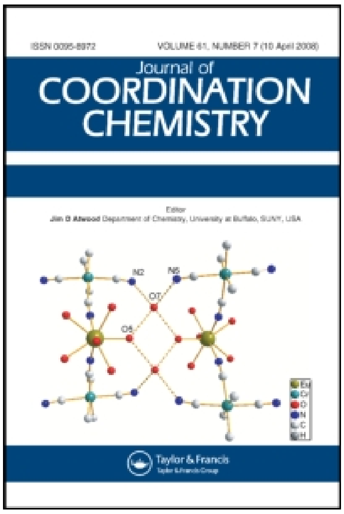

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SYNTHESIS, VIBRATIONAL AND PROTON RESONANCE SPECTRA, AND REACTIONS OF TETRAKIS (TRIMETHYLPLATINUM THIOCYANATE)

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SYNTHESIS, VIBRATIONAL AND PROTON RESONANCE SPECTRA, AND REACTIONS OF TETRAKIS (TRIMETHYLPLATINUM THIOCYANATE)[1]

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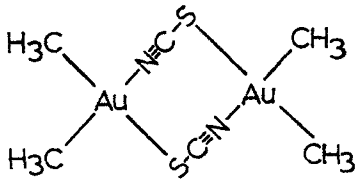
Trimethylplatinum(IV) thiocyanate has been synthesized and found to be tetrameric in benzene solution. On the basis of proton magnetic resonance, Raman, and infrared spectra an acentric D_{2d} structure has been assigned. This involves a tetrahedral array of platinum atoms linked by bridging thiocyanates. Within any one of the four large faces of the rectangular parallelepiped defined by the skeleton, the bonding is analogous to that in $[(CH_3)_2AuNCS]_2$, but in $[(CH_3)_3PtNCS]_4$ the sulfur atoms are three coordinate. The coordination about the thiocyanate is similar to that reported for $Pr^n_3PAgNCS$. Pyridine, triphenylphosphine, and triphenylarsine react in a 4 : 1 mole ratio with $[(CH_3)_3PtNCS]_4$ to yield the dimeric compounds $[(CH_3)_3Pt(NCS)L]_2$. These are assigned a bridged structure similar to $[(CH_3)_2AuNCS]_2$. Complete Raman, infrared, and pmr spectra are given for the parent compound and its derivatives.

INTRODUCTION

Although trimethylplatinum(IV) chloride, bromide, and iodide have been known for sixty years,[3] the pseudo-halides, in general, do not appear to have been investigated. One early report[4] suggested that trimethylplatinum(IV) cyanide was formed when KCN was added to an aqueous solution of trimethylplatinum nitrate or sulfate. The compound was described as noncrystalline and insoluble in organic solvents. No analytical data were given. It seems likely that this reaction gave a mixed hydroxide–cyanide compound. Trimethylplatinum hydroxide itself is only very slightly soluble in water and is precipitated readily from solutions containing $(CH_3)_3Pt(OH_2)_3^+$ by the addition of base.

In 1947, Rundle and Sturdivant[5] showed that $[(CH_3)_3PtCl]_4$ had the cubane type of structure, and the iodide has been found to have a similar but slightly less symmetric structure.[6] Three different groups[7–9] have studied the structure of $[(CH_3)_3PtOH]_4$ and found it to have the same skeleton as the chloride.

Recently the synthesis of $[(CH_3)_2AuNCS]_2$ was reported,[10] and the thiocyanate ion was found to bridge through both the nitrogen and sulfur atoms giving (1).



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Although the stereochemistry of trimethylplatinum(IV) compounds is typical of d^6 octahedral complexes while that of dimethylgold(III) is characteristic of the square planar structure expected for a d^8 transition metal, these moieties often react in a very similar way. In mononuclear complexes, stretching frequencies for comparable platinum and gold—ligand bonds are usually within a few wavenumbers of one another indicating that the bond strengths are very similar. Chemical shifts for methyl protons in analogous compounds often are separated by only a few hundredths of a ppm from each other, presumably a reflection of the very similar bond lengths, bond angles, and charge distributions. Since bridging halides in the $[(CH_3)_2AuX]_2$ compounds are two-coordinate while those in the $[(CH_3)_3PtX]_4$ molecules are three-coordinate, trimethylplatinum(IV) thiocyanate was synthesized in an effort to prepare a compound with a three-coordinate bridging thiocyanate ligand. The reactions of trimethylplatinum thiocyanate with ligands containing nitrogen, phosphorus, and arsenic donor atoms have been examined.

