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Synthesis and Structure of a Series of Thiophosphinato-Bridged Platinum Complexes. Crystal and Molecular Structure of $[Pt\{SP(C_2H_5)_2\}P(OC_6H_5)_3]_2(Pt\text{-}Pt)$

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Received June 26, 1974

AIC404158

Reaction of the platinum(0) complexes PtL_4 with various substituted diphosphine disulfides $[R_2P(S)]_2$ (L = various phosphines, R = alkyl or aryl) in refluxing toluene is shown to give the first reported examples of the thiophosphinato-bridged platinum dimers $[Pt(SPR_2)L]_2$. The crystal and molecular structure of one of these, $[Pt\{SP(C_2H_5)_2\}P(OC_6H_5)_3]_2$, formally a complex of Pt(I), has been determined. The complex crystallizes with one molecule per triclinic unit cell of symmetry $P\bar{1}$, with dimensions $a = 10.036$ (2), $b = 13.051$ (2), $c = 9.512$ (2) Å; $\alpha = 101.35$ (2), $\beta = 101.87$ (2), $\gamma = 87.74$ (2)°. Full-matrix isotropic–anisotropic least-squares refinement on 2249 independent counter data gave a final unweighted R factor of 2.5%. The structure consists of discrete molecular units with the halves of each molecule linked by bridging $SP(C_2H_5)_2^-$ anions and a Pt–Pt bond length of 2.628 (1) Å. The sulfur atoms, with two lone pairs, are each considered to form single covalent bonds with one platinum and a bridge phosphorus atom, the latter donating (formally) two electrons to the other metal atom. Only slight distortion is observed in the essentially planar Pt–P–S–Pt–P–S six-atom framework, visualized primarily as the result of mutual twisting of the bridging groups with respect to one another about a line at right angles to the Pt–Pt bond.

Introduction

Tetraorganodiphosphine disulfides, $R_2P(S)P(S)R_2$, are reported to function as bidentate ligands in a number of metal complexes, coordinating to the metal through the sulfur atoms. This behavior was first observed by Meek and Nicpon;[1] the complexes $[Cu\{R_2P(S)P(S)R_2\}_2]ClO_4$ ($R = CH_3, C_2H_5$) were obtained from copper(II) perchlorate and the appropriate diphosphine disulfide. Later preliminary X-ray data on the chloride and bromide salts were reported to confirm the suggested structure.[2] Adducts of tetramethyldiphosphine disulfide having the same metal–ligand stoichiometry were subsequently reported for Zn(II), Sb(III), Bi(III), Sn(II), and Hg(II)[3] and are presumed also to have the same structure. The same mode of coordination of this ligand was also suggested for the complexes $[Co(NO)_2\{(CH_3)_2P(S)P(S)(CH_3)_2\}]Br$, these species being isolated in reactions of this ligand with $[Co(NO)_2Br]_2$.[4]

The only apparent deviation in reactions of tetraorganodiphosphine disulfides with metals appears with $CdCl_2$. This reaction is reported to give a complex $(CH_3)_2P(S)P(S)(CH_3)_2{\cdot}2CdCl_2$, and it is proposed that monodentate coordination of each sulfur to cadmium(II) is involved.[5]

We felt reasonably encouraged from these data to look further at complexes derived from tetraorganodiphosphine disulfides. In particular, the possibility of coordination to low-valent metals seemed a reasonable one, in view of the earlier observation of the reduction of copper(II) to copper(I);[1] the relative "soft" base character anticipated for sulfur also accorded with this idea. However the first attempts to pursue this subject in reactions of platinum(0) complexes led to entirely different results. We have characterized from these reactions the dinuclear platinum species $[Pt(SPR_2)L]_2$. A single-crystal X-ray crystallographic study has provided unambiguous structural characterization of these complexes which contain discrete thiophosphinato groups bridging platinum atoms; these species obviously arise through phosphorus–phosphorus bond cleavage in these reactions.

Experimental Section

A. Synthesis and Characterization. All reactions were carried out under a nitrogen atmosphere in solvents deaerated with nitrogen. Infrared spectra (4000–400 cm^{-1}) were recorded on a Beckman IR-10 or Perkin-Elmer Model 457 grating spectrometer as Nujol mulls. Proton nmr spectra were recorded on a Varian A-60 spectrometer using deuteriochloroform as a solvent and TMS as the internal standard. Molecular weights were determined with a Mechrolab vapor pressure osmometer on $\sim 1 \times 10^{-3}$ *m* chloroform or benzene solutions. Melting points were taken on a Kofler hot stage and are uncorrected. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Tetramethyl- and tetraethyldiphosphine disulfide were synthesized from alkylmagnesium bromide and $PSCl_3$.[6] The *dl*-dimethyldiphenyldiphosphine disulfide was synthesized from $C_6H_5PSCl_2$ and methylmagnesium bromide and was separated from the meso product by extraction with ethanol.[7] Tetrakis(triphenylphosphine)- and tetrakis(diphenylmethylphosphine)platinum(0) were prepared by the reduction of K_2PtCl_4 with alcoholic KOH in the presence of excess phosphine.[8] Tetrakis(triphenyl phosphite)platinum(0) was obtained from $Pt[P(C_6H_5)_3]_4$ by phosphite exchange.[9]

Preparation of $[Pt\{SP(C_2H_5)_2\}P(C_6H_6)_3]_2$. The preparation of this compound illustrates the general procedure used.

A solution of $[(C_2H_5)_2P(S)]_2$ (0.28 g, 1.17 mmol) in 15 ml of toluene was added dropwise to a refluxing toluene solution of $Pt[P(C_6H_5)_3]_4$ (1.40 g, 1.15 mmol). After 6-hr reflux, the initially deep yellow-orange solution turned yellow-green and a light-colored solid was observed. Partial removal of solvent and addition of 25 ml of absolute ethanol followed by cooling at −20° gave the product, together with a small amount of amorphous gray solid. Recrystallization from chloroform–hexane gave the pure product (0.38 g, 57%) as pale yellow-green crystals, mp 295–296° dec.

Anal. Calcd for $C_{44}H_{50}P_4S_2Pt_2{\cdot}0.25CHCl_3$: C, 44.8; H, 4.27; P, 10.44; S, 5.40; mol wt 1157. Found: C, 45.2; H, 4.08; P, 10.09; S, 5.81; mol wt 1172 ($CHCl_3$). (Products generally retained some solvent of crystallization.) Ir spectrum (cm^{-1}): 1588 w, 1570 w, 1477 m, 1432 s, 1308 w, 1170 w, 1095 m, 1040 w, 1022 w, 995 w, 748 m, 742 m, 736 m, 705 w, 690 s, 672 w, 652 m, 550 w, 520 s, 508 m, 485 m, 450 w.

