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Supplementary Material Available. Table V, showing planes and dihedral angles, Table VII, showing intermolecular contact distances, and 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 \$4.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-279.

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Mixed Thiocyanate Complexes of Platinum(II). Crystal Structure of *cis*-Thiocyanatoisothiocyanatobis(3,3-dimethylbutynyldiphenylphosphine)platinum(II)

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Mixed thiocyanate complexes of the type *cis*-$\mathrm{Pt(NCS)(SCN)(Ph_2PC{\equiv}CR)_2}$ (R = Ph, Et, *i*-Pr, *t*-Bu) have been prepared and characterized. The purely N-bonded compound *cis*-$\mathrm{Pt(NCS)_2(Ph_2PC{\equiv}C}$-*t*-Bu)$_2$ and the chloride complexes *cis*-$\mathrm{PtCl_2(Ph_2PC{\equiv}CR)}$ are also described. Infrared vibrational frequencies for the coordinated $\mathrm{CNS^-}$ ion have been assigned using ^{15}N isotopically substituted compounds. *cis*-$\mathrm{Pt(NCS)(SCN)(Ph_2PC{\equiv}C}$-*t*-Bu)$_2$ crystallizes in space group $Pca2_1$ with a = 18.272 (13), b = 13.287 (5), and c = 16.470 (17) Å. Observed and calculated densities are 1.47 and 1.40 g cm^{-3}, respectively, for mol wt 843.9 and Z = 4. The structure was solved by a combination of Patterson, Fourier, and least-squares refinement techniques. The final discrepancy index for 1951 observed, independent reflections is R = 0.057. The platinum atom is coordinated in square-planar fashion by two phosphorus atoms of the acetylenic phosphines, a nitrogen atom of an isothiocyanate group, and a sulfur atom of a thiocyanate group. Relevant intramolecular distances include Pt–P(1) (2.275 (6) Å), Pt–P(2) (2.244 (7) Å), Pt–S(1) (2.374 (8) Å), and Pt–N(1) (2.061 (29) Å). Factors influencing the bonding mode of the thiocyanate ion in platinum(II) complexes are discussed.

Despite the existence of a wide variety of metal thiocyanate complexes only a relatively small number contain *both* M-NCS and M-SCN linkages.[1,2] X-Ray studies have confirmed the presence of nonbridging mixed thiocyanato bonding in *cis*-$\mathrm{Pd(NCS)(SCN)(Ph_2P(CH_2)_3NMe_2)}$,[3] *cis*-$\mathrm{Pd(NCS)(SCN)(Ph_2P(CH_2)_2PPh_2)}$,[4] and *cis*-$\mathrm{Pd(NCS)(SCN)(Ph_2PC{\equiv}C}$-*t*-Bu)$_2$[5] while infrared spectroscopic measurements indicate probable mixed bonding modes in Pd(NCS)(SCN)[$\mathrm{Ph_2P}$(*o*-$\mathrm{C_6H_4AsPh_2}$)],[6] $\mathrm{Pd(NCS)(SCN)(Ph_2P(CH_2)_2NMe_2)}$,[6] [$\mathrm{M(NCS)(SCN)(Ph_2PC{\equiv}CPPh_2)}$]$_2$ (M = Pd, Pt),[7] Pd(NCS)(SCN)L (L = 4,4′-dimethylbipyridyl),[8] and Cu(NCS)(SCN)L (L = tri-2-pyridylamine, phenyldi-2-pyridylamine).[9] As a continuation of our work on the novel coordinating properties of acetylenic phosphines we recently discovered[10] that the complex $\mathrm{Pd(CNS)_2(Ph_2PC{\equiv}C}$-*t*-Bu)$_2$ could be isolated in three isomeric forms, two of which were *cis*-$\mathrm{Pd(NCS)(SCN)(Ph_2PC{\equiv}C}$-*t*-Bu)$_2$ while the third, *trans*-$\mathrm{Pd(SCN)_2(Ph_2PC{\equiv}C}$-*t*-Bu)$_2$, was an example of a hitherto unknown structural type namely a *trans*-dithiocyanatophosphine complex of Pd(II). In an attempt to prepare and study other phosphine complexes of the transition metals containing mixed thiocyanate and purely S-bonded thiocyanate groups, in order to test current ideas on factors controlling $\mathrm{CNS^-}$ bonding,[1,3-6,10,11] the work has been extended to Pt(II) systems. This paper describes the synthesis and characterization of the complexes *cis*-$\mathrm{Pt(CNS)_2(Ph_2PC{\equiv}CR)_2}$ (R = Ph, Et, *i*-Pr, *t*-Bu) which can be isolated in the N-bonded form *cis*-$\mathrm{Pt(NCS)_2(Ph_2PC{\equiv}CR)_2}$ (R = *t*-Bu) or mixed forms *cis*-$\mathrm{Pt(NCS)(SCN)(Ph_2PC{\equiv}CR)_2}$. Solid-state and solution infrared measurements including assignments of $\mathrm{CNS^-}$ vibrational modes from ^{15}N isotopic substitution studies are reported. A full three-dimensional X-ray structure determination of the complex *cis*-$\mathrm{Pt(NCS)(SCN)(Ph_2PC{\equiv}C}$-*t*-Bu)$_2$ has been carried out to confirm spectroscopic measurements and to provide further insight into factors influencing the bonding mode of the thiocyanate ion.

Experimental Section

The ligands $\mathrm{Ph_2PC{\equiv}CR}$ (R = Et, Ph, *i*-Pr, *t*-Bu) were synthesized as previously described.[12]

Preparation of Compounds. (1) $\mathrm{PtCl_2(Ph_2PC{\equiv}CEt)_2}$. $\mathrm{K_2PtCl_4}$ (0.5 g) dissolved in $\mathrm{H_2O}$ (30 ml) and ethanol (20 ml) was stirred at room temperature for 12 hr with $\mathrm{Ph_2PC{\equiv}CEt}$ (0.8 g). The solution was taken to dryness and the solid extracted with dichloromethane. The solution was filtered, the volume reduced to *ca.* 5 ml, and diethyl ether (20 ml) added. Yellowish white crystals of the complex were obtained on cooling. *Anal.* Calcd for $\mathrm{PtCl_2(Ph_2PC{\equiv}CEt)_2}$: C, 51.75; H, 4.05. Found: C, 52.39; H, 3.75.

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(2) We use the term "mixed thiocyanate bonding" to imply the presence of two (or more) thiocyanate groups coordinated in monodentate fashion but differing in their mode of attachment to the metal. Throughout the paper we represent metal–isothiocyanate bonding as M(NCS) and metal–thiocyanate bonding as M(SCN). When no specific bonding mode is implied M(CNS) is used.

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The following complexes were similarly obtained. $PtCl_2(Ph_2PC{\equiv}CPh)_2$ appeared as yellowish white crystals. *Anal.* Calcd: C, 57.27; H, 3.57. Found: C, 57.53; H, 3.64. $PtCl_2(Ph_2PC{\equiv}C\text{-}i\text{-}Pr)_2$ appeared as yellowish white crystals. *Anal.* Calcd: C, 52.98; H, 4.41. Found: C, 52.75; H, 4.37. $PtCl_2(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)_2$ appeared as colorless crystals. *Anal.* Calcd: C, 54.13; H, 4.76. Found: C, 54.20; H, 4.54.

