Preparation and Crystal and Molecular Structure of [MoO(SCH$_2$CH$_2$PPh$_2$)$_2$] †

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The title complex has been prepared by reaction of [MoO$_2$(acac)$_2$] (acac = pentane-2,4-dionate) with an excess of Ph$_2$PCH$_2$CH$_2$SH in methanol or toluene. The oxo-group can be protonated with anhydrous HBF$_4$ in benzene to give [Mo(OH$_2$)(SCH$_2$CH$_2$PPh$_2$)$_2$][BF$_4$]$_2$ but does not undergo condensation-type reactions with hydrazines even under forcing conditions. The complex [MoO(SCH$_2$CH$_2$PPh$_2$)$_2$] crystallises in the orthorhombic space group $P2_12_12_1$ with four molecules in a unit cell of dimensions a = 10.263(3), b = 10.246(1), and c = 26.657(5) Å. The structure has been solved using 2 179 symmetry-independent reflections with $I > 2.58\sigma(I)$ collected by counter techniques using Cu-K_α radiation. Refinement by full-matrix least squares, using anisotropic temperature factors for all non-carbon and non-hydrogen atoms, gives a final R factor of 0.063. The co-ordination polyhedron is intermediate between trigonal-bipyramidal and square-pyramidal geometries. The bond distances to Mo are Mo–O 1.733(9), Mo–S(av.) 2.360(4), and Mo–P(av.) 2.484(4) Å.

THE co-ordinated dinitrogen in the complexes [M(N$_2$)$_2$(PMe$_2$Ph)$_4$] (M = Mo or W) is activated towards protonation and ammonia is produced on treatment with acid.[1] However recent EXAFS measurements on the iron–molybdenum protein of nitrogenase have suggested that the molybdenum in the enzyme is ligated by sulphur.[2] In an effort to investigate the chemistry of molybdenum in an intermediate mixed sulphur–phosphorus environment we have prepared some complexes of the phosphinothiol Ph$_2$PCH$_2$CH$_2$SH. Prior to this work the only known molybdenum complex of this ligand was [Mo(CO)$_4$(SCH$_2$CH$_2$PPh$_2$)] prepared from the carbonyl anion [Mo(CO)$_5$X]$^-$ by reaction with the thallium salt of the phosphinothiol.[3] We here report the preparation, reactivity, and crystal structure of the five-co-ordinate molybdenum(IV) oxo-complex [MoO(SCH$_2$CH$_2$PPh$_2$)$_2$].

EXPERIMENTAL

The [MoO$_2$(acac)$_2$] (acac = pentane-2,4-dionate) (Climax Molybdenum Company) and ethylene sulphide (Aldrich Chemical Co. Ltd.) were used as supplied without further purification. 2-(Diphenylphosphino)ethane-1-thiol was prepared as described in detail below by slight modification of the method briefly reported in a patent.[4] All solvents were distilled under nitrogen prior to use and all manipulations were performed under nitrogen. The instrumentation employed is as described previously.[5] Microanalyses were made by Mr. and Mrs. A. Olney of the University of Sussex and by A. Berhardt, West Germany.

2-(Diphenylphosphino)ethane-1-thiol.—To diphenylphosphine (prepared according to ref. 6) (29.9 g, 0.16 mol) dissolved in tetrahydrofuran (thf) (100 cm^3) was added dropwise a solution of methyl-lithium in diethyl ether until methane evolution ceased to give a clear orange solution. Ethylene sulphide (7.2 g, 0.15 mol) was added dropwise at room temperature, discharging the orange colouration. Methanol (65 cm) and a degassed, saturated, aqueous solution of ammonium chloride were added (50 cm^3) and the solution stirred for 30 min. The ether layer was siphoned off, dried over Mg[SO$_4$], and the ether removed by distillation. The resulting viscous residue was fractionally distilled at 0.4 Torr,‡ collecting the fraction boiling in the range 180—190 °C.

Bis[2-(diphenylphosphino)ethane-1-thiolato]oxomolybdenum(IV).—Dioxobis(pentane-2,4-dionato)molybdenum(VI) (1.0 g, 0.003 mol) and 2-(diphenylphosphino)ethanethiol (2.2 g, 0.009 mol) in benzene (50 cm^3) were heated under reflux for 1 h. The resulting dark green solution was cooled and evaporated to low volume (10 cm^3) at 10^{-2} Torr and the complex precipitated by addition of hexane (40 cm^3). The product was recrystallised from benzene–hexane as green needles in *ca.* 70% yield (Found: C, 56.0; H, 4.0. C$_{28}$H$_{28}$MoOP$_2$S$_2$ requires C, 55.8; H, 4.7%).

