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Synthesis and Properties of the Hybrid Te, P Ligand Phenyl *o*-(Diphenylphosphino)phenyl Telluride. X-ray Structure of $[Pt\{PhTe(o\text{-}PPh_2C_6H_4)\}_2][Pt(SCN)_4]\cdot 2DMF$

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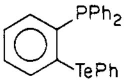
The first example of a bidentate hybrid ligand incorporating a tellurium donor atom, $PhTe(o\text{-}PPh_2C_6H_4)$, was prepared by the reaction of $PPh_2(o\text{-}LiC_6H_4)$ with PhTeBr in THF. Its reaction with $K_2Pt(SCN)_4$ gave the monomeric complex $Pt(SCN)_2PhTe(o\text{-}PPh_2C_6H_4)$, formulated as a thiocyanato complex (Pt–SCN bonding) on the basis of infrared spectroscopy. Recrystallization of this complex from dimethylformamide (DMF) gave the double salt $[Pt\{PhTe(o\text{-}PPh_2C_6H_4)\}_2][Pt(SCN)_4]\cdot 2DMF$, which was characterized by single-crystal X-ray diffraction.

Introduction

Hybrid ligands incorporating various combinations of groups 5A and 6A donor atoms have been reported.[1-4] The incorporation of such ligands in transition-metal complexes can result in unusual stereochemistries and bonding modes of ambidentate ligands in the coordination sphere.[1-3] Illustrative of the first effect is the complex $[Ni(bitas)Cl]BPh_4$ (bitas = tris(*o*-(dimethylarsino)phenyl)bismuthine), which has square-pyramidal geometry.[5] Indeed, the very coordination of the bismuth atom is noteworthy, because simple organobismuth derivatives are poor ligands.[6] The complexes [PdL(SCN)(NCS)] (L = $Ph_2PCH_2CH_2CH_2NMe_2$,[7a,8] $Ph_2P(o\text{-}C_6H_4AsPh_2)$[7]), which contain both N- and S-bonded thiocyanate, illustrate the unusual bonding modes.

The ligand chemistry of tellurium, long neglected in favor of the lighter chalcogenide elements, has been the subject of increasing recent interest.[9,10] Although a variety of transition-metal complexes with monodentate tellurium ligands have been reported,[9,10] no examples with bidentate ligands have appeared. We report here the first example of a hybrid bidentate ligand, diphenyl(*o*-phenyltellurenyl)phosphine (tep):



The monomeric complex $[Pd(tep)(SCN)_2]$ isolated from the reaction of $K_2[Pt(SCN)_4]$ with tep isomerizes upon recrystallization from hot DMF to give the Magnus-type salt $[Pt(tep)_2][Pt(SCN)_4]\cdot 2DMF$, which has been characterized by single-crystal X-ray diffraction.

Experimental Section

Starting Materials. Diphenyl ditelluride[11] and $K_2[Pt(SCN)_4]$[12] were prepared as described. (*o*-Bromophenyl)diphenylphosphine was obtained from Orgmet, Inc. All other materials were obtained from Kodak Laboratory Chemicals. A nylon column of SiO_2 (activity 3, ICN Nutritional Biochemicals) was used for dry column chromatography.[13] Air-sensitive reagents were handled in Schlenk vessels.[14]

Physical Measurements. Infrared spectra were measured as mineral oil mulls on a Nicolet Series 7000 Fourier-transform infrared spectrometer. Field-desorption mass spectra were recorded on a Varian MAT 731 mass spectrometer. TGA scans were recorded on a Du Pont Model 900 thermal analyzer.

Microanalyses were done by the Analytical Sciences Division of the Kodak Research Laboratories.