Run in benzene solvent, the reaction is far from complete after a 24-hr reflux period and only small amounts of $[Pt\{SP(C_2H_5)_2\}P(C_6H_5)_3]_2$ could be recovered from the system. Also, using excess $[(C_2H_5)_2P(S)]_2$ decreased the yield of desired product and a small amount of $(C_6H_5)_3PS$ could be recovered from the toluene solution.

Data on other compounds prepared by this route are given below.

$[Pt\{SP(CH_3)_2\}P(C_6H_5)_3]_2$. Pale green crystals recrystallized from chloroform–heptane (mp 296–298° dec) in 51% yield.

Anal. Calcd for $C_{40}H_{42}P_4S_2Pt_2{\cdot}0.5CHCl_3$: C, 41.9; H, 3.69; P, 10.7; S, 5.53; mol wt 1101. Found: C, 41.5; H, 3.79; P, 10.6; S, 5.80; mol wt 1130 ($CHCl_3$). Ir spectrum (cm^{-1}): 1583 m, 1572 w, 1567 w, 1476 s, 1432 s, 1418 m, 1409 m, 1331 w, 1309 m, 1286 m, 1275 m, 1187 w, 1176 m, 1160 w, 1157 w, 1096 s, 1088 m, 1067 w, 1027 m, 998 m, 942 s, 927 m, 900 s, 850 m, 836 m, 757 s, 744 s, 720 m, 703 vs, 620 m, 553 m, 530 vs, 515 s, 497 s, 457 m, 432 m, 383 m, 316 m.

$[Pt\{SP(C_2H_5)_2\}P(C_6H_5)_2CH_3]_2$. Yellow-green crystals recrystallized from chloroform–heptane (mp 235–238°) in 13% yield. The preparation required a longer reflux time (88 hr).

Anal. Calcd for $C_{34}H_{46}P_4S_2Pt_2{\cdot}0.25CHCl_3$: C, 38.7; H, 4.39; P, 11.7; S, 6.03; mol wt 1032. Found: C, 38.8; H, 4.51; P, 12.0; S, 5.41; mol wt 986 ($CHCl_3$). Ir spectrum (cm^{-1}): 1585 w, 1569 w, 1480 m, 1433 s, 1408 w, 1027 m, 997 w, 989 w, 880 s, 752 m, (sh), 746 s, 721 m, 694 s, 679 m, 655 m, 545 m, 508 s, 472 m, 440 m, 422 w, 369 w, 348 w, 304 w.

$[Pt\{SP(CH_3)_2\}P(C_6H_5)_2CH_3]_2$. Pale yellow-green crystals, 29% yield, were obtained after 40 hr at reflux; they were recrystallized from chloroform–heptane (mp 267–269°).

Anal. Calcd for $C_{30}H_{38}P_4S_2Pt_2 \cdot 1.5CHCl_3$: C, 32.7; H, 3.43; P, 10.7; S, 5.55. Found: C, 32.5; H, 3.63; P, 11.2; S, 5.61. Ir spectrum (cm^{-1}): 1583 w, 1570 w, 1480 m, 1434 s, 1418 w, 1308 w, 1291 w, 1284 w, 1270 w, 1224 w, 1099 m, 1069 w, 1027 w, 998 w, 945 m, sh, 937 s, 900 m, sh, 890 s, 880 s, 831 w, 748 s, 724 m, 698 s, 660 w, 550 m, 516 s, 510 s, sh, 491 m, 442 m, 435 m, sh, 425 w, sh, 383 m, 343 w, 314 w.

$[Pt\{SP(C_2H_5)_2\}P(OC_6H_5)_3]_2$. Off-white crystals, 11% yield, were obtained after 40 hr at reflux; they were recrystallized from benzene–ethanol (mp 183–185°).

Anal. Calcd for $C_{44}H_{50}O_6P_4S_2Pt_2$: C, 43.7; H, 4.13; P, 9.59; mol wt 1253. Found: C, 43.6; H, 4.23; P, 10.6; mol wt 1242 (C_6H_6). Ir spectrum (cm^{-1}): 1593 s, 1585 s, 1484 vs, 1405 w, 1332 w, 1285 w, 1249 w, sh, 1232 w, sh, 1212 m, 1180 vs, 1162 s, 1149 m, 1070 w, 1065 w, 1040 w, 1023 m, 1000 w, 912 vs, 883 s, 822 w, 774 s, 764 s, 751 s, 740 m, 727 w, 717 s, 696 m, 687, 656 w, 617 s, 595 s, 541 s, 506 m, 486 m, 471 m, 442 w, 410 w, 398 w, 365 m, 301 m. Pmr spectrum: τ 9.13 (d of t, $J_{P-CH_3} = 19$ Hz, $J_{CH_2-CH_3} = 7$ Hz, P–CH_2CH_3), τ 8.26 (m, P–CH_2), τ 2.72 (m, O–C_6H_5).

This compound could be prepared in 96% yield by the dropwise addition of a benzene solution of triphenyl phosphite (0.78 mmol) to a suspension of $[Pt\{SP(C_2H_5)_2\}P(C_6H_5)_3]_2$ (0.22 mmol) in refluxing benzene. The original green suspension went into solution within 10 min. The hot benzene solution was filtered, ethanol was added, and the resulting solution was evaporated until crystals began to form. After standing 2 hr at −20°, the product was filtered.

$[Pt\{SP(CH_3)_2\}P(OC_6H_5)_3]_2$. Very pale green crystals, 90% yield, were prepared by the reaction of triphenyl phosphite and $[Pt\ SP(CH_3)_2\ P(C_6H_5)_3]_2$ in refluxing benzene; they were recrystallized from benzene–ethanol (mp 170–171°).

Anal. Calcd for $C_{40}H_{42}O_6P_4S_2Pt_2$: C, 40.1; H, 3.54; P, 10.3; mol wt 1197. Found: C, 40.2; H, 3.47; P, 9.93; mol wt 1172 (C_6H_6). Infrared spectrum (cm^{-1}): 1588 s, 1485 vs, 1420 w, 1402 w, 1290 w, 1275 w, 1220 s, 1188 vs, 1164 s, 1070 w, 1020 m, 1003 w, 940 m, 908 s, 880 vs, 835 w, 767 s, 730 m, 715 m, 700 w, 683 m, 610 w, 595 m, 550 m, 495 m, 475 m, sh, 430 w. Pmr spectrum: τ 8.37 (t of d, $J_{Pt-P-H} = 47$ Hz, $J_{P-CH_3} = 10.5$ Hz, P–CH_3), τ 2.82 (s, P–OC_6H_5).

