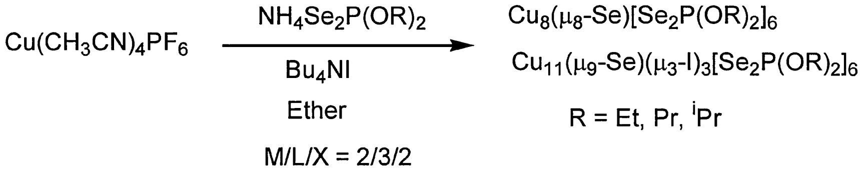
SCHEME 2



$$\mathrm{Cu(CH_3CN)_4PF_6} \xrightarrow[\substack{\mathrm{Bu_4NBr} \\ \mathrm{CH_2Br_2} \\ \mathrm{M/L/X = 2/3/2}}]{\mathrm{NH_4Se_2P(OR)_2}} \begin{array}{l} \mathrm{Cu_8(\mu_8\text{-}Se)[Se_2P(OR)_2]_6} \\ \mathrm{Cu_8(\mu_8\text{-}Br)[Se_2P(OR)_2]_6(PF_6)} \\ \mathrm{Cu_{11}(\mu_9\text{-}Se)(\mu_3\text{-}Br)_3[Se_2P(OR)_2]_6} \\ \mathrm{R = Et,\ Pr,\ {}^iPr} \end{array}$$

SCHEME 3

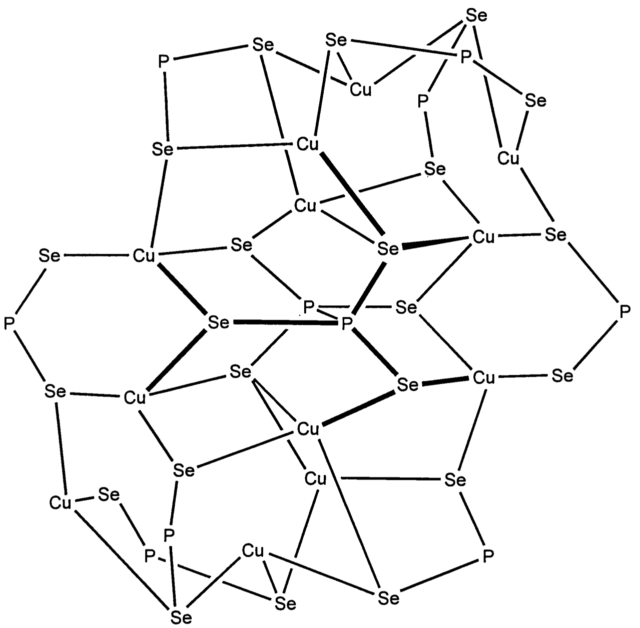
one is the undecanuclear copper cage in a pentacapped trigonal prism. The copper cage is further stabilized by three bromine atoms and six dsep ligands with a selenium atom in the center. Among the eleven Cu atoms, there are only nine Cu atoms having bonding interactions with the central Se atom because two Cu atoms cap the two triangular faces of the trigonal prismatic structure are too far away from the central Se atom. Thus a novel nonacoordinate bridging selenido ligand in a tricapped trigonal prismatic geometry is formed. The iodide analogue of undecanuclear copper cage was obtained in a similar fashion (Scheme 4). However, the synthesis of iodo-centered Cu_8 cube cannot be achieved. This is probably due to the steric effect in which the size of the iodide ion is too big. An intriguing ^{77}Se NMR pattern of the dsep ligands coupled with both ^{31}P and ^{1}H NMR suggests a local C_{3h} symmetry is retained in solution for the undecanuclear copper cluster.[14] Both chemically and magnetically inequivalent selenium nuclei of the dsep ligand exhibit significantly different scalar coupling patterns with adjacent chemically equivalent but magnetically nonequivalent phosphorus nuclei.