Synthesis of $Ph_2P(o\text{-}PhTeC_6H_4)$. To a solution of $Ph_2P(o\text{-}BrC_6H_4)$ (3.4 g, 10 mmol) in 150 mL of ether at −78 °C was added 4 mL of 2.5 M *n*-C_4H_9Li in hexane via a syringe. The solution was then stirred in an ice bath for 1 h. A solution of PhTeBr was prepared by addition of Br_2 (0.8 g, 5 mmol) in 12 mL of benzene to a −78 °C solution of Ph_2Te_2 (2.05 g, 5 mmol) in 125 mL of ether. The solution was stirred for 15 min in an ice bath. The resulting suspension of the black PhTeBr[15] was transferred via a Teflon tube to the above lithium reagent. The solution was then stirred at room temperature for 0.5 h, diluted with 150 mL of petroleum ether, and extracted with 500 mL of aqueous NH_4Cl. The organic phase was dried over $MgSO_4$, and the solvent was removed on a rotary evaporator, giving a viscous orange residue. This crude product, which contained some Ph_2Te_2, was dissolved in 25 mL of CH_2Cl_2 and adsorbed on SiO_2. The adsorbed material was loaded on top of an SiO_2 dry column and eluted with hexane. A leading pink band of Te_2Ph_2 was observed with a second yellow band near the top of the column. When the yellow band was resolved from the origin, it was extracted with CH_2Cl_2. Field-desorption mass spectroscopy (FDMS) of this extract showed mainly the desired product (*m*/*e* 468, ^{130}Te) with a trace of the phosphine oxide (*m*/*e* 484, ^{130}Te). Removal of the solvent gave a yellow gum, which was further purified by dry column chromatography with toluene elution and recrystallization from isopropyl alcohol (2.1 g, 45%). Anal. Calcd for $C_{24}H_{19}TeP$ (M_r 465.96): C, 61.86; H, 4.11; Te, 27.38; P, 6.65. Found: C, 61.9; H, 4.3; Te, 27.1; P, 6.7 [M_r (FDMS, CH_2Cl_2) 468 (based on ^{130}Te)].

$[Pt(tep)_2][Pt(SCN)_4]\cdot 2DMF$. To a solution of $K_2Pt(SCN)_4$ (0.51 g, 1 mmol) in 40 mL of water was added a solution of tep (0.47 g, 1 mmol) in 20 mL of acetone. A precipitate formed immediately, and the mixture was stirred for 15 h. A peach solid was isolated by filtration, washed with 20-mL portions of water, ethanol, and ether, and recrystallized from hot DMF (0.55 g, 70.7%). Anal. Calcd for $C_{58}H_{52}N_6P_2Pt_2S_4Te_2O_2$ (M_r 1700.68): C, 40.96; H, 3.08; N, 4.94; S, 7.54; Pt, 22.94; DMF, 8.6. Found:

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(1) McAuliffe, C. A., Ed. "Transition Metal Complexes of Phosphorus, Arsenic, and Antimony Ligands"; Wiley: New York, 1973.

(2) McAuliffe, C. A.; Levason, W. "Phosphine, Arsine, and Stibine Complexes of the Transition Elements"; Elsevier: Amsterdam, 1979.

(3) Mason, R.; Meek, D. W. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 183.

(4) Uriarte, R.; Mazanec, T. J.; Tau, K. D.; Meek, D. W. *Inorg. Chem.* **1980**, *19*, 79.

(5) Levason, W.; McAuliffe, C. A.; Murray, S. G. *J. Chem. Soc., Chem. Commun.* **1975**, 164.

(6) Levason, W.; Sheikh, B.; McCullough, F. P. *J. Coord. Chem.* **1982**, *12*, 53.

(7) (a) Meek, D. W.; Nicpon, P. E.; Meek, V. I. *J. Am. Chem. Soc.* **1970**, *92*, 5351. (b) Nicpon, P.; Meek, D. W. *Inorg. Chem.* **1967**, *6*, 145.

(8) Clark, G. R.; Palenik, G. J.; Meek, D. W. *J. Am. Chem. Soc.* **1970**, *92*, 1077.

(9) Gysling, H. J. *Coord. Chem. Rev.* **1982**, *42*, 133.

(10) Gysling, H. J. *Kodak Lab. Chem. Bull.* **1982**, *53(1)*, 1.

(11) Haller, W. S.; Irgolic, K. J. *J. Organomet. Chem.* **1972**, *38*, 97.

(12) DeStefano, N. J.; Burmeister, J. L. *Synth. React. Inorg. Met.-Org. Chem.* **1977**, *3*, 313.

(13) Loev, B.; Goodman, M. M. "Progress in Separation and Purification"; Interscience: New York, 1970; Vol. 3, p 73.

(14) (a) Shriver, D. F. "The Manipulation of Air-Sensitive Compounds"; McGraw-Hill: New York, 1969. (b) Gysling, H. J.; Thunberg, A. L. In "Physical Methods of Chemistry", 5th ed.; Rossiter, B. W., Hamilton, J. F., Eds.; Interscience: New York, in press.