Reaction with tetrafluoroboric acid. The above complex (0.10 g) in benzene (40 cm^3) was treated dropwise with anhydrous tetrafluoroboric acid–diethyl ether until the green colour of the solution was completely discharged, yielding a brown precipitate (Found: C, 42.6; H, 4.2. C$_{28}$H$_{30}$B$_2$F$_8$MoOP$_2$S$_2$ requires C, 43.2; H, 3.9%). Recrystallisation from methanol–diethyl ether gave a brown crystalline product (Found: C, 50.0; H, 4.9. C$_{32}$H$_{38}$BF$_5$MoOP$_2$S$_2$ requires C, 50.1; H, 5.0%).

Collection and Reduction of Diffraction Data.—Green prismatic crystals of [MoO(SCH$_2$CH$_2$PPh$_2$)$_2$] were formed by slow evaporation from methylene chloride–methanol and mounted along the long axis. Preliminary cell dimensions were obtained from Weissenberg and precession photographs of the crystals taken with Cu-K_α (λ = 1.541 8 Å) radiation. Using these approximate cell dimensions from the film measurements, 24 reflections with $50 < 2\theta < 90°$ were accurately centred in the counter window of a Picker FACS-I-OOS diffractometer. A least-squares procedure was used to obtain a best fit between the observed and calculated values of χ, ω, and 2θ for these reflections.

Crystal Data.—C$_{28}$H$_{28}$MoOP$_2$S$_2$, Orthorhombic, a = 10.263(3), b = 10.246(1), c = 26.657(5) Å, $\alpha = \beta = \delta$ = 90°, U = 2 803.4 Å^3, D_m = 1.44(2) g cm^{-3}, Z = 4, D_c = 1.43 g cm^{-3}, $F(000)$ = 1 232, space group $P2_12_12_1$ from systematic absences $h00$ for h odd, $0k0$ for k odd, and $00l$ for l odd, λ(Cu-K_α) = 1.541 8 Å, μ(Cu-K_α) = 65.5 cm^{-1}.

Intensity data were collected on the Picker FACS-I using Cu-K_α radiation filtered through Ni foil and a crystal of dimensions 0.23 × 0.47 × 0.15 mm. The take-off angle was 2.8°. A scan speed of 1° min^{-1} was employed in measuring each reflection by the moving-crystal–moving-

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† Bis (2-diphenylphosphinoethane-1-thiolato)oxomolybdenum(IV).

‡ Throughout this paper: 1 Torr = (101 325/760) Pa.

counter (ω—2θ) scan method with a scan range of 1.6° in 2θ for 20 s on a stationary crystal with a stationary counter. Three standard reflections, (112), ($\bar{1}50$), and ($1\bar{2}\bar{6}$), scanned after every 97 observations, were employed to monitor diffractometer and crystal stability. Fluctuations in the integrated intensities of the standard reflections were less than $\pm 1.5\%$.

The observed intensities were corrected for background, Lorentz and polarisation effects, the attenuation, and absorption. Only reflections with $I > 2.58\sigma(I)$ were included in the refinement. The observed data were not corrected for secondary extinction.

Solution and Refinement of the Structure.—A sharpened Patterson map was computed using the corrected data.[7] The map was contoured and solved for the co-ordinates of the molybdenum atom ($R = 0.43$). The positional co-ordinates were used to produce a set of phased structure factors for a difference Fourier synthesis. This revealed the positions of the oxygen, two sulphur, and two phosphorus atoms. These positional co-ordinates were refined by least-squares methods for two cycles ($R = 0.32$), and phasing on these atoms resulted in the location of all non-hydrogen atoms in the [$MoO(SCH_2CH_2PPh_2)_2$] molecule. Five cycles of refinement on the positional and isotropic temperature factors of the 34 atoms led to convergence at values of 0.085 and 0.092 for the discrepancy factors $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$, respectively, where the weights, w, were $4F^2/\sigma^2(F^2)$. Scattering factors for the zerovalent Mo, S, O, and C atoms were taken from ref. 8, with the effects of anomalous dispersion being included in the contributions of Mo and S to the calculated structure factors.