$$\mathrm{Cu(CH_3CN)_4PF_6} \xrightarrow[\substack{\mathrm{Bu_4NI} \\ \mathrm{Ether} \\ \mathrm{M/L/X = 2/3/2}}]{\mathrm{NH_4Se_2P(OR)_2}} \begin{array}{l} \mathrm{Cu_8(\mu_8\text{-}Se)[Se_2P(OR)_2]_6} \\ \mathrm{Cu_{11}(\mu_9\text{-}Se)(\mu_3\text{-}I)_3[Se_2P(OR)_2]_6} \\ \mathrm{R = Et,\ Pr,\ {}^iPr} \end{array}$$

SCHEME 4

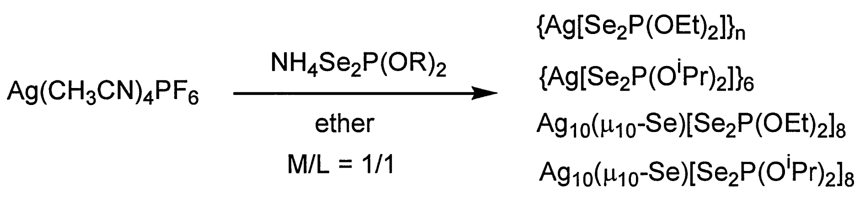
During the preparation of selenide-centered Cu_8 cubes, a dodecanuclear copper cluster was isolated serendipitously.[20] Its line drawing with the alkoxyl groups omitted is displayed in Scheme 5. It turned out to be the first molecular cluster containing an ethane-like hexaselenodiphosphato ($P_2Se_6^{4-}$) bridging group in an unprecedented μ_8-η^3, η^2, η^2, η^3, η^2, η^2 coordination mode. The four, outer-copper atoms are further connected to the eight, inner-copper atoms by eight dsep ligands.



SCHEME 5

The variable temperature ^{31}P NMR study of the Cu_{12} cluster indicates that while the peripheral, eight dsep ligands are fluxional in solution, the $Cu_8(P_2Se_6)$ core remains intact in solution and the resonance frequency for the P(+4) of the $P_2Se_6^{4-}$ anion is centered at 134 ppm. Unfortunately the plausible mechanism regarding the formation of this hexaselenodiphosphato anion remains unknown.

The rich coordination chemistry exhibited by the diselenophosphato copper complexes encourages us to extend the cluster synthesis to silver atom. Shown in Scheme 6 are the general syntheses of the phosphor-1, 1-diselenolato silver complexes.[12] Depending on the alkyl groups, the isolated products can be a polymeric species or a hexanuclear cluster,

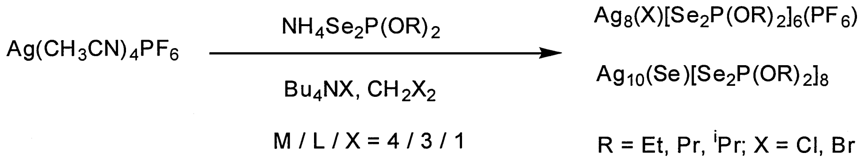


$$\mathrm{Ag(CH_3CN)_4PF_6} \xrightarrow[\substack{\text{ether} \\ M/L\,=\,1/1}]{\mathrm{NH_4Se_2P(OR)_2}} \begin{array}{l} \{\mathrm{Ag[Se_2P(OEt)_2]}\}_n \\ \{\mathrm{Ag[Se_2P(O^iPr)_2]}\}_6 \\ \mathrm{Ag_{10}(\mu_{10}\text{-}Se)[Se_2P(OEt)_2]_8} \\ \mathrm{Ag_{10}(\mu_{10}\text{-}Se)[Se_2P(O^iPr)_2]_8} \end{array}$$

SCHEME 6

which are isostructural with their respective sulfur analogue.[2,3,21] In addition, a decanuclear silver cluster encapsulated with a selenide anion also is structurally characterized and the Ag_{10} cluster has no counterpart for the dithiophosphato ligands. The coordination number for the central selenium atom in the decanuclear silver cluster is extended to ten. That is distorted, cis-bicapped trapezoidal prismatic. Moreover, the dsep ligands exhibit three different bridging patterns in the Ag_{10} cluster and this phenomenon has never been found in any dithiophosphato metal complexes.