(15) Schulz, P.; Klar, G. *Z. Naturforsch. B*, **1975**, *30*, 40; **1975**, *30*, 43.

0276-7333/84/2303-0596$01.50/0

C, 40.8; H, 3.1; N, 4.9; S, 7.2; Pt, 22.9; DMF, 8.3 (TGA).

X-ray Structure Determination of $[Pt(tep)_2][Pt(SCN)_4]\cdot 2DMF$. An orange, chunky crystal (0.15 × 0.18 × 0.27 mm) obtained from the DMF recrystallization was glued onto a thin glass rod and used for data collection. The unit cell parameters were obtained by least-squares refinement of the setting angles for 24 accurately centered reflections. The space group and cell data are as follows: triclinic, $P\bar{1}$, $a = 11.175$ (3) Å, $b = 12.438$ (1) Å, $c = 11.003$ (1) Å, $\alpha = 99.954$ (9)°, $\beta = 97.51$ (2)°, $\gamma = 80.30$ (2)°, $V = 1476.7$ (7) Å^3, $Z = 1$, d(calcd) = 1.912 g cm^{-3}, μ(Mo Kα) = 59.9 cm^{-1}, $F(000) = 812$, formula weight = 1700.68. The ω–2θ scan technique was used to measure 8591 unique reflections ($2\theta < 60°$) on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation. Each reflection was scanned from 2θ(Mo Kα_1) − 0.85° to 2θ(Mo Kα_2) + 0.85° at a scan rate that varied from 2° to 20° 2θ min^{-1}, depending on the intensity of the reflection. The scan width was extended 25% at each end to measure background intensities. As a check on crystal and electronic stability, the intensities of three reflections were monitored every hour of exposure. All data were corrected for the slow but steady decrease (maximum of 11.6%) in these intensities during data collection.

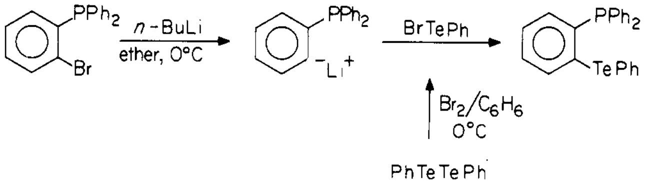
The net intensities were calculated according to $I = ASK(C - RB)$, and the standard deviations were $\sigma^2(I) = (ASK)^2(C + R^2B)$ and $\sigma(F_o) = [(I + \sigma(I))/Lp]^{1/2} - F_o$, where A is the attenuator factor, S is the scan rate, K is a scale factor, C is total integrated peak count, R is the ratio of peak to background time, B is the total background count, $(Lp)^{-1}$ is the Lorentz–polarization correction, and $F_o = (I/Lp)^{1/2}$ is the observed structure factor. An empirical absorption correction was applied.[16] A total of 6996 reflections with $I > \sigma(I)$ were considered observed and used in further calculations.

The structure was solved by the heavy-atom method.[17] Examination of the largest intensities showed pseudo-body centering, indicating that the Pt atoms occupied the centers of symmetry at 0,0,0 and 1/2,1/2,1/2. The Patterson map vectors confirmed this relationship and also gave the Te atom position. Subsequent electron-density maps gave all the remaining atoms. There is a disorder in the $Pt(SCN)_4$ ion involving alternate positions for S and C atoms (labeled S1A, S2A, C25A, and C26A). The N atoms appear to be in about the same positions for either orientation and could not be resolved. The disordered C and S positions were well resolved, the closest distance being 0.79 Å between C25A and C26. From relative peak heights in the electron-density maps and comparison of the isotropic thermal parameters, an occupancy ratio of 75/25 for S1/S1A, etc., was estimated.

The structure was refined by the full-matrix least-squares method with isotropic thermal parameters applied to the disordered SCN atoms and anisotropic thermal parameters to all other atoms. Hydrogen atoms were not located or included in the calculations. Atomic scattering factors and anomalous dispersion corrections were obtained from ref 18. The function minimized was $\sum w(|F_o| - K|F_c|)^2$ with $w^{-1} = \sigma^2(F_o) + (0.03F_o)^2$. The final discrepancy indices were 0.038 for $R = \sum||F_o| - K|F_c||/\sum|F_o|$ and 0.051 for $R_w = [\sum w(|F_o| - K|F_c|)^2/\sum wF_o^2]^{1/2}$. The scale factor K refined to 1.219 (1).

