Preparation and Crystal Structures of $[PPh_4]_2[M_2(SPh)_6]$ (M = Zn or Cd)†

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The compounds $[PPh_4]_2[Zn_2(SPh)_6]$ and $[PPh_4]_2[Cd_2(SPh)_6]$ have been prepared by reaction between the hydrated metal(II) nitrate and $[PPh_4][SPh]$ in methanol–acetonitrile solution. The compounds are isostructural (space group $P2_1/c$) and the dimeric anion has crystallographic inversion symmetry, imposing an *anti* arrangement of the two bridging benzenethiolate ligands. The metal atoms have a distorted tetrahedral co-ordination with two terminal and two bridging ligands. The central M_2S_2 rings are exactly planar and essentially square [Zn–S 2.424(1), 2.431(1) Å, S–Zn–S 90.7(1)°; Cd–S 2.611(1), 2.611(1) Å, S–Cd–S = 91.8(1)°]. Proton and ^{13}C n.m.r. spectra indicate a rapid exchange of terminal and bridging ligands of the anions in solution.

The thiolate chemistry of Zn^{II} and Cd^{II} is characterised by tetrahedral co-ordination. Mononuclear complexes $[M(SR)_4]^{2-}$[1] and $[M(SCH_2CH_2S)_2]^{2-}$,[2] binuclear $[M_2(SR)_6]^{2-}$,[3] and tetranuclear $[M_4(SR)_{10}]^{2-}$[4,5] complexes have been prepared and studied. Also, the complexes $[M_4(SPh)_{10-n}X_n]^{2-}$ (X = halide, n = 1—4), with substitution of terminal thiolate groups by halide ions, have been formed in the reaction of $ZnCl_2$ with PhS^- to give $[Zn_4(SPh)_8Cl_2]^{2-}$,[6] and by the oxidation of $[Cd_4(SPh)_{10}]^{2-}$ by I_2 giving, in solution, a number of intermediate iodide-substituted products.[7] The reaction of $ZnCl_2$ with PhS^- has also yielded $[Zn_8(SPh)_{16}Cl]^-$, containing a μ_4-Cl atom at the centre of a $Zn_8(SPh)_{16}$ icosahedral cage.[8]

Reaction of $[M_4(SPh)_{10}]^{2-}$ with elemental sulphur or selenium has been shown to give the products $[M_{10}E_4(SPh)_{16}]^{4-}$ (M = Zn or Cd, E = S or Se), which contain a 'super-tetrahedral' fragment of the cubic (sphalerite) metal chalcogenide lattice structure, involving four fused rings with μ_3-bridging E^{2-} ions in an adamantane-like arrangement.[9] Crystalline $Cd(SPh)_2$ is an inorganic polymer consisting of $Cd_4(SPh)_6$ adamantane-like cages, each of which is linked by μ-SPh groups to four adjacent cages; the compound dissolves in dimethylformamide as $[Cd_{10}(SPh)_{20}]$ which has a tetra-adamantanoid structure.[10]

The binuclear complex ions $[M_2(SEt)_6]^{2-}$ contain two bridging and four terminal thiolate ligands.[3] We report here the preparation and characterisation of the corresponding benzenethiolate complexes as their bis(tetraphenylphosphonium) salts, $[PPh_4]_2[M_2(SPh)_6]$, [M = Zn (**1**) or Cd (**2**)], which display small but significant structural differences from their ethanethiolate analogues.

Experimental

Reactions were carried out under an atmosphere of purified dinitrogen using standard Schlenk techniques. Acetonitrile was distilled from CaH_2 and degassed before use. Infrared spectra were recorded for Nujol mulls on a Perkin-Elmer 577 spectrometer, u.v.-visible spectra on a Shimadzu UV260 spectrometer, 300-MHz ^1H n.m.r. spectra on a Varian XL300 spectrometer, and 20-MHz ^{13}C n.m.r. spectra on a Bruker WP80 spectrometer.

