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Synthesis and Characterization of Zinc and Cadmium Compounds with Arenephosphinothiol Ligands. Crystal and Molecular Structures of $[Cd_2\{2\text{-}(Ph_2PO)C_6H_4S\}_4]$, $[Zn\{2\text{-}(Ph_2P)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_2]$, $[Cd\{2\text{-}(Ph_2PO)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_2(CH_3OH)]$, and $[Zn\{PhPO(C_6H_4S\text{-}2)_2\}(bipy)]$

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The electrochemical oxidation of a metallic anode (zinc or cadmium) in an acetonitrile solution of a series of arenephosphinothiol ligands, $2\text{-}(Ph_2P)C_6H_4SH$, $2\text{-}(Ph_2P)\text{-}6\text{-}(Me_3Si)C_6H_3SH$, $2\text{-}(Ph_2PO)\text{-}6\text{-}(Me_3Si)C_6H_3SH$, and $PhP(C_6H_4SH\text{-}2)_2$ [abbreviated $RP\text{-}(SH)_x$, $x = 1$ or 2], affords $[M(RP\text{-}S)_2]$ and $[M(RP\text{-}S_2)]$, M = Zn, Cd. Adducts of several of these compounds with 1,10-phenanthroline and 2,2′-bipyridine have also been obtained by addition of these coligands to the electrolysis phase. The compounds obtained have been characterized by microanalysis, IR, UV−visible, FAB spectrometry and ^1H, ^{31}P NMR spectroscopic studies. The compounds, $[Cd_2\{2\text{-}(Ph_2PO)C_6H_4S\}_4]CH_3CN$ (**1**), $[Zn\{2\text{-}(Ph_2P)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_2]$ (**2**), $[Cd\{2\text{-}(Ph_2PO)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_2(CH_3OH)]$ (**3**), and $[Zn\{PhPO(C_6H_4S\text{-}2)_2\}(bipy)]$ (**4**), have been also characterized by single-crystal X-ray diffraction. Compound **1** is binuclear with a $\{Cd_2S_2\}$ core and distorted trigonal bipyramidal $\{CdO_2S_3\}$ geometry about the Cd sites. Compounds **2**, **3**, and **4** are mononuclear with distorted tetrahedral $\{ZnP_2S_2\}$, distorted square pyramidal $\{CdO_3S_2\}$, and distorted trigonal bipyramidal $\{ZnON_2S_2\}$ geometries, respectively. Crystal data: **1**, $C_{42}H_{37}N_3O_2P_2S_2Cd$, triclinic, $P\bar{1}$, $a = 13.5780(2)$ Å, $b = 13.8505(2)$ Å, $c = 13.9526(2)$ Å, $\alpha = 106.622(1)°$, $\beta = 109.693(1)°$, $\gamma = 107.137(1)°$, $V = 2133.30(5)$ Å^3, $Z = 2$, 9560 reflections, $R = 0.0483$; **2**, $C_{46}H_{50}N_2P_2S_2Si_2Zn$, monoclinic, $C2/c$, $a = 21.332(4)$ Å, $b = 9.391(2)$ Å, $c = 25.938(5)$ Å, $\beta = 113.84(3)°$, $V = 4753(2)$ Å^3, $Z = 4$, 2564 reflections, $R = 0.0377$; **3**, $C_{43}H_{48}CdO_3P_2S_2Si_2$, triclinic, $P\bar{1}$, $a = 12.1237(4)$ Å, $b = 14.0568(4)$ Å, $c = 15.0938(2)$ Å, $\alpha = 70.836(2)°$, $\beta = 83.410(2)°$, $\gamma = 65.397(2)°$, $V = 2208.7(1)$ Å^3, $Z = 2$, 4936 reflections, $R = 0.0738$; **4**, $C_{29}H_{22}Cl_3N_2OP_2S_2Zn$, triclinic, $P\bar{1}$, $a = 8.9556(3)$ Å, $b = 12.7911(4)$ Å, $c = 14.0598(5)$ Å, $\alpha = 82.671(1)°$, $\beta = 73.140(1)°$, $\gamma = 74.113(1)°$, $V = 1480.44(9)(1)$ Å^3, $Z = 2$, 3820 reflections, $R = 0.0511$.

Introduction

Neutral thiolate complexes of zinc or cadmium $[M(SR)_2]$ form in general infinite lattices with bridging ligands and tetrahedral metal centers.[1−3] Their polymeric nature renders these materials of low volatility and unsuitable for deposition of metal chalcogenides under typical MOCVD conditions. Volatility may be improved by modifying the degree of aggregation of these species by blocking some coordination sites either with donor atoms from the thiolate ligand or with coligands, such as 2,2′-bipyridine or 1,10-phenanthroline. In previous studies we have used this strategy for the synthesis of monomeric[4] and dimeric compounds[5] of zinc and cadmium with heterocyclic thiones. As a continuation of this work this paper reports the synthesis of zinc and cadmium complexes with phosphinothiols, ligands incorporating both thiolate sulfur and tertiary phosphorus atoms as donor groups, following an electrochemical procedure where the metal is the anode of a cell containing the ligand in an acetonitrile solution. This method is simple and high-yielding, and the presence in the cell of coligands such as 1,10-phenanthroline or 2,2′-bipyridine allows the synthesis of mixed-ligand complexes in one step.

Compounds with arenephosphinothiol ligands have been previously reported by Dilworth and Zubieta, mainly of the heavier transition metals, such as molybdenum,[6] technetium and rhenium,[7] ruthenium,[8] and rhodium and iridium[9] metals. In contrast, the chemistry of the main group metals remains

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unexplored, and compounds of zinc or cadmium with these ligands have not been reported previously.

Experimental Section

General Considerations. All manipulations were carried out under an inert atmosphere of dry nitrogen. Zinc and cadmium (Aldrich Chemie) were used as plates (ca. 2 × 2 cm). All other reagents, including 1,10-phenanthroline and 2,2′-bipyridine, were used as supplied. Syntheses of ligands were carried out using minor modifications of the standard literature procedure.[10]

Elemental analyses were performed in a Carlo-Erba EA microanalyzer, and IR spectra were recorded as KBr mulls on a Brucker IFS-66V. FAB mass spectra were recorded on a Kratos-MS-50T connected to a DS90 data system, using 3-nitrobenzyl alcohol (3-NBA) as matrix material. ^{1}H NMR spectra were recorded on a Brucker AMX 300 MHz instrument and ^{31}P in a Brucker 500 MHz, using $CDCl_3$ or DMSO-d_6 as solvents; ^{1}H NMR chemical shifts were recorded against TMS as internal standard while ^{31}P chemical shifts were determined against H_3PO_4 (85%).

Electrochemical Synthesis. The complexes were obtained following an electrochemical procedure. An acetonitrile solution of the ligand containing about 15 mg of tetramethylammonium perchlorate as a current carrier was electrolyzed using a platinum wire as the cathode and a metal plate as the sacrificial anode. For the synthesis of mixed complexes, the corresponding coligand, 1,10-phenanthroline or 2,2′-bipyridine, was also added to the solution. Applied voltages of 10−15 V allowed sufficient current flow for smooth dissolution of the metal. During electrolysis, nitrogen was bubbled through the solution to provide an inert atmosphere and also to stir the reaction mixture. The cell can be summarized as $Pt_{(-)}/CH_3CN + RP\text{-}(SH)_x/M_{(+)}$.

