

Synthesis and characterization of Group 11 and 12 complexes containing a new thioether-functionalized and pyridine-based bis(phosphine) ligand, 2,6-bis[2-(diphenylphosphino)ethylsulfanylmethyl]pyridine

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The new ligand 2,6-bis[2-(diphenylphosphino)ethylsulfanylmethyl]pyridine, 2,6-(Ph₂PCH₂CH₂SCH₂)₂C₅H₃N (L¹), has been synthesized. Reaction of [Cu(MeCN)₄][CF₃SO₃] or AgNO₃ with 1 molar equivalent of L¹ gave [CuL¹][CF₃SO₃] **1** or [AgL¹][NO₃] **2**, in good yield. Reaction of equimolar quantities of L¹ and Au^I, followed by precipitation with AgO₃SCF₃, gave [AuL¹][CF₃SO₃] **3**. In the crystal structure of **2**·H₂O, L¹ co-ordinates to Ag via a P₂S₂ donor set in a distorted tetrahedral geometry. Reaction of M(O₃SCF₃)₂ (M = Zn or Cd) with 1 molar equivalent of L¹ gave [ML¹(O₃SCF₃)₂] (M = Zn **4** or Cd **5**). Crystal structure analysis of **5** showed that the molecule has symmetry 2, with all five donor atoms of L¹ and a pair of monodentate CF₃SO₃[−] ligands arranged in an unusual distorted pentagonal bipyramidal co-ordination geometry about the cadmium centre.

Acyclic phosphine ligands are well known to form stable complexes with many metal ions, whereas acyclic thioether complexes tend to be less stable and often hydrolyse readily.¹ As the NS₂ donor set in 2,6-bis(*R*-sulfanylmethyl)pyridine has been found to be good for the stabilization of transition-metal ions,² we reasoned that the incorporation of heteroatom donors, such as nitrogen or sulfur, on sites within a diphosphine bridge might result in transition-metal complexes co-ordinated by sulfur (or nitrogen) and the phosphorus centres. We anticipated that, as phosphines are better σ donors compared to thioethers, stabilization of a mixed phosphine–thioether co-ordination complex could be achieved by inhibiting decomplexation of the more weakly bound thioether in solution. In this context, recent reports by Darensbourg and co-workers³ and Reid and co-workers⁴ have demonstrated the development and co-ordination chemistry of dithiobis(phosphine) chelates. We report here the synthesis and characterization of Group 11 and 12 complexes with a new thioether-functionalized and pyridine-based bis(phosphine) ligand, 2,6-bis[2-(diphenylphosphino)ethylsulfanylmethyl]pyridine, 2,6-(Ph₂PCH₂CH₂SCH₂)₂-C₅H₃N (L¹), which displays an unusual co-ordination mode toward Cd²⁺.

Experimental

General procedure, measurement and materials

All reactions were routinely carried out under a nitrogen atmosphere using Schlenk techniques. The solvents were purified by standard methods. The ¹H and ¹³C-{¹H} NMR spectra were recorded on a Bruker-300 spectrometer using SiMe₄ as the external standard and CDCl₃ as solvent, ³¹P-{¹H} NMR spectra on a Bruker-500 spectrometer at 202.45 MHz using (PhO)₃P as the external standard and CDCl₃ as solvent and mass spectra on a Hewlett-Packard 5989B spectrometer. The compounds [Cu(MeCN)₄][CF₃SO₃]⁵ and M(O₃SCF₃)₂ (M = Zn or Cd)⁶ were prepared by the literature procedures.

Preparations

2,6-Bis[2-(diphenylphosphino)ethylsulfanylmethyl]pyridine, L¹. A solution of LiBuⁿ in hexane (1.60 M, 17.0 cm³) was added dropwise to a solution of Ph₂PH (4.65 g, 25 mmol) in tetrahy-