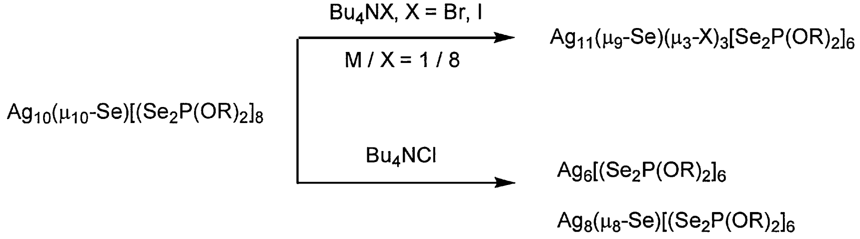
Discrete halide-centered, cuboidal silver clusters of the type, $Ag_8(\mu_8\text{-}X)[Se_2P(OR)_2]_6(PF_6)$ (X = Cl, Br) were isolated from the reaction of $[Ag(CH_3CN)_4](PF_6)$, $NH_4[Se_2P(OR)_2]$, and Bu_4NX in a molar ratio of 4:3:1 in CH_2X_2 (Scheme 7).[15,22] When the reaction is performed in alcohol, the anion of the cluster is the halide ion instead of PF_6^-. More intriguingly, the structural analysis for $Ag_8Cl_2[Se_2P(OEt)_2]_6$ is confirmed to be a rare example containing a combination of discrete clusters and chains where two chloride-centered Ag_8^I cubes are connected by the chloride ion and form a polymeric chain.[22]



SCHEME 7

Another intriguing result during the cluster synthesis is the characterization of a rare example of cocrystallization with clusters, $Ag_8(\mu_8\text{-}Se)[Se_2P(O^iPr)_2]_6$ and $Ag_6[Se_2P(O^iPr)_2]_6$, superimposing along the three-fold axis of the trigonal lattice.[11] Subsequently we found that the reaction of Ag_{10} cluster with halides produced the cocrystallization products and undecanuclear silver clusters[15] depending on which halide ion being used (Scheme 8). The Ag_{11} clusters which are isostructural with the Cu_{11} clusters display a strong orange luminescence in both solid and solution state. Its photophysical properties and the possible role for which halide ions may play in the cluster transformation in solution will be reported soon.

It has been reported that the total range of ^{77}Se chemical shift is about 3300 ppm;[23,24] the extremes are marked by selenoaldehydes and some molybdenum selenides (up to $\delta = 2400$ ppm) on the high-frequency side and bridging (μ) selenium in tungsten complexes ($\delta = -900$ ppm) on the low frequency side. We have been interested in the identification of hypercoordinate selenide ions by ^{77}Se NMR with



SCHEME 8

the hope to see if *the* ^{77}Se *shielding can be used to monitor bonding situation prior to detailed crystallographic studies*. Listed in the Table I are solution $^{31}P\{^1H\}$ and $^{77}Se\{^1H\}$ NMR data for hypercoordinated, selenide-centered clusters. The cluster nuclearities range from 8–11 and the chemical shifts lie in the range of −1150–1400 ppm. Since these data are outside the reported range of ^{77}Se chemical shift, several efforts have been tried including the MAS ^{77}Se experiments in order to certify these data. From the outset we failed to get any signals assigned to the resonance frequency of the central selenide ion. Later we realized that the accumulation time is the key to obtain a good NMR spectrum. A typical experiment requires 4 to 5 days for the accumulation with the recycle times in ~10 seconds.