Preparation of $[PPh_4]_2[Zn_2(SPh)_6]$ (**1**).—This was initially isolated as one product from a reaction of $[NMe_4]_2[Zn_4(SPh)_{10}]$ with $[PPh_4]_2[MoS_4]$; subsequently a direct, rational synthesis was developed. The salt $Zn(NO_3)_2\cdot6H_2O$ (1.5 g, 5 mmol) was dissolved in methanol (10 cm^3) and added to a solution of $[PPh_4][SPh]$ (7.0 g, 15 mmol) in MeCN (25 cm^3). The yellow solution immediately became colourless. Storage at −20 °C overnight yielded a mass of colourless hexagonal-shaped plate crystals, which were collected by filtration, washed with cold MeCN (5 cm^3) and diethyl ether, and dried *in vacuo* (yield 2.1 g, 60%) (Found: C, 67.7; H, 4.8; P, 4.3; S, 12.2; Zn, 8.9. Calc. for $C_{84}H_{70}P_2S_6Zn_2$: C, 68.9; H, 4.8; P, 4.3; S, 13.1; Zn, 9.0%).

Preparation of $[PPh_4]_2[Cd_2(SPh)_6]$ (**2**).—(*i*) A solution of $Cd(NO_3)_2\cdot4H_2O$ (1.0 g, 3 mmol) in methanol (10 cm^3) was added to $[PPh_4][SPh]$ (4.7 g, 10 mmol) in MeCN (10 cm^3), to give an immediate white precipitate, which redissolved on stirring and heating to *ca.* 70 °C. The hot filtered solution was cooled to −20 °C, to yield a colourless microcrystalline precipitate, which was filtered off, washed with methanol (5 cm^3) and diethyl ether (30 cm^3), and dried *in vacuo* (yield 1.6 g, 65%).

(*ii*) Alternatively, $[PPh_4][SPh]$ (2.35 g, 5 mmol) in MeCN (20 cm^3) was added to a suspension of $Cd(SPh)_2$ (1.1 g, 5 mmol) in MeCN (20 cm^3). The $Cd(SPh)_2$ dissolved over a period of *ca.* 10 min. The resulting colourless solution was heated to 60 °C and concentrated to a volume of *ca.* 10 cm^3 under a reduced pressure. Slow cooling to room temperature produced colourless hexagonal-shaped crystals, which were washed with MeCN (3 × 5 cm^3 at −20 °C) and diethyl ether (30 cm^3) and dried *in vacuo* (yield 3.0 g, 80%). The two products had essentially identical elemental analyses (Found: C, 64.2; H, 4.3; Cd, 14.4; P, 4.0; S, 12.0. Calc. for $C_{84}H_{70}Cd_2P_2S_6$: C, 64.7; H, 4.5; Cd, 14.4; P, 4.0; S, 12.3%).

Crystal Structure Determinations.—Crystal data. For (**1**). $C_{84}H_{70}P_2S_6Zn_2$, M = 1 464.5, monoclinic, space group $P2_1/c$,

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† Bis(tetraphenylphosphonium) di-μ-benzenethiolato-bis[bis(benzenethiolato)zincate(II)] and di-μ-benzenethiolato-bis[bis(benzenethiolato)cadmate(II)].

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Atomic co-ordinates (× 10^4)

(*a*) $[PPh_4]_2[Zn_2(SPh)_6]$

Atom	*x*	*y*	*z*
Zn	6 226(1)	4 692(1)	4 978(1)
S(1)	4 790(1)	3 805(1)	5 203(1)
C(11)	5 164(2)	3 415(2)	6 065(1)
C(12)	6 034(2)	2 831(2)	6 296(1)
C(13)	6 330(3)	2 497(2)	6 966(2)
C(14)	5 772(3)	2 758(2)	7 403(2)
C(15)	4 910(3)	3 333(3)	7 179(2)
C(16)	4 596(3)	3 664(2)	6 510(1)
S(2)	7 749(1)	4 917(1)	5 827(1)
C(21)	7 504(2)	5 754(2)	6 421(1)
C(22)	6 559(2)	5 802(2)	6 574(1)
C(23)	6 415(3)	6 432(2)	7 066(2)
C(24)	7 213(3)	7 026(3)	7 417(2)
C(25)	8 148(3)	6 993(3)	7 275(2)
C(26)	8 300(2)	6 368(2)	6 783(2)
S(3)	6 503(1)	3 799(1)	4 092(1)
C(31)	7 559(2)	4 312(2)	3 860(1)
C(32)	7 393(2)	4 748(2)	3 228(2)
C(33)	8 221(3)	5 135(3)	3 019(2)
C(34)	9 225(3)	5 085(2)	3 445(2)
C(35)	9 395(2)	4 642(2)	4 067(2)
C(36)	8 581(2)	4 268(2)	4 279(1)
P	7 589(1)	279(1)	4 473(1)
C(41)	6 198(2)	443(2)	4 200(1)
C(42)	5 761(2)	1 314(2)	4 305(2)
C(43)	4 696(3)	1 464(3)	4 090(2)
C(44)	4 063(3)	743(3)	3 782(2)
C(45)	4 480(3)	−123(3)	3 661(3)
C(46)	5 545(3)	−280(3)	3 862(2)
C(51)	8 132(2)	791(2)	5 311(1)
C(52)	8 629(2)	179(2)	5 846(1)
C(53)	9 051(3)	556(3)	6 489(2)
C(54)	8 970(3)	1 528(3)	6 603(2)
C(55)	8 507(3)	2 162(3)	6 078(2)
C(56)	8 086(2)	1 792(2)	5 427(2)
C(61)	8 192(2)	858(2)	3 893(1)
C(62)	9 067(2)	1 438(2)	4 131(2)
C(63)	9 571(3)	1 818(3)	3 686(2)
C(64)	9 203(3)	1 598(3)	3 004(2)
C(65)	8 329(3)	1 014(3)	2 755(2)
C(66)	7 818(3)	656(2)	3 206(2)
C(71)	7 882(2)	−1 007(2)	4 503(1)
C(72)	8 601(2)	−1 381(2)	4 208(1)
C(73)	8 832(3)	−2 374(2)	4 255(2)
C(74)	8 356(3)	−2 980(2)	4 607(2)
C(75)	7 646(3)	−2 610(2)	4 915(2)
C(76)	7 395(2)	−1 630(2)	4 855(2)