(2) $Pt(NCS)(SCN)(Ph_2PC{\equiv}CEt)$. To $PtCl_2(Ph_2PC{\equiv}CEt)_2$ (0.45 g) in acetone (100 ml) was added potassium thiocyanate (0.90 g). The mixture was warmed to dissolve the thiocyanate and then stirred at room temperature for 20 hr. The solution was taken to dryness, the solid extracted with dichloromethane, and the volume of solution reduced to a few milliliters. Diethyl ether (10 ml) was added and the solution cooled. Colorless crystals of the complex were obtained. *Anal.* Calcd for $Pt(CNS)_2(Ph_2PC{\equiv}CEt)_2$: C, 51.84; H, 3.81. Found: C, 51.91; H, 3.60.

The following compounds were similarly prepared. $Pt(NCS)(SCN)(Ph_2PC{\equiv}CPh)_2$ appeared as yellowish white crystals from dichloromethane–ethanol. *Anal.* Calcd: C, 57.07; H, 3.40. Found: C, 56.91; H, 3.31. $Pt(NCS)(SCN)(Ph_2PC{\equiv}C\text{-}i\text{-}Pr)_2$ appeared as colorless crystals from petroleum ether–ethanol. *Anal.* Calcd: C, 53.00; H, 4.17. Found: C, 53.55; H, 4.02. $Pt(NCS)_2(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)_2$ appeared as colorless crystals from dichloromethane–diethyl ether. *Anal.* Calcd: C, 54.08; H, 4.50. Found: C, 53.64; H, 4.12.

Recrystallization of the colorless crystals of $Pt(NCS)_2(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)_2$ from acetonitrile at 0° afforded colorless crystals of a different complex, shown by infrared spectroscopy (*vide infra*) to be $Pt(NCS)(SCN)(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)_2$.

Attempts were made, without success, to obtain a $Pt(SCN)_2(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)_2$ complex by crystallization and precipitation at low temperatures from acetonitrile and dichloromethane.

The isotopically substituted complexes $Pt(^{15}NCS)_2(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)_2$, $Pt(^{15}NCS)(SC^{15}N)(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)_2$, and $Pt(^{15}NCS)(SC^{15}N)(Ph_2PC{\equiv}CEt)_2$ were prepared on a 20-mg scale from the halo complexes by metathesis with 95% isotopically enriched $NaSC^{15}N$ (Stohler Isotope Chemicals). Purity was checked by a careful comparison of infrared spectra with the natural-abundance spectra.

Infrared Spectra. Solid-state spectra were measured as Nujol mulls on cesium iodide windows. Solution spectra were obtained in a variety of solvents using matched silver chloride cells of path length 0.5 mm. Integrated intensity measurements were made as previously described.[6,10] All infrared spectra were recorded on a Perkin-Elmer 180 spectrophotometer.

Collection and Reduction of X-Ray Data

Crystals of *cis*-$Pt(NCS)(SCN)(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)_2$ from dichloromethane–ethanol are colorless prisms. Weissenberg and precession photographs established the cell constants, which were refined by least-squares methods from the 2θ values (Mo Kα) measured from a General Electric XRD-6 diffractometer for 13 reflections. The crystal data are summarized here for *cis*-thiocyanatoisothiocyanatobis(3,3-dimethylbutynyldiphenylphosphine)platinum(II), $C_{38}H_{38}N_2P_2PtS_2$: mol wt 843.9; orthorhombic; $a = 18.272$ (13), $b = 13.287$ (5), $c = 16.470$ (17) Å; $V = 3998.6$ Å^3; $d_m = 1.47$ g cm^{-3} (by flotation); $Z = 4$; $d_c = 1.40$ g cm^{-3}; $F(000) = 1680$; space group $Pca2_1$ (C_{2v}^5); μ(Mo Kα) = 39.0 cm^{-1}.

A crystal with dimensions of 0.10 × 0.10 × 0.25 mm was mounted on a glass fiber and aligned with c^* along the ϕ axis of the General Electric XRD-6 automatic spectrogoniometer equipped with scintillation counter, pulse height analyzer, and Hewlett-Packard Scaler-Timer (5201L). Zirconium-filtered Mo Kα radiation at a takeoff angle of 4° was employed.

The θ–2θ scan method with scan speed of 2° min^{-1} was used and the scan range was $\pm(0.9 + 0.3 \tan\theta)°$. The background was measured at the beginning and end of each scan with a 10-sec stationary count. The stability was monitored with three standard reflections which were measured after each 100 reflections. The variation was within 6%. The standard deviations were estimated from counting statistics. Among 2226 independent reflections measured, 1951 with intensities greater than 1.5σ were considered as observed and used throughout the structural analyses. Lorentz and polarization factors were applied to the derivation of structure amplitudes. Revised versions of least-squares (by Doedens and Ibers) and Fourier (by Zalkin) programs were used. Other programs were developed in this laboratory. The calculations were done on an IBM 360/75 computer at the University of Waterloo.

Structure Determination and Refinement

The systematic absences were $0kl$, $k = 2n + 1$, and $h0l$, $l = 2n + 1$, and these indicate a possible space group of $Pbcm$. The measured density indicates that there are 4 molecules per unit cell and therefore the molecule is required to have a mirror plane, if the space group is $Pbcm$. The axes can also be chosen to fit the space group $Pca2_1$; then the systematic absences become $h0l$, $h = 2n + 1$, and $0kl$, $l = 2n + 1$. The coordinates for the platinum atom were derived from a three-dimensional Patterson map assuming a space group $Pca2_1$ which proved to be correct by the successful solution of the structure with the heavy-atom method. With all the nonhydrogen atoms having isotropic thermal parameters, the structure was refined to an R factor of 0.07 using full-matrix least-squares methods. The atomic scattering factors of ref 13 were used for all the atoms with dispersion corrections made for platinum. Anisotropic thermal parameters were then introduced for Pt, P, and the atoms of the thiocyanate groups. The function minimized was $\Sigma w\Delta^2$, where $w = (40 + |F_o| + 0.055|F|^2)^{-1}$ and $\Delta = |F_o| - |F_c|$. An attempt to locate the hydrogen atoms was unsuccessful through a difference Fourier synthesis and the refinement was stopped at discrepancy indices R and R_w of 0.057 and 0.079, respectively. At this stage, structure factors were also calculated using $-x, -y, -z$ (a negative model) with the previous data. Even though the agreement was less satisfactory, only relatively small differences were found in each reflection. It was therefore difficult to predict conclusively the absolute configuration from measurements of a few reflections with $\bar{h}\bar{k}\bar{l}$.