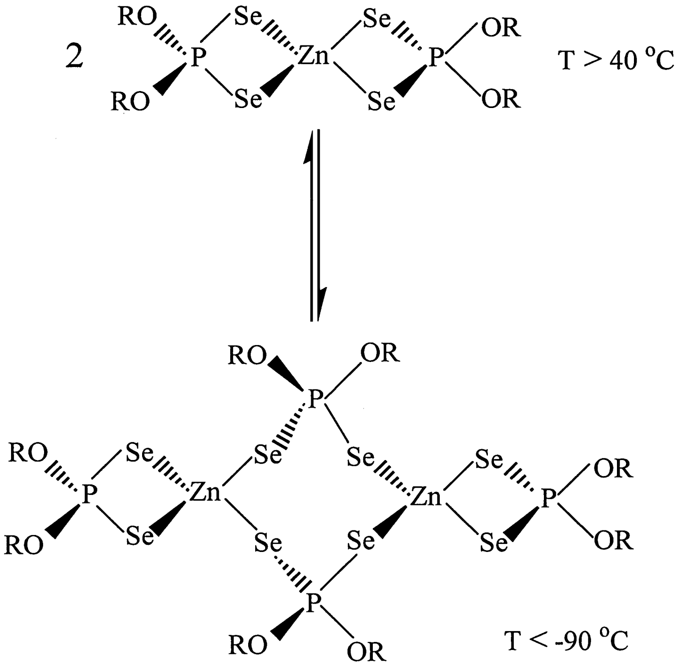
ZINC AND CADMIUM COMPLXES CONTAINING DISELENOPHOSPHATE LIGANDS

Although Zn^{II} and Cd^{II} compounds consisting of dsep ligands were first reported by Zingaro and coworkers, their solution behaviors as well as the detailed solid state structures had never been studied.[6] Thus, complexes $[Zn\{Se_2P(OEt)_2\}_2]_\infty$ and $[Zn_2\{Se_2P(O^iPr)_2\}_4]$ were prepared from the reaction of $Zn(ClO_4)_2{\cdot}6H_2O$ and $(NH_4)[Se_2P(OR)_2]$ (R = Et and ^{i}Pr) in deoxygenated water.[25] While the solid state structure of the ethyl derivative is one dimensional polymer via symmetrically bridging dsep ligands, the isopropyl one in the crystalline state exists as a dimer. In both structures, the zinc atoms are connected by two bridging dsep ligands with an additional chelating ligand at each zinc atom. Thus each zinc atom is coordinated by four selenium atoms from two bridging and one chelating dsep ligands and the geometry around zinc is distorted tetrahedral. From variable temperature ^{31}P NMR studies it has been found that monomer and dimer of the complex are in equilibrium in solution via exchange of bridging and chelating ligands (Scheme 9). However, at temperature above 40°C the complex exists as a monomer

TABLE I ^{31}**P &** ^{77}**Se NMR Data for Hypercoordinated Selenide-Centered Clusters**