[Zn{2-(Ph$_2$P)C$_6$H$_4$S}$_2$]. Electrochemical oxidation of a zinc anode in a solution of 2-diphenylphosphinobenzenethiol, 2-$(Ph_2P)C_6H_4SH$ (0.220 g, 0.748 mmol), in acetonitrile (50 cm^3), at 16 V and 10 mA for 2 h caused 25 mg of zinc to be dissolved, $E_f = 0.51$ mol F^{-1}. During the electrolysis process, hydrogen was evolved at the cathode, and at the end of the reaction white crystalline needles appeared at the bottom of the vessel. The solid was filtered off, washed with acetonitrile and ether, and dried under vacuum (0.21 g, 87%). Anal. Calcd for $C_{36}H_{28}ZnP_2S_2$: C, 66.3; H, 4.30; S, 9.82. Found: C, 66.03; H, 4.25; S, 9.70. IR (cm^{-1}): 1572 (m), 1480 (m), 1436 (s), 1421 (m), 1248 (m), 1096 (m), 743 (s), 693 (s). ^{1}H NMR (DMSO-d_6, ppm): δ 8.0−6.8 (m, 28 H). ^{31}P NMR (DMSO-d_6, ppm): δ 42.3.

[Cd{2-(Ph$_2$P)C$_6$H$_4$S}$_2$]. A similar experiment (12 V, 10 mA, 2 h) with cadmium as anode and 0.220 g (0.748 mmol) of 2-$(Ph_2P)C_6H_4SH$ in 50 cm^3 of acetonitrile dissolved 40 mg of metal, $E_f = 0.47$ mol F^{-1}. At the end of the electrolysis white crystals deposited in the cell were recovered, washed with cool acetonitrile and diethyl ether, and dried under vacuum (0.19 g, 77%). Anal. Calcd for $C_{36}H_{28}CdP_2S_2$: C, 61.9; H, 4.01; S, 9.16. Found: C, 61.9; H, 4.00; S, 8.97. IR (KBr, cm^{-1}): 1570 (m), 1479 (m), 1435 (s), 1418 (m), 1247 (m), 1094 (m), 743 (s), 693 (s). ^{1}H NMR ($CDCl_3$, ppm): δ 8.0−6.5 (m, 28). ^{31}P NMR ($CDCl_3$, ppm): δ 32.4. Air concentration of the resulting solution yielded crystals of $[Cd_2\{2\text{-}(Ph_2PO)C_6H_4S\}_4]\cdot 3CH_3CN$ (**1**) suitable for X-ray studies.

[Cd{2-(Ph$_2$P)C$_6$H$_4$S}$_2$(bipy)]. Electrochemical oxidation of cadmium in an acetonitrile solution (50 cm^3) containing 2-$(Ph_2P)C_6H_4SH$, 0.220 g, 0.748 mmol, and 2,2′-bipyridine, 0.060 g, 0.384 mmol, using a current of 10 mA, 11 V, for 2 h resulted in the dissolution of 44 mg of metal, $E_f = 0.52$ mol F^{-1}. As the reaction proceeded the solution color changed from colorless to yellow, and a microcrystalline solid was deposited in the cell. The solid was recovered, washed with acetonitrile, dried under vacuum, and identified by elemental analysis (0.21 g, 67%). Anal. Calcd for $C_{46}H_{36}CdN_2P_2S_2$: C, 64.6; H, 4.21; N, 3.27; S, 7.49. Found: C, 64.5; H, 4.19; N, 3.19; S, 7.39%. IR (KBr, cm^{-1}): 1588 (m), 1568 (m), 1479 (m), 1435 (s), 1419 (m), 1246 (m), 1095 (m), 761 (m), 747 (s), 695 (s). ^{1}H NMR ($CDCl_3$, ppm): δ 8.8 (d, 2H), 8.4 (d, 2H), 7.9 (m, 2H), 7.7 (m,2H), 7.4−6.6 (m, 28H). ^{31}P NMR ($CDCl_3$, ppm): δ 37.6 ppm.

[Cd{2-(Ph$_2$P)C$_6$H$_4$S}$_2$(phen)]. A similar experiment (10 mA, 10 V, 1.5 h) using 0.166 g (0.333 mmol) of 2-$(Ph_2P)C_6H_4SH$ (0.565 mmol) and 0.060 g (0.282 mmol) of 1,10-phenanthroline dissolved 31 mg of cadmium from the anode, $E_f = 0.49$ mol F^{-1}. The color of the solution changed from colorless to yellowish. At the end of the reaction yellow needles were recovered, washed with acetonitrile, and dried (0.18 g, 75%). Anal. Calcd for $C_{48}H_{36}N_2P_2S_2Cd$: C, 65.6; H, 4.10; N, 3.19; S, 7.28. Found: C, 65.0; H, 4.02; N, 3.14; S, 7.18. IR (KBr, cm^{-1}): 1587 (m), 1569 (s), 1513 (m), 1479 (m), 1435 (s), 1416 (s), 1242 (m), 1091 (s), 847 (m), 748 (s), 731 (m), 696 (s). ^{1}H NMR ($CDCl_3$, ppm): δ 9.1 (d, 2H), 8.1 (d, 2H), 7.6 (s, 2H), 7.4 (m,2H), 7.3−6.4 (m, 28H). ^{31}P NMR ($CDCl_3$, ppm): δ 36.6.

[Zn{2-(Ph$_2$P)-6-(Me$_3$Si)C$_6$H$_3$S}$_2$]. A solution of acetonitrile (50 cm^3) containing 2-diphenylphosphino-6-trimethylsilylbenzenethiol (0.273 g, 0.746 mmol) was electrolyzed at 10 mA, 20 V, during 2 h, and 24 mg of zinc metal was dissolved from the anode, $E_f = 0.49$ mol F^{-1}. A white crystalline compound was obtained directly from the cell at the end of the reaction. The crystals were recovered by filtration, washed with acetonitrile, dried, and identified by elemental analysis (0.24 g, 82%). Anal. Calcd for $C_{42}H_{44}P_2S_2Si_2Zn$: C, 63.4; H, 5.53; S, 8.05. Found: C, 62.4; H, 5.59; S, 8.15. IR (KBr, cm^{-1}): 3053 (m), 2949 (m), 2893 (m), 1555 (m), 1482 (m), 1436 (m), 1352 (s), 1243 (m), 1096 (m), 853 (s), 743 (s), 692 (s). ^{1}H NMR ($CDCl_3$, ppm): δ 8.1−6.8 (m, 26H), 0.5 (s, 18H). ^{31}P NMR ($CDCl_3$, ppm): δ 43.2.

X-ray quality crystals of $[Zn\{2\text{-}(Ph_2P)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_2]\cdot 2CH_3CN$ (**2**) were obtained by crystallization from CH_3CN.

[Cd{2-(Ph$_2$P)-6-(Me$_3$Si)C$_6$H$_3$S}$_2$]. A similar experiment (16 V, 10 mA, 2 h) with 0.273 g (0.746 mmol) of the ligand 2-(Ph_2P)-6-$(Me_3Si)C_6H_3SH$ in 50 cm^3 of acetonitrile dissolved 42 mg of cadmium, $E_f = 0.50$ mol F^{-1}. A white microcrystalline solid was obtained at the end of the reaction. The solid was collected, washed with cool acetonitrile and diethyl ether, and dried under vacuum (0.27 g, 86%). Anal. Calcd for $C_{42}H_{44}CdP_2S_2Si_2$: C, 59.8; H, 5.22; S, 7.60. Found: C, 59.2; H, 5.21; S, 7.66. IR (KBr, cm^{-1}): 3055 (m), 2947 (m), 2893 (m), 1553 (m), 1480 (m), 1435 (m), 1351 (s), 1243 (m), 1095 (m), 851 (s), 743 (s), 693 (m). ^{1}H NMR ($CDCl_3$, ppm): δ 7.8−6.5 (m, 26 H), 0.35 (s, 18H). ^{31}P NMR ($CDCl_3$, ppm): δ 37.3.