drofuran (thf, 50 cm³) at −78 °C. To this mixture, a solution of ethylene sulfide (thiirane) (1.50 cm³, 25 mmol) in thf (20 cm³) was added. The resulting solution was continuously stirred until 0 °C was reached, and a solution of 2,6-bis(chloromethyl)pyridine (2.20 g, 12.5 mmol) in thf (80 cm³) was then added over a period of 3 h with the temperature maintained at 0 °C. After the addition the mixture was stirred at room temperature for 48 h. The thf was removed in vacuum and water (100 cm³) added. The water phase was next extracted with diethyl ether (3 × 50 cm³) and the organic phase dried with anhydrous Na₂SO₄ overnight. Most of the diethyl ether was removed in vacuum and hexane (100 cm³) was added. Cooling to −30 °C for 8 h yielded a colourless solid. Recrystallization from CH₂Cl₂–hexane afforded L¹ as an analytically pure product, 5.30 g (71%) (Found: C, 70.24; H, 5.88; N, 2.27. C₃₅H₃₅NP₂S requires C, 70.56; H, 5.92; N, 2.35%), m.p. 52–53 °C. ¹H NMR (CDCl₃): δ 7.52 (t, *J* = 3.5, 1 H), 7.36–7.25 (m, 20 H), 7.05 (d, *J* = 2.2 Hz, 2 H), 3.73 (s, 4 H), 2.50 (m, 4 H) and 2.26 (m, 4 H). ¹³C-{¹H} NMR (CDCl₃): δ 28.73 (d, *J* = 20.3), 28.96 (d, *J* = 14.9 Hz), 38.56 (s) and 121.65–138.57 (m). ³¹P-{¹H} NMR: δ −4.54. FAB mass spectrum: *m/z* = 596; Calc. 595 for (Ph₂PCH₂CH₂-SCH₂)₂C₅H₃N.

[CuL¹][CF₃SO₃] **1.** To a solution containing compound L¹ (0.30 g, 0.5 mmol) in CH₂Cl₂ (20 cm³) was added solid [Cu(MeCN)₄][CF₃SO₃] (0.19 g, 0.5 mmol). The resulting solution was stirred at room temperature for 2 h. Subsequent diffusion of diethyl ether into the concentrated solution gave complex **1** as air-stable colourless crystals (yield 0.34 g, 84%) (Found: C, 53.21; H, 4.71; N, 1.78. C₃₆H₃₅CuF₃NO₃P₂S₃ requires C, 53.49; H, 4.36; N, 1.73%). ³¹P-{¹H} NMR: δ 34.72.

[AgL¹][NO₃] **2.** The procedure used was similar to that above, except that AgNO₃ (0.09 g, 0.5 mmol) was employed instead of [Cu(MeCN)₄][CF₃SO₃]. Recrystallization of the product from CH₂Cl₂–diethyl ether afforded complex **2**·H₂O as colourless crystals. Yield: 0.29 g (76%) (Found: C, 54.99; H, 4.61; N, 3.55. C₃₅H₃₅AgN₂O₃P₂S₂·H₂O requires C, 54.86; H, 4.72; N, 3.57%). ³¹P-{¹H} NMR: δ 43.14.

[AuL¹][CF₃SO₃] **3.** The complex K[AuCl₄]·2H₂O (0.10 g, 0.25 mmol) was reduced to Au^I by 2,2'-thiodiethanol (0.06 g, 0.5

mmol) in methanol (20 cm³) for 30 min. Compound L¹ (0.15 g, 0.25 mmol) in CH₂Cl₂ (10 cm³) was added and stirred for 10 min, and then AgO₃SCF₃ (0.26 g, 1.0 mmol) in methanol (20 cm³) was added to the mixture and stirred for 30 min. Filtration followed by solvent removal and subsequent recrystallization from CH₂Cl₂–hexane afforded complex **3** as colourless crystals. Yield: 0.15 g (81%) (Found: C, 45.78; H, 3.77; N, 1.41. C₃₆H₃₅AuF₃NO₃P₂S₃ requires C, 45.91; H, 3.75; N, 1.49%). ³¹P-{¹H} NMR: δ 42.91.

[ZnL¹][CF₃SO₃]₂ 4. To a solution containing compound L¹ (0.30 g, 0.5 mmol) in CH₂Cl₂ (20 cm³) was added solid Zn(O₃SCF₃)₂ (0.18 g, 0.5 mmol). The resulting solution was stirred at room temperature for 2 h. Subsequent diffusion of diethyl ether into the concentrated solution gave complex **4** as air-stable colourless crystals (yield 0.40 g, 77%) (Found: C, 43.95; H, 3.67; N, 1.33. C₃₇H₃₅F₆NO₃P₂S₄Zn·CH₂Cl₂ requires C, 43.71; H, 3.57; N, 1.34%). ³¹P-{¹H} NMR: δ 56.53.