This compound could not be prepared directly from $Pt[P(OC_6H_5)_3]_4$ and $[(CH_3)_2P(S)]_2$.

$[Pt\{SP(C_6H_5)(CH_3)\}P(C_6H_5)_3]_2$. The reaction of $Pt[P(C_6H_5)_3]_4$ and *dl*-$[(C_6H_5)(CH_3)P(S)]_2$ gave two isomers which could only be partially separated. The best data for each isomer are given below:

Isomer A. Pale green needles, 31% yield after 4.5-hr reflux, were obtained from cooled chloroform–hexane solution, (mp 309–310° dec). Ir spectrum (cm^{-1}): 1588 w, 1570 w, 1432 s, 1305 w, 1270 w, 1210 m, 1180 m, 1155 w, 1090 s, 1065 w, 993 w, 875 m, 750 s, 737 s, 720 m, 690 s, 625 w, 553 m, 520 s, 505 s, 485 m, 445 m.

Isomer B. Pale yellow cubic crystals, 43% yield, were obtained as the second crop from the above crystallization (mp 276–278° dec). Ir spectrum (cm^{-1}): same as that for isomer A except band at 875 split into 885 m, 869 w; bands at 750, 737, and 505 lessened in intensity; new band at 679 s.

Analyses and molecular weight determination were carried out on a mixture of isomers. *Anal.* Calcd for $C_{50}H_{46}P_4S_2Pt_2 \cdot 0.5CHCl_3$: C, 47.2; H, 3.65; P, 9.64; S, 4.99; mol wt 1225. Found: C, 47.0; H, 3.84; P, 9.19; S, 4.67; mol wt 1234 ($CHCl_3$).

Reaction of $Pt[P(C_6H_5)_2CH_3]_4$ and *dl*-$[(C_6H_5)(CH_3)P(S)]_2$. The mixture of two products obtained after 2 hr at reflux was isolated from toluene–ethanol and recrystallized giving the following compounds.

Isomer A was formed as yellow-green crystals from chloroform–ethanol (mp ~210°). Ir spectrum (cm^{-1}) (low resolution): 1585 w, 1570 w, 1486 m, 1432 s, 1305 w, 1282 w, 1150 w, 1093 m, 1063 w, 1020 w, 875 s, 756 s, 738 s, 690 s, 555 m, 505 s, 478 m, 452 m, 440 m.

Isomer B was a yellow powder, obtained as the second crop from the above recrystallization (mp 243–245°). Ir spectrum (cm^{-1}) (low resolution): same as that for isomer A to 875 band, 738 s, 690 s, 555 m, 500 s, 484 m, 440 m, 432 w, sh.

As for the previous reaction, recrystallization did not give the two isomers pure and the analytical data are taken from a mixture of isomers A and B. *Anal.* Calcd for $C_{40}H_{42}P_4S_2Pt_2 \cdot 0.5C_6H_6$: C, 45.3; H, 3.98; P, 10.9; mol wt 1100. Found: C, 44.8; H, 3.83; P, 11.1; mol wt 1045 (C_6H_6).

B. Determination of the Structure of $[Pt\{SP(C_2H_5)_2\}P(OC_6H_5)_3]_2$. Single-Crystal X-Ray Data. A single crystal of $[Pt\{SP(C_2H_5)_2\}P(OC_6H_5)_3]_2$ with an approximately rectangular cross section and dimensions (each defined by the perpendicular distance between the opposite pair of crystal faces) of 0.45 mm (001) × 0.20 mm (100) × 0.15 mm (010) was obtained by vapor diffusion of ethyl ether into a dichloromethane solution of the complex at room temperature. The crystal was placed on a Syntex $P\bar{1}$ four-circle computer-controlled diffractometer equipped with a graphite monochromator and after careful optical crystal and X-ray tube alignment, 15 diffraction maxima were automatically centered in 2θ, χ, and ω, with the crystal mounted approximately along the b direction. Mo Kα radiation (λ 0.7107 Å) was used throughout the alignment and data collection procedures. After being assigned indices, these reflections were used in a least-squares procedure to give the lattice and orientation parameters.[10]

Intensity data (20°) were collected by the θ–2θ scan technique with stationary-crystal, stationary-counter background counts taken at the beginning and end of each scan. In the Syntex procedure, variable-scan rates (2.0–24.0°/min) and scan ranges are determined according to the intensity and width of the peak being measured. For each peak the total time spent in taking the two background counts was set equal to the total scan time.[10] A total of 2433 reflections were measured, of which 2249 were Laue independent, distributed through the four octants hkl, $h\bar{k}l$, $\bar{h}kl$, and $\bar{h}\bar{k}l$, and for which $3.0° \leq 2\theta \leq 40.0°$. During the entire data collection process, the intensity of the two standard reflections $(31\bar{4})$ and $(22\bar{3})$, measured every 50 reflections as a check of electronic and crystal stability, varied by only ±3% as measured on I, making corrections for crystal decay unnecessary.

The data were corrected for Lorentz and polarization effects[11] and used to calculate structure factor amplitudes $|F_o| = (I/Lp)^{1/2}$, where Lp is the Lorentz–polarization factor, and their estimated standard deviations of $\sigma(F) = \sigma(I)/(2|F_o|Lp)$. The instrument instability or "ignorance" factor E was set equal to $0.003(I^2)$ and introduced into $\sigma(I)$ to avoid overweighting the strong reflections in least squares. A given reflection was considered statistically unobserved if the net intensity was $I < 2\sigma(I)$, as calculated from standard expressions.[12] The merged data set gave a total of 2140 observed reflections, all of which were used in the structure determination. Based on the linear absorption coefficient[13] for Mo Kα radiation of 63.48 cm^{-1}, transmission factors were calculated and found to vary in their extreme range from 0.2941 to 0.4220 and, accordingly, the appropriate absorption corrections were made.[14]

Unit Cell and Space Group. The reduced primitive triclinic unit cell of symmetry $P\bar{1}$ (C_i^1, No. 2) and cell parameters $a = 10.036$ (2) Å, $b = 13.051$ (2) Å, $c = 9.512$ (2) Å, $\alpha = 101.35$ (2)°, $\beta = 101.87$ (2)°, and $\gamma = 87.74$ (2)° contains one formula unit of $[Pt\{SP(C_2H_5)_2\}P(OC_6H_5)_3]_2$. The volume of the unit cell is 1194.9 (3) Å^3. The observed density of 1.71 (1) g cm^{-3}, obtained by flotation in a mixture of methyl iodide and carbon tetrachloride (20°), is in satisfactory agreement with the calculated value of 1.734 g cm^{-3}. The total number of electrons per cell is $F(000) = 874$.