[Zn{2-(Ph$_2$PO)-6-(Me$_3$Si)C$_6$H$_3$S}$_2$]. The electrochemical oxidation of zinc in a solution of 2-(Ph_2PO)-6-$(Me_3Si)C_6H_3SH$ (0.214 g, 0.560 mmol) in acetonitrile (60 mL) for 1.5 h at 10 V and 10 mA resulted in the loss of 19 mg of zinc from the anode, $E_f = 0.52$ mol F^{-1}. At the end of the electrolysis the reaction mixture was filtered to remove any precipitated particles of metal, and the filtrate was left to concentrate by evaporation at room temperature. A white crystalline product was isolated and identified by elemental analysis (0.190 g, 82%). Anal. Calcd for $C_{42}H_{44}ZnP_2O_2S_2Si_2$: C, 60.9; H, 5.32; S, 7.73. Found: C, 61.3; H, 5.43; S, 7.70. IR (KBr, cm^{-1}): 3057 (m), 2951 (m), 2893 (m), 1556 (m), 1438 (s), 1354 (s), 1242 (m), 1128 (s), 1060 (m), 854 (s), 748 (m), 692 (s). ^{1}H NMR ($CDCl_3$, ppm): δ 7.7−6.5 (m, 26H), 0.35 (s, 18H). ^{31}P($CDCl_3$, ppm): δ 45.1.

[Cd{2-(Ph$_2$PO)-6-(Me$_3$Si)C$_6$H$_3$S}$_2$]. Electrolysis of an acetonitrile solution (50 cm^3) containing 2-(Ph_2PO)-6-$(Me_3Si)C_6H_3SH$ (0.214 g, 0.560 mmol) using 10 mA, 10 V electric current for 1.5 h caused the dissolution of 32 mg of cadmium ($E_f = 0.51$ mol F^{-1}). The final reaction mixture was concentrated to produce a white solid (0.20 g, 80%). Anal. Calcd $C_{42}H_{44}CdP_2O_2S_2Si_2$: C, 57.6; H, 5.03; S, 7.32. Found: C, 58.0; H, 5.17; S, 7.25. IR (KBr, cm^{-1}): 3055 (m), 2952 (m), 2895 (m), 1555 (m), 1438 (s), 1353 (s), 1242 (s), 1130 (s), 1065 (m), 845 (s), 748 (s), 692 (s). ^{1}H NMR ($CDCl_3$, ppm): δ 7.7−6.6 (m, 26H), 0.35 (s, 18H). ^{31}P($CDCl_3$, ppm): δ 40.7. Crystals of $[Cd\{2\text{-}(Ph_2PO)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_2(CH_3OH)]$ (**3**) suitable for X-ray studies were obtained by crystallization from CH_2Cl_2/CH_3OH.

[Zn{PhP(C$_6$H$_4$S-2)$_2$}]. The electrochemical oxidation of zinc in a solution of $PhP(C_6H_4SH\text{-}2)_2$ (0.122 g, 0.374 mmol) in acetonitrile (40 mL) for 2 h at 20 V and 10 mA resulted in the loss of 24 mg of zinc from the anode, $E_f = 0.49$ mol F^{-1}. A white insoluble solid precipitated in the cell within a few minutes. This solid was washed with acetonitrile and ether, dried under vacuum, and identified by elemental analysis (0.13 g, 94%). Anal. Calcd for $C_{18}H_{13}PS_2Zn$: C, 55.5; H, 3.34; S, 16.4.

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Table 1. Summary of Crystallographic Data for the Compounds [$Cd_2\{2\text{-}(Ph_2PO)C_6H_4S\}_4$]·$3CH_3CN$ (**1**), [$Zn\{2\text{-}(Ph_2P)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_2$]·$2CH_3CN$ (**2**), [$Cd\{2\text{-}(Ph_2PO)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_2(CH_3OH)$] (**3**), and [$Zn\{PhPO\ (C_6H_4S\text{-}2)_2\}(bipy)$]·$CHCl_3$ (**4**)

	1	**2**	**3**	**4**
empirical formula	$C_{42}H_{37}N_3P_2S_2O_2Cd$	$C_{46}H_{50}N_2P_2S_2Si_2Zn$	$C_{43}H_{48}P_2O_3S_2Si_2Cd$	$C_{29}H_{22}N_2POS_2Cl_3Zn$
fw	854.10	878.49	907.4	681.30
temp (K)	298(2)	293(2)	298(2)	296(2)
wavelength (Å)	0.710 73	1.541 78	0.710 73	0.710 73
cryst syst	triclinic	monoclinic	triclinic	triclinic
space group	$P\bar{1}$	$C2/c$	$P\bar{1}$	$P\bar{1}$
unit cell dimens				
a (Å)	13.5780(2	21.332(4)	12.1237(4)	8.9556(3)
b (Å)	13.8505(2)	9.391(2)	14.0586(4)	12.7911(4)
c (Å)	13.9526(2)	25.938(5)	15.0938(2)	14.0598(5)
α (deg)	106.622(1)		70.836(2)	82.671(1)
β (deg)	109.693(1)	113.84(3)	83.410(2)	73.140(1)
γ (deg)	107.137(1)		65.397(2)	74.113(1)
vol (Å^3)	2133.30(5)	4753(2)	2208.7(1)	1480.44(9)
Z	2	4	2	2
d_{cal}, g cm^{-3}	1.329	1.228	1.364	1.528
μ, mm^{-1}	0.713	2.899	0.752	1.322
R^a	0.0517	0.0396	0.0885	0.0567
$R_w{}^b$	0.1613	0.0953	0.1553	0.1322

[a] $R = \sum(|F_o| - |F_c|)|\sum|F_o|$. [b] $R_w = [(|\sum w(|F_o| - |F_c|)^2|\sum w|F_o|^2]^{1/2}$.

Found: C, 55.3; H, 3.35; S, 16.2. IR (KBr, cm^{-1}): 1574 (m), 1440 (s), 1421 (s), 1253 (m), 1101 (s), 744 (s), 694 (m). ^{1}H NMR ($CDCl_3$, ppm): δ 7.9−6.6 (m, 13H). ^{31}P ($CDCl_3$, ppm): δ 47.7.

[Zn{PhP(C_6H_4S-2)$_2$}(bipy)]. Electrolysis of an acetonitrile solution (50 cm^3) containing $PPh(C_6H_4SH\text{-}2)_2$ (0.122 g, 0.374 mmol) and 2,2′-bipyridine (0.060 g, 0.384 mmol), using a 10 mA, 12 V electric current for 1.5 h caused the dissolution of 18 mg of zinc from the anode, E_f = 0.50 mol F^{-1}. The solid obtained was washed with acetonitrile and ether and dried under vacuum. A second crop of the compound was obtained by concentration of the resulting solution (0.12 g, 73%). Anal. Calcd for $C_{28}H_{21}N_2PS_2Zn$: C, 61.6; H, 3.85; S, 11.7; N, 5.12. Found: C, 61.9; H, 4.05; S, 11.8; N, 5.17. IR (KBr, cm^{-1}): 1597 (m), 1573 (m), 1473 (m), 1441 (s), 1417 (m), 1246 (m), 1094 (m), 1046 (m), 1020 (m), 768 (s), 742 (s), 699 (m). ^{1}H NMR ($CDCl_3$, ppm): δ 8.7 (d, 2H), 8.1 (d, 2H), 7.9 (s, 2H), 7.6 (m,2H), 7.4−6.7 (m, 13H). ^{31}P ($CDCl_3$, ppm): δ 48.4. Crystals of [Zn{PhPO(C_6H_4S-2)$_2$}(bipy)]·$CHCl_3$ (**4**) suitable for X-ray studies were obtained by recrystallization from $CHCl_3/CH_3OH$.