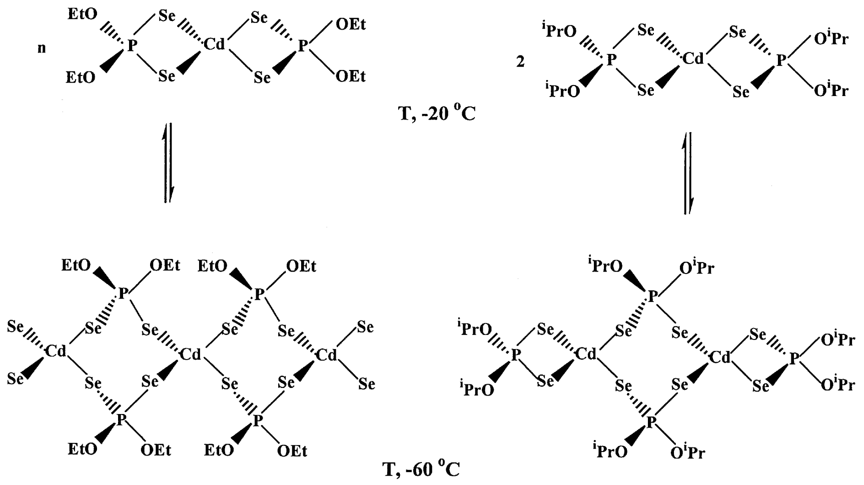
Compound	$\mathit{Se}_2\mathit{P}(\mathrm{OR})_2^-$ δ/ppm. [J/Hz]	$\mathit{Se}_2\mathrm{P}(\mathrm{OR})_2^-$ δ/ppm. [J/Hz]	Se^{2-} δ/ppm
$\mathrm{Cu_8(\mu_8\text{-}Se)[Se_2P(OEt)_2]_6}$	78.5 [s, 6P, $J_{\mathrm{PSe}} = 674.0$ Hz]	−76.9 [12Se, $J_{\mathrm{PSe}} = 672.5$]	−1169.4
$\mathrm{Cu_8(\mu_8\text{-}Se)[Se_2P(OPr^i)_2]_6}$	73.0 [s, 6P, $J_{\mathrm{PSe}} = 671.0$ Hz]	−54.7 [12Se, $J_{\mathrm{PSe}} = 671.0$]	−1147.4
$\mathrm{Cu_8(\mu_8\text{-}Se)[Se_2P(OPr)_2]_6}$	78.0 [s, 6P, $J_{\mathrm{PSe}} = 670.0$ Hz]	−17.1 [12Se, $J_{\mathrm{PSe}} = 670.0$]	−1172.6
$\mathrm{Cu_{11}(\mu_9\text{-}Se)(\mu_3\text{-}Br)_3[Se_2P(OEt)_2]_6}$	81.7 [s, 6P, $J_{\mathrm{PSe}} = 651, 675$ Hz]	44.4 [6Se, $J_{\mathrm{PSe}} = 651.0$] −5.69 [6Se, $J_{\mathrm{PSe}} = 676.6$]	−1220.1
$\mathrm{Cu_{11}(\mu_9\text{-}Se)(\mu_3\text{-}Br)_3[Se_2P(OPr^i)_2]_6}$	74.8 [s, 6P, $J_{\mathrm{PSe}} = 647, 668$ Hz]	61.7 [6Se,$J_{\mathrm{PSe}} = 650.0$] 0.1 [6Se,$J_{\mathrm{PSe}} = 668.9$]	−1201.0
$\mathrm{Cu_{11}(\mu_9\text{-}Se)(\mu_3\text{-}Br)_3[Se_2P(OPr)_2]_6}$	79.6 [s, 6P, $J_{\mathrm{PSe}} = 650, 675$ Hz]	70.0 [6Se, $J_{\mathrm{PSe}} = 651.0$] 9.2 [6Se, $J_{\mathrm{PSe}} = 676.6$]	−1193.9
$\mathrm{Cu_{11}(\mu_9\text{-}Se)(\mu_3\text{-}I)_3[Se_2P(OEt)_2]_6}$	81.7 [s, 6P, $J_{\mathrm{PSe}} = 651.3, 676.6$ Hz]	36.6 [6Se, $J_{\mathrm{PSe}} = 651.1$] −6.7 [6Se, $J_{\mathrm{PSe}} = 676.6$]	−1184.8
$\mathrm{Cu_{11}(\mu_9\text{-}Se)(\mu_3\text{-}I)_3[Se_2P(OPr^i)_2]_6}$	76.2 [s, 6P, $J_{\mathrm{PSe}} = 644.9, 673.0$ Hz]	50.3 [6Se, $J_{\mathrm{PSe}} = 644.9$] 12.5 [6Se,$J_{\mathrm{PSe}} = 673.0$]	−1210.8
$\mathrm{Cu_{11}(\mu_9\text{-}Se)(\mu_3\text{-}I)_3[Se_2P(OPr)_2]_6}$	83.0 [s, 6P, $J_{\mathrm{PSe}} = 651.3, 677.4$ Hz]	34.0 [6Se, $J_{\mathrm{PSe}} = 651.3$] −12.1 [6Se, $J_{\mathrm{PSe}} = 676.6$]	−1187.0
$\mathrm{Ag_{10}(\mu_{10}\text{-}Se)[Se_2P(OEt)_2]_8}$	81.0 [s, 8P, $J_{\mathrm{PSe}} = 672.0$ Hz]	77.9 [16Se, $J_{\mathrm{PSe}} = 672.0$]	−1396.1
$\mathrm{Ag_{10}(\mu_{10}\text{-}Se)[Se_2P(OPr^i)_2]_8}$	75.6 [s, 8P, $J_{\mathrm{PSe}} = 669.0$ Hz]	108.0 [16Se, $J_{\mathrm{PSe}} = 668.0$]	−1395.4