EXPERIMENTAL

General Data The starting material for the synthesis of trimethylplatinum thiocyanate was $[(CH_3)_3PtI]_4$ which was prepared by the method of Morgan *et al.*[11] Microanalyses were performed by Schwarzkopf Microanalytical Laboratory or by the microanalytical laboratory in this Department. Molecular weights were determined osmometrically by the Purdue microanalytical laboratory. Melting points were determined with a Thomas-Hoover Capillary Melting Point Apparatus. Chloroform used as an nmr solvent was treated with sulfuric acid and freshly distilled before use.

Tetrakis(trimethylplatinumthiocyanate) To a solution of $[(CH_3)_3PtI]_4$ (0.467 g, 0.3 mmol) in 40 ml of 50% (v/v) benzene-acetone was added a five-fold excess of AgSCN. In order to prevent the formation of $[(CH_3)_3PtOH]_4$, all reactions were carried out under a dry nitrogen atmosphere, and all solvents were dried carefully. The mixture was refluxed for two hours, the hot solution was filtered under nitrogen, and the solvent was removed by a stream of nitrogen gas. The white, amorphous product was stored under vacuum over P_4O_{10}. Yield: 0.20 g, 54% mp (decompn), 203–205°. The compound tends to explode as it melts. *Anal.* Calcd. for C_4H_9NSPt: C, 16.1; H, 3.02; N, 4.69; S, 10.7; Pt, 65.4. Found: C, 16.0; H, 3.11; N, 4.66; S, 11.1; Pt, 64.9%. Mol. Wt. in benzene, 1050. (Accuracy ca. ±5%.) Calculated for $[(CH_3)_3PtSCN]_4$, 1192 amu.

Di-μ-thiocyanato(N,S)bis(pyridine)hexamethyldiplatinum To a suspension of 150 mg (0.005 monomol) of $[(CH_3)_3PtNCS]_4$ in benzene was added the stoichiometric amount of pyridine. After shaking for a few minutes, the solution became clear. Upon evaporation of the solvent, an oil was obtained which was washed with dry ether and stored in a vacuum desiccator over P_4O_{10}. After three days, the oil crystallized to an opalescent white product. mp, 84–8°. *Anal.* Calcd. for $C_9H_{14}N_2SPt$: C, 28.6; H, 3.71; N, 7.42; S, 8.48; Pt, 51.7. Found: C, 28.9; H, 3.73; N, 7.59; S, 8.18; Pt, 51.5%. Mol. wt. in benzene, 752; calculated for a dimer, 755 amu.

Di-μ-thiocyanato(N,S)bis(triphenylphosphine) hexamethyldiplatinum From the solution obtained by reacting a suspension of $[(CH_3)_3PtNCS]_4$ in benzene with four equivalents of triphenylphosphine, well formed crystals precipitated after ½ hour. The compound was washed with benzene and ether and dried. mp, 166°–167°. *Anal.* Calcd for $C_{22}H_{24}NPSPt$: C, 47.1; H, 4.28; N, 2.50; P, 5.53; S, 5.71; Pt, 34.8. Found: C, 47.1; H, 4.50; N, 2.45; P, 5.83; S, 5.42; Pt, 35.0. Mol. wt. in $CHCl_3$, 1002. Calcd. for a dimer, 1120. (Because of the low solubility of the compound, the accuracy of the determination was estimated to be ±15%.)

Di-μ-thiocyanato(N, S) bis(triphenylarsine)hexamethyldiplatinum The solution obtained by reaction of $[(CH_3)_3PtNCS]_4$ with four equivalents of triphenylarsine in benzene was stored at 0° overnight during which time a precipitate formed. The product was washed with methanol and CCl_4. mp, 182°. *Anal.* Calcd. for $C_{22}H_{24}NAsSPt$: C, 43.7; H, 3.97; N, 2.32; S, 5.29; Pt, 32.3. Found: C, 43.5; H, 4.21; N, 2.09; S, 5.46; Pt, 32.4. Mol. wt. in $CHCl_3$, 697 (0.0066 *M*), 854 (0.012 *M*). Calcd for a dimer, 1208.

Raman spectra These were obtained using He-Ne and Ar^+ excitation and an instrument which has been described briefly elsewhere.[12] The compounds were contained in sealed capillary tubes and the transillumination technique was employed. Calibration of the monochromator was effected with the exciting lines, background plasma lines, and neat indene. Frequencies of sharp lines are accurate within to $\pm 2\ cm^{-1}$.