[Zn{PhP(C_6H_4S-2)$_2$}(phen)]. A similar experiment (10 mA, 10 V, 1.5 h) using 0.122 g (0.374 mmol) of $PhP(C_6H_4SH\text{-}2)_2$ and 0.08 g (0.44 mmol) of 1,10-phenanthroline dissolved 19 mg of zinc from the anode, E_f = 0.51 mol F^{-1}. The color of the solution changed from colorless to yellow. At the end of the reaction a yellow crystalline solid was recovered, washed with acetonitrile, and dried, 0.14 g (85%). Anal. Calcd for $C_{30}H_{21}N_2PS_2Zn$: C, 63.2; H, 3.69; N, 4.93; S, 11.2. Found: C, 63.0; H, 3.72; N, 5.02, S, 10.2%. IR (KBr, cm^{-1}): 1574 (m), 1544 (w), 1516 (m), 1477 (w), 1422 (s), 1247 (m), 1095 (s), 849 (m), 744 (s), 727 (m), 699 (s). ^{1}H NMR ($CDCl_3$, ppm): δ 9.0 (d, 2H), 8.4 (d, 2H), 7.9 (s, 2H), 7.7 (m, 2H), 7.6−6.7 (m, 13H). ^{31}P ($CDCl_3$, ppm): δ 45.3.

[Cd{PhP(C_6H_4S-2)$_2$}]. An acetonitrile solution (50 mL) containing 0.122 g (0.374 mmol) of $PhP(C_6H_4SH\text{-}2)_2$ was electrolyzed using a 10 mA, 14 V electric current for 2 h, resulting in the loss of 41 mg of cadmium from the anode, E_f = 0.49 mol F^{-1}. A white insoluble solid precipitated in the cell within a few minutes (0.14 g, 88%). This solid was washed with acetonitrile and ether, dried under vacuum, and identified as [Cd{PhP(C_6H_4S-2)$_2$}]. Anal. Calcd for $C_{18}H_{13}CdPS_2$: C, 49.5; H, 2.98; S, 14.7. Found: C, 50.1; H, 2.95; S, 15.0. IR (KBr, cm^{-1}): 1572 (m), 1440 (s), 1421 (s), 1252 (m), 1098 (s), 1042 (m), 744 (s), 695 (m). ^{1}H NMR ($CDCl_3$, ppm): δ 7.8−6.5 (m, 13H). ^{31}P ($CdCl_3$, ppm): δ 38.1.

[Cd{PhP(C_6H_4S-2)$_2$}(bipy)]. Electrolysis of an acetonitrile solution (60 cm^3) containing 0.120 g (0.374 mmol) of $PPh(C_6H_4SH\text{-}2)_2$ and 0.060 g (0.0384 mmol) of 2,2′-bipyridine using a 10 mA, 17 V electric current for 2 h caused the dissolution of 41 mg of cadmium from the anode, E_f = 0.49 mol F^{-1}. At the end of the experiment a white insoluble solid was recovered from the cell. Concentration of the filtered solution allowed a second crop of compound. The product was identified as [Cd{PhP(C_6H_4S-2)$_2$}(bipy)] (0.17 g, 80%). Anal. Calcd for $C_{28}H_{21}N_2PS_2Cd$: C, 56.7; H, 3.54; S, 10.8; N, 4.72. Found: C, 56.5; H, 3.62; S, 10.5; N, 4.67. IR (KBr, cm^{-1}): 1593 (m), 1572 (m), 1478 (m), 1439 (s), 1420 (m), 1251 (m), 1098 (s), 1041 (m), 744 (s), 696 (m). ^{1}H NMR ($CDCl_3$, ppm): δ 8.6−6.6 (m, 21H). ^{31}P NMR ($CDCl_3$, ppm): δ 39.9.

[Cd{PhP(C_6H_4S-2)$_2$}(phen)]. A similar experiment (10 mA, 10 V, 1.5 h) using 0.18 g of $PhP(C_6H_4SH\text{-}2)_2$ (0.552 mmol) and 0.10 g (0.55 mmol) of 1,10-phenanthroline dissolved 32 mg of cadmium from the anode, E_f = 0.51 mol F^{-1}. The color of the solution changed from colorless to yellow. At the end of the reaction yellow needles were recovered, washed with acetonitrile, and dried (0.13 g, 74%). Anal. Calcd for $C_{30}H_{21}N_2PS_2Cd$: C, 58.40; H, 3.41; N, 4.54; S, 10.38. Found: C, 58.27; H, 3.36; N, 4.53; S, 9.87. IR (KBr, cm^{-1}): 1589 (m), 1570 (s), 1512 (m), 1479 (w), 1435 (w), 1424 (s), 1245 (m), 1098 (s), 844 (m), 743 (s), 729 (m), 700 (m). ^{1}H NMR ($CDCl_3$, ppm): δ 9.2 (d, 2H), 8.3 (d, 2H), 7.8 (s, 2H), 7.7 (m,2H), 7.6−6.5 (m, 13H). ^{31}P ($CDCl_3$, ppm): δ 37.4.

X-ray Crystallography. Compounds [$Cd_2\{2\text{-}(Ph_2PO)C_6H_4S\}_4$] (**1**), [$Cd\{2\text{-}(Ph_2PO)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_2(CH_3OH)$] (**3**), and [$Zn\{PhPO(C_6H_4S\text{-}2)_2\}(bipy)$] (**4**) were studied on a Siemens Smart diffractometer, and compound [$Zn\{2\text{-}(Ph_2P)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_2$] (**2**) was studied on a Nicolet P3 apparatus. Data collections were carried out under ambient conditions, using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) for **1**, **3**, and **4** and Cu Kα radiation (λ = 1.541 78 Å) for (**2**). The crystal parameters and other experimental details of the data collection are summarized in Table 1. A complete description of the details of the crystallographic methods is given in the Supporting Information. The structures were solved by direct methods and refined by a full-matrix least-squares procedure. Neutral atom scattering factors were taken from Cromer and Waber,[11] and anomalous dispersion factors were taken from Cromer.[12] Data were corrected for absorption using SADABS (T_{max}/T_{min}: 0.935/0.786 (**1**); 0.928/0.735 (**2**); 0.894/0.562 (**3**); 0.954/0.876 (**4**)). All calculations were performed using SHELXTL PLUS (PC version)[13] for **1**, **3**, and **4**, and using DECMicroVAX 3500 computer for **2**. Refinements were based on F^2. No anomalies were encountered in the refinements of any of the structures. In the case of **1**, an acetonitrile molecule of crystallization is disordered over three

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(11) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A.

(12) Cromer, D. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

(13) Sheldrick, G. M. *SHELXTL-PLUS* program package (PC Version) for the determination of crystal structures, Release 4.0; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1990.

sites with concomitant large thermal parameters. Atomic positional parameters and isotropic temperature factors for the structures are presented in the Supporting Information.

Results and Discussion

Arenephosphinothiolate complexes of zinc and cadmium, and some adducts with 2,2′-bipyridine (bipy) or 1,10 phenanthroline (phen), are easily prepared in good yield, by the simple one-step electrochemical procedure described above.

The electrochemical efficiency, defined as the amount of metal dissolved per Faraday of charge, was in all cases close to 0.5 mol F^{-1}. This and the evolution of hydrogen at the cathode are consistent with the following reaction scheme:

$$\text{cathode:} \quad 2\text{RP-SH} + 2e^- \rightarrow 2\text{RP-S}^- + \text{H}_2$$

$$\text{anode:} \quad 2\text{RP-S}^- + \text{M} \rightarrow [\text{M(RP-S)}_2] + 2e^-$$

$$2\text{RP-S}^- + \text{M} + \text{L}' \rightarrow [\text{M(RP-S)}_2\text{L}']$$

$$\text{M} = \text{Zn, Cd; L}' = \text{bipy, phen}$$

A similar mechanism is proposed for the synthesis of metal complexes with the RP-(SH)$_2$ ligand.