Determination of the Structure. The crystal structure, which involved the location of half of one molecule as the asymmetric unit, was solved by the heavy-atom method. A Fourier synthesis,[15] phased on the platinum atom, the trial positional parameters of which were obtained from the interpretation of a three-dimensional Patterson map, gave initial coordinates for one sulfur, two phosphorus, three oxygen, and 15 of the 22 carbon atoms. These parameters conformed to the centrosymmetric space group $P\bar{1}$ and this choice of space group was subsequently corroborated by the satisfactory least-squares refinement of the structure. All crystallographically independent atoms were found to occupy the general twofold set of positions (2i): $\pm(x, y, z)$.[16] After four cycles of full-matrix least-squares refinement[17] varying individual positional and isotropic thermal parameters, the discrepancy indices R_1 and R_2[18] were 10.8% and 16.5%, respectively. A three-dimensional Fourier difference map revealed the positions of the remaining seven nonhydrogen atoms and also indicated strong thermal anisotropy about the Pt, P, and S atoms. Another least-squares refinement cycle as before, but now including all nonhydrogen

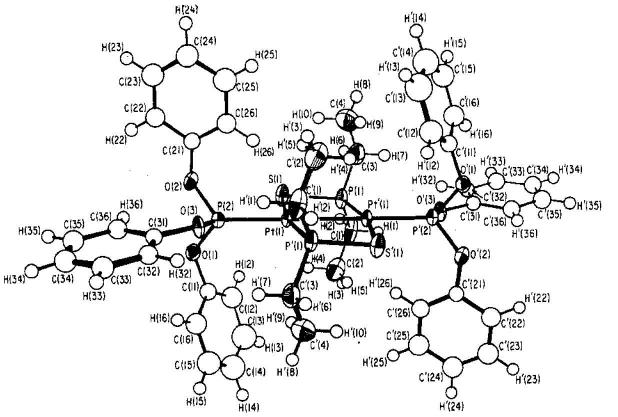


Figure 1. A view of $[Pt\{SP(C_2H_5)_2\}P(OC_6H_5)_3]_2$, centrosymmetric about a point midway between the two Pt atoms, showing anisotropic thermal ellipsoids (at 30% probability) and the atom numbering scheme.

atoms, gave $R_1 = 7.1\%$, $R_2 = 10.1\%$. Further refinement was accomplished by varying positional and anisotropic temperature factors for all Pt, P, and S atoms and for the carbon atoms of the ethyl groups. The positional and isotropic parameters of the remaining carbon atoms were allowed to vary, and ideal coordinates[19] for all hydrogen atoms adjusted after every second least-squares cycle were included as fixed-atom contributions, with $B_{iso} = 6.0$ Å^2. Anomalous dispersion corrections for the Pt, P, and S atoms[20] were also included and the final three cycles of full-matrix least-squares refinement resulted in convergence at $R_1 = 2.5\%$ and $R_2 = 3.7\%$. No value of shift/error > 0.1 was observed in the final cycle. The final data to parameter ratio was approximately 8:1.

All least-squares refinements were based on the minimization of $\sum w_i \| F_o | - | F_c \|^2$. The atomic scattering factors used for all nonhydrogen atoms were those compiled by Hanson, *et al.*,[21] while those used for hydrogen atoms were from Stewart, *et al.*[22] The calculated and observed structure factor amplitudes obtained from the last cycle of anisotropic–isotropic least-squares refinement are listed in Table I.[23] The positional and thermal parameters for all atoms are given in Table II. Interatomic bonding distances and bond angles, with estimated standard deviations calculated with the Busing–Martin–Levy function and error program[24] from the full inverse matrix (with inclusion of the estimated unit cell uncertainties), are presented in Table III. Equations of least-squares planes and the dihedral angles between the normals to these planes are listed in Table IV.[25] The root-mean-square thermal displacements along the directions of the principal axes are given for those atoms varied anisotropically in Table V.

Description of the Structure

The crystal structure of $[Pt\{SP(C_2H_5)_2\}P(OC_6H_5)_3]_2$, shown in Figure 1, consists of discrete molecules, separated by normal van der Waals distances. The closest nonbonding intermolecular distance observed is 3.125 Å between S(1) and H(34) of a different molecule. Hence the molecular structure appears unaffected by packing interactions.

The molecule can be formally regarded as a complex of Pt(I) consisting of two $Pt\{SP(C_2H_5)_2\}P(OC_6H_5)_3$ units; the halves of the molecule are linked by bridging $SP(C_2H_5)_2^-$ anions and by a metal–metal bond. The structure is centrosymmetric with the center of symmetry at a point midway between the two platinum atoms. The sulfur atom, with two lone pairs, can be regarded as forming single covalent bonds with one platinum and a bridge phosphorus atom, the latter donating (formally) two electrons to the other metal atom.

The Pt–Pt distance of 2.628 (1) Å in this compound is within the range expected for a single-bond distance. It is in good agreement with the sum of the proposed covalent metal radii (2.62 Å)[26] and is essentially equal to the metal–metal bond distances of 2.627 (2) Å reported for the compound $Pt_2S(CO)[P(C_6H_5)_3]_3$[27] and 2.633 (1) Å reported for $FePt_2(CO)_5[P(OC_6H_5)_3]_3$.[28] Other measured platinum–platinum bond distances do vary somewhat more however: from somewhat shorter values (2.581 Å in $Pt_2(C_5H_5)_4$[29] and in $Pt_3(C_8H_{12})_3(SnCl_3)_2$[30]) to longer values (2.66 Å in several $[Pt(CO)_2]_n^{2-}$ anions[31] and 2.75 and 2.79 Å in $Pt_4(CO)_5[P(C_6H_5)(CH_3)_2]_4$[32]).