Results and Discussion

The first example of a bidentate ligand containing the Te, P donor set was prepared by the following route:



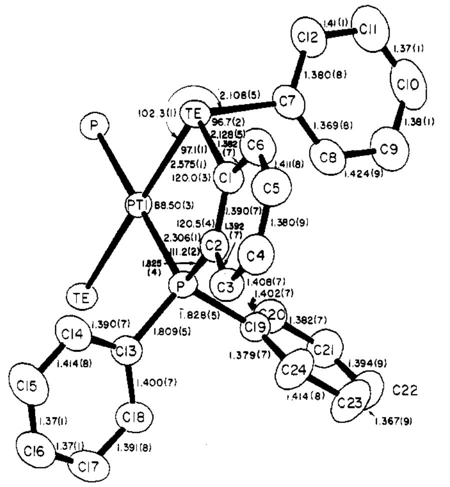


Figure 1. Bond lengths and selected angles in the $[Pt(tep)_2]^{2+}$ cation. Estimated standard deviations are given in parentheses. The thermal vibration ellipsoids were drawn at the 50% probability level.

This new ligand is air stable and can be conveniently purified by dry column chromatography, a rapid technique that requires relatively little solvent.[13,14b]

In view of the thiocyanate complexes containing both bonding modes of this ambidentate ligand previously reported for P,N[7a,8] and P,As[7] bidentate hybrid ligands, the related complex with tep was prepared. Reaction of an aqueous solution of $K_2Pt(SCN)_4$ with 1 equiv of tep in acetone gave an immediate precipitate of a material whose elemental analysis supports the formulation $Pt(SCN)_2(tep)$. The IR spectrum of this peach powder had two sharp bands in the ν_{CN} region at 2102 and 2118 cm^{-1}; the positions, shapes, and doublet character of these absorptions all supported a monomeric cis complex with S-bonded thiocyanates.[19]

This complex was insoluble in most organic solvents but was recrystallized from hot DMF, giving an orange crystalline material. Elemental analysis, thermogravimetric analysis (8.3% solvent lost in the range 150–210 °C), and IR spectroscopy (one sharp ν_{CN} band at 2108 cm^{-1}) all supported a solvated Magnus-salt formulation, $[Pt(tep)_2][Pt(SCN)_4]\cdot 2DMF$. This formulation, with the first example of a hybrid bidentate tellurium ligand, was confirmed by a single-crystal X-ray diffraction structural determination.

The positional and thermal parameters are given in Table I. Both lengths and selected angles are given in Figures 1 and 2. Additional bond angles were omitted for clarity and are included in supplementary tables. The structure consists of discrete, centrosymmetric $Pt(tep)_2^{2+}$ and $Pt(SCN)_4^{2-}$ ions, and the coordination about both Pt atoms is strictly square planar by symmetry. The coordination about Te is tetrahedral with the lone pair of electrons occupying one of the sp^3 orbitals. In this orientation, π bonding to Pt is unlikely. The bond angles about Te are all less than the tetrahedral angle, as predicted by VSEPR theory.[20,21]

No crystal structures of Pt complexes with organotellurium ligands have been reported, but a comparison can be made with the structure of *trans*-$Pd(SCN)_2$(Te-

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(16) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A* **1968**, *A24*, 351.

(17) Programs for structure solution and refinement were part of the Structure Determination Package (SDP), Enraf-Nonius Corp., Delft, Holland, Rev. 18, 1981.

(18) "International Tables for X-ray Crystallography", Kynoch Press: Birmingham, 1974; Vol. 4, Chapter 2.

(19) (a) Burmeister, J. L. "Chemistry and Biochemistry of Thiocyanic Acid and Its Derivatives"; Newman, H. A., Ed.; Academic Press: London, 1975; Chapter 2. (b) Chia, L. Y.; McWhinnie, W. R. *J. Organomet. Chem.* **1978**, *148*, 165. (c) McAuliffe, C. A.; Niven, I. E.; Parish, R. V. *Inorg. Chim. Acta* **1977**, *22*, 239.

(20) Gillespie, R. J.; Nyholm, R. S. *Q. Rev., Chem. Soc.* **1957**, *11*, 339.

(21) Gillespie, R. J. *J. Chem. Educ.* **1970**, *47*, 18.