[M{2-(Ph$_2$P)C$_6$H$_4$S}$_2$] Compounds. The electrochemical oxidation of anodic zinc or cadmium in a cell containing 2-(Ph$_2$P)C$_6$H$_4$SH in acetonitrile gave the complexes [Zn{2-(Ph$_2$P)C$_6$H$_4$S}$_2$] and [Cd{2-(Ph$_2$P)C$_6$H$_4$S}$_2$] in good yield. The compounds are insoluble in the reaction solvent and are obtained as crystalline white air-stable solids in the bottom of the cell. The compounds are sparingly soluble in chloroform and in a range of other chlorinated organic solvents.

The IR spectra of these complexes do not show the band attributed to ν(S−H), which in the ligand appears at 2494 cm^{-1}. This is indicative of the anionic thiolate form of the ligand in the complex. The spectra also show bands in the aromatic region, 1580−1500 cm^{-1}, characteristic of the ν(C═C) vibrations and also a band at 720−730 cm^{-1} attributable to ν(P−C).

The room temperature ^{1}H NMR spectra of complexes exhibit only multiplet resonances in the aromatic region, δ 8.0−6.5 ppm, as the signal attributable to the SH hydrogen, which in the free ligand appears at δ 4.0 ppm as a doublet due to the coupling to the phosphorus atom, is now absent. The ^{31}P NMR spectra show a single signal at δ 42.3 and 32.4 ppm for the zinc and cadmium complexes, respectively. This signal appears in the free ligand at δ −14.6 ppm. The downfield shift is a consequence of the coordination of the phosphorus atom to the metal.

The FAB mass spectrum of the cadmium compound shows a peak at *m*/*z* 699 (23%), due to the molecular ion, but also a signal at *m*/*z* 1102 (56%) due to [Cd$_2${2-(Ph$_2$P)C$_6$H$_4$S}$_3$]$^+$, formed by loss of one ligand from the dimer species. This can be taken as indicative of a dimeric structure for this compound, similar to that found in the case of complex **1**, vide infra. For solubility reasons, the FAB spectra of the zinc complex could not be recorded, but the structure of this compound is presumably analogous to that of the trimethylsilyl derivative complex **2** discussed below.

Concentration of the mother liquor from the synthesis of [Cd{2-(Ph$_2$P)C$_6$H$_4$S}$_2$] in air yielded crystals of the dimeric phosphine oxide complex [Cd$_2${2-(Ph$_2$PO)C$_6$H$_4$S}$_4$] (**1**). Such facile oxidation of phosphine to phosphine oxides has been observed in other complexes containing this type of ligand.[14]

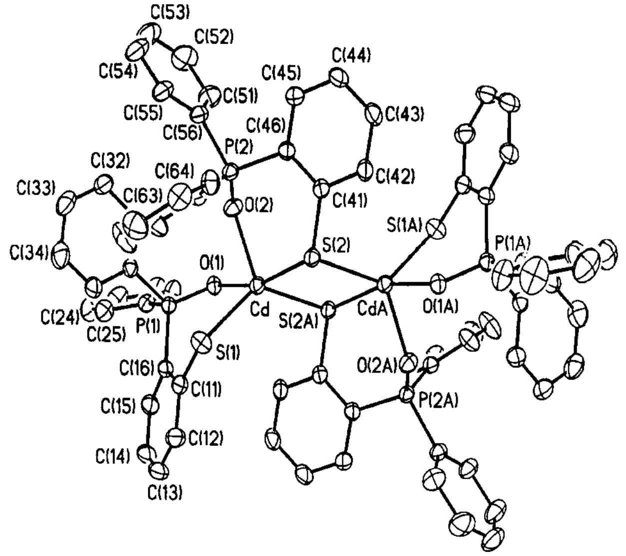

Figure 1. Molecular structure of [Cd$_2${2-(Ph$_2$PO)C$_6$H$_4$S}$_4$].

The incorporation of additional bidentate ligands to the cell allows the synthesis of cadmium mixed-ligand complexes such as [Cd{2-(Ph$_2$P)C$_6$H$_4$S}$_2$(bipy)] and [Cd{2-(Ph$_2$P)C$_6$H$_4$S}$_2$(phen)]. These complexes show IR bands characteristic of the coordinated phosphinothiolate ligand and also bands at 761 and 747 cm^{-1} and 748 and 731 cm^{-1} typical of coordinated 2,2′-bipyridine and 1,10-phenanthroline, respectevily.[15,16] The ^{1}H NMR spectra of these mixed complexes also show additional signals due to coordinated 2,2′-bypiridine at δ 8.8, 8.4, 7.9, and 7.7 ppm and 1,10-phenantroline at δ 9.3, 8.3, 7.9, and 7.7 ppm.[17] The FAB mass spectra of these cadmium mixed-ligand compounds do not show the molecular ion, but show peaks at *m*/*z* 563 (17%) and *m*/*z* 587 (30%) corresponding to [Cd{2-(Ph$_2$P)C$_6$H$_4$S}(bipy)]$^+$ and [Cd{2-(Ph$_2$P)C$_6$H$_4$S}(phen)]$^+$, respectively. The presence of additional ligands in the coordination sphere of the metal leads us to suggest an octahedral monomeric structure for these complexes.

Attempts to obtain mixed-ligand complexes in the case of zinc were unsuccessful, as the analytical data did not show the incorporation of the additional coligand. In all cases, the recovered compound was [Zn{2-(Ph$_2$P)C$_6$H$_4$S}$_2$]. This behavior can be ascribed to the different atomic sizes of zinc and cadmium, which makes the zinc atom more reluctant than the cadmium atom to achieve octahedral environments, especially in the case of bulky ligands such as the arenephosphinothiolate ones.

Crystal Structure of [Cd$_2${2-(Ph$_2$PO)C$_6$H$_4$S}$_4$] (1). Figure 1 shows a view of the molecule together with the atomic numbering scheme. Bond lengths and angles with the standard uncertainties are listed in Table 2. The structure consists of dimers in which two thiolate sulfur atoms of two ligands bridge both cadmium atoms. The molecule possesses a crystallographic inversion center. In addition, each cadmium is coordinated to an oxygen atom of the bridging ligand and to the thiolate sulfur atom and the oxygen atom of an additional ligand. The value of 0.63 for the geometrical parameter τ ($\tau = \beta - \alpha/60$)[18] suggests that the cadmium atom is in a distorted [CdO$_2$S$_3$]

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[16] Schilt, A. A.; Taylor, R. C. *J. Inorg. Nucl. Chem.* **1959**, *9*, 211.

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[Cd_2\{2\text{-}(Ph_2PO)C_6H_4S\}_4]$ (**1**)[a]

Cd−O(2)	2.219(3)	Cd−S(1)	2.508(1)
Cd−S(2)$^{\#1}$	2.5351(9)	Cd−O(1)	2.374(3)
Cd−S(2)	2.8700(9)	S(2)−Cd$^{\#1}$	2.5351(9)
P(1)−O(1)	1.511(3)	P(2)−O(2)	1.509(3)
S(1)−C(11)	1.758(4)	S(2)−C(41)	1.787(4)
P(1)−C(16)	1.809(4)	P(1)−C(36)	1.806(4)
O(2)−Cd−O(1)	86.68(9)	O(2)−Cd−S(1)	106.44(8)
O(1)−Cd−S(1)	90.63(7)	O(2)−Cd−S(2)$^{\#1}$	125.75(8)
O(1)−Cd−S(2)$^{\#1}$	97.31(6)	S(1)−Cd−S(2)$^{\#1}$	127.47(4)
O(2)−Cd−S(2)	79.67(7)	O(1)−Cd−S(2)	165.56(7)
S(1)−Cd−S(2)	97.72(3)	S(2)$^{\#1}$−Cd−S(2)	86.97(3)

[a] Symmetry transformations used to generate equivalent atoms: (#1) $-x + 1, -y + 1, -z + 1$.

trigonal bipyramidal environment with O(1) and S(2) at axial sites and O(2), S(1), and S(2A) in the equatorial plane. The cadmium metal is 0.085 Å out of the equatorial plane. Angular distortions are observed both in the equatorial plane, with bond angles in the range 106.44(8)−127.47(4)°, and along the axial direction of the bipyramid with an O(1)−Cd−S(2) angle of 165.56(7)°.