Anisotropic temperature factors were introduced for Mo, O, S, and P atoms. A further five cycles of full-matrix least-squares refinement on all positional and thermal parameters resulted in discrepancy factors $R = 0.063$ and $R' = 0.072$. Since the introduction of anisotropic temperature factors for the 28 carbon atoms produced no significant improvement in the discrepancy indices, the additional 140 variables are not reported in the Supplementary Publication. A final difference-Fourier map calculated from phases for the fully refined structure exhibited no excursions of electron density greater than 1.2 e Å^{-3} on a scale where the average carbon value is 7.1 e Å^{-3}. Although a number of these peaks with density 0.8—1.2 e Å^{-3} were located at positions consistent with hydrogen sites, no attempt was made to locate hydrogen atoms.

Final positional and thermal parameters, observed and calculated structure-factor amplitudes, and details of least-squares planes are available as Supplementary Publication No. SUP 22547 (34 pp.).*

RESULTS AND DISCUSSION

Preparation and Reactions of [$MoO(SCH_2CH_2PPh_2)_2$].—Dioxobis(pentane-2,4-dionato)molybdenum, [$MoO_2(acac)_2$], reacted with an excess of $Ph_2PCH_2CH_2SH$ in refluxing benzene to give the green molybdenum(IV) oxo-complex [$MoO(SCH_2CH_2PPh_2)_2$] in 60—70% yield. The complex is moderately air-stable in the solid state, monomeric in 1,2-dichloroethane solution, and its mass spectrum shows a molecular ion with appropriate isotope splitting. Its i.r. spectrum has a strong band at 955 cm^{-1} assigned to ν(Mo=O) and there are no bands assignable to ν(S–H). The ^1H n.m.r. spectrum in $CDCl_3$ showed multiplets at 2.14(2), 2.93(2), 7.10(6), 7.59(2), and 8.14(2) p.p.m. (integrated values in parentheses). The first two are assigned to PCH_2 and CH_2S respectively and the remaining three to phenyl protons. The ^{31}P n.m.r. spectrum exhibited a single peak at −81.6 p.p.m. relative to H_3PO_4 indicating a *trans* configuration for the phosphorus atoms.

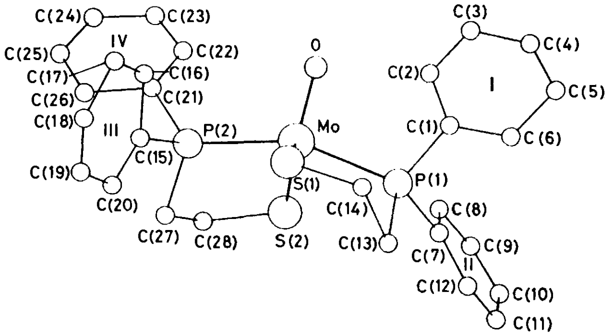

FIGURE 1 Perspective view of the molecule [$MoO(SCH_2CH_2PPh_2)_2$] showing the atom-labelling scheme

The complex reacted rapidly with anhydrous HBF_4 in benzene to give a brown product which no longer had an i.r. band due to Mo=O, but showed strong broad bands at *ca.* 3 600 and 1 650 cm^{-1} attributable to H_2O. Its elemental analysis was in accord with the formulation [$Mo(OH_2)(SCH_2CH_2PPh_2)_2$][$BF_4$]$_2$. However, decomposition in solution precluded measurements of its conductivity, and recrystallisation from methanol–diethyl ether gave a further yellow-brown product. The i.r. spectrum of this product showed no absorptions due to H_2O but characteristic bands of diethyl ether were present. Elemental analysis fitted the formulation [$MoF(OEt_2)(SCH_2CH_2PPh_2)_2$][$BF_4$] but again instability in solution prevented measurement of its conductivity. While the protonation of molybdenum oxo-groups to hydroxyl or water is well documented, it is comparatively rare to isolate a complex where the water is retained in the co-ordination sphere.

Although many molybdenum oxo-complexes undergo condensation-type reactions with amines and hydrazines to generate species with molybdenum–nitrogen multiple bonds,[9] [$MoO(SCH_2CH_2PPh_2)_2$] was completely inert to these reagents even under forcing conditions. The reasons for this lack of reaction are not obvious, but the steric constraints provided by the PPh_2 groups (see below) would be expected to hinder the formation of any intermediate involving the hydrazine bound *cis* to the oxo-group prior to the elimination of water. Attempts at chemical reduction of the complexes using magnesium, zinc, or sodium amalgam yielded intractable brown residues. However, cyclic voltammetry (in thf with 0.2 mol dm^{-3} [NBu^n_4][BF_4] as support electrolyte and a vitreous carbon electrode) showed the complex to undergo a reversible one-electron reduction step at