(*b*) $[PPh_4]_2[Cd_2(SPh)_6]$

Atom	*x*	*y*	*z*
Cd	6 278(1)	4 647(1)	4 975(1)
S(1)	4 739(1)	3 698(1)	5 205(1)
C(11)	5 123(2)	3 398(2)	6 073(1)
C(12)	5 986(3)	2 837(3)	6 328(2)
C(13)	6 280(3)	2 584(3)	7 004(2)
C(14)	5 721(3)	2 871(3)	7 430(2)
C(15)	4 870(3)	3 419(3)	7 178(2)
C(16)	4 553(3)	3 688(3)	6 502(2)
S(2)	7 862(1)	4 891(1)	5 901(1)
C(21)	7 565(2)	5 743(2)	6 464(1)
C(22)	6 615(2)	5 807(3)	6 586(2)
C(23)	6 439(3)	6 457(3)	7 051(2)
C(24)	7 210(3)	7 054(3)	7 419(2)
C(25)	8 161(3)	6 999(3)	7 303(2)
C(26)	8 340(3)	6 355(3)	6 833(2)
S(3)	6 581(1)	3 665(1)	4 038(1)
C(31)	7 609(2)	4 245(2)	3 819(1)
C(32)	7 440(3)	4 705(3)	3 199(2)
C(33)	8 239(3)	5 146(3)	3 006(2)
C(34)	9 214(3)	5 109(3)	3 421(2)
C(35)	9 392(3)	4 658(3)	4 034(2)
C(36)	8 596(2)	4 237(2)	4 233(2)
P	7 626(1)	255(1)	4 490(1)
C(41)	6 256(2)	390(3)	4 222(2)
C(42)	5 797(3)	1 222(3)	4 356(2)
C(43)	4 744(3)	1 336(3)	4 134(2)
C(44)	4 162(3)	621(3)	3 799(2)
C(45)	4 603(3)	−209(3)	3 642(3)
C(46)	5 650(3)	−328(3)	3 854(2)
C(51)	8 146(2)	767(2)	5 321(1)
C(52)	8 643(3)	157(3)	5 843(1)
C(53)	9 042(3)	536(3)	6 483(2)
C(54)	8 941(3)	1 512(3)	6 599(2)
C(55)	8 469(3)	2 137(3)	6 082(2)
C(56)	8 078(3)	1 772(3)	5 440(2)
C(61)	8 220(3)	859(2)	3 920(2)
C(62)	9 067(3)	1 453(3)	4 155(2)
C(63)	9 550(3)	1 849(3)	3 711(2)
C(64)	9 205(3)	1 634(3)	3 039(2)
C(65)	8 366(3)	1 048(3)	2 796(2)
C(66)	7 858(3)	659(3)	3 231(2)
C(71)	7 927(2)	−1 036(2)	4 515(1)
C(72)	8 645(3)	−1 401(2)	4 218(2)
C(73)	8 887(3)	−2 394(3)	4 267(2)
C(74)	8 430(3)	−3 006(3)	4 624(2)
C(75)	7 731(3)	−2 651(3)	4 930(2)
C(76)	7 470(3)	−1 668(2)	4 874(2)