Infrared spectra These were recorded with a Beckman IR-12 spectrometer using split mulls or KBr disks. The instrument was calibrated with polystyrene film and indene. The frequencies for sharp bands are accurate to $\pm 2\ cm^{-1}$, while those for broad bands should be within $\pm 5\ cm^{-1}$. Far infrared spectra were run as Nujol mulls between polyethylene windows on a Beckman IR-11 for which we are indebted to Professor W. F. Edgell.

Proton magnetic resonance spectra Varian A-60 and XL-100 spectrometers were used for pmr spectra. The ambient probe temperature was ca. 40° C. Coupling constants are believed to be accurate to ±0.5 Hz and chemical shifts to ±0.01 ppm. Chemical shifts were measured relative to an internal TMS reference. For time averaging, a Varian Model C-1024 computer was employed.

Conductivity measurements Conductances were determined with nitrobenzene solutions at 25° using a simple bridge designed in the Department Electronics Laboratory. The cell constant was obtained by measuring the conductance of 0.02 *M* KCl.

DATA AND RESULTS

Proton Resonance Spectra

Trimethylplatinum(IV) thiocyanate is only slightly soluble in organic solvents, and it is tetrameric in benzene solution. The proton magnetic resonance spectrum of a nearly saturated solution in chloroform (ethanol free) is illustrated in Figure 1. Two signals with intensity ratios of 2 : 1 are observed at $\tau = 8.65$ and 9.02 ppm with coupling constants $^2J(^{195}\text{Pt}–^1\text{H})$ of 76.4 and 75.1 Hz. This indicates that the structure is stereochemically rigid at 40°. The proton chemical shifts are very similar to those for $[(CH_3)_2AuNCS]_2$ $\tau = 8.70$ and 9.05 ppm in $CHCl_3$ solution. Data from the pmr spectra for these and $[(CH_3)_3Pt(NCS)L]_2$ compounds are collected in Table I. The spectrum of $[(CH_3)_3Pt(NCS)py]_2$ is illustrated in Figure 2.

Raman and Infrared Spectra

The observed frequencies together with qualitative assignments for $[(CH_3)_3PtNCS]_4$ are collected in Table II. The Raman spectrum is illustrated in Figure 3, and the infrared spectrum in Figure 4. The frequencies associated with the thiocyanate ligands are similar to those for $[(CH_3)_2AuNCS]_2$ where the following values were observed: $\nu(C{\equiv}N)$ 2163(ir) and 2151(R), $\nu(C—S)$ 775(ir), and $\delta(NCS)$ 444, 430 cm^{-1}(R). The other assignments were made by comparison with the spectra of the

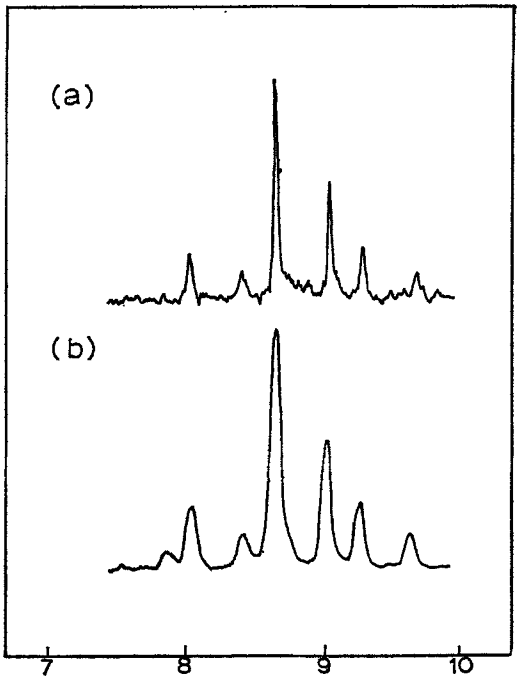


FIGURE 1 Proton magnetic resonance spectrum of $[(CH_3)_3PtNCS]_4$ in chloroform solution: (a) single scan, (b) 20 scans with CAT.