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

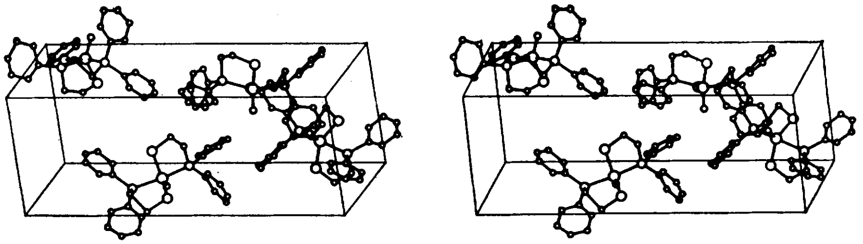

FIGURE 2 Stereoscopic view of the packing of symmetry-related molecules in the unit cell

$E_\mathrm{p}^\mathrm{red} = -1.86$ V followed by a slow decomposition of the reduced species to a further, unidentified, product. The only observable oxidation process occurred at $E_\mathrm{p}^\mathrm{ox} = +0.69$ V and was irreversible, with a peak height corresponding to a two-electron process.

Crystal Structure.—Table 1 contains some relevant bond lengths and valence angles for the complex, and Table 2 presents the non-bonding interactions defining the polytopal edges or suggestive of some interaction. A perspective view of the molecular geometry giving the atom-labelling scheme is presented in Figure 1, while Figure 2 illustrates the packing of the symmetry-related molecules in the unit cell.

The structure consists of monomeric molecules $[\mathrm{MoO(SC_2H_4PPh_2)_2}]$ of geometry intermediate between trigonal bipyramidal and square or tetragonal pyramidal and exhibiting approximate C_{2v} local symmetry. The distortions from regular trigonal-bipyramidal geometry are evident in the P(1)–Mo–P(2) angle of 154.7(1)° compared to 180° for the regular polyhedron, and in the angles in the basal plane, 122.3(3), 117.3(3), and 120.4(3)° for S(1)–Mo–S(2), S(1)–Mo–O, and S(2)–Mo–O, respectively, rather than 120°. The significantly different P(1)–Mo–P(2) and S(1)–Mo–S(2) angles [154.7(1) and 122.3(1)°, respectively] and the concomitant deviations of the sulphur and phosphorus atoms from the best least-squares planes through these positions, ± 0.30 Å, illustrate the distortion from tetragonal-pyrimidal geometry. Analysis of the molecular geometry in terms of ideal polytopal forms as shown in Table 3 confirms that the structure is intermediate between the limiting ideal shapes.[10] The Table presents not only the ideal dihedral angles calculated by Muetterties and Guggenburger,[10] but also the interplanar angles for idealised C_{2v} polyhedra which take into account the bond-length distortion inherent as a result of the strong π-substituent effects of the oxo-ligand.

TABLE 1

Selected bond lengths (Å) and angles (°) for $[\mathrm{MoO(SCH_2CH_2PPh_2)_2}]$

(*a*) Lengths

Mo–P(1)	2.481(4)	P(2)–C(15)	1.85(1)
Mo–P(2)	2.486(3)	P(2)–C(21)	1.88(1)
Mo–S(1)	2.372(4)	P(2)–C(27)	1.84(1)
Mo–S(2)	2.348(4)	S(2)–C(28)	1.87(1)
Mo–O	1.733(9)	C–C av., ring I	1.43(2)
P(1)–C(1)	1.85(2)	C–C av., ring II	1.42(3)
P(1)–C(7)	1.83(1)	C–C av., ring III	1.43(2)
P(1)–C(13)	1.91(2)	C–C av., ring IV	1.42(2)
S(1)–C(14)	1.91(2)	C(13)–C(14)	1.54(2)
		C(27)–C(28)	1.55(2)