and shows a very sharp peak while lowering the temperature the percentage of dimer increases gradually at the expense of monomer. Below −90°C the complex exists as a dimer and observed two peaks with equal intensities which are due to bridging and chelating ligands. It is of great interest to uncover the equilibrium behavior in solution in this system because the structure in solution phase of their corresponding sulfur analogues, widely used as additives in lubricating oils, was not studied before.[26–30]



SCHEME 9

For cadmium compounds the preparation method is very similar to that of zinc complexes except using methanol as solvent.[15] The solid-state structure of the ethyl derivative is a polymer via bridging dsep ligands solely. All cadmium atoms are connected by bridging dsep ligands. The isopropyl one is isostructural with its zinc analogue. The cadmium atoms in both structures are coordinated by four selenium atoms in a distorted tetrahedral geometry. From variable temperature ^{31}P NMR studies it has been found that both complexes exist as monomers in solution at room temperature, while polymers in the case of ethyl group and dimers for isopropyl one at lower temperature ∼ −60°C (Scheme 10).



SCHEME 10

During the preparation of the n-propyl derivative of the zinc compound, a selenide-centered Zn_4 cluster was isolated in ~70% yield, $[Zn_4(\mu_4\text{-Se})\{Se_2P(OPr)_2\}_6]$.[15] Four zinc atoms are located in the apex of a near regular tetrahedron with each edge of the tetrahedron bridged by a dsep ligand. This cluster decomposed in solution and became $[Zn_2\{Se_2P(OPr)_2\}_4]$ at low temperature as evidenced from the VT ^{31}P NMR studies. Interestingly, treatment of $[Zn\{Se_2P(OR)_2\}_2]_n$ (R = Et, ^iPr) with Et_3N in CCl_4 produces the oxide-centered Zn_4 clusters, $[Zn_4(\mu_4\text{-O})\{Se_2P(OR)_2\}_6]$, in ~ 45% yield.[15] They are isostructural with the sulfur analogues and have a typical beryllium acetate type structure.[31]

REFERENCES

[1] C. W. Liu, R. T. Stubbs, R. J. Staples, and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **117,** 9778 (1995).

[2] C. W. Liu, J. T. Pitts, and J. P. Fackler, Jr., *Polyhedron*, **16,** 3899 (1997).

[3] J. P. Fackler, Jr., R. J. Staples, C. W. Liu, R. T. Stubbs, C. Lopez, and J. T. Pitts, *Pure Appl. Chem.*, **70,** 839 (1998).

[4] C. W. Liu, R. J. Staples, and J. P. Fackler, Jr., *Coord. Chem. Rev.*, **174,** 147 (1998).

[5] M. V. Kudchadker, R. A. Zingaro, and K. J. Irgolic, *Can. J. Chem.*, **46,** 1415 (1968).