A separate refinement was carried out with the negative model which gave higher values of 0.063 and 0.086 for R and R_w, respectively. The negative model also gave unreasonable platinum–ligand distances: Pt–P(1), 2.368 Å; Pt–P(2), 2.189 Å. The difference of 0.179 Å is too large even considering the relative trans bond lengthening influences of thiocyanate and isothiocyanate groups.[4,5,10,14] In fact Pt–P(1) is longer than any of the other Pt–P bond lengths in Table I.[14-19] Pt–S(2), 2.285 Å, is short and Pt–N(2), 2.123 Å, is too long when compared with *trans*-$Pt(SC_6F_5)_2(Bu_3P)_2$[18] and α- and β-$Pt_2Cl_2(NCS)_2(n\text{-}Pr_3P)_2$.[14] These structural anomalies together with the larger R values from the negative model led us to conclude that the previous model was correct. The atomic coordinates and thermal parameters are given in Table II. A table of structure factors is available.[20]

Results and Discussion

Synthesis and Infrared Spectra. The complexes *cis*-$PtCl_2(Ph_2PC{\equiv}CR)_2$ (R = Et, Ph, *i*-Pr, *t*-Bu) were characterized by elemental analysis and the appearance of two strong ν(Pt–Cl) bands at *ca.* 290 and *ca.* 315 cm^{-1} in the far-infrared spectrum (Table III). There was no evidence for bands near 340 cm^{-1} attributable to the trans complexes. Confirmation of the cis geometry of $PtCl_2(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)_2$ was provided by the solid-state Raman spectrum. Two ν(Pt–Cl) bands coincident with the far-infrared bands were found at 319 and 299 cm^{-1} but the intense Ag mode of a centrosymmetric trans compound normally observed near 330 cm^{-1} was absent.[21] These compounds are analogous to a series of cis palladium complexes recently described.[22] Metathesis of *cis*-$PtCl_2(Ph_2PC{\equiv}CR)_2$ with KSCN in acetone gave the thiocyanates $Pt(CNS)_2(Ph_2PC{\equiv}CR)_2$. The compounds $Pt(CNS)_2(Ph_2PC{\equiv}CR)_2$ (R = Et, Ph, *i*-Pr) exhibited, in addition to strong bands due to ν(C≡C) near 2200 cm^{-1}, a sharp band at

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Table I. Pertinent Bond Distances in Some Platinum(II) Complexes

Compd	Pt-P, Å	Pt-S, Å	Pt-N, Å	Ref
α-Pt$_2$Cl$_2$(NCS)$_2$(*n*-Pr$_3$P)$_2$	2.244 (4)	2.327 (5)	2.078 (13)	14
β-Pt$_2$Cl$_2$(NCS)$_2$(*n*-Pr$_3$P)$_2$	2.262 (4)	2.408 (4)	1.965 (13)	14
cis-Pt(NCS)(SCN)(Ph$_2$PC≡C-*t*-Bu)$_2$	2.275 (6), 2.244 (7)	2.374 (8)	2.061 (29)	This work
cis-Pt(CN)(C≡CN)(Ph$_3$P)$_2$	2.32 (1), 2.33 (1)			15
cis-PtCl$_2$(Me$_3$P)$_2$	2.25 (1)			16
trans-Pt$_2$Cl$_4$(*n*-Pr$_3$P)$_2$	2.230 (9)			17
trans-Pt(SC$_6$F$_5$)$_2$(*n*-Bu$_3$P)$_2$	2.329 (8)	2.355 (8)		18
trans-PtBr$_2$(Et$_3$P)$_2$	2.315			19
trans-PtCl$_2$(Et$_3$P)$_2$	2.30			19

Table II

Atomic Coordinates (Fractional, $\times 10^4$) and Thermal Parameters

Atom	*x*	*y*	*z*	*B*, Å^2
Pt	0758 (1)	1022 (1)	2500	
S(1)	1496 (4)	0468 (6)	3599 (5)	
S(2)	0914 (6)	−2220 (7)	1271 (7)	
P(1)	0068 (3)	1407 (5)	1393 (4)	
P(2)	0667 (3)	2539 (5)	3090 (4)	
N(1)	1306 (16)	−1597 (28)	3693 (20)	
N(2)	0794 (12)	−0406 (23)	2011 (16)	
C(01)	1375 (19)	−0795 (22)	3591 (23)	
C(02)	0858 (13)	−1150 (22)	1718 (18)	
C(1)	0530 (15)	0930 (19)	0485 (18)	4.6 (6)
C(2)	1242 (14)	1218 (20)	0363 (17)	4.7 (5)
C(3)	1649 (18)	0835 (25)	−0282 (21)	5.2 (7)
C(4)	1295 (17)	0153 (25)	−0792 (22)	6.2 (7)
C(5)	0592 (18)	−0144 (26)	−0654 (23)	5.2 (8)
C(6)	0208 (13)	0220 (20)	0005 (17)	4.5 (6)
C(7)	−0838 (12)	0922 (20)	1420 (17)	3.1 (5)
C(8)	−1008 (14)	0141 (21)	2003 (17)	4.0 (5)
C(9)	−1728 (15)	−0221 (22)	2022 (20)	5.3 (6)
C(10)	−2244 (15)	0132 (22)	1471 (20)	5.6 (6)
C(11)	−2067 (18)	0897 (26)	0864 (22)	5.9 (8)
C(12)	−1361 (16)	1251 (22)	0838 (18)	4.8 (6)
C(13)	−0059 (16)	2643 (22)	1139 (17)	4.1 (6)
C(14)	−0268 (14)	3446 (21)	0907 (18)	4.4 (6)
C(15)	−0511 (17)	4410 (25)	0568 (21)	5.8 (7)
C(16)	0146 (19)	4907 (30)	0142 (23)	8.0 (8)
C(17)	−1157 (27)	4174 (32)	−0006 (32)	8.4 (9)
C(18)	−0699 (21)	5182 (34)	1337 (32)	8.8 (9)
C(19)	1069 (10)	3620 (15)	2603 (19)	3.1 (4)
C(20)	0860 (18)	4508 (28)	2748 (23)	7.0 (9)
C(21)	1167 (14)	5413 (21)	2354 (18)	5.3 (6)
C(22)	1723 (15)	5249 (24)	1893 (21)	5.7 (7)
C(23)	1974 (15)	4291 (22)	1649 (19)	5.1 (6)
C(24)	1657 (14)	3452 (21)	2066 (17)	3.8 (5)
C(25)	1099 (13)	2638 (19)	4065 (15)	3.8 (5)
C(26)	0676 (13)	2350 (22)	4797 (18)	4.4 (6)
C(27)	1003 (18)	2274 (25)	5509 (22)	6.3 (7)
C(28)	1776 (23)	2576 (33)	5590 (26)	7.4 (1)
C(29)	2151 (17)	2867 (25)	4906 (22)	6.9 (8)
C(30)	1817 (16)	2938 (23)	4132 (20)	4.6 (7)
C(31)	−0208 (14)	2863 (21)	3262 (18)	5.0 (6)
C(32)	−0868 (14)	3061 (22)	3356 (19)	4.7 (6)
C(33)	−1655 (15)	3265 (22)	3543 (18)	5.1 (6)
C(34)	−1822 (19)	4336 (26)	3560 (23)	6.4 (8)
C(35)	−1925 (21)	2780 (28)	4269 (26)	8.2 (9)
C(36)	−2062 (19)	2700 (27)	2762 (24)	8.1 (9)