TABLE I

Nuclear magnetic resonance data for $[(CH_3)_3PtNCS]_4$ and the $[(CH_3)_3Pt(NCS)L]_2$ compounds, L = C_5H_5N, $P(C_6H_5)_3$ and $AS(C_6H_5)_3$ at 40°. Coupling constants are given within parentheses and integrated intensities[a] within brackets

Compound	Solvent	Methyl groups *trans* to: N $\tau(^2J(^{195}Pt–H))$	S $\tau(^2J(^{195}Pt–H))$	L $\tau(^2J(^{195}Pt–H))$ ppm. Hz
$[(CH_3)_3Pt(NCS)]_4$	$CHCl_3$	9.02 ($75._1$) [1][b]	8.65 ($76._4$) [1.95 ± 0.06][b]	
$[(CH_3)_2Au(NCS)]_2$	$CHCl_3$	9.05[c]	8.70[d]	
$[(CH_3)_3Pt(NCS)py]_2$	C_6H_6	8.98 ($73._0$) [1]	8.72 ($71._7$) [1.0 ± 0.1]	8.49 ($70._5$) [0.8 ± 0.1]
$[(CH_3)_3Pt(NCS)PPh_3]_2$[e]	CHCl	9.50 (73 [1][f]	9.05 (71) [1]	8.77 (59) [1]
	($^3J(^{31}P–H)$ =	7.5	= 7.5	= 7.5 Hz)
$[(CH_3)_3Pt(NCS)AsPh_3]_2$[e]	$CHCl_3$	9.37 (g) [1]	9.00 (72) [1.0 ± 0.1]	8.77 (66) [0.8 ± 0.1]

[a] Intensities are the average of four integrations.
[b] Intensities from 20 scans accumulated with a CAT.
[c] Assigned to methyls *trans* to nitrogen, ref. 10.
[d] Assigned to methyls *trans* to sulfur, ref. 10.
[e] Spectra recorded at both 60 and 100 MHz; the temperature in the latter case was 35°.
[f] Precise integration was not possible because of the complexity of the spectrum.
[g] Value uncertain. The compound is only very slightly soluble, and there appears to be slight dissociation in solution.

TABLE II

Infrared and laser Raman (He–Ne) spectra of $[(CH_3)_3PtNCS]_4$

Infrared ν, cm^{-1}	Raman ν, cm^{-1}	Assignment
2978 s	2987 w, bd	$\nu_{as}(CH_3)$
2913 s	2911 m[a]	$\nu_s(CH_3)$
	2905 s[a]	
	2900 s[a]	
2815 w		$2 \times \delta_{as}(CH_3) = 2 \times 1415$
2190 vs	2182 vs[b]	$\nu(C{\equiv}N)$
2184 vs		
1418 m bd		$\delta_{as}(CH_3)$
1285 m	1281 m	$\delta_s(CH_3)$
1278 m		
1238 s	1238 s	
1228 s	1223 s	
749 m	747 vw	$\nu(C—S)$
729 m		
	592 vw	$\nu(Pt—C)$
	582 vs	
	566 vs	
454 w	456 vw	$\delta(NCS)$, $\nu(Pt—N)$
	446 vw	
253 m	263 m	$\delta(PtNCSPt)$, $\nu(Pt—S)$, $\delta(Pt—C_3)$
243 m, bd	238 m	
194 m	broad scattering	

s, strong; m, medium; w, weak; v, very; sh, shoulder; bd, broad.

[a] Determined with Ar$^+$ laser excitation, since He–Ne excitation gives a strong Lyman ghost in this region.

[b] Scanned with 0.5Å slits (1.2 cm^{-1}) using an Ar$^+$ laser at 4880 Å. Even with this resolution, only one Raman line was observed.

trimethylplatinum halides.[13-16] Data for the $(C{\equiv}N)$ and $(Pt—C)$ stretching and the symmetric methyl deformations vibrations of the $[(CH_3)_3Pt(NCS)L]_2$ compounds are collected in Table III. None of these compounds mulled well and all infrared spectra showed marked Christiansen filter effects. The Raman spectra of $[(CH_3)_3Pt(NCS)L]_2$ (L = py, PPh_3, $AsPh_3$) are illustrated in Figure 5.

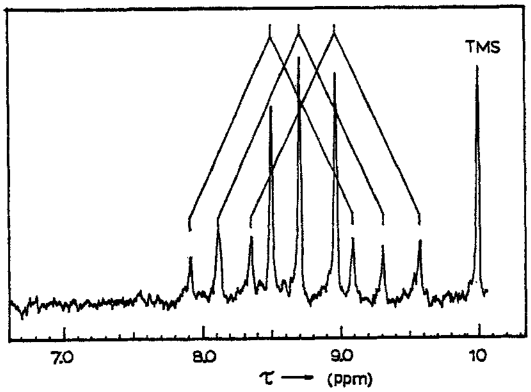


FIGURE 2 Proton magnetic resonance spectrum of $[(CH_3)_3Pt(NCS)py]_2$ in benzene.