[CdL¹(O₃SCF₃)₂] 5. The procedure used was similar to that above, except that Cd(O₃SCF₃)₂ (0.21 g, 0.5 mmol) was used instead of Zn(O₃SCF₃)₂. Recrystallization of the product from CH₂Cl₂–hexane afforded complex **5** as colourless crystals. Yield: 0.32 g (64%) (Found: C, 43.37; H, 3.49; N, 1.34. C₃₇H₃₅CdF₆NO₃P₂S₄ requires C, 44.16; H, 3.51; N, 1.39%). ³¹P-{¹H} NMR: δ 55.09.

X-Ray crystallography

Intensity data for complexes **2**·H₂O and **5** were collected at 294 K in the variable ω-scan mode on a four-circle diffractometer (Siemens R3m/V) using Mo-Kα radiation (λ = 0.710 73 Å, 50 kV, 25 mA; 2θ_{min} = 3, 2θ_{max} = 55°). Empirical absorption corrections were applied by fitting a pseudo-ellipsoid to the ψ-scan data of 25 selected strong reflections over a range of 2θ angles.^{7a}

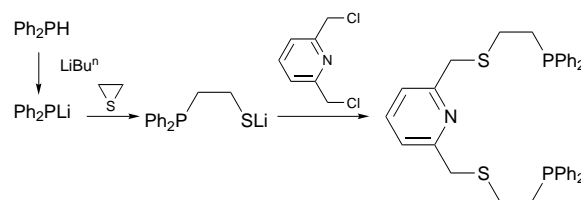
Structure solution by the direct method yielded the positions of all non-hydrogen atoms, which were refined using anisotropic thermal parameters. Hydrogen atoms were all generated geometrically (C–H bond lengths fixed at 0.96 Å), assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms. All the H atoms were held stationary and included in the structure-factor calculation in the final stage of full-matrix least-squares refinement. All computations were performed on an IBM-compatible 486 personal computer with the SHELTX PC, version 5.03, program package.^{7b}

Information concerning X-ray data collection and structure refinement of all compounds is summarized in Table 1.

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Results and Discussion

The synthesis of a new thioether-functionalized and pyridine-based bis(phosphine) ligand, namely 2,6-bis[2-(diphenylphosphino)ethylsulfanyl]methylpyridine (L¹), was accomplished in two steps in good yield, as outlined in Scheme 1. Reaction of Ph₂PLi (prepared *in situ* from Ph₂PH and LiBuⁿ) with ethylene sulfide at low temperature gave the lithium 2-diphenylphosphinoethanethiolate salt, which then reacted with 2,6-bis-(chloromethyl)pyridine to give the designed phosphine ligand. The structure of 2,6-(Ph₂PCH₂CH₂SCH₂)₂C₅H₃N, L¹, was confirmed by elemental analysis and ¹H, ¹³C-{¹H}, ³¹P-{¹H} NMR spectroscopy and FAB mass spectrometry. In the ¹H NMR spectrum the SCH₂C₅H₃N methylene protons appeared as a singlet at δ 3.73 and two groups of signals attributed to the SCH₂CP and SCCH₂P methylene protons coupled with the phosphorus atoms were observed at δ 2.50 and 2.26. In the ¹³C-{¹H} NMR spectrum the SCC₅H₃N carbon atom appeared as a singlet at δ 38.56, whereas the SCCP carbon atoms appeared as



Scheme 1

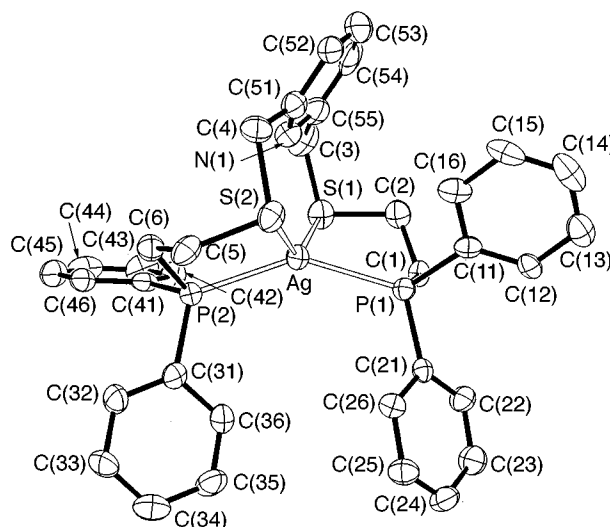


Fig. 1 Perspective view of the cation in [Ag{(Ph₂PCH₂CH₂SCH₂)₂-C₅H₃N}][NO₃]·H₂O, 2·H₂O. The atoms are shown as 35% thermal ellipsoids