(*b*) Angles

P(1)–Mo–P(2)	154.7(1)	C(15)–P(2)–Mo	121.9(4)
S(1)–Mo–S(2)	122.3(1)	C(21)–P(2)–Mo	114.8(5)
O–Mo–P(1)	101.6(3)	C(27)–P(2)–Mo	105.3(4)
O–Mo–P(2)	103.6(3)	C(14)–S(1)–Mo	110.6(5)
O–Mo–S(1)	117.3(3)	C(28)–S(2)–Mo	109.1(5)
O–Mo–S(2)	120.4(3)	P(1)–C(13)–C(14)	103(1)
P(1)–Mo–S(1)	81.9(1)	C(13)–C(14)–S(1)	109(1)
P(1)–Mo–S(2)	87.4(1)	P(2)–C(27)–C(28)	106(1)
P(2)–Mo–S(1)	84.6(1)	C(27)–C(28)–S(2)	110(1)
P(2)–Mo–S(2)	81.9(1)	C–C–C av., ring I	120(2)
C(1)–P(1)–Mo	123.2(5)	C–C–C av., ring II	120(2)
C(7)–P(1)–Mo	112.1(5)	C–C–C av., ring III	120(2)
C(13)–P(1)–Mo	107.7(5)	C–C–C av., ring IV	120(1)

TABLE 2

Non-bonding interactions

(*a*) Defining the polyhedral edges for $[\mathrm{MoO(SCH_2CH_2PPh_2)_2}]$

P(1) ··· S(1)	3.181(5)	P(1) ··· O	3.30(1)
P(2) ··· S(2)	3.169(5)	P(2) ··· O	3.347(9)
P(1) ··· S(2)	3.338(5)	S(1) ··· O	3.52(1)
P(2) ··· S(1)	3.271(6)	S(2) ··· O	3.554(9)

(*b*) Distances less than 4.0 Å between ring carbon and sulphur atoms

S(1) ··· C(15), III	3.40(1)	S(2) ··· C(2), I	3.47(2)
S(1) ··· C(16), III	3.82(2)	S(2) ··· C(1), I	3.54(2)
S(1) ··· C(11), II	3.89(2)	S(2) ··· C(11), II	3.89(2)
S(1) ··· C(20), III	3.93(2)	S(2) ··· C(18), III	3.81(2)

The distorted geometry found for $[\mathrm{MoO(SCH_2CH_2PPh_2)_2}]$ appears to be atypical for five-co-ordinate molybdenum complexes. The monomeric molybdenum(IV) species $[\mathrm{MoO(S_2CNPr_2)_2}]$ [11] and $[\mathrm{MoO}(\eta^2\text{-}\mathrm{S_2CSPr})(\eta^3\text{-}\mathrm{S_2CSPr})]$ [12] exhibit local C_{4v} symmetry, *i.e.* tetragonal-pyramidal geometry; the monomeric molybdenum(V) complex $[\mathrm{MoOCl_3(SPPh_3)}]$ [13] also displays approximate tetragonal-pyramidal geometry. Square-pyramidal molybdenum environments with apical oxo-groups are also found in the dimeric molecules $[\mathrm{Mo_2O(S_2CNEt_2)_2(PhCON_2)_2}]\cdot\mathrm{CH_2Cl_2}$,[14] $[\mathrm{Mo_2O(S_2CNEt_2)_2(ClC_6H_4CSN_2)_2}]\cdot\mathrm{CHCl_3}$,[15] $[\mathrm{Mo_2O_4(S_2CNEt_2)_2}]$,[16] and $[\mathrm{Mo_2O_2S_2\{S_2C_2(CN)_2\}_2}]^{2-}$.[17] Although trigonal-bipyramidal geometry is not common for molybdenum complexes, distorted trigonal-bipyramidal geometry has been observed for $[\mathrm{Mo_2O_4(cysteine\ ethyl\ ester)_2}]$ [18] and $[\mathrm{Mo_2O_2S_2(cysteine\ methyl\ ester)_2}]$,[19] where the terminal oxo-group, the cysteine sulphur, and a bridging oxo- or sulphido-group define the equatorial plane.

The distortions from regular polytopal forms exhibited by $[\mathrm{MoO(SCH_2CH_2PPh_2)_2}]$ are similar to those previously observed for $[\mathrm{ReNCl_2(PPh_3)_2}]$,[20] where the bulky phosphine ligands are in approximately apical positions and the π-substituent nitrido-group in the equatorial plane. Since equatorial π bonding has been shown to be stronger than axial for the trigonal bipyramid,[21] the approximately equatorial location of the π-donor ligands in these distorted molecules may be anticipated as the substitutional preference. Although tetragonal-pyramidal geometry is more commonly observed for d^1 and d^2 complexes where the apical interaction between the π-donor oxo-group and the metal d_{xz} and d_{yz} orbitals may be maximised, while the destabilisation of the d electrons is minimised, it is apparent that the conformational preference is due not only to electronic effects but to steric requirements of the co-ordinated ligands.[22] Thus, the bulky trimethylamine groups in $[VOCl_2(NMe_3)_2]$ [23] occupy apical positions of a distorted trigonal bipyramid rather than basal positions in the tetragonal-pyramidal geometry more commonly observed for vanadyl complexes.[24,25] Similarly, it appears that non-bonding interactions play an important role in determining the conformational preference of $[MoO(SCH_2CH_2PPh_2)_2]$. Reference to Table 2(*b*) shows a number of S–C(ring) distances of 3.4—3.5 Å. Although these distances are quite short and suggest steric interaction, any further deviation from trigonal-bipyramidal toward square-pyramidal geometry could only make the S–C ring distances shorter and the interactions more unfavourable.