DISCUSSION

The proton resonance data indicate that $(CH_3)_3PtNCS]_4$ is a stereochemically rigid molecule

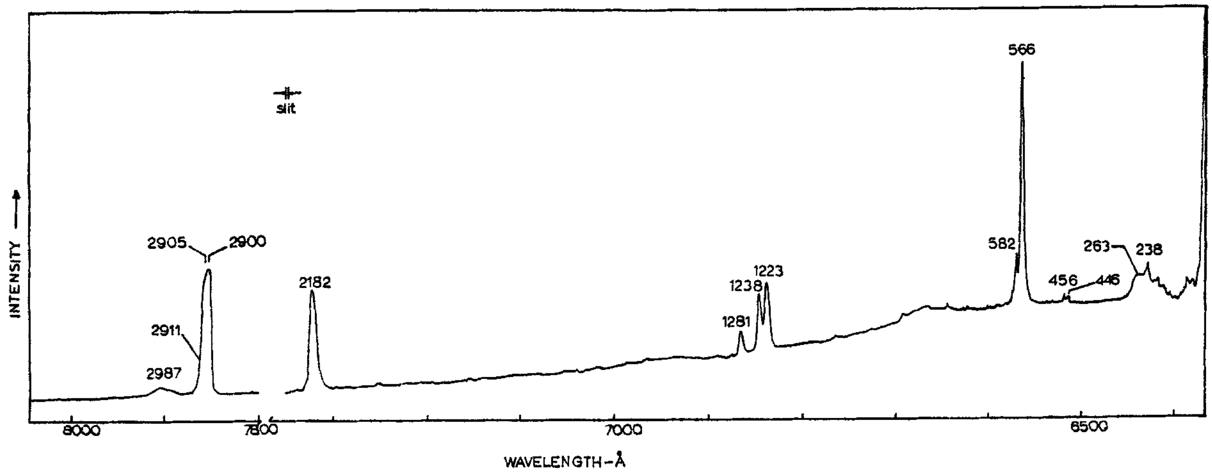


FIGURE 3 Laser Raman spectrum of $[(CH_3)_3PtNCS]_4$ recorded with a He–Ne laser and a crystalline powder sample. Scan rate = 2.5 Å/min (~6 cm^{-1}/min), slits 3.2Å (~7 cm^{-1}), time constant 10 sec. Much of the scattering at Δ = 2903 cm^{-1} arises from the Lyman ghost characteristic of the Bausch and Lomb gratings used.

TABLE III

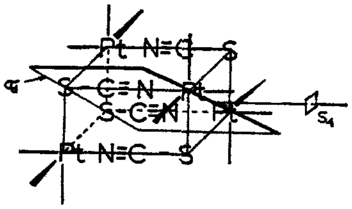
Vibrational frequencies for $[(CH_3)_3Pt(NCS)L]_2$ compounds, L = C_5H_5N, $P(C_6H_5)_3$, and $As(C_6H_5)_3$

Frequency (cm^{-1})	L = C_5H_5N		$P(C_6H_5)_3$		$As(C_6H_5)_3$		$[(CH_3)_3Pt(NCS)]_4$	
	ir	Raman	ir	Raman	ir	Raman	ir	Raman
$\nu(C{\equiv}N)$	2149 vs	2143 m	2130 vs	2134 m, bd	2141 vs	2132 w, bd	2190 vs	2182
	2100 s	—	2119 s	—	—	—	2184 vs	—
$\delta_s(CH_3)$							1285 m	—
	1272 m	1277 w	1275 m	—	1275 m	—	1278 m	1281 m
	1240 m	1241 w	1235 m	1235 vw	1236 m	1236 vw	1238 s	1238 s
	1228 w	1222 w	1216 w	1216 w	1220 w	1222 w	1228 s	1223 s
$\nu(PtC_3)$	579 w	578 m, bd	[a]	578 m	—	575 w	—	592 vw
	565 w	562 vs	[a]	548 vs	558 vw	558 vs	—	582 vs
	—	—	—	—	—	—	—	566 vvs

Abbreviations as in Table II.