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
Pt1	0.0	0.0	0.0	2.280 (4)	C19	0.2126 (5)	0.0085 (4)	−0.1958 (4)	2.99 (9)
Pt2	0.5	0.5	0.5	3.094 (5)	C20	0.1784 (5)	0.1221 (4)	−0.1599 (5)	3.7 (1)
Te	0.15520 (3)	−0.07863 (3)	0.16881 (3)	2.871 (6)	C21	0.2412 (6)	0.1949 (5)	−0.1981 (6)	4.6 (1)
P	0.1300 (1)	−0.0878 (1)	−0.1450 (1)	2.55 (2)	C22	0.3383 (6)	0.1562 (5)	−0.2695 (6)	4.9 (1)
C1	0.2741 (5)	−0.1836 (4)	0.0476 (5)	3.1 (1)	C23	0.3706 (6)	0.0454 (6)	−0.3051 (7)	5.6 (2)
C2	0.2475 (4)	−0.1892 (4)	−0.0802 (5)	2.96 (9)	C24	0.3073 (6)	−0.0308 (5)	−0.2681 (6)	4.7 (1)
C3	0.3152 (5)	−0.2709 (4)	−0.1575 (5)	3.5 (1)	C27	0.1072 (7)	−0.3851 (6)	0.0163 (7)	5.6 (2)
C4	0.4117 (6)	−0.3425 (5)	−0.1051 (6)	4.3 (1)	C28	0.078 (1)	−0.4172 (9)	0.2188 (9)	8.9 (3)
C5	0.4388 (6)	−0.3329 (5)	0.0219 (6)	4.5 (1)	C29	0.225 (1)	−0.5472 (8)	0.092 (1)	10.5 (4)
C6	0.3691 (5)	−0.2522 (5)	0.1014 (6)	4.2 (1)	O	0.0359 (5)	−0.2980 (4)	0.0259 (6)	6.7 (1)
C7	0.2655 (5)	0.0467 (4)	0.2240 (5)	3.6 (1)	N3	0.1368 (5)	−0.4477 (5)	0.1075 (6)	5.3 (1)
C8	0.3144 (7)	0.0882 (6)	0.1374 (7)	5.7 (2)	S1	0.3135 (2)	0.6149 (2)	0.5099 (2)	5.05 (4)*
C9	0.3838 (8)	0.1765 (6)	0.1760 (8)	6.8 (2)	S1A	0.2924 (6)	0.5427 (6)	0.5256 (7)	4.7 (1)*
C10	0.4002 (7)	0.2176 (6)	0.3008 (9)	6.1 (2)	S2	0.4527 (2)	0.4042 (2)	0.6453 (2)	4.91 (4)*
C11	0.3535 (7)	0.1737 (7)	0.3867 (8)	6.7 (2)	S2A	0.4686 (7)	0.6226 (6)	0.3580 (7)	5.0 (1)*
C12	0.2850 (6)	0.0863 (7)	0.3490 (7)	5.7 (2)	N1	0.3256 (8)	0.8094 (7)	0.4222 (8)	7.7 (2)*
C13	0.0612 (4)	−0.1625 (4)	−0.2854 (5)	3.00 (9)	N2	0.2228 (7)	0.4667 (6)	0.7198 (8)	7.4 (2)*
C14	0.0123 (6)	−0.2561 (5)	−0.2760 (6)	4.5 (1)	C25	0.3250 (9)	0.7267 (8)	0.4514 (9)	5.0 (2)*
C15	−0.0428 (7)	−0.3146 (6)	−0.3847 (7)	5.7 (2)	C25A	0.264 (2)	0.485 (2)	0.637 (2)	3.6 (4)*
C16	−0.0522 (7)	−0.2782 (6)	−0.4967 (6)	5.3 (2)	C26	0.3116 (8)	0.4506 (7)	0.6813 (9)	4.8 (2)*
C17	−0.0035 (7)	−0.1858 (6)	−0.5045 (6)	5.4 (2)	C26A	0.387 (2)	0.729 (2)	0.408 (2)	4.5 (5)*
C18	0.0523 (6)	−0.1261 (5)	−0.4001 (5)	4.2 (1)					