Anisotropic Thermal Parameters in the Form $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})] \times 10^{-3}$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	36.8 (5)	38.9 (7)	35.2 (5)	3.1 (4)	−3.1 (6)	−0.1 (7)
S(1)	67 (5)	64 (5)	56 (4)	14 (4)	−28 (3)	−2 (4)
S(2)	134 (8)	48 (5)	92 (8)	20 (5)	−15 (6)	−24 (5)
P(1)	38 (3)	51 (4)	40 (4)	7 (2)	−7 (3)	6 (3)
P(2)	41 (3)	35 (4)	39 (4)	4 (2)	−6 (3)	−7 (3)
N(1)	128 (20)	61 (23)	60 (20)	15 (18)	−19 (15)	38 (19)
N(2)	59 (15)	72 (19)	48 (16)	1 (13)	2 (12)	−22 (15)
C(01)	92 (25)	24 (16)	80 (23)	1 (17)	−26 (19)	14 (16)
C(02)	55 (14)	29 (19)	29 (16)	1 (13)	11 (10)	−24 (14)

ca. 2130 cm^{-1} and a broad band at *ca.* 2090–2100 cm^{-1} assignable to ν(C≡N) of S- and N-coordinated CNS$^-$ groups, respectively (Table III). Similar ν(C≡N) band intensities, frequencies, and patterns characterize the complexes *cis*-Pd(NCS)(SCN)(Ph$_2$P(CH$_2$)$_2$PPh$_2$),[4] *cis*-Pd(NCS)(SCN)(Ph$_2$P(CH$_2$)$_3$NMe$_2$),[3] and *cis*-Pd(CNS)(SCN)(Ph$_2$PC≡C-*t*-Bu)$_2$.[5] The complex Pt(CNS)$_2$(Ph$_2$PC≡C-*t*-Bu)$_2$ obtained in the same fashion as above showed a broad doublet due to ν(C≡N) at 2101, 2082 cm^{-1} due to N-bonded thiocyanate (Table III). Recrystallization of Pt(NCS)$_2$(Ph$_2$PC≡C-*t*-Bu)$_2$ from acetonitrile at 0° afforded colorless crystals of an isomeric complex with ν(C≡N) at 2127 and 2088 cm^{-1} analogous to the spectra of Pt(NCS)(SCN)(Ph$_2$PC≡CR)$_2$ (R = Et, Ph, *i*-Pr). Although it is conceivable that an isomeric mixture of purely S-bonded and N-bonded thiocyanate complexes could give rise to the same type of spectrum, the X-ray structure determination of *cis*-Pt(NCS)(SCN)(Ph$_2$PC≡C-*t*-Bu)$_2$ (*vide infra*) together with the marked similarity of ν(C≡N) and far-infrared spectra for all these derivatives renders this possibility unlikely. The complexes are therefore *cis*-Pt(NCS)(SCN)(Ph$_2$PC≡CR)$_2$ (R = Et, Ph, *i*-Pr, *t*-Bu). Assignments of vibrational frequencies for the coordinated CNS$^-$ moieties utilizing the ^{15}N isotopically substituted compounds *cis*-Pt(^{15}NCS)(SC^{15}N)(Ph$_2$PC≡CR)$_2$ (R = Et, *t*-Bu) and *cis*-Pt(^{15}NCS)$_2$(Ph$_2$PC≡C-*t*-Bu) are given in Table III. Without isotopic data ν(C-S) and δ(CNS) bands are difficult to locate due to their low intensities and overlap with ligand bands.

As Table III illustrates, overtones of δ(CNS) vibrations may also be mistakenly identified for C-S stretches.[23] The unambiguous assignments in Table III are generally in accord with empirical correlations of vibrational frequencies and bonding mode in the literature.[1d] For *cis*-Pt(NCS)(SCN)(Ph$_2$PC≡CR)$_2$ (R = *t*-Bu) two bands in the region 830–860 cm^{-1} are isotope sensitive. The stronger band in this case is due to ν(C-S) of the N-bonded thiocyanate and the weaker shoulder to the first overtone of the δ(SCN) vibration of the S-bonded thiocyanate. For *cis*-Pt(NCS)$_2$(Ph$_2$PC≡C-*t*-Bu)$_2$ two weak isotope-sensitive bands appear at 857, 847 cm^{-1} as expected for cis isothiocyanate groups.

For *cis*-Pt(NCS)(SCN)(Ph$_2$PC≡CR)$_2$ ν(Pt-N) appears as a strong band in the region 260–300 cm^{-1}. This band is absent from the spectra of *cis*-PtCl$_2$(Ph$_2$PC≡CR)$_2$. Strong, broad ν(Pd-N) bands at similar frequencies are present for *cis*-Pd(NCS)(SCN)(Ph$_2$PC≡CR)$_2$ (R = Et, Ph, *i*-Pr, *t*-Bu) but absent for *trans*-Pd(SCN)$_2$(Ph$_2$PC≡C-*t*-Bu)$_2$[10] and *cis*-PdCl$_2$(Ph$_2$PC≡CR)$_2$ (R = Et, Ph, *i*-Pr, *t*-Bu).[22] As expected in view of the small change in effective mass of the CNS$^-$ group and the large mass of the platinum atom, ^{15}N substitution gave no experimentally observable shift in the ν(Pt-N) frequency. As expected the N-bonded complex Pt(NCS)$_2$(Ph$_2$PC≡C-*t*-Bu)$_2$ exhibits two bands in the same spectral region as ν(Pt-N) in the mixed complexes. By analogy with assignments for K$_2$[Pt(SCN)$_4$] [ν(Pt-S) 283 (m), 293 (w) cm^{-1}],[23] K$_2$PtCl$_4$ [ν(Pt-Cl) 321 cm^{-1} (ir)],[24] and *cis*-PtCl$_2$(Et$_3$P)$_2$ [ν(Pt-Cl) 303, 281 cm^{-1}],[21,25] ν(Pt-S) for *cis*-Pt(NCS)(SCN)-

(23) See also ref 1b and A. Sabatini and I. Bertini, *Inorg. Chem.*, **4**, 1665 (1965).

Table III. Solid-State Infrared and Far-Infrared Spectra of Complexes (cm^{-1})[f]

Complex	$\nu(C\equiv C)$	$\nu(C\equiv N)$	$\nu(C-S)$[a]	$\delta(SCN)$[b]	$\nu(Pt-Cl)$ or $\nu(Pt-N)$
$PtCl_2(Ph_2PC\equiv CEt)_2$	2190 m, sp				318 s, 292 s
$PtCl_2(Ph_2PC\equiv CPh)_2$	2171 m, sp				314 s, 294 s, 285 s
$PtCl_2(Ph_2PC\equiv C\text{-}i\text{-}Pr)_2$	2180 m, sp				312 s, 293 s
$PtCl_2(Ph_2PC\equiv C\text{-}t\text{-}Bu)_2$	2208 m, sp, 2197 m, sp, 2166 s, sp, 2156 s, sp				319 s, 299 s
$Pt(NCS)(SCN)(Ph_2PC\equiv CEt)_2$	2191 s, sp	2130 s, sp, 2097 s, br	856 w	416 w	273 m, 259 sh
$Pt(^{15}NCS)(SC^{15}N)(Ph_2PC\equiv CEt)_2$	2192 s, sp	2130 w, sp,[e] 2101 s, sp, 2068 s, br	843 w	413 w	273 m, 259 sh
$Pt(NCS)(SCN)(Ph_2PC\equiv C\text{-}i\text{-}Pr)_2$	2185 s, sp	2124 s, sp, 2098 s, br	856 w	418 w	280 m, br, 266 sh
$Pt(NCS)(SCN)(Ph_2PC\equiv CPh)_2$	2173 s, sp	2127 s, sp, 2122 sh, 2091 s, br	*d*	*d*	295 m, 277 m
$Pt(NCS)(SCN)(Ph_2PC\equiv C\text{-}t\text{-}Bu)_2$	2208 s, sp, 2167 s, sp	2127 s, sp, 2088 s, br	862 w, 851 sh, 843 vw,[c] 840 sh, vw[c]	420 m	282 m, br
$Pt(^{15}NCS)(SC^{15}N)(Ph_2PC\equiv C\text{-}t\text{-}Bu)_2$	2208 s, sp, 2167 s, sp	2127 w, sp,[e] 2100 s, sp, 2070 s, br	844 w, 834 sh[c]	417 m	282 m, br
$Pt(NCS)_2(Ph_2PC\equiv C\text{-}t\text{-}Bu)_2$	2213 m, sp, 2204 m, sp, 2173 s, sp, 2159 s, sp	2101 s, br, 2082 s, br	857 w, 847 w		284 m, br, 269 m, br
$Pt(^{15}NCS)_2(Ph_2PC\equiv C\text{-}t\text{-}Bu)_2$	2214 m, sp, 2203 m, sp, 2173 s, sp, 2159 s, sp	2074 s, br, 2057 s, br	844 w, 838 w		284 m, br, 269 m, br