[a] Weak bands obscured by strong absorptions of PPh_3.

in solution at 40° with four methyl groups in one set and eight in another. The similarity of the τ values of the methyl protons and the high $\nu(C{\equiv}N)$ values to the corresponding values of $[(CH_3)_2AuNCS]_2$ suggests similar bridging *via* both the nitrogen and sulfur atoms of thiocyanate. In both dimethylgold (III) and trimethylplatinum(IV) compounds, the methyl proton resonances seem to shift consistently to lower field when the *trans* ligands become more polarizable.[10,14,17] The $^2J(^{195}Pt\text{-}H)$ coupling constants also seem to depend markedly on the nature of the *trans* ligand,[17,18] and they decrease as the *trans* ligand becomes more polarizable. Here the signal with the relative intensity of 2 which results from methyl protons in the groups *trans* to sulfur is, indeed, at lower field. This also is consistent with the assignments for $[(CH_3)_2AuNCS]_2$.[10] A structure which is in accord with these data is **2**. The skeletal



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symmetry (or the effective symmetry assuming free rotation of the methyl groups) is D_{2d} compared to T_d for the simple halides. If the thiocyanate bridged by either the nitrogen or the sulfur atoms only, of which the latter is the more reasonable, the symmetry should also be T_d. These structures are ruled

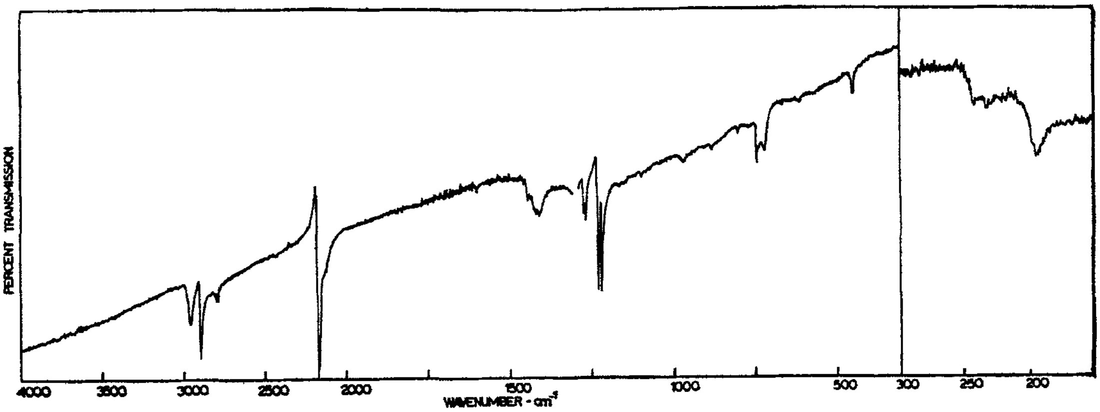


FIGURE 4 Infrared spectrum of $[(CH_3)_3PtNCS]_4$ recorded using split mulls.

out by the nmr data. With **2**, the methyl protons are split into two sets, one with 12 and the other with 24 protons. The bonding with the structure **2** is certainly more reasonable too. This mode of bridging by the thiocyanate is supported by the high ($C\equiv N$) stretching frequencies.

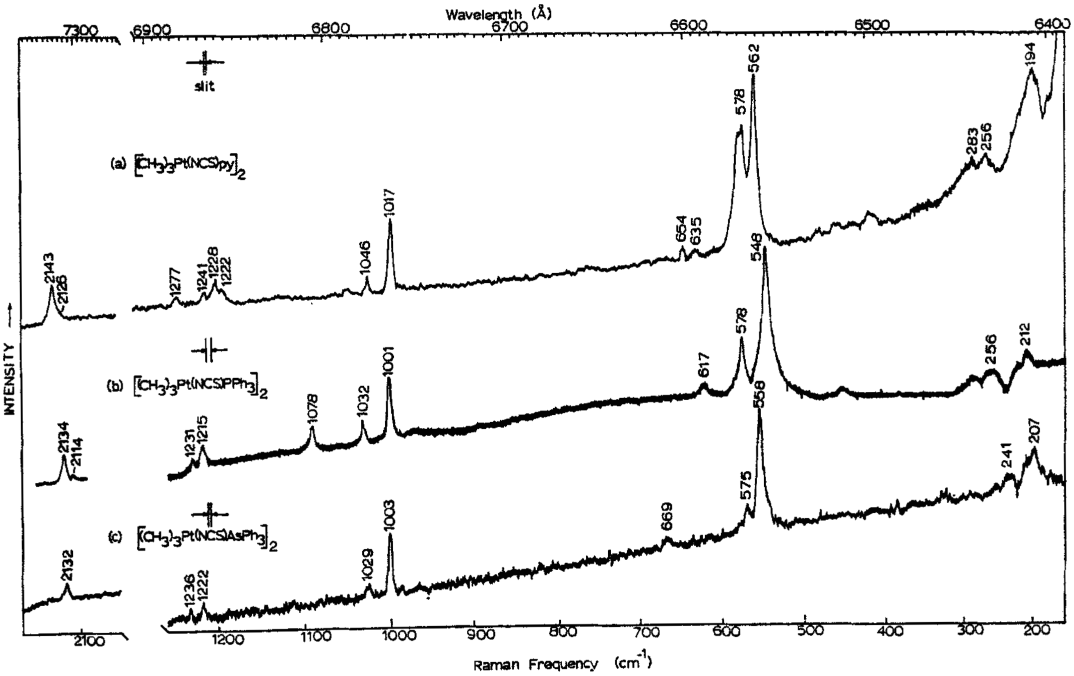
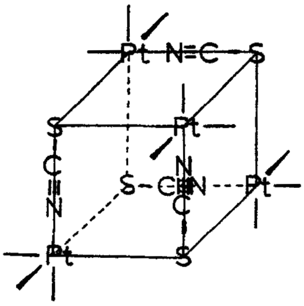