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

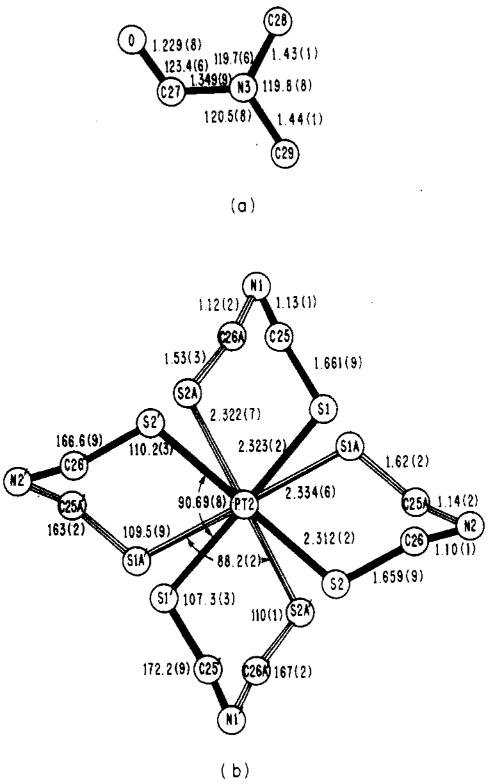

Figure 2. Bond lengths and angles for DMF (a) and $[Pt(SCN)_4]^{2-}$ (b). Atoms were given arbitrary radii in this figure.

$(CH_2CH_2CH_2SiMe_3)_2)_2$,[22] because the covalent radii of Pt and Pd are the same (1.31 Å).[23] The Pt–Te bond (2.575 (1) Å) is slightly shorter than the 2.606 (1) Å found in the above Pd complex and the sum of covalent radii (2.63 Å, using 1.32 Å for tetrahedral Te).[23] The Pt–P bond (2.306 (1) Å) is shorter than the sum of covalent radii (2.35 Å, using 1.05 Å for P)[3] but is at the upper end of the range of Pt–P bonds commonly found,[3,24] showing that dπ–dπ back-bonding is not significant. Bonds within the ligand average 1.821 Å for P–C_{sp^2}, 2.118 Å for Te–C_{sp^2}, and 1.39 Å for C_{sp^2}–C_{sp^2} and are normal values.

Although numerous $PtL(SCN)_2$ structures have been published, the $Pt(SCN)_4^{2-}$ anion here is the first known structure reported except for $K_2Pt(SCN)_4$[25] and the Pd analogue.[26] The Pt–S bond distances average 2.323 Å, slightly less than the sum of covalent radii (2.35 Å),[23] so S–Pt π bonding is probably not significant.[19a] The comparable distance in $Pd(SCN)_4^{2-}$ is 2.312 (9) Å.[26] A second Pd–S distance is longer (2.392 Å) but is affected by a Pd–S intermolecular interaction. The S–C and C–N bond lengths are affected by the disorder but compare well with tabulated values for S-bonded SCN groups in several Pd complexes.[27]

There are no short intermolecular interactions and no apparent steric reason for the unequal occupancy in the SCN disorder. It is interesting though that the torsion angles for S2–Pt2–S1–C25 and S1–Pt2–S2–C26 are 18.4° and 4.2°, respectively, vs. 6.9° and 43.9° for the comparable angles in the minor (A) component. A 44° tilt of the SCN group from the PtS_4 plane minimizes the overlap between one of the S π molecular orbitals and a Pt dπ orbital,[19a] and to the extent that π bonding is important, this configuration is less energetically favored.

We are continuing our studies of hybrid tellurium ligands that incorporate additional group 5A and 6A donor sites.

Registry No. $[Pt(tep)_2][Pt(SCN)_4]\cdot 2DMF$, 88905-10-6; tep, 88905-11-7; $Ph_2P(o\text{-}BrC_6H_4)$, 62336-24-7.

Supplementary Material Available: Tables of anisotropic thermal parameters, remaining angles in the cation, and structure factor amplitudes (55 pages). Ordering information is given on any current masthead page.

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(22) Gysling, H. J.; Luss, H. R.; Smith, D. L. *Inorg. Chem.* **1979**, *18*, 2696.

(23) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

(24) Manojlovic-Muir, L.; Muir, K. W.; Solomun, T. *J. Organomet. Chem.* **1977**, *142*, 265.

(25) Zvonkova, Z. V. *Zh. Fiz. Khim.* **1952**, *26*, 1804.

(26) Mawby, A.; Pringle, G. E. *J. Chem. Soc. D* **1970**, 385.

(27) Beran, G.; Carty, A. J.; Chieh, P. C.; Patel, H. A. *J. Chem. Soc., Dalton Trans.* **1973**, 488.