[a] N-bonded CNS^- only. Bands due to $\nu(C-S)$ of the S-bonded CNS^- are obscured by ligand absorptions. [b] S-bonded CNS^- only. Bands due to $\delta(NCS)$ of N-bonded CNS^- are obscured by ligand absorptions. [c] Assigned to first overtone of $\delta(SCN)$. [d] Bands due to $\nu(C-S)$ and $\delta(SCN)$ are obscured by ligand vibrations. [e] Residual $\nu(C\equiv N)$ from ^{14}N-containing species. [f] Key: w, weak; s, strong; m, medium; br, broad; sp, sharp; sh, shoulder; vw, very weak.

$(Ph_2PC\equiv C\text{-}t\text{-}Bu)_2$ should appear at *ca.* 260-270 cm^{-1}. We conclude that the expected $\nu(Pt-S)$ band is either very weak or obscured by the $\nu(Pt-N)$ band.

Solution Spectra. $\nu(C\equiv N)$ bands of the complexes *cis*-$Pt(CNS)(SCN)(Ph_2PC\equiv CR)_2$ (R = Et, *t*-Bu) and *cis*-$Pt(NCS)_2(Ph_2PC\equiv C\text{-}t\text{-}Bu)_2$ were recorded in a variety of solvents (Table IV). The data elicit the following conclusions: (1) Spectra are independent of the isomer dissolved (for R = *n*-Bu). (2) Bands due to S-bonded thiocyanate are strongest in acetone, acetonitrile, ethanol, and dichloromethane, weaker in DMF and benzonitrile, and very weak in benzene and chloroform. (3) Integrated intensities of 1.19×10^4 and 8.3×10^4 cm^{-2} mol^{-1} were found for the $\nu(C\equiv N)$ bands of *cis*-$Pt(NCS)(SCN)(Ph_2PC\equiv C\text{-}t\text{-}Bu)_2$ in acetonitrile, the solvent apparently most favoring S-bonding. These values are typical of S- and N-bonded CNS^-, respectively.[1,6] (4) On the whole, N bonding appears to be marginally more favored for these Pt(II) complexes than for the analogous Pd(II) species. (5) The results qualitatively agree with the observations of Burmeister and coworkers,[26] in that solvents of high dielectric constant inhibit conversion to Pt-NCS bonding. However there was no evidence for complete conversion of either *cis*-$Pt(NCS)_2(Ph_2PC\equiv C\text{-}t\text{-}Bu)_2$ or *cis*-$Pt(NCS)(SCN)(Ph_2PC\equiv C\text{-}t\text{-}Bu)_2$ to the S-bonded isomer as was found for *trans*-$Pd(NCS)_2(Ph_3P)_2$ in Burmeister's group A solvents.[26]

Table IV. $\nu(C\equiv N)$ Solution Spectra of $Pt(NCS)(SCN)(Ph_2PC\equiv CEt)_2$ and $Pt(NCS)(SCN)(Ph_2PC\equiv C\text{-}t\text{-}Bu)_2$ in Various Solvents (cm^{-1})

Solvent	$Pt(NCS)(SCN)$-$(Ph_2PC\equiv CEt)_2$	$Pt(NCS)(CNS)$-$(Ph_2PC\equiv C\text{-}t\text{-}Bu)_2$
$CHCl_3$	2125 m, sp, 2099 s, br	2124 sh, 2098 s, br
C_6H_6	2124 sh, 2100 s, br	2123 sh, 2100 s, br
CH_3CN	2126 m, sp, 2097 s, br	2128 s, sp, 2103 s, br
CH_2Cl_2		2128 m, sp, 2098 s, br
C_2H_5OH	2127 s, sp, 2097 s, br	2127 s, sp, 2099 s, br
CH_3COCH_3	2124 m, sp, 2094 s, br	2128 s, sp, 2096 s, br
DMF		2128 m, sp, 2098 s, br
C_6H_5CN		2127 m, sp, 2100 s, br

Description and Discussion of the Structure of *cis*-$Pt(NCS)(SCN)(Ph_2PC\equiv C\text{-}t\text{-}Bu)_2$

A perspective view of the molecule illustrating the atomic numbering scheme is shown in Figure 1 which also includes pertinent bond distances and angles. Selected interatomic distances are given in Table V together with bond angles. Figure 2 is a packing diagram for the molecules in the unit cell. The platinum atom is coordinated in approximately square-planar fashion by two tertiary phosphine ligands, a nitrogen atom of one thiocyanate, and a sulfur atom of the other thiocyanate group. The bond angles around the platinum atom are unexceptional although it is worth noting that the P(1)-Pt-P(2) angle of 96.0 (2)° is smaller than the corresponding angle in *cis*-$Pt(CN)(C\equiv CPh)(PPh_3)_2$[15] (101.8 (3)°) but similar to the value of 96.2 (4)° found for P-Pt-P in *cis*-

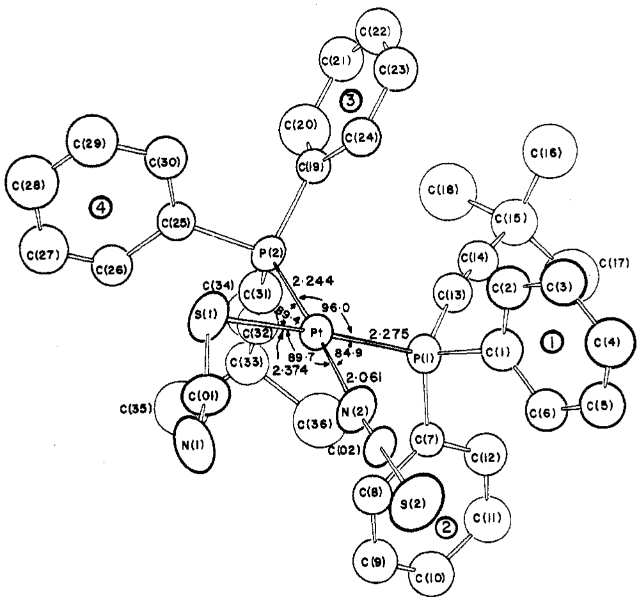

Figure 1. A view of the molecular structure of *cis*-$Pt(NCS)(SCN)(Ph_2PC\equiv C\text{-}t\text{-}Bu)_2$ showing the atomic numbering and pertinent bond angles and distances.

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(24) J. R. Ferraro, "Low Frequency Vibrations of Inorganic and Coordination Compounds," Plenum Press, New York, N. Y., 1971, p 132.