FIGURE 5 Laser Raman spectra of $[(CH_3)_3Pt(NCS)L]_2$, L = py(a), PPh_3(b), $AsPh_3$(c), recorded with a He–Ne laser.

This structure is basically a dimer of the dimethylgold thiocyanate, structure, I, and it leads to the stable six coordination for platinum(IV). The molecular weight data[10] for $[(CH_3)_2AuNCS]_2$ suggest that there may be some slight association of these dimeric dimethylgold thiocyanate molecules in solution. Other structures which might give nmr spectra similar to the one observed, e.g. **3**, could be ruled out on the basis of their unreasonable bond lengths and angles.

For structure **2**, the $C\equiv N$ internal coordinates transform as $A_1 + B_1 + E$. Since these will not couple strongly with other internal coordinates, we should expect three frequencies arising primarily from $C\equiv N$ bond stretching. All three should be Raman active but only the E mode is infrared active. An intense infrared band is observed which under high resolution is found to consist of two equal intensity components at 2184 and 2190 cm^{-1}. The splitting presumably results from lattice effects.

A very intense Raman band occurs at 2182 cm^{-1}, and most of the scattering certainly must arise from the A_1 mode. Since this is essentially the same as the frequency of the doubly degenerate mode, it implies that all three modes are almost accidentally degenerate. For $[(CH_3)_2AuNCS]_2$ where mutual exclusion operates, these stretches were observed at 2163(ir) and 2151(R) cm^{-1}.



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The twelve Pt–C internal coordinates transform as $2A_1 + A_2 + B_1 + 2B_2 + 3E$. Again there should be normal modes of these symmetry species which involve mainly Pt–C bond stretching. In contrast to the halides or the hydroxide, $[(CH_3)_3PtX]_4$

where $\Gamma PtC = A_1 + E + T_1 + 2T_2$, for which there are four Raman active (A_1, E, $2T_2$) and two infrared active modes ($2T_2$), the thiocyanate should exhibit eight Raman active [$2A_1$, B_1, $2B_2$, $3E$) and 5 infrared active modes ($2B_2$, $3E$). Because of accidental degeneracy, all that would be expected is somewhat more structure in the 550–600 cm^{-1} region with the thiocyanate compared to the other compounds. Raman spectra of the chloride[15], bromide[15], iodide[15], and hydroxide[19] have been obtained with crystalline samples using a relatively low resolution instrument and only one band was reported for (Pt–C_3) stretching for each of these. Under high resolution, we have found that $(CH_3)_3PtI$ shows two Raman signals at 560, 568 cm^{-1} corresponding to the 566 and 582 cm^{-1} bands of the thiocyanate. Similar data for the iodide have been reported recently by Bulliner, Maroni, and Spiro.[13] Obviously, coupling of the Pt–C coordinates through the cage structure is minimal.

Using the local symmetry coordinates for the methyl groups (C_{3v} symmetry), the coordinates for symmetric deformation of the twelve methyl groups transform according to the same representation as for the Pt–C coordinates. Thus there will be eight Raman active modes of this type but only three bands are observed at 1223, 1238, and 1281 cm^{-1}. Only four of the five infrared active modes are observed at 1228, 1238, 1278 and 1285 cm^{-1}. In each case more modes are observed than reported for $[(CH_3)_3PtOH]_4$[13, 19] in agreement with the lower symmetry of the thiocyanate. Coupling of the internal methyl vibrations through the cage is also very slight as expected. The vibrational data are consistent with the suggested D_{2d} structure, but because of the considerable accidental degeneracy, the structure could not have been assigned from these vibrational data alone.