a pair of doublets centred at δ 28.73 (*J* = 20.3) and 28.96 (*J* = 14.9 Hz). On the basis of literature data for P–C coupling constants⁸ and the observed chemical shifts for related phosphine-containing ligands, we assigned the first and second doublets to the carbon atoms located in the α and β positions, respectively, with respect to the phosphorus atom. The FAB mass spectrum showed the molecular ion at *m/z* = 596, and the ³¹P-{¹H} NMR spectrum exhibited a singlet at δ –4.54.

Reaction of [Cu(MeCN)₄][CF₃SO₃] or AgNO₃ with 1 molar equivalent of L¹ in degassed dichloromethane, followed by precipitation with diethyl ether, gave [CuL¹][CF₃SO₃] **1** or [AgL¹][NO₃] **2**, as white solids in good yield. Reaction of equimolar amounts of L¹ and Au^I, generated *in situ* by the reduction of K[AuCl₄] with 2,2′-thiodiethanol in methanol, gave a colourless solution at room temperature. Addition of AgO₃SCF₃ to the solution precipitated [AuL¹][CF₃SO₃] **3**, as a white solid.

The ³¹P-{¹H} NMR spectra of complexes **1** and **2** at 298 K showed a singlet at δ 34.72 and 43.14, respectively, and no Ag–P coupling was observed for **2**. For complex **3** the ³¹P-{¹H} NMR spectrum displayed a high-frequency shift of 47.4 ppm relative to the free phosphine. This shift is similar to those of the complexes [Au{(Ph₂PCH₂CH₂SCH₂)₂}[PF₆] (49.2 ppm) and [Au{(Ph₂PCH₂CH₂SCH₂)₂CH₂}[PF₆] (46.1 ppm),^{4b} both of which involve averaged P₂ co-ordination in solution. In view of the similarity of these species, we expect that in the solid state **3** also adopts a similar primary P₂ co-ordination about Au^I and a distorted linear geometry.

Crystals of [AgL¹][NO₃]·H₂O suitable for single-crystal X-ray study were obtained by layering a solution of the complex in CH₂Cl₂ at ca. –20 °C with toluene. The structure of the molecular cation with the atom numbering scheme is depicted in Fig. 1. The co-ordination geometry around silver(I) may be described as a very distorted tetrahedron with a P–Ag–P angle of 144.4(1)° (Table 2), far higher than the idealized value of 109.5°. This is certainly caused by the repulsion between two phenyl rings [C(26)⋯C(36) 3.690 Å] which has the further consequence of narrowing the S–Ag–P bond angles to 80.2(1) and 81.3(1)°. A similar effect has been reported in [Ag(Ph₂P-

Table 1 Crystal and structural data for complexes **2**·H₂O and **5**

| | | |
|---|--|---|
| Formula | C ₃₅ H ₃₅ AgN ₂ O ₃ P ₂ S ₂ ·H ₂ O 2 ·H ₂ O | C ₃₇ H ₃₅ CdF ₆ NO ₆ P ₂ S ₄ 5 |
| <i>M</i> | 783.6 | 1006.2 |
| Crystal system | Orthorhombic | Trigonal |
| Space group | <i>P</i> 2 ₁ 2 ₁ 2 ₁ | <i>P</i> 3 ₂ 21 |
| <i>a</i> /Å | 9.875(1) | 18.072(3) |
| <i>b</i> /Å | 12.585(5) | 18.072(3) |
| <i>c</i> /Å | 28.362(3) | 12.099(2) |
| <i>U</i> /Å ³ | 3524.7(12) | 3425(2) |
| <i>Z</i> | 4 | 3 |
| <i>F</i> (000) | 1608 | 1524 |
| <i>D</i> _c /g cm ⁻³ | 1.477 | 1.464 |
| <i>μ</i> /cm ⁻¹ | 0.821 | 0.797 |
| Goodness of fit | 1.22 | 1.10 |
| No. unique reflections | 4909 (0.027) | 4876 (0.030) |
| (<i>R</i> _{int}) | | |
| No. observed reflections | 3183 | 4561 |
| [<i>F</i> ≥ 4σ(<i>F</i>)] | | |
| No. variables, <i>p</i> | 410 | 263 |
| <i>R</i> _F ^a | 0.053 | 0.049 |
| <i>R</i> _F ^{2b} | 0.087 | 0.052 |