The Pt–S distance of 2.377 (2) Å is comparable to the Pt–SR distance of 2.37 (1) Å trans to the tertiary phosphine ligand in the nonplanar sulfur-bridged dimer $[PtCl(SC_2H_5)P(C_3H_7)_3]_2$[33] and is approximately the length expected for a single bond. These distances, however, are significantly longer than the Pt–S bond lengths of 2.218 (9) and 2.227 (9) Å in $Pt_2S(CO)[P(C_6H_5)_3]_3$[27] and the mean distance of 2.22 (1) Å found in the sulfur-bridged complex $Pt_2Br_4[S(C_2H_5)_2]_2$[34] where π as well as σ bonding is thought to occur. The Pt–P(1)(bridge) and Pt–P(2)(phosphite) distances are 2.227 (2) and 2.219 (3) Å, respectively, as shown in Table III. The S–P(1) bonding distance of 2.046 (3) Å is only slightly shorter than that of 2.090 (5) Å found in P_4S_3.[35] All the above distances are shorter than the sums of the corresponding covalent and metallic radii.[26]

The platinum–phosphite phosphorus bonding distance of 2.219 (3) Å found here is identical with the average value of 2.22 Å found in $FePt_2(CO)_5[P(OC_6H_5)_3]_3$,[28] the only other example of such a distance reported in the literature. The principal bonding parameters in the triphenyl phosphite ligand are comparable to the parameters for other complexes of this ligand.

Although the coordination about each platinum atom is essentially planar, the angles the metal makes with the ligand phosphorus and bridge atoms deviate substantially from 90°. As shown in Table IV by plane (b), no atoms directly bonded to the platinum deviate from the plane containing them and the metal by more than ±0.025 Å. Indeed, all members of the central, strongly bonded six atom framework are essentially coplanar (plane (a)) and the two phosphine phosphorus atoms are situated above and below this plane by only ±0.08 Å respectively. Similarly, the phosphorus and sulfur atoms in the framework are coplanar, Pt(1) lying 0.046 Å above and Pt'(1) an equal distance below the plane (plane (c), Table IV) due to the center of symmetry. The marked angular distortions around each essentially square-planar platinum atom which arise primarily as a result of restrictions imposed by the S–P bridge bond, are emphasized in Table III by the strongly bent S–Pt–P angles of 164.70°, the acute P–Pt–Pt angles of 77.17°, and the correspondingly obtuse values of 102.41° for the P(1)–Pt–P(2) angles. The distortion of the essentially planar central framework can therefore be visualized as primarily the result of mutual twisting of the two $SP(C_2H_5)_2$ bridging units with respect to each other, about a line at right angles to the Pt–Pt bond. The angle of twist is small however, with a value of only 1.77° as shown by the angle between planes (d) and (e) in Table IV, indicating little steric crowding or ring strain is present in the structure.

The distorted pseudotetrahedral coordination about the bridge phosphorus atoms is shown by the data collected in Table III and in Figure 2. Thus, the Pt–P–C(1) and Pt–P–C(3) angles of 114.8 and 116.0°, respectively, result in a correspondingly smaller value of 102.9 (5)° for C(1)–P–C(3) with the ethyl groups angled away from the center of the molecule and slightly inclined toward each of the bare sulfur atoms. This serves to minimize steric crowding immediately above and below the central six-membered Pt–S–P–Pt–S–P framework. The other angles about P(1), including the bridge angle of 108.5 (1)°, are close to the expected tetrahedral value. The average P(1)–C(ethyl) distance of 1.82 (1) Å appears normal.

Table II. Final Atomic and Thermal Parameters for $[Pt\{SP(C_2H_5)_2\}P(OC_6H_5)_3]_2$[a]

	x	y	z	B, Å^2
Pt(1)	99061 (2)	10241 (2)	2326 (3)	*b*
P(1)	10842 (2)	−623 (2)	−2106 (2)	*b*
P(2)	9725 (2)	2753 (1)	629 (2)	*b*
S(1)	10839 (2)	969 (1)	−1885 (2)	*b*
O(1)	8644 (4)	3286 (3)	−518 (5)	*b*
O(2)	10967 (5)	3457 (3)	491 (5)	*b*
O(3)	9404 (5)	3269 (4)	2216 (5)	*b*
C(1)	9811 (12)	−1147 (6)	−3911 (8)	*b*
C(2)	8360 (12)	−771 (8)	−4126 (10)	*b*
C(3)	12529 (11)	−1067 (7)	−2288 (13)	*b*
C(4)	13597 (12)	−635 (10)	−1072 (18)	*b*
C(11)	7364 (7)	2837 (6)	−1118 (8)	4.0 (2)
C(12)	7187 (10)	2155 (8)	−2387 (11)	7.1 (2)
C(13)	5838 (13)	1755 (10)	−3032 (14)	9.8 (3)
C(14)	4838 (12)	2066 (10)	−2291 (14)	8.9 (3)
C(15)	5032 (11)	2737 (9)	−1060 (12)	7.5 (2)
C(16)	6312 (9)	3123 (7)	−427 (10)	5.8 (2)
C(21)	12231 (7)	3503 (5)	1404 (7)	3.5 (1)
C(22)	12942 (8)	4434 (7)	1632 (9)	5.3 (2)
C(23)	14212 (10)	4550 (8)	2548 (11)	6.8 (2)
C(24)	14790 (9)	3772 (8)	3184 (11)	6.5 (2)
C(25)	14088 (10)	2825 (8)	2957 (11)	6.8 (2)
C(26)	12809 (8)	2711 (6)	2032 (9)	4.8 (2)
C(31)	9011 (7)	4286 (6)	2765 (8)	3.3 (1)
C(32)	8441 (7)	4385 (6)	3971 (8)	4.0 (2)
C(33)	8001 (8)	5351 (6)	4579 (9)	4.8 (2)
C(34)	8130 (8)	6197 (7)	3974 (9)	5.1 (2)
C(35)	8733 (8)	6120 (7)	2800 (9)	5.1 (2)
C(36)	9190 (8)	5140 (7)	2152 (9)	4.4 (2)
H(1)[c]	9822	−1918	−4029	
H(2)	10257	−928	−4653	
H(3)	7882	−1089	−5130	
H(4)	8372	4	−4007	
H(5)	7937	−986	−3383	
H(6)	12724	−844	−3190	
H(7)	12552	−1831	−2422	
H(8)	14507	−900	−1234	
H(9)	13423	−838	−160	
H(10)	13594	150	−929	
H(12)	7920	1946	−2914	
H(13)	5648	1265	−3999	
H(14)	3904	1751	−2716	
H(15)	4259	2944	−583	
H(16)	6454	3611	530	
H(22)	12548	5013	1114	
H(23)	14694	5226	2733	
H(24)	15709	3863	3833	
H(25)	14516	2243	3425	
H(26)	12319	2037	1824	
H(32)	8316	3758	4390	
H(33)	7593	5427	5465	
H(34)	7774	6891	4405	
H(35)	8848	6739	2361	
H(36)	9624	5044	1251	