(25) D. M. Adams, J. Chatt, J. Gerratt, and A. D. Westland, *J. Chem. Soc.*, 734 (1964).

(26) J. L. Burmeister, R. L. Hassell, and R. J. Phelan, *Inorg. Chem.*, 10, 2032 (1971).

Table V. Intramolecular Bond Distances and Angles for *cis*-Pt(NCS)(SCN)($Ph_2PC{\equiv}C$-*t*-Bu)$_2$

Atoms	Distance, Å	Atoms	Angle, deg
Platinum–Ligand Bonds			
Pt–S(1)	2.374 (8)	S(1)–Pt–P(1)	174.6 (2)
Pt–P(1)	2.275 (6)	S(1)–Pt–P(2)	89.4 (2)
Pt–P(2)	2.244 (7)	S(1)–Pt–N(2)	89.7 (7)
Pt–N(2)	2.061 (29)	P(1)–Pt–P(2)	96.0 (2)
		P(1)–Pt–N(2)	84.9 (7)
		P(2)–Pt–N(2)	176.4 (7)
Thiocyanate Bonds			
S(1)–C(01)	1.69 (3)	Pt–S(1)–C(01)	103 (1)
S(2)–C(02)	1.60 (3)	Pt–N(2)–C(02)	175 (1)
N(1)–C(01)	1.09 (5)	S(1)–C(01)–N(1)	171 (2)
N(2)–C(02)	1.11 (4)	S(2)–C(02)–N(2)	177 (1)
Phosphorus–Carbon Bonds			
P(1)–C(1)	1.83 (3)	Pt–P(1)–C(1)	109 (1)
P(1)–C(7)	1.78 (2)	Pt–P(1)–C(7)	115 (1)
P(1)–C(13)	1.71 (3)	Pt–P(1)–C(13)	119 (1)
		C(1)–P(1)–C(7)	109 (1)
		C(1)–P(1)–C(13)	101 (1)
		C(7)–P(1)–C(13)	103 (1)
P(2)–C(19)	1.80 (2)	Pt–P(2)–C(19)	120 (1)
P(2)–C(25)	1.79 (3)	Pt–P(2)–C(25)	115 (1)
P(2)–C(31)	1.68 (3)	Pt–P(2)–C(31)	112 (1)
		C(19)–P(2)–C(25)	121 (1)
		C(19)–P(2)–C(31)	105 (1)
		C(25)–P(2)–C(31)	104 (1)
Phenyl Rings			
C(1)–C(2)	1.37 (4)	P(1)–C(1)–C(2)	118 (1)
C(2)–C(3)	1.39 (4)	P(1)–C(1)–C(6)	121 (1)
C(3)–C(4)	1.39 (5)	C(2)–C(1)–C(6)	121 (2)
C(4)–C(5)	1.36 (5)	C(1)–C(2)–C(3)	121 (2)
C(5)–C(6)	1.38 (5)	C(2)–C(3)–C(4)	117 (2)
C(6)–C(1)	1.36 (4)	C(3)–C(4)–C(5)	122 (2)
		C(4)–C(5)–C(6)	121 (2)
		C(5)–C(6)–C(1)	119 (2)
Phenyl Rings			
C(7)–C(8)	1.45 (4)	P(1)–C(7)–C(8)	119 (1)
C(8)–C(9)	1.40 (4)	P(1)–C(7)–C(12)	120 (1)
C(9)–C(10)	1.39 (4)	C(8)–C(7)–C(12)	122 (2)
C(10)–C(11)	1.46 (5)	C(7)–C(8)–C(9)	118 (2)
C(11)–C(12)	1.37 (4)	C(8)–C(9)–C(10)	121 (2)
C(12)–C(7)	1.42 (4)	C(9)–C(10)–C(11)	122 (2)
		C(10)–C(11)–C(12)	118 (2)
		C(11)–C(12)–C(7)	120 (2)
C(19)–C(20)	1.26 (4)	P(2)–C(19)–C(20)	122 (2)
C(20)–C(21)	1.48 (5)	P(2)–C(19)–C(24)	118 (1)
C(21)–C(22)	1.29 (4)	C(20)–C(19)–C(24)	119 (2)
C(22)–C(23)	1.41 (4)	C(19)–C(20)–C(21)	124 (2)
C(23)–C(24)	1.40 (4)	C(20)–C(21)–C(22)	115 (2)
C(24)–C(19)	1.46 (4)	C(21)–C(22)–C(23)	125 (2)
		C(22)–C(23)–C(24)	117 (2)
		C(23)–C(24)–C(19)	118 (2)
C(25)–C(26)	1.48 (4)	P(2)–C(25)–C(26)	119 (1)
C(26)–C(27)	1.32 (5)	P(2)–C(25)–C(30)	121 (1)
C(27)–C(28)	1.47 (5)	C(26)–C(25)–C(30)	121 (2)
C(28)–C(29)	1.38 (6)	C(25)–C(26)–C(27)	121 (2)
C(29)–C(30)	1.42 (5)	C(26)–C(27)–C(28)	120 (2)
C(30)–C(25)	1.38 (4)	C(27)–C(28)–C(29)	119 (2)
		C(28)–C(29)–C(30)	123 (2)
		C(29)–C(30)–C(25)	118 (2)
3,3-Dimethylbutynyl Groups			
C(13)–C(14)	1.20 (4)	P(1)–C(13)–C(14)	168 (1)
C(31)–C(32)	1.24 (4)	C(13)–C(14)–C(15)	176 (2)
		P(2)–C(31)–C(32)	176 (1)
		C(31)–C(32)–C(33)	175 (2)
C(15)–C(14)	1.47 (4)	C(14)–C(15)–C(16)	108 (2)
C(15)–C(16)	1.54 (5)	C(14)–C(15)–C(17)	107 (2)
C(15)–C(17)	1.54 (6)	C(14)–C(15)–C(18)	108 (2)
C(15)–C(18)	1.67 (6)	C(16)–C(15)–C(17)	114 (2)
		C(16)–C(15)–C(18)	104 (2)
		C(17)–C(15)–C(18)	116 (2)
C(33)–C(32)	1.50 (4)	C(32)–C(33)–C(34)	113 (2)
C(33)–C(34)	1.46 (5)	C(32)–C(33)–C(35)	115 (2)
C(33)–C(35)	1.44 (5)	C(32)–C(33)–C(36)	101 (2)
		C(34)–C(33)–C(36)	111 (2)
		C(35)–C(33)–C(36)	107 (2)

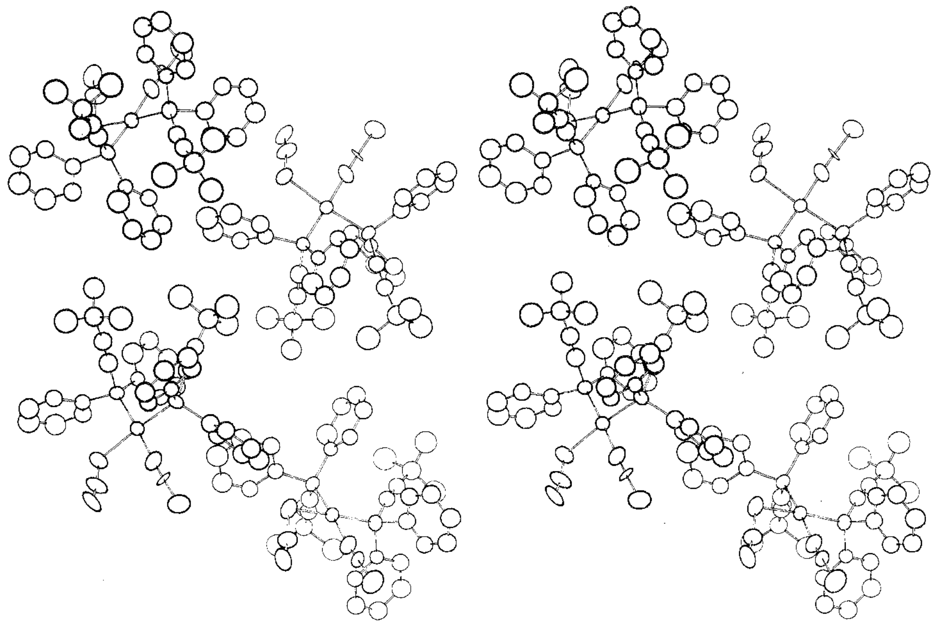

Figure 2. Stereoscopic packing diagram showing the contents of one unit cell.