[6] V. Krishnan, and R. A. Zingaro, *J. Coord. Chem.*, **1,** 1 (1971).

[7] C. K. Jorgenson, *Mol. Phys.*, **5,** 485 (1962).

[8] A. A. J. Tomlinson, *J. Chem. Soc. A*, 1409 (1971).

[9] G. M. Larin and M. E. Dyatkina, *Izv. Akad. Nauk. SSSR. Ser. Khim.*, **6,** 1413 (1972).

[10] C. W. Liu, H.-C. Chen, J.-C. Wang, and T.-C. Keng, *Chem. Commun.*, 1831 (1998).

[11] C. W. Liu, I.-J. Shang, J.-C. Wang, and T.-C. Keng, *Chem. Commun.*, 995 (1999).

[12] C. W. Liu, I.-J. Shang, C.-M. Hung, J.-C. Wang, and T.-C. Keng, *J. Chem. Soc. Dalton Trans.*, 1974 (2002).

[13] C. W. Liu, C.-M. Hung, H.-C. Chen, J.-C. Wang, T.-C. Keng, and K. Guo, *Chem. Commun.*, 1897 (2000).

[14] C. W. Liu, C.-M. Hung, J.-C. Wang, and T.-C. Keng, *J. Chem. Soc., Dalton Trans.*, 3482 (2002).

[15] C. W. Liu, unpublished results.

[16] S. L. Lawton, W. J. Rohrbaugh, and G. T. Kokotailo, *Inorg. Chem.*, **11,** 612 (1972).

[17] H. Haiduc, D. B. Snowerby, and S.-F. Lu, *Polyhedron*, **14,** 3389 (1995).

[18] C. W. Liu, C.-M. Hung, B. K. Santra, J.-C. Wang, H.-M. Kao, and Z. Lin, *Inorg. Chem.*, **42,** 8551 (2003).

[19] C. W. Liu, C.-M. Hung, B. K. Santra, H.-C. Chen, H.-H. Hseuh, and J.-C. Wang, *Inorg. Chem.*, **42,** 3216 (2003).

[20] C. W. Liu, H.-C. Chen, J.-C. Wang, and T.-C. Keng, *Angew. Chem. Int. Ed.*, **40,** 2342 (2001).

[21] W. Kuchen and H. Mayatepek, *Chem. Ber.*, **101,** 3454 (1968).

[22] C. W. Liu, C.-M. Hung, H.-C. Hsia, B.-J. Liaw, L.-S. Liou, Y.-F. Tsai, and J.-C. Wang, *Chem. Commun.*, 976 (2003).

[23] H. Duddeck, *Prog. NMR Spectrosc.*, **27,** 1 (1995).

[24] H. Duddeck, *Encyclopedia of Nuclear Magnetic Resonance*, D. M. Grant and R. K. Harris (Eds.), John Wiley & Sons, New York (1996).

[25] B. K. Santra, B.-J. Liaw, C.-M. Hung, C. W. Liu, and J.-C. Wang, *Inorg. Chem.*, **42,** 8866 (2003).

[26] S. L. Lawton and G. T. Kokotailo, *Inorg. Chem.*, **8,** 2410 (1969).

[27] V. P. Wystrach, E. O. Hook, and G. L. M. Christopher, *J. Org. Chem.*, **21,** 705 (1956).

[28] D. E. Goldberg, W. C. Fernelius, and M. Shamma, *Inorg. Synth.*, **11,** 21 (1960).

[29] J. S. Ashford, L. Bretherick, and P. Gould, *J. Appl. Chem.*, **15,** 170 (1965).

[30] I. Heilweil, *J. Am. Chem. Soc., Div. Petroleum Chem., Preprints*, **10,** 19 (1965).

[31] A. Tulinsky, C. R. Worthington, and E. Pignataro, *Acta Crystallogr.*, **12,** 623 (1959).