a = 13.379(2), b = 13.654(2), c = 20.480(3) Å, β = 106.50(2)°, U = 3 587.2 Å^3 (from 2θ values of 28 reflections centred at $\pm\omega$, λ = 0.710 69 Å), Z = 2, D_c = 1.356 g cm^{-3}, F(000) = 1 520. Crystal dimensions 0.7 × 0.6 × 0.5 mm, μ(Mo-K_α) = 0.94 mm^{-1}.

For (**2**). $C_{84}H_{70}Cd_2P_2S_6$, M = 1 558.6, monoclinic, space group $P2_1/c$, a = 13.599(1), b = 13.584(1), c = 20.655(2) Å, β = 106.06(1)°, U = 3 666.7 Å^3 (from 32 reflections), Z = 2, D_c = 1.411 g cm^{-3}, F(000) = 1 592. Crystal dimensions 0.2 × 0.2 × 0.5 mm, μ(Mo-K_α) = 0.83 mm^{-1}.

The compounds are isostructural; the dimeric anion has inversion symmetry in each case.

Data collection and processing. Compound (**1**) [in square brackets for (**2**) if different]: Stoe-Siemens AED diffractometer, θ—ω scan mode, graphite-monochromated Mo-K_α radiation, on-line profile fitting.[11] 6 298 [7 714] Reflections measured ($h \leqslant 0$, $k \geqslant 0$, $2\theta \leqslant 50°$) [$h \geqslant 0$, $k \leqslant 0$ and some reflections with k = 1 or 2, $2\theta \leqslant 50°$], 6 298 unique reflections [6 439 unique reflections, R_{int} = 0.018], 4 987 [4 918] with $F > 4\sigma(F)$. Semiempirical absorption corrections based on azimuthal scan measurements: transmission 0.49—0.55 [0.71—0.79]. No extinction correction; no significant variation in three standard reflection intensities.

Structural analysis and refinement. Direct methods and difference syntheses. Blocked-cascade least-squares refinement on F with all non-hydrogen atoms anisotropic. Hydrogen atoms on external bisectors of ring angles with C–H 0.96 Å and U(H) = 1.2U_{eq}(C). Automatic optimisation of weighting scheme, $w^{-1} = \sigma^2(F) + gF^2$ where g = 0.000 13 [0]. 424 Parameters, R = 0.037 [0.036], $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$ = 0.040 [0.030], slope of normal probability plot = 1.37 [1.53], no significant features in a final difference synthesis. Scattering factors from ref. 12. Programs: SHELXTL;[13] diffractometer control program by W. C.

Atomic co-ordinates are given in Table 1, selected geometrical parameters in Table 2.

Table 2. Selected bond lengths (Å) and angles (°) for $[PPh_4]_2$-$[M_2(SPh)_6]$

	M = Zn	M = Cd
M-S(1)	2.424(1)	2.611(1)
M-S(1′)	2.431(1)	2.611(1)
M-S(2)	2.293(1)	2.477(1)
M-S(3)	2.302(1)	2.478(1)
S(1)-C(11)	1.775(3)	1.772(3)
S(2)-C(21)	1.766(3)	1.764(4)
S(3)-C(31)	1.759(3)	1.769(4)
S(1)-M-S(1′)	90.7(1)	91.8(1)
S(1)-M-S(2)	120.3(1)	119.7(1)
S(1)-M-S(3)	101.5(1)	101.0(1)
S(2)-M-S(3)	111.2(1)	112.2(1)
S(1′)-M-S(2)	109.9(1)	107.9(1)
S(1′)-M-S(3)	122.4(1)	123.3(1)
M-S(1)-M′	89.3(1)	88.2(1)
M-S(1)-C(11)	108.9(1)	105.7(1)
M′-S(1)-C(11)	113.1(1)	109.8(1)
M-S(2)-C(21)	108.1(1)	106.7(1)
M-S(3)-C(31)	108.9(1)	105.9(1)

The prime denotes an atom generated by the inversion symmetry operator 1 − *x*, 1 − *y*, 1 − *z*.