The four-membered ring Cd−S(2)−S(2A)−Cd(A) is planar, and the thiolate bridge is clearly asymmetric, with Cd−S bond distances of 2.5351(9) and 2.8700(9) Å. Although asymmetric bridging thiolate bonds have been found in dimeric pentacoordinated cadmium complexes, for instance 2.667(2) and 2.597(2) Å in $[Cd_2(3\text{-}Me_3Si(pyt))_4]$ ($pyt^- =$ pyridinethionate),[5] the value of 2.8700(9) Å is considerably larger than the sum of the covalent radii of tetrahedral cadmium and sulfur atoms, 2.52 Å.[19] This is indicative of weak interaction between the metal and this donor atom. The other bridge bond distance, 2.5351(9) Å, and the cadmium−terminal sulfur bond distance, 2.5082(11) Å, are normal and agree with those found in other dimeric cadmium complexes with pentacoordinated environments around the cadmium, such as in $[Cd_2(3\text{-}Me_3Si(pyt))_4]$, and with Cd−($\mu$-SR) bond distances in general.[20]

The Cd−O bond distances, 2.219(3) and 2.374(3) Å, are also different, with the Cd−O(1) for the chelating ligand longer by 0.155 Å. However, for example, both distances are in the range found in **3**, vide supra, and similar to those found in other pentacoordinated cadmium complexes involving O-donor ligands, e.g., 2.34 Å in $[Cd(thiourea)_3(SO_4)]$,[21] or 2.387(9) and 2.353(9) Å in dinitrato bis(2-methylmercaptoaniline) Cd(II).[22]

$[M\{2\text{-}(Ph_2P)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_2]$ Compounds. In order to evaluate the possible steric effects upon the metal−phosphinothiolate system, anodic zinc and cadmium were oxidized in a solution of 2-(diphenylphosphino)-6-trimethylsilylbenzenethiol in acetonitrile. In both cases the compounds are obtained directly from the cell as microcrystalline solids deposited at the bottom of the cell.

The IR spectra of both compounds are similar to those of $[M\{2\text{-}(Ph_2P)C_6H_4S\}_2]$ described above, with additional medium-intensity bands at 3100−2900 cm^{-1} corresponding to the methyl group vibrations, and a strong-intensity band at 850 cm^{-1} characteristic of the ν(Si−C) group. The ^1H NMR spectra show the aromatic resonances at δ 8.0−6.5 ppm and singlets at δ 0.55 and 0.35 ppm for zinc and cadmium complexes, respectively, characteristic of the $SiMe_3$ group. The ^{31}P NMR spectra show a singlet at δ 43.2, M = Zn, and 37.3 ppm, M = Cd.

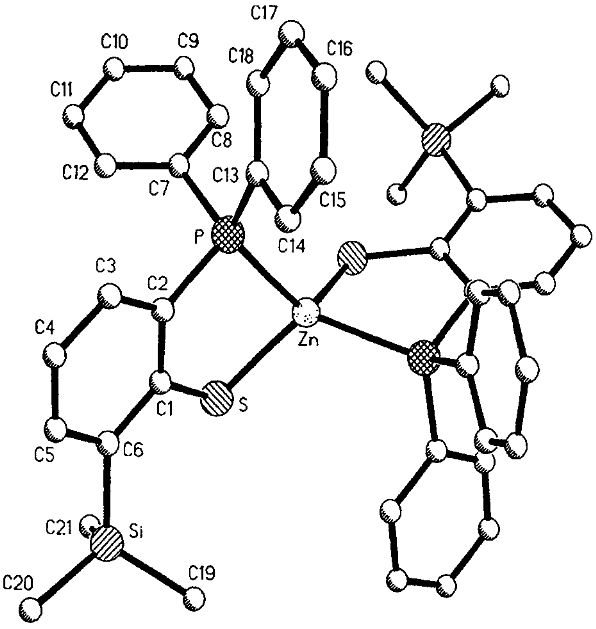

Figure 2. Molecular structure of $[Zn\{2\text{-}(Ph_2P)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_2]$.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[Zn\{2\text{-}(Ph_2P)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_2]$ (**2**)[a]

Zn−S	2.2791(9)	Zn−S$^{\#}$	2.2791(9)
Zn−P	2.387(1)	Zn−P$^{\#}$	2.387(1)
S−C(1)	1.768(3)	P−C(2)	1.804(3)
P−C(7)	1.808(3)	P−C(13)	1.821(3)
S−Zn−S$^{\#1}$	122.82(5)	S−Zn−P$^{\#1}$	119.12(3)
S$^{\#1}$−Zn−P$^{\#1}$	87.60(3)	S−Zn−P	87.60(3)
S$^{\#1}$−Zn−P	119.12(3)	P$^{\#1}$−Zn−P	124.62(5)

[a] Symmetry transformations used to generate equivalent atoms: (#1) $-x + 1, y, -z + {}^1/_2$.

The FAB mass spectra of both compounds show the molecular ion at *m*/*z* 795 (12%) and 843 (4%) for the zinc complex and the cadmium complex, respectively. None of them show peaks of *m*/*z* higher than that of the molecular ion, suggesting that both compounds are monomeric molecular species. The X-ray structure of $[Zn\{2\text{-}(Ph_2P)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_2]$, vide infra, confirms this conclusion. In the case of cadmium, the monomeric structure can be taken as a consequence of the steric hindrance introduced by the trimethylsilyl group, which prevents the formation of dimeric species.

Crystal Structure of $[Zn\{2\text{-}(Ph_2P)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_2]$ (2). Figure 2. shows a view of the molecule together with the atomic numbering scheme. Bond lengths and angles with the estimated standard deviations are listed in Table 3.

The structure consists of discrete molecules with the zinc atom located on a crystallographic 2-fold axis and coordinated to the thiolate sulfur atoms and phosphorus atoms of two symmetry-related ligand moieties. Thus both phosphinothiolate ligands assume five-membered chelate ring geometries. The geometry about the zinc atom is best described as distorted tetrahedral $[ZnP_2S_2]$, as a result of the small bite angle of the ligands, 87.60(3)°. The bond angles S−Zn−S$^{\#}$ and S−Zn−P$^{\#}$, 122.82(5), and 119.12(3)°, also deviate from the theoretical 109°. The dihedral angle between the P−Zn−S and P$^{\#}$−Zn−S$^{\#}$ planes is 94.1°.

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(19) Pauling, L. *The Nature of the Chemical Bond*; 3rd ed.; Cornell University Press: Ithaca, New York, 1960; p 246.

(20) See, for example: (a) Gonzalez-Duarte, P.; Clegg, W.; Casals, I.; Sola, J.; Ruis, J. *J. Am. Chem. Soc.* **1998**, *120*, 1260. (b) Vossmeyer, T.; Reck, G.; Schulz, B.; Katsikas, L.; Weller, H. *J. Am. Chem. Soc.* **1995**, *117*, 12881. (c) Vossmeyer, T.; Reck, G.; Katsikas, L.; Houpt, E. T. K.; Schulz, B.; Weller, H. *Science 267*, 1476 and references therein.