^a Σ(|*F*_o| − |*F*_c|)/Σ|*F*_o|. ^b {w[Σ(|*F*_o| − |*F*_c|)²]/Σ|*F*_o|²]^{1/2}.

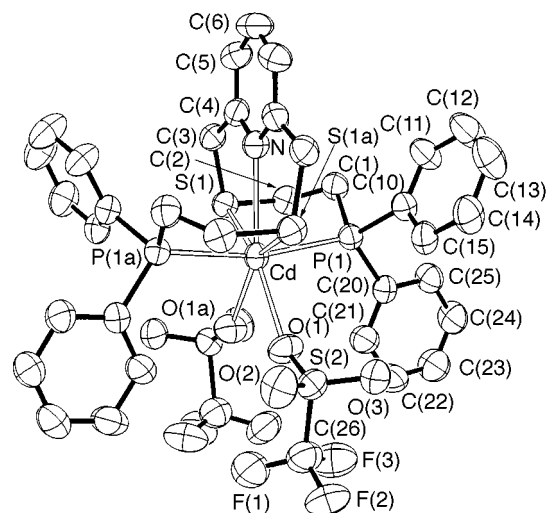
Table 2 Selected bond lengths (Å) and angles (°) of complexes **2**·H₂O and **5**

| | | | |
|----------------------------|----------|---------------|----------|
| 2 ·H ₂ O | | | |
| Ag–P(1) | 2.455(3) | Ag–P(2) | 2.448(3) |
| Ag–S(1) | 2.869(3) | Ag–S(2) | 2.846(3) |
| P(1)–Ag–P(2) | 144.4(1) | P(1)–Ag–S(1) | 80.2(1) |
| P(1)–Ag–S(2) | 110.5(1) | P(2)–Ag–S(1) | 111.2(1) |
| S(1)–Ag–S(2) | 142.7(1) | P(2)–Ag–S(2) | 81.3(1) |
| 5 | | | |
| Cd–P(1) | 2.590(1) | Cd–S(1) | 2.821(1) |
| Cd–O(1) | 2.455(2) | Cd–N(1) | 2.695(3) |
| P(1)–Cd–S(1) | 79.9(1) | P(1)–Cd–O(1) | 97.1(1) |
| S(1)–Cd–O(1) | 75.8(1) | P(1)–Cd–N | 83.4(1) |
| S(1)–Cd–N | 70.1(1) | O(1)–Cd–N | 145.2(1) |
| P(1)–Cd–P(1a) | 166.8(1) | S(1)–Cd–S(1a) | 140.1(1) |
| O(1)–Cd–O(1a) | 69.5(2) | P(1)–Cd–S(1a) | 95.6(1) |
| P(1)–Cd–O(1a) | 93.8(1) | S(1)–Cd–O(1a) | 143.7(1) |

CH₂CH₂SEt)₂][ClO₄] with a P–Ag–P angle of 148.9(1)°. The Ag(1)···N(1) distance of 2.689 Å, much longer than the corresponding distance of 2.368(6) Å in [AgL₂][PF₆] [L² = 6,9,12-trioxa-3,15-dithia-21-azabicyclo[15.3.1]henicosa-1(21),17,19-triene],¹⁰ indicates that the Ag···N interaction is very feeble, which is consistent with the fact that the nitrogen lone pair does not point directly toward the silver atom (Fig. 1). The Ag–P distances of 2.455(3) and 2.448(3) Å are within the expected range for silver tertiary phosphine complexes. The Ag–S distances of 2.869(3) and 2.846(3) Å, which are longer than 2.694(2) Å in [Ag(Ph₂PCH₂CH₂SEt)₂][ClO₄]⁹ and 2.589(2) Å (average) in [Ag_n(PhSCH₂CH₂CH₂SPh)_{2n}][BF₄]_n·0.5*n*H₂O,¹¹ suggest that the silver ion is weakly bound to the sulfur atoms.