$PtCl_2(PMe_3)_2$.[16] This may reflect, in part, reduced steric bulk of the acetylenic phosphine[22] compared to triphenylphosphine or alkyldiphenylphosphines and this appears consistent with the P–M–P bond angles in *cis*-Pd(NCS)(SCN)($Ph_2PC{\equiv}C$-*t*-Bu)$_2$[5] and *cis*-Pt(NCS)(SCN)($Ph_2PC{\equiv}C$-*t*-Bu)$_2$. The platinum–phosphorus bond lengths are significantly different presumably as a result of the higher trans influence of a sulfur-bonded CNS^- group than an N-bonded thiocyanate. Table I shows that the Pt-P(1) bond length of 2.275 (6) Å compares favorably with the Pt-P distance of 2.262 (4) Å in the β isomer of $Pt_2Cl_2(SCN)_2(P\text{-}n\text{-}Pr_3)_2$[14] where the phosphorus atoms are trans to the sulfur atoms of bridging thiocyanate groups. In similar fashion Pt-P(2) of 2.244 (7) Å is identical with the Pt-P (trans to N) distance in α-$Pt_2Cl_2(SCN)_2(P\text{-}n\text{-}Pr_3)_2$.[14] Indeed comparison of structurally analogous bond lengths in *cis*-$Pt(NCS)(SCN)(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)_2$ and α- and β-$Pt_2Cl_2(SCN)_2(P\text{-}n\text{-}Pr_3)_2$ reveals a remarkable consistency of trans bond lengthening influences for the phosphines and thiocyanate ion even though the latter has a bridging role in α- and β-$Pt_2Cl_2(SCN)_2(P\text{-}n\text{-}Pr_3)_2$.

Within the 3,3-dimethylbutynyldiphenylphosphine ligands the P-C(sp^2) bond lengths vary between 1.78 (2) and 1.83 (3) Å, the mean value being 1.81 Å. The average P-C(sp) bond length is 1.70 (3) Å, somewhat shorter than expected by comparison with the sum of covalent radii for P (1.10 Å) and C(sp) (0.69 Å)[27] and with average values of 1.78, 1.765, and 1.765 Å for P-C(sp) in $P(CN)_3$,[28] $P(C{\equiv}CPh)_3$,[29] and $Ph_2PC{\equiv}CPPh_2$.[30] A similar P-C(sp) shortening is apparent in *trans*-$Pd(SCN)_2(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)_2$.[10] This effect may be due to $P(d\pi)$-$C(sp)(p\pi)$ interaction similar to that postulated previously to account for the molecular configuration of $Ph_2PC{\equiv}CPPh_2$,[30] bond lengths in $P(C{\equiv}CPh)_3$,[29] and -C≡C- stretching frequencies in complexes of $Ph_2PC{\equiv}CPPh_2$.[31] The most interesting aspect of the structure is the presence of both S- and N-bonded thiocyanate ions for a Lewis acid, Pt^{2+} normally considered to favor N bonding in phosphine complexes.[32] The S-bonded thiocyanate group is bent out of the square plane away from phenyl ring 4 (Figure 1) with a Pt-S(1)-C(01) angle (103 (1)°) similar to the angle of 104.9 (1.1)° recently found in $[Co(SCN)(NH_3)_5]Cl_2$[33] and intermediate between extremes of 97.6 (5) and 111.8 (6)° obtained for S-bonded thiocyanates in $Hg(SCN)_2$[34] and *cis*-$Pd(NCS)(SCN)(Ph_2P(CH_2)_2PPh_2)$.[4] The S(1)-C(01) distance in the S-bonded thiocyanate group (1.69 (3) Å) is shorter than the S(2)-C(02) bond length (1.60 (3) Å) in the N-bonded ion, and the Pt-N-C-S linkage deviates only slightly from linearity. The mixed thiocyanate coordination in *cis*-$Pt(NCS)(SCN)(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)_2$ prompted a search for intra- and intermolecular repulsive nonbonded contacts which might be responsible for the presence of an S-bonded thiocyanate group. While the S(1)-C(01)-N(1) group is twisted about the Pt-S(1) bond away from phenyl ring 4,[35] there is no obvious crystallographic rationale disfavoring a linear Pt-NCS linkage for this group. Conversely, however, S bonding of the N(2)-C(02)-S(2) group would inevitably lead to additional repulsive contacts with S(1)-C(01)-N(2) or phenyl groups 1 and 2. We conclude therefore that for this complex the mixed Pt(NCS)(SCN) bonding is due mainly to steric inhibition of dithiocyanato coordination.

Comments on Platinum-Thiocyanate Ion Bonding

An assessment of the relative importance of factors influencing the preferential bonding of -N or -S sites of the CNS^- ion to $PdL_2{}^{2+}$ or $PtL_2{}^{2+}$ (L = phosphine) in the solid state or in solution must take note of the following points. (a) Pd^{2+} and Pt^{2+} are intrinsically "soft" ions. In the *absence of other effects* these ions might be expected to favor M-SCN bonding. Examples of this are the $M(SCN)_4{}^{2-}$ ions[36] which are both -S bonded (but see ref 11). (b) For the isomerization process *cis*-$M(SCN)_2L_2 \rightleftarrows$ *trans*-$M(SCN)_2L_2$ or *cis*-$M(NCS)_2L_2 \rightleftarrows$ *trans*-$M(NCS)_2L_2$ in solution ΔH for bond strength changes and solvation should favor the cis isomers where the ligands of highest trans influence (L) are cis to one another and the dipole moment is highest.[37] ΔS of solvation should favor the trans compound. Steric effects influence ΔS by reducing internal degrees of freedom and may reduce internal bond strengths by increasing bond lengths. Internal steric crowding will depend on the ligand sizes (particularly phosphine size) but it is difficult to predict whether this will disfavor most the cis or trans S-bonded species. The major role which steric effects may play in phosphine complexes has however been unambiguously demonstrated elsewhere.[10,38] Available thermodynamic data for Pd(II)[39] and Pt(II)[40] complexes indicate that the isomerization process is entropy controlled and that the cis isomers are thermodynamically favored, more so for Pd(II) than Pt(II). (c) For the isomerization *cis*-$M(SCN)_2L_2 \rightleftarrows$ *cis*-$M(NCS)_2L_2$ ΔH for internal bond energy changes should favor the cis N-bonded complex.[37,39,40] (d) Internal bond energies will be dependent on the σ-donor-π-acceptor properties, trans influences of the ligands, and steric repulsions. Usually it has been assumed that π acidity decreases in the order $PR_3 >$ -SCN > -NCS. The trans influence of the ligands decreases in the order $PR_3 >$ -SCN > -NCS according to X-ray data.[3-5,10] Also the trans influence increases in importance from the first to the third row of the transition series.[37] (e) Nonpolar solvents should favor the trans S-bonded complexes. (f) For solids isomerization may be slow while ΔH and ΔS of solvation are irrelevant. However packing factors and internal bond energy differences will still be important.