(21) Corao, E.; Baggio, S. *Inorg. Chim. Acta* **1969**, *3*, 617

(22) Griffith, E. A. H.; Charles, N. G.; Rodesiler, P.F.; Amma, E. L. *Polyhedron* **1985**, *4*, 615.

The Zn−S bond distance, 2.2791(9) Å, is comparable to those of tetrahedral zinc thiolates with five-membered chelating rings, such as in [Zn{$SCH_2CH_2N(CH_3)_2$}$_2$], 2.266 Å (average value),[23] or in other distorted tetrahedral thiolate zinc complexes.[24] The Zn−S(thiolate) distances are consistently shorter than Zn−S(dithiocarbamate) distances in four-coordinate complexes.[25] The Zn−P bond distance, 2.387(1) Å, is also similar to those found in tetrahedral zinc complexes with tertiary phosphines as ligands, 2.376(1) Å (average value) in [$ZnCl_2(PMe_3)_2$][26] or in the anion [$ZnCl_3PPh_3$]$^-$, 2.392(1) Å.[27]

The phenyl rings of the ligand are essentially planar, the maximum deviation being less than 0.02 Å. The P and the S atoms are practically on the plane of the ring to which they are bonded.

[M{2-(Ph_2PO)-6-(Me_3Si)C_6H_3S}$_2$] Compounds. Compounds with ligands 2-(Ph_2PO)-6-(Me_3Si)C_6H_3SH were obtained by oxidation of zinc or cadmium in a cell containing 2-(diphenylphosphinyl)-6-trimethylsilylbenzenethiol following the general procedure described previously. In these cases at the end of the electrolysis the clear solutions were filtered to remove any particles of the metal. The [Zn{2-(Ph_2PO)-6-(Me_3Si)-C_6H_3S}$_2$] and [Cd{2-(Ph_2PO)-6-(Me_3Si)C_6H_3S}$_2$] were obtained as white crystalline solids by concentration of the solution in a vacuum at room temperature. Crystals of [Cd{2-(Ph_2PO)-6-(Me_3Si)C_6H_3S}$_2$(CH_3OH)] (**3**) suitable for X-ray studies were obtained by crystallization of the initial compound from $CHCl_3$/CH_3OH.

Both compounds show IR spectra similar to those of [M{2-(Ph_2P)-6-(Me_3Si)C_6H_3S}$_2$] described above, with an additional strong-intensity band at 1130 cm^{-1} corresponding to the vibration characteristic of the ν(P−O) group. The ^{31}P NMR spectra show a resonance at δ 45.1 and 40.7 ppm for the zinc and cadmium compounds, respectively, downfield respect to the same signal in the free ligand, δ 34.1 ppm.

The FAB mass spectra of both compounds also show the molecular ion at *m*/*z* 828 (6%), M = Zn, and 875 (6%), M = Cd. None of them show peaks of higher *m*/*z* than that of the molecular ion. All of these results suggest that both compounds have a monomeric structure. The monomeric structure of [Cd{2-(Ph_2PO)-6-(Me_3Si)C_6H_3S}$_2$] may be compared with the dimeric structure of [Cd_2{2-(Ph_2PO)C_6H_4S}$_4$]. Once more, the steric hindrance of the trimethylsilyl group prevents the formation of a dimer compound.

Crystal Structure of [Cd{2-(Ph_2PO)-6-(Me_3Si)C_6H_3S}$_2$-(CH_3OH)] (3). The molecular structure of [Cd{2-(Ph_2PO)-6-(Me_3Si)C_6H_3S}$_2$(CH_3OH)] is shown in Figure 3 together with the atomic numbering scheme adopted. Final atomic coordinates amd selected bond distances and angles are listed in Table 4.

The cadmium atom is coordinated to the thiolate sulfur and oxygen atoms of two bidentate monanionic ligands and also weakly coordinated to a molecule of methanol.

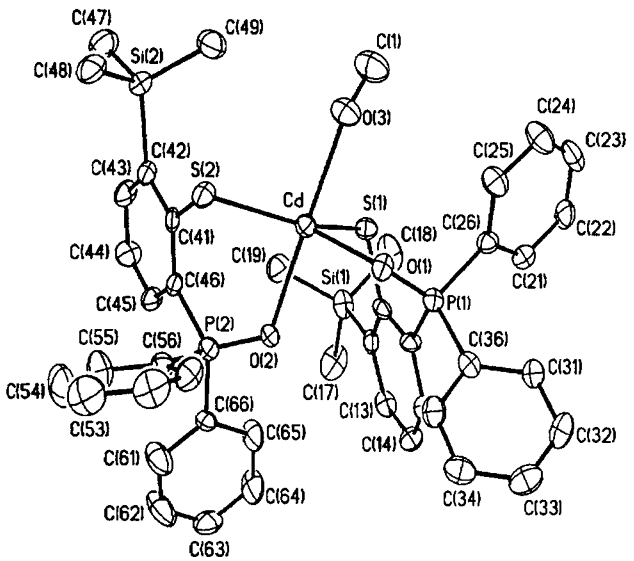

Figure 3. Molecular structure of [Cd{2-(Ph_2PO)-6-(Me_3Si)C_6H_3S}$_2$(CH_3-OH)].

Table 4. Selected Bond Lengths (Å) and Angles (deg) for [Cd{2-(Ph_2PO)-6-(Me_3Si)C_6H_3S}$_2$(CH_3Oh)] (**3**)

Cd−O(1)	2.290(6)	P(1)−C(36)	1.803(10)
Cd−O(2)	2.374(6)	P(1)−C(26)	1.800(10)
Cd−S(2)	2.460(3)	P(2)−O(2)	1.490(7)
Cd−S(1)	2.474(3)	P(2)−C(66)	1.809(10)
Cd−O(3)	2.551(7)	P(2)−C(56)	1.795(11)
P(1)−O(1)	1.504(6)	P(2)−C(46)	1.816(10)
P(1)−C(16)	1.808(9)	S(1)−C(11)	1.760(9)
S(2)−C(41)	1.765(10)		
O(1)−Cd−O(2)	86.5(2)	S(2)−Cd−S(1)	140.04(9)
O(1)−Cd−S(2)	129.8(2)	O(1)−Cd−O(3)	81.3(2)
O(2)−Cd−S(2)	84.8(2)	O(2)−Cd−O(3)	160.4(2)
O(1)−Cd−S(1)	90.1(2)	S(2)−Cd−O(3)	91.3(2)
O(2)−Cd−S(1)	100.0(2)	S(1)−Cd−O(3)	95.4(2)

The environment around the cadmium atom may be described as a [CdO_3S_2] distorted square pyramid, $\tau = 0.34$, with the O(1) atom as the apical atom. In this description, S(1) and S(2) are 0.53 and 0.65 Å above the best least-squares plane of S(1)-S(2)O(2)O(3), and O(2) and O(3) are 0.53 and 0.65 Å below. The cadmium atom is 0.24 Å out of this plane.

The two Cd−S bond distances in the complex are similar, 2.460(3) and 2.474(3) Å, and not very different from those observed in **3**. Similarly, the Cd−O bond distances corresponding to oxygen atoms of the bidentate chelate ligands, 2.290(6) and 2.374(6) Å, are in the range for the mentioned pentacoordinated cadmium complexes. Nevertheless the bond distance Cd−O(3), 2.551(7) Å, is considerably longer, but less than the sum of the van der Waals radii for cadmium and oxygen, 3.10 Å, and indicative of the methanol being only weakly bonded to the cadmium, with a bond order of ca. 0.4.