The Mo–O distance of 1.733(9) Å is significantly longer than the distances of 1.664(8) and 1.66(1) Å observed for the molybdenum(IV) complexes $[MoO(S_2CNPr^n{}_2)_2]$ [11] and $[MoO(S_2CSR)_2]$,[12] respectively. It is not obvious whether this difference is electronic in nature or results from the large steric requirements of the donor ligands (Table 3).

TABLE 3

Ideal and observed dihedral angles (°) for five-co-ordinate complexes [a]

Complex	Shape-determining angles	Remaining angles
Ideal trigonal bipyramid, D_{3h}	53.1 53.1, 53.1	101.5, 101.5, 101.5, 101.5, 101.5, 101.5
Ideal MOL_4, C_{2v} [b]	54.6 36.2, 36.2	85.8, 85.8, 113.4, 113.4, 113.4, 113.4
$[MoO(SCH_2CH_2PPh_2)_2]$ Approx. C_{2v}	27.7 57.2, 57.8	88.5, 90.0, 111.5, 111.8, 112.8, 113.8
Ideal MOL_4, C_{4v} [c]	0.0 72.8, 72.8	72.8, 72.8, 122.4, 122.4, 123.5, 123.5
Ideal square pyramid, C_{4v}	0.0 72.7, 75.7	75.7, 75.7, 119.8, 119.8, 119.8, 119.8

[a] Angles are defined in ref. 10. [b] The calculation assumed a Mo–O distance of 1.70 Å and Mo–L distances of 2.42 Å. The oxo-group occupied a position on the equatorial plane. [c] The distances used for the idealised C_{2v} symmetry were employed. The oxo-group occupied the apical position.

The average Mo–S distance [2.360(4) Å] is shorter than the distances commonly observed for Mo–S in dithiocarbamate complexes which range from 2.45 to 2.55 Å.[26] These longer distances are due in part to structural *trans* effects produced by *trans* terminal oxo- or bridging oxo-groups, to differences in the hybridisation at the sulphur, and to the steric requirements of the four-membered chelate rings in these complexes. Four-membered rings display decreased angles at the metal atom resulting in poorer metal–ligand overlap and consequently longer bond lengths.[27] The expansion of the chelate ring to a five-membered system in $[MoO(SCH_2CH_2PPh_2)_2]$ increases the chelate angle at the metal from average values of *ca.* 73° in the four-membered dithiocarbamate rings to 82°, a value significantly closer to the usual metal valence angle of 90°. The Mo–S distance should be compared to the value of 2.38 Å observed for $[Mo_2O_4(\text{cysteine ethyl ester})_2]$ [18] and $[Mo_2O_2S_2(\text{cysteine methyl ester})_2]$,[19] where the S atom not only displays the same hybridisation but is also present in a five-membered chelate ring in equatorial position of a distorted trigonal-bipyramidal co-ordination.

The average Mo–P distance [2.484(4) Å] is comparable to the distances found in other molybdenum(IV) complexes: $[MoOCl_2(PMe_2Ph)_3]$ [2.550(9) and 2.500(3) Å],[28] $[MoOCl_2(PEt_2Ph)_3]$ [2.567(4) and 2.522(4) Å],[29] $[MoOCl(Ph_2PC_2H_4PPh_2)_2]^+$,[30] $[MoH_4(PMePh_2)_4]$ (2.503 Å),[31] and $[MoCl_4(PMe_2Ph)_3]$ [2.577(4) Å],[32] although the larger co-ordination numbers of these complexes may effect some bond lengthening as a result of the large non-bonding interactions associated with phosphine ligands in complexes of co-ordination number six or greater.

Reference to Table 2 shows that the intraligand bond angles and distances are not unusual. There are no significant intermolecular interactions as shown in the unit-cell packing stereogram (Figure 2).

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