	$10^5\beta_{11}$	$10^5\beta_{22}$	$10^5\beta_{33}$	$10^5\beta_{12}$	$10^5\beta_{13}$	$10^5\beta_{23}$
Pt(1)	942 (5)	241 (3)	767 (6)	−20 (2)	237 (3)	62 (2)
P(1)	1479 (28)	358 (14)	1076 (29)	−17 (15)	587 (23)	77 (16)
P(2)	985 (23)	307 (13)	929 (27)	15 (14)	238 (20)	117 (15)
S(1)	1809 (32)	374 (14)	1176 (30)	−45 (16)	747 (25)	133 (16)
O(1)	1089 (61)	459 (35)	1219 (71)	−4 (36)	62 (52)	235 (41)
O(2)	1160 (63)	442 (35)	1256 (71)	−145 (36)	237 (53)	208 (40)
O(3)	1473 (66)	330 (34)	989 (69)	142 (36)	465 (54)	60 (38)
C(1)	3085 (194)	503 (63)	888 (114)	−267 (86)	407 (117)	107 (68)
C(2)	2438 (173)	986 (89)	1592 (151)	−445 (99)	−367 (129)	444 (93)
C(3)	1898 (152)	617 (72)	3111 (212)	92 (82)	1376 (154)	273 (101)
C(4)	1763 (168)	1259 (116)	4860 (351)	217 (115)	998 (203)	725 (170)

[a] The Pt positional Parameters have been multiplied by 10^5, all others, by 10^4. The estimated standard deviations of the last significant figures are given in parentheses here and in succeeding tables. [b] Anisotropic temperature factors of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ here used for these atoms. [c] The hydrogen parameters are the idealized coordinates used for the final three least-squares cycles.

Discussion

The reaction of tetraorganodiphosphine disulfides and several platinum(0) phosphine complexes proceeded according to the reaction

$$PtL_4 + [R_2P(S)]_2 \xrightarrow[\text{reflux}]{\text{toluene}} [Pt(SPR_2)L]_2$$

Table III. Interatomic Distances and Bond Angles

A. Bonding Intramolecular Distances, Å

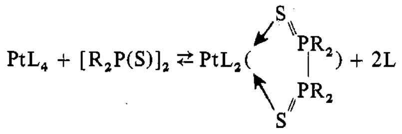
Metal-metal	Pt(1)-Pt′(1)	2.628 (1)		
Metal-sulfur	Pt(1)-S(1)	2.377 (2)		
Metal-phosphorus	Pt(1)-P(1)	2.227 (2)		
	Pt(1)-P(2)	2.219 (3)		
Phosphorus-sulfur	P(1)-S(1)	2.046 (3)		
Ethyl bonds	Phosphorus-carbon		Carbon-carbon	
	P(1)-C(1)	1.831 (9)	C(1)-C(2)	1.505 (14)
	P(1)-C(3)	1.799 (10)	C(3)-C(4)	1.444 (16)
	Av	1.817	Av	1.482
Phosphite bonds	Phosphorus-oxygen		Carbon-oxygen	
	P(2)-O(1)	1.613 (5)	C(11)-O(1)	1.395 (8)
	P(2)-O(2)	1.619 (5)	C(21)-O(2)	1.379 (8)
	P(2)-O(3)	1.617 (5)	C(31)-O(3)	1.401 (9)
	Av	1.619	Av	1.393
Phenyl ring 1	Carbon-carbon			
Phenyl ring 1	C(11)-C(12)	1.334 (12)	C(14)-C(15)	1.301 (14)
	C(12)-C(13)	1.439 (15)	C(15)-C(16)	1.371 (13)
	C(13)-C(14)	1.347 (16)	C(16)-C(11)	1.358 (11)
			Av	1.361
Phenyl ring 2	C(21)-C(22)	1.391 (11)	C(24)-C(25)	1.404 (13)
	C(22)-C(23)	1.384 (12)	C(25)-C(26)	1.395 (12)
	C(23)-C(24)	1.336 (12)	C(26)-C(21)	1.346 (10)
			Av	1.376
Phenyl ring 3	C(31)-C(32)	1.365 (10)	C(34)-C(35)	1.360 (12)
	C(32)-C(33)	1.376 (11)	C(35)-C(36)	1.409 (12)
	C(33)-C(34)	1.364 (11)	C(36)-C(31)	1.388 (11)
			Av	1.380

B. Intramolecular Angles, Deg

Angles Centered on Platinum			
P(2)-Pt(1)-Pt′(1)	179.38 (6)	P′(1)-Pt(1)-Pt′(1)	77.17 (7)
P(2)-Pt(1)-S(1)	92.80 (8)	S(1)-Pt(1)-P′(1)	164.70 (7)
P(2)-Pt(1)-P′(1)	102.41 (8)	S(1)-Pt(1)-Pt′(1)	87.63 (6)
Angles Centered on Phosphorus			
S(1)-P(1)-Pt′(1)	108.5 (1)	Pt(1)-P(2)-O(1)	118.9 (2)
S(1)-P(1)-C(1)	106.9 (3)	Pt(1)-P(2)-O(2)	119.9 (2)
S(1)-P(1)-C(3)	107.1 (3)	Pt(1)-P(2)-O(3)	114.3 (2)
C(1)-P(1)-Pt′(1)	114.8 (3)	O(1)-P(2)-O(2)	92.4 (2)
C(1)-P(1)-C(3)	102.9 (5)	O(1)-P(2)-O(3)	104.8 (3)
C(3)-P(1)-Pt′(1)	116.0 (4)	O(2)-P(2)-O(3)	103.5 (3)
Angles Centered on Carbon (Ethyl Groups), Sulfur, and Oxygen			
P(1)-C(1)-C(2)	114.0 (6)	P(2)-O(1)-C(11)	120.3 (4)
P(1)-C(3)-C(4)	114.7 (8)	P(2)-O(2)-C(21)	123.4 (4)
Pt(1)-S(1)-P(1)	86.63 (9)	P(2)-O(3)-C(31)	130.7 (4)
Angles Centered on Phenyl Ring Carbon Atoms			
O(1)-C(11)-C(12)	119.2 (7)	C(13)-C(14)-C(15)	122.9 (12)
O(1)-C(11)-C(16)	119.6 (7)	C(14)-C(15)-C(16)	120.0 (11)
C(11)-C(12)-C(13)	118.2 (10)	C(15)-C(16)-C(11)	119.8 (9)
C(12)-C(13)-C(14)	117.9 (12)	C(16)-C(11)-C(12)	121.2 (8)
O(2)-C(21)-C(26)	124.5 (6)	C(23)-C(24)-C(25)	119.8 (9)
O(2)-C(21)-C(22)	115.8 (6)	C(24)-C(25)-C(26)	118.7 (9)
C(21)-C(22)-C(23)	119.5 (8)	C(25)-C(26)-C(21)	121.0 (8)
C(22)-C(23)-C(24)	121.3 (9)	C(26)-C(21)-C(22)	119.7 (7)
O(3)-C(31)-C(36)	123.3 (6)	C(33)-C(34)-C(35)	121.5 (8)
O(3)-C(31)-C(32)	114.9 (6)	C(34)-C(35)-C(36)	119.7 (8)
C(31)-C(32)-C(33)	119.3 (7)	C(35)-C(36)-C(31)	117.6 (7)
C(32)-C(33)-C(34)	120.0 (8)	C(36)-C(31)-C(32)	121.9 (7)