[M{PhP(C_6H_4S-2)$_2$}] Complexes. Zinc and cadmium compounds of the ligand PhP(C_6H_4SH-2)$_2$ were prepared following the standard procedure. White-yellow powdered insoluble solids precipitated immediately at the anode of the cell. Analytical data confirm the formation of [M{PhP(C_6H_4S-2)$_2$}] compounds. The lack of bands assignable to ν(S−H) is indicative of the dianionic tridentate nature of the ligands in the complexes. The high insolubility of both compounds in normal solvents suggests that these complexes are either dimeric or polymeric species in the solid state. The FAB spectrum of [Zn{PhP(C_6H_4S-2)$_2$}] shows, in addition to a signal at *m*/*z* 391 (37%) due to [Zn{PhP(C_6H_4S-2)$_2$}]$^+$, a signal at *m*/*z* 780 (4%) corresponding to [Zn_2{PhP(C_6H_4S-2)$_2$}$_2$]$^+$ and another strong intensity peak at *m*/*z* 456 (100%) due to [Zn_2{PhP(C_6H_4S-2)$_2$}]$^+$, formed by loss

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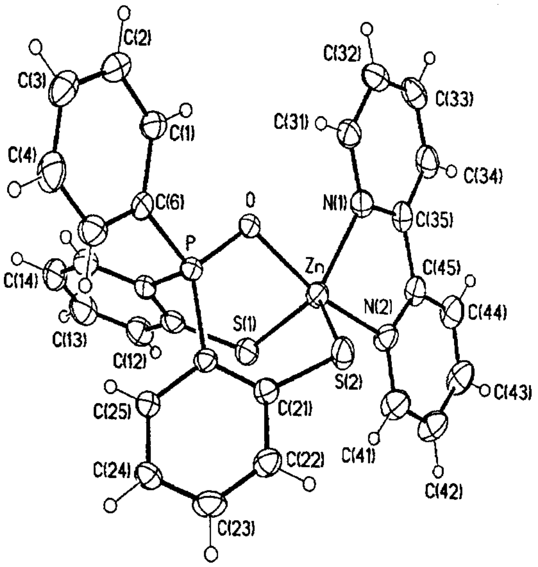

Figure 4. Molecular structure of [Zn{PhPO(C_6H_4S-2)$_2$}(bipy)].

of one ligand from the dimer species. For the Cd{PhP(C_6H_4S-2)$_2$}] complex, the FAB spectrum shows a peak at *m/z* 438 (4%), corresponding to [Cd{PhP(C_6Y_4S-2)$_2$}]$^+$, and additional peaks at *m/z* 547 (7%), corresponding to [Cd_2{PhPH(C_6H_4S-2)$_2$}]$^+$.

The addition of 2,2′-bipyridine and 1,10-phenanthroline into the cell as coligands affords the synthesis of the mixed-ligand compounds [M{PhP(C_6H_4S-2)$_2$}L′] (M = Zn, Cd; L′ = bipy, phen), as yellow-white crystalline solids moderately soluble in the reaction medium and also soluble in a range of other organic solvents. The IR spectra of the complexes confirm the presence of both coordinated ligands. ^{1}H NMR spectra show signals in the range δ 9.2−7.7 ppm corresponding to bipyridine or phenanthroline and a multiplet at δ 7.6−6.5 ppm, due to the aromatic protons of the arenephoshinothiol ligand. The FAB mass spectra of the zinc and cadmium mixed-ligand complexes with bipyridine show in both cases the molecular ion, at *m/z* 545 (65%) and 595 (2%), respectively, and also peaks at *m/z* 389 (30%) and 438 (4%) due to [M{PhP(C_6H_4S-2)$_2$}]$^+$, formed by loss of the bipyridine ligand from both complexes. The FAB mass spectra of the mixed-ligand compounds with phenanthroline show the molecular ion, at *m/z* 569 (100%), M = Zn, and 616 (5%), M = Cd.

Crystals of [Zn{PhPO(C_6H_4S-2)$_2$}(bipy)]·$CHCl_3$ suitable for X-ray studies were obtained by crystallization of [Zn{PhP(C_6H_4S-2)$_2$}bipy] from $CHCl_3$/CH_3OH. Once more, the presence of a phosphinyl group in the resulting compound shows the extreme sensitivity to oxidation of the phosphorus atom in this type of ligand.

Crystal Structure of [Zn{PhPO(C_6H_4S-2)$_2$}bipy] (4). The structure of [Zn{PhPO(C_6H_4S-2)$_2$}(bipy)] is shown in Figure 4. Positional parameters and selected bond lengths and angles are given in Table 5. The complex consists of monomer units in which a pentacoordinated [$ZnON_2S_2$] zinc atom is bound to two sulfur atoms and one oxygen atom of a tridentate ligand and also to two nitrogen atoms of a bidentate chelating bipyridine molecule. The environment of the zinc atom can be described a distorted trigonal bipyramidal, $\tau = 0.7$, with both sulfur atoms and one of the nitrogen atoms of the bipyridine molecule in the equatorial plane of the molecule. The zinc atom is nearly on the equatorial plane, with a deviation of 0.07 Å out of the least-squares plane. Equatorial bond angles, in the range 116.62(5)−122.67(11)°, are close to the idealized 120°, but angular deviation is observed along the axial direction of the trigonal bipyramid with an O−Zn−N(2) angle of 164.58(14)°, significantly distorted from the theoretical 180°. The small bite of the bipyridine ligand, N(1)−Zn−N(2) bond angle of 76.0(2)°, is the principal source of distortion. This value is similar to those found in other pentacoordinated zinc complexes containing 2,2′-bipyridine as chelating ligand.[28]

Table 5. Selected Bond Lengths (Å) and Angles (deg) for [Zn{PhPO(C_6H_4S-2)$_2$}(bipy)] (**4**)

Zn−O	2.093(3)	Zn−N(1)	2.108(4)
Zn−N(2)	2.184(4)	Zn−S(2)	2.314(1)
Zn−S(1)	2.398(2)	P−O	1.509(3)
N(1)−C(35)	1.357(6)	N(2)−C(45)	1.347(6)
N(1)−C(31)	1.340(6)	N(2)−C(41)	1.342(7)
S(1)−C(11)	1.771(5)	S(2)−C(21)	1.769(5)
O−Zn−N(1)	90.29(14)	N(2)−Zn−S(2)	101.21(12)
O−Zn−N(2)	164.58(14)	O−Zn−S(1)	92.98(10)
N(1)−Zn−N(2)	76.0(2)	N(1)−Zn−S(1)	120.43(11)
O−Zn−S(2)	92.11(10)	N(2)−Zn−S(1)	88.00(13)
N(1)−Zn−S(2)	122.67(11)	S(2)−Zn−S(1)	116.62(5)

The bond distances around the zinc atom are similar to those reported for other pentacoordinated complexes containing the same donor atoms. Thus, the Zn−S bond distances, 2.356(2) Å (average value), although longer than those of [Zn{$SCH_2CH_2N(CH_3)_2$}$_2$],[23] are of the same order as the value of 2.334(4) Å found for Zn−S in the pentacoordinated mixed-ligand compound [(2,2′-bipyridine){2-(2-mercaptophenyl)iminophenoxy}]zinc(II).[28] In addition, the values of 2.146(4) and 2.093 Å for the Zn−N and Zn−O bond distances, respectively, are similar to those found in the above-mentioned complex, and in other pentacoordinate complexes of Zn with Schiff bases containing N and O as donor atoms.[29]

The bipyridine ligand is essentially planar, with no atom deviating from thr least-squares plane by more than 0.02 Å. Bond lengths and angles within the ligand are similar to those found in other bipyridine.[30, 31]

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Supporting Information Available: X-ray crystallographic files, in CIF format, for the structures of **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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