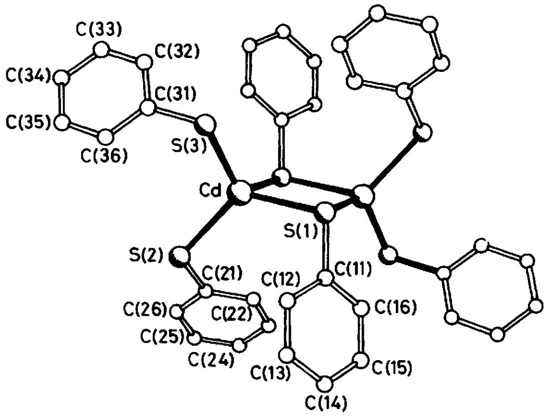

Figure. Structure of the $[Cd_2(SPh)_6]^{2-}$ anion

Results and Discussion

The complexes $[PPh_4]_2[Zn_2(SPh)_6]$ and $[PPh_4]_2[Cd_2(SPh)_6]$ are isostructural (Figure). The dimeric anion in each case has inversion symmetry, with an exactly planar M_2S_2 ring. The phenyl substituents of the bridging ligands are arranged *anti* to each other. The central ring shows only slight deviations from a perfectly square geometry, with four almost exactly equal M-S bonds and with angles within 2° of 90°. Table 3 compares the main geometrical parameters with those of the previously determined $[M_2(SEt)_6]^{2-}$ anions. The major differences are (*i*) a greater variation in M-S bond lengths in the ring for the SEt^- complexes, (*ii*) a more marked compression of the ring along the M-M vector for these complexes, producing larger ring angles at M and smaller at S. The bond lengths and angles *exo* to the ring are not markedly different in the two pairs of complexes. The reasons for the differences between the EtS^- and PhS^- structures are not clear.

Vibrational spectra show features above 400 cm^{-1} which can all be assigned to internal vibrations of the cations and benzenethiolate ligands. Metal–sulphur modes are observed at 250—270 and 330—350 cm^{-1}, with weaker bands in the region 275—300 cm^{-1}, small shifts to lower frequency occurring on substitution of Cd for Zn. The main feature in the u.v.-visible spectra is a structured band at 260—275 nm, to which aromatic $\pi \longrightarrow \pi^*$ transitions make the major contribution, masking the metal–sulphur charge-transfer transitions [$\lambda_{max.}$ for the zinc complex 272 ($\varepsilon = 10.5 \times 10^4$); for the cadmium complex, 270 nm ($\varepsilon = 9.5 \times 10^4$ dm^3 mol^{-1} cm^{-1})].

Table 3. Comparison of structural results for $[M_2(SR)_6]^{2-}$ complexes. Distances in Å, angles in °

M	Zn	Zn	Cd	Cd
SR	SEt	SPh	SEt	SPh
$M-S_{bridging}$	2.456(1)	2.431(1)	2.635(2)	2.611(1)
	2.394(1)	2.424(1)	2.589(2)	2.611(1)
$M-S_{terminal}$	2.304(1)	2.302(1)	2.487(2)	2.478(1)
	2.296(1)	2.293(1)	2.471(2)	2.477(1)
$M \cdots M$	3.179(1)	3.421(1)	3.483(2)	3.692(1)
S_b-M-S_b	98.1(1)	90.7(1)	96.4(1)	91.8(1)
S_t-M-S_t	113.9(1)	111.2(1)	115.3(1)	112.2(1)
$M-S_b-M$	81.9(1)	89.3(1)	80.5(1)	88.2(1)

In the ^1H n.m.r. spectra the protons of the benzenethiolate ligands give rise to three distinct resonances, which can be assigned, in order of increasing chemical shift, as *para* [triplet, 1 H, δ 6.76 (Zn), 6.85 (Cd)], *meta* [triplet, 2 H, δ 6.90 (Zn), 6.95 (Cd)], and *ortho* [doublet, 2 H, δ 7.40 (Zn), 7.35 (Cd)]. The signals are sharp, and cannot be resolved into separate signals for terminal and bridging ligands; this indicates a rapid chemical exchange of the ligand sites in solution at room temperature. A similar averaging of terminal and bridging ligand signals is observed in the ^{13}C n.m.r. spectra. Resonances due to the thiolate ligands are assigned as follows (δ/p.p.m.): *ipso* 146.16 (Zn), 145.55 (Cd); *ortho* 132.28 (Zn), 132.27 (Cd); *meta* 126.87 (Zn), 127.01 (Cd); *para* 120.39 (Zn), 120.61 (Cd).

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