Keeping in mind that solid and solution data are not necessarily compatible since solid-state structures may not necessarily reflect solution thermodynamic stabilities and that the solid phase crystallizing may have only a minor solution concentration (*e.g.*, *trans*-$Pd(SCN)_2(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)_2$), our results appear consistent with the reduced steric demands of the phosphinoacetylene increasing the possibility of S bonding[41] together with the expected higher trans influence of the phosphines in the platinum complexes.

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Registry No. $PtCl_2(Ph_2PC\equiv CEt)_2$, 42847-15-4; $PtCl_2(Ph_2PC\equiv CPh)_2$, 42847-16-5; $PtCl_2(Ph_2PC\equiv CPr\text{-}i)_2$, 42847-17-6; $PtCl_2(Ph_2PC\equiv CBu\text{-}t)_2$, 42847-18-7; $Pt(NCS)(SCN)(Ph_2PC\equiv CEt)_2$, 42921-68-6; $Pt(NCS)(SCN)(Ph_2PC\equiv CPh)_2$, 42847-19-8; $Pt(NCS)(SCN)(Ph_2PC\equiv CPr\text{-}i)_2$, 42847-20-1; $Pt(NCS)_2(Ph_2PC\equiv CBu\text{-}t)_2$, 42847-21-2; $Pt(NCS)(SCN)(Ph_2PC\equiv CBu\text{-}t)$, 42847-22-3; $Pt(^{15}NCS)(SC^{15}N)(Ph_2PC\equiv CEt)_2$, 42847-23-4; $Pt(^{15}NCS)(SC^{15}N)(Ph_2PC\equiv CBu\text{-}t)_2$, 42847-24-5; $Pt(^{15}NCS)_2(Ph_2PC\equiv CBu\text{-}t)_2$, 42847-25-6.

Supplementary Material Available. 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 \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-284.

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(41) Solid $Pt(CNS)_2(Ph_3P)_2$ is N bonded and cis in the solid state although *trans*-$PtCl_2(Ph_3P)_2$ apparently yields the S-bonded species initially on reaction with CNS^- ion.[42]

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Crystal Structure of Ammonium Samarium Sulfate Tetrahydrate

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The structure of $NH_4Sm(SO_4)_2\cdot 4H_2O$ has been determined by single-crystal X-ray diffraction techniques. The positions of all nonhydrogen atoms were deduced, from 1145 diffractometer-measured intensities, by means of Patterson and Fourier methods. Refinement by the method of least-squares calculations, with anisotropic thermal motion for each atom, resulted in an R value of 0.046. The monoclinic cell has the dimensions $a = 6.582$ (2), $b = 18.886$ (7), $c = 8.736$ (4) Å, and $\beta = 96.88$ (4)°; it contains four formula units. The space group is $P2_1/c$. The unit cell dimensions for the isostructural ammonium lanthanide sulfates (La–Tb) have also been determined. The samarium atom is coordinated by six oxygen atoms, belonging to sulfate ions, at distances of 2.378–2.559 Å and by three water molecules at distances of 2.442–2.512 Å. The nine oxygen atoms form a polyhedron, which can equally well be described either as a tricapped trigonal prism or as a monocapped square antiprism. Cross-linking of samarium atoms occurs through sharing of sulfate ions; in this way layers are formed which are held together by hydrogen bonds. Ir and thermal data for the compound have also been measured and are discussed.

Introduction

The lanthanides form a variety of double sulfates with the alkali and ammonium ions. The composition and properties of these sulfates have been studied extensively. However, the knowledge of their structure is very scarce and based on thermal and spectroscopic studies; no X-ray structural determination seems to have been done.

The present investigation was undertaken to elucidate the crystal structure of the double sulfate of ammonium and samarium. The existence of such a phase with the formula $NH_4Sm(SO_4)_2\cdot 4H_2O$ has been confirmed earlier.[2] This compound is isostructural with $NH_4Nd(SO_4)_2\cdot 4H_2O$[3] and $NH_4Ce(SO_4)_2\cdot 4H_2O$.[4] The present report also describes the unit cell dimensions of the isostructural double sulfate series from lanthanum to terbium. The heavier lanthanides form double sulfates with ammonium, which have the same composition but different structure as indicated by the published powder pattern of $NH_4Dy(SO_4)_2\cdot 4H_2O$.[5]

Experimental Section

Preparation of the Compounds. The crystals were prepared as described earlier; aqueous solutions of lanthanide sulfate and ammonium sulfate were mixed in the approximate molar ratio of 1:4 and the solution was left to stand in air.[2] Upon evaporation prismatic crystals were obtained which showed the characteristic color of the lanthanide ion. The crystals were washed with small amounts of water, ethanol, and ether. The lanthanide sulfate solutions were prepared from lanthanide oxides of 99.5–99.9% purity; all other reagents were of analytical reagent grade.

Spectroscopic and Thermal Studies. Infrared spectra in the region 4000–400 cm^{-1} were recorded with a Perkin-Elmer 125 spectrophotometer using the KBr pellet technique. The sample showed no reaction with KBr.

Tg, dtg, and dta curves were recorded simultaneously with a Mettler Thermoanalyzer. The furnace atmosphere was a dynamic air atmosphere with a flow rate of 90 cm^3/min. The heating rate was 2°/min and two kinds of platinum crucibles were employed: (i) long and relatively narrow ones (diameter 7 mm, depth 19 mm, weight 2.0 g) and (ii) small and broad ones (diameter 6 mm, depth 5 mm, weight 0.25 g). Alumina was used as reference material.

Data Collection and Reduction. The accurate unit cell dimensions were calculated for the eight ammonium lanthanide sulfates from powder photographs. These were obtained at 25° in a Guinier-Hagg focusing camera of 80-mm diameter, with strictly monochromatized Cu Kα_1 radiation (λ 1.54050 Å). Potassium chloride ($a = 6.29228$ Å)[6] was used as internal standard. The powder photographs were measured and interpreted to $\sin^2\theta = 0.35$.

Single-crystal intensity data for $NH_4Sm(SO_4)_2\cdot 4H_2O$, chosen for the complete crystal structure analysis, were obtained on a Philips PW 1100 computer-controlled four-circle diffractometer. Graphite-monochromatized Cu K radiation and a scintillation counter with pulse height discrimination were used. The dimensions of the crystal were 0.09 × 0.08 × 0.07 mm^3. The θ–2θ scan technique was employed, with a scan range of 1.5° and a speed of 0.015°/sec; the background was measured for 50 sec at each end of the scan interval. Three test reflections were measured hourly to check for the possible deterioration of the crystal in the X-ray beam, but the intensity was found to remain constant within ±2%. Therefore no correction for radiation damage was made. The background intensities were calculated as averages of the intensities at each end of the scan interval.

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