Reactions of M(O₃SCF₃)₂ (M = Zn or Cd) with 1 molar equivalent of L¹ in dichloromethane at room temperature gave a colourless solution which on addition of diethyl ether gave [ML¹(O₃SCF₃)₂] (M = Zn **4** or Cd **5**). The ³¹P-{¹H} NMR spectra of **4** and **5** at 298 K showed a singlet at δ 56.53 and 55.09, respectively, and no Cd–P coupling was observed for **5**.

Diffraction-quality crystals of [CdL¹(O₃SCF₃)₂] **5** were obtained by vapour diffusion of diethyl ether into a solution of the complex in CH₂Cl₂ at room temperature. A perspective view of the molecular structure of **5**, which possesses a crystallographically imposed two-fold axis passing through Cd, N and C(6), is illustrated in Fig. 2. The co-ordination geometry about the cadmium centre is a distorted pentagonal bipyramid, with

**Fig. 2** An ORTEP¹² view of the [Cd{(Ph₂PCH₂CH₂SCH₂)₂C₅H₅N}-(O₃SCF₃)₂] molecule, **5**. The atoms are shown as 35% thermal ellipsoids. Note that a two-fold symmetry axis passes through the Cd, N and C(6) atoms

coplanar O(1), S(1), N, S(1a) and O(1a) atoms at the equatorial sites, and P(1) and P(1a) occupying the axial positions. The seven-co-ordinate geometry observed in this complex is largely a result of the constraints imposed by the pentadentate ligand. Since there is no ligand-field stabilization effect in Cd²⁺, the stereochemistry of its complexes is in general determined by ionic size, electrostatics, and covalent bonding energies.¹³ Owing to its size, Cd²⁺ commonly has a co-ordination number of six as in CdCl₂, [CdCl₂(NH₃)₂], [CdCl(OH)], K₄[CdCl₄], CdI₂ and Cd(OH)₂.¹⁴ However, a seven-co-ordinate, distorted pentagonal bipyramidal complex of Cd²⁺ containing a thioether ligand is known, namely [Cd([15]aneS₅)](ClO₄)₂·H₂O ([15]-aneS₅ = 1,4,7,10,13-pentathiacyclopentadecane).¹⁵

The P(1)–Cd–S(1) and P(1)–Cd–N angles are somewhat acute [79.9(1) and 83.4(1)°, respectively], while P(1)–Cd–S(1a) and P(1)–Cd–O(1) are somewhat obtuse [95.6(1) and 97.1(1)°]. This distortion is attributable to the geometrical constraints imposed by the ligand, as the ethylene bridges between S and P atoms do not allow P(1) and P(1a) to pull away far enough from each other. The P(1)–Cd–P(1a) angle of 166.8(1)° is accordingly less than the ideal value of 180°.

The P–Cd bond length of 2.590(1) Å is close to the sum of covalent radii for cadmium and phosphorus (1.48 + 1.10 = 2.58 Å)¹⁶ and also comparable to 2.602(2) Å found in [Cd{P(C₆H₁₁)₃}]₂[NO₃]₂·CH₂Cl₂.¹⁷ The Cd–S bond length of 2.821(1) Å is comparable to those of [Cd([15]aneS₅)](ClO₄)₂·H₂O (Cd–S_{av} 2.76 Å)¹⁵ and significantly longer than 2.703(1) Å in the six-co-ordinate complex [{CdL²Cl₂·H₂O}]₂ [L² = 2,6-bis(ethylsulfanylmethyl)pyridine]¹⁸ and four-co-ordinate complex [Cd([16]aneS₄)](ClO₄)₂ (Cd–S_{av} 2.65 Å) ([16]aneS₄ = 1,5,9,13-tetrathiacyclohexadecane).¹⁹ It has been observed that in mercury(II) thioether complexes²⁰ the metal–sulfur bond lengths are a function of the number of donor atoms. As the co-ordination number of the metal centre goes up, its bonds to sulfur are lengthened. Hence it is not surprising that the seven-co-ordinate complex **5** has such long Cd–S bonds compared to those of an analogous six- or four-co-ordinate complex. The Cd–N bond distance of 2.695(3) Å is also longer than 2.380(3) Å in the six-co-ordinate, dimeric complex [{CdL²Cl₂·H₂O}]₂.¹⁸

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