where L = $P(C_6H_5)_3$, $P(C_6H_5)_2CH_3$, $P(OC_6H_5)_3$; SPR_2 = $SP(CH_3)_2$, $SP(C_2H_5)_2$, $SP(C_6H_5)(CH_3)$. The dimeric thiophosphinato-bridged species, $[Pt(SPR_2)L]_2$, were the only platinum-containing complexes to be isolated and were generally obtained in good yield.

The conditions necessary for this reaction, toluene reflux for 6 hr or more, were quite severe. They were clearly in excess of the conditions anticipated if platinum(0) complexes were being sought; formation of a complex derived simply by ligand replacement might be expected to occur rapidly at room temperature since the lability of the platinum(0) complexes is well established. The failure to obtain such complexes suggests that the formation of these species is not favored; it does not rule out some sort of equilibrium in solution, however, *viz.*



$$PtL_4 + [R_2P(S)]_2 \rightleftarrows PtL_2(S{=}PR_2{-}PR_2{=}S) + 2L$$

We prefer to view this reaction as proceeding with oxidative addition to the platinum(0) complex, possibly *via* the intermediate species derived from ligand replacement. This latter suggestion seems quite attractive, in that the simple bonding picture for an intermediate complex appears to indicate

Table IV. Equations of Best Least-Squares Planes, Distances of Selected Atoms from These Planes, and Dihedral Angles between Them[a,b]

A. Equations of Planes and Perpendicular Distances (Å) of Selected Atoms from the Planes

(a) Plane Containing Pt(1), Pt'(1), P(1), P'(1), S(1), S'(1)

$-0.832X + 0.053Y - 0.553Z + 8.362 = 0$

Pt(1)	0.025	S(1)	−0.015
Pt'(1)	−0.025	S'(1)	0.015
P(1)	0.017	P(2)	0.084
P'(1)	−0.017	P'(2)	−0.084

(b) Plane Containing Pt(1), Pt'(1), P'(1), S(1), P(2)

$-0.829X + 0.031Y - 0.559Z + 8.351 = 0$

Pt(1)	0.010	S(1)	−0.023
Pt'(1)	0.021	P(2)	0.018
P'(1)	−0.025		

(c) Plane Containing P(1), P'(1), S(1), S'(1)

$-0.833X + 0.069Y - 0.549Z + 8.379 = 0$

P(1)	0.000	S(1)	0.000
P'(1)	0.000	S'(1)	0.000
Pt(1)	0.046	P(2)	0.141
Pt'(1)	−0.046	P'(2)	−0.141

(d) Plane Containing Pt(1), Pt'(1), S(1), S'(1)

$-0.821X + 0.037Y - 0.569Z + 8.261 = 0$

Pt(1)	0.000	S(1)	0.000
Pt'(1)	0.000	S'(1)	0.000

(e) Plane Containing Pt(1), Pt'(1), P(1), P'(1)

$-0.839X + 0.032Y - 0.544Z + 8.433 = 0$

Pt(1)	0.000	P(1)	0.000
Pt'(1)	0.000	P'(1)	0.000

B. Dihedral Angles (deg) between Normals to Planes

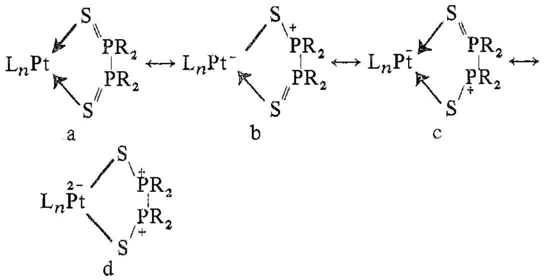
(a)-(b)	1.33	(b)-(d)	0.83
(a)-(c)	0.92	(b)-(e)	1.00
(a)-(d)	1.42	(c)-(d)	2.24
(a)-(e)	1.38	(c)-(e)	2.13
(b)-(c)	2.25	(d)-(e)	1.77

[a] The equation of each least-squares plane is expressed in orthogonal coordinates (X, Y, Z) which are related to the triclinic cell coordinates (x, y, z) by the transformations $X = x \sin\gamma + 2\cos\phi$, $Y = y + z\cos\alpha + x\cos\gamma$, and $Z = z\cos\rho$ where $\cos\phi = (\cos\beta - \cos\gamma\cos\alpha/\sin\gamma$ and $\cos\rho = (1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma)^{1/2}\sin\gamma$. In this transformation X lies in the xy plane, Y coincides with y, and Z is perpendicular to the xy plane. [b] Unit weights were used for all atoms in the application of the Smith[25] least-squares program.

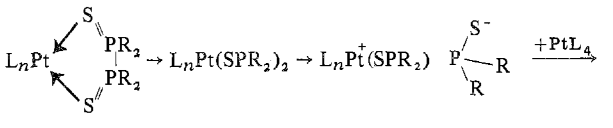
Table V. Root-Mean-Square Thermal Displacements along the Direction of the Principal Axes (in Å)

Atom	Axis 1	Axis 2	Axis 3
Pt(1)	0.141 (1)	0.178 (1)	0.216 (1)
P(1)	0.172 (3)	0.189 (3)	0.277 (3)
P(2)	0.159 (3)	0.196 (3)	0.220 (3)
S(1)	0.171 (3)	0.193 (3)	0.307 (3)
O(1)	0.187 (7)	0.217 (7)	0.250 (6)
O(2)	0.175 (8)	0.231 (7)	0.247 (6)
O(3)	0.156 (9)	0.201 (7)	0.273 (6)
C(1)	0.190 (12)	0.198 (13)	0.393 (12)
C(2)	0.234 (12)	0.259 (12)	0.395 (13)
C(3)	0.225 (13)	0.242 (12)	0.388 (13)
C(4)	0.278 (14)	0.320 (15)	0.454 (16)

phosphorus–phosphorus bond weakening (particularly resonance form d). Following oxidative addition, rearrangement



(ligand isomerization) and subsequent further reaction with the platinum(0) species would yield the observed product



$[Pt(SPR_2)L]_2$

No other thiophosphinato-bridged complexes have been authenticated, although a secondary product formulated as $[Pt\{SP(CF_3)_2\}S_2P(CF_3)_2]_2$ has been reported in the reaction of $PtCl_2$ and $HS_2P(CF_3)_2$, and this is suggested to contain bridging $SP(CF_3)_2$ groups. There are, of course, numerous reports of phosphinato groups (OPR_2) serving in a bridging capacity.[37-40]

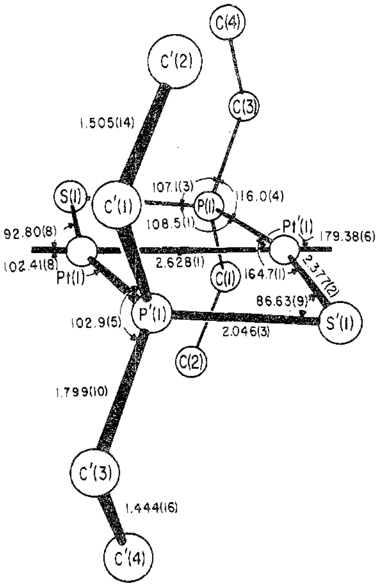


Figure 2. A view of the central portion of $[Pt\{SP(C_2H_5)_2\}P(OC_6H_5)_3]_2$ showing the detailed geometry including the principal bonding distances (Å) and bond angles (deg) with their standard deviations. Hydrogen atoms have been omitted for clarity.

Acknowledgment. We are pleased to acknowledge support from the University of Wisconsin Graduate School for this work. The Syntex diffractometer system was obtained by the department through a National Science Foundation major instrument grant.

Registry No. $[Pt\{SP(C_2H_5)_2\}P(C_6H_5)_3]_2$, 54020-36-9; $[Pt\{SP(CH_3)_2\}P(C_6H_5)_3]_2$, 54020-37-0; $[Pt\{SP(C_2H_5)_2\}P(C_6H_5)_2CH_3]_2$, 54020-33-6; $[Pt\{SP(CH_3)_2\}P(C_6H_5)_2CH_3]_2$, 54020-34-7; $[Pt\{SP(C_2H_5)_2\}P(OC_6H_5)_3]_2$, 54020-39-2; $[Pt\{SP(CH_3)_2\}P(OC_6H_5)_3]_2$, 54020-40-5; $[Pt\{SP(C_6H_5)(CH_3)\}P(C_6H_5)_3]_2$, 54020-38-1; $[Pt\{SP(C_6H_5)(CH_3)\}P(C_6H_5)_2CH_3]_2$, 54020-35-8; $[(C_2H_5)_2P(S)]_2$, 3790-23-6; $Pt[P(C_6H_5)_3]_4$, 14221-02-4; $P(OPh)_3$, 101-02-0.

Supplementary Material Available. Table I, a listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC404158.

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Structural and Magnetic Characterization of Di-μ-hydroxo-bis[bis(1,10-phenanthroline)chromium(III)] Iodide Tetrahydrate

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Received August 22, 1974 AIC40599Q

The crystal and molecular structure of di-μ-hydroxo-bis[bis(1,10-phenanthroline)chromium(III)] iodide tetrahydrate, $[Cr(phen)_2OH]_2I_4 \cdot 4H_2O$, has been determined from three-dimensional counter X-ray data. The material crystallizes in the triclinic space group $P\bar{1}$ with two dimeric formula units in a cell of dimensions $a = 11.463$ (12), $b = 9.893$ (11), $c = 22.757$ (25) Å; $\alpha = 90.06$ (2), $\beta = 93.04$ (2), $\gamma = 82.82$ (2)°. Least-squares refinement of 4453 independent data has led to an R factor of 0.074. The complex cation consists of two chromium(III) ions symmetrically bridged by two hydroxides, the remaining coordination sites being occupied by two bidentate 1,10-phenanthroline groups on each metal center. The coordination around each chromium center is roughly octahedral; the average Cr–N and Cr–O bond lengths are 2.056 (8) and 1.920 (3) Å, respectively, while the Cr–Cr separation is 2.986 (4) Å and the average Cr–O–Cr bridging angle is 102.1 (3)°. The magnetic susceptibility of a powdered sample of the complex has been examined in the temperature range 15–283°K. The dimer exhibits an antiferromagnetic exchange interaction, with the best fit to the Van Vleck equation including biquadratic exchange yielding $2J = -43.8$ cm^{-1} and $j = +1.5$ cm^{-1} with $\langle g \rangle = 2.00$. These data lead to a singlet–triplet splitting of -53.6 cm^{-1}. A comparison of the structural and magnetic properties of this complex with those of the glycinato complex $[Cr(gly)_2OH]_2$ leads to the conclusion that the correlation between bridging angle and singlet–triplet splitting observed for the analogous copper(II) complexes $[Cu(L)OH]_2^{2+}$ may also obtain for the chromium(III) systems.

Introduction

There has been considerable recent interest in the structural and magnetic properties of hydroxo-bridged copper(II) complexes of formulation $[Cu(L)OH]_2^{2+}$, where L is a bidentate ligand, and a number of structural and magnetic investigations on systems of this type have been reported.[1-13] These structural and magnetic data have demonstrated a nearly linear correlation between the Cu–O–Cu bridging angle, ϕ, and the singlet–triplet splitting, $2J$, with a slope of -79.1 cm^{-1} deg^{-1} and an intercept of 7730 cm^{-1}.[11] From molecular orbital considerations, it has been suggested that a similar relationship should exist for the analogous chromium(III) complexes $[Cr(L)_2OH]_2^{n+}$ but that the magnitude of the slope should be smaller for chromium(III) than for copper(II) because of the poor overlap between the chromium t_{2g} orbitals and the oxygen p orbitals relative to that between the copper $d_{x^2-y^2}$ orbital and the oxygen p orbitals.[12,14]

We have recently extended our experimental studies to the chromium complexes and have reported the structural and magnetic properties of the glycinato dimer,[15,16] $[Cr(gly)_2OH]_2$, and of the chloride salt of the phenanthroline dimer,[17] $[Cr(phen)_2OH]_2Cl_4 \cdot 6H_2O$. These latter data, which showed a singlet–triplet splitting of approximately -55 cm^{-1} for the chloride salt of the phen complex, are of considerable interest since, on the basis of high-temperature data, Earnshaw and Lewis[18] have calculated a singlet–triplet splitting of ap-