A related structure has been reported for $Pr^n_3PAgNCS$[20] which is polymeric in the crystal, and this is illustrated in 4. In solution the structure appears to break down, for the degree of polymerization of $Pr_3{}^nPAgNCS$ was reported to vary from 2.2 to 3.0 and that of $Pr_3{}^iPAgNCS$ was 2.0. The R_3PAg^+ cation behaves rather like the $(CH_3)_3Pt^+$ ion. It is conceivable that trimethylplatinum thiocyanate could, in the solid state, have a similar polymeric structure. On the basis of the stereochemical rigidity of the tetrameric molecule shown to be present in solution, such a marked structural change on going from crystal to solution is considered unlikely.

A somewhat similar bridging thiocyanate with three coordinate sulfur has been reported recently[21] to occur in $K_2[Pd(SCN)_4]$. In this case, the thiocyanates are coordinated to palladium only through the sulfur atoms. The nitrogen lone pairs are uninvolved in the bonding.

The tetrakis (trimethylplatinum thiocyanate) is cleaved readily by bases. It would be expected that comparable reactions would take place between trimethylplatinum halides and bases, although there appears to be only one compound of this type reported in the literature. Gibson *et al.*[22, 23] reported the following reaction with pyridine:

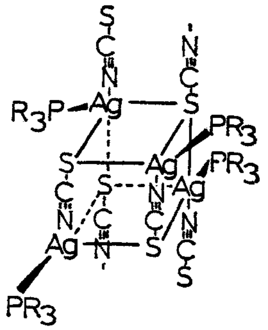
$$2[(CH_3)_3PtIpy_2] \underset{Py}{\overset{H^+}{\rightleftharpoons}} [(CH_3)_3PtIpy]_2 + 2py \qquad (1)$$

Workers subsequently appear to have been unable to reproduce this dimerization. Gel'man and Gorushkina[24] report that $[(CH_3)_3PtIpy_2]$ is very stable and does not lose pyridine. Clegg[14] found no tendency for the dimer to form in benzene solution.

The solid products obtained from reaction of $[(CH_3)_3Pt(NCS)]_4$ with py and PPh_3 gave molecular weights in solution corresponding to dimers, i.e. the reaction is (2).

$$[(CH_3)_3Pt(NCS)]_4 + 4L \longrightarrow 2[(CH_3)_2Pt(NCS)L]_2 \qquad (2)$$

A solution of $[(CH_3)_3Pt(NCS)PPh_3]_2$ in nitrobenzene showed no significant conductivity. The pyridine derivative gives sharp methyl proton resonances comparable in line width to the TMS reference as can be seen from Figure 2. The methyl proton resonances are broadened somewhat with the phosphine derivative, and with the arsine compound the width at half intensity is ca. 2.5 times that of the internal TMS standard. It is possible that this broadening might be caused by coupling with ^{75}As, $I = 3/2$; however, the experimental molecular weights for the arsine complex are less than the value for the dimer and increase with



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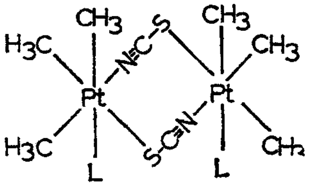
concentration suggesting dissociation occurs in chloroform solution. The pmr spectrum also contains weak signals suggesting the presence of some $[(CH_3)_3Pt(NCS)]_4$.

The pmr spectra indicate that the six methyl groups of these dimeric molecules split into three sets each containing two methyl groups. Both structures 5 and 6 are in accord with this, although 5 seems the more likely assuming that bridge cleavage occurs by nucleophilic attack at a Pt–S bond. The pmr spectra again exclude bridging by the sulfur atoms alone or by only the nitrogen atoms of the thiocyanates.



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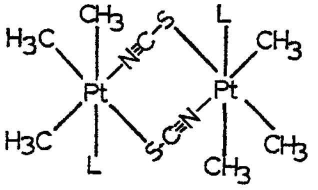

6

The appearance of two strong infrared bands in the $(C{\equiv}N)$ stretching region for $[(CH_3)_3Pt(NCS)py]_2$ and $[(CH_3)_3Pt(NCS)PPh_3]_2$ is not in accord with a centric structure such as 6, although this could result from lattice effects. The $(C{\equiv}N)$ stretching frequencies are 10 to 30 cm^{-1} lower than with $[(CH_3)_2AuNCS]_2$, although the values are still higher than those normally associated with terminal, sulfur bonded thiocyanate ligands. These binuclear complexes are presumed to have a bridge similar to that in bis(dimethylgold thiocyanate). The (C–S) stretching and (N–C–S) bending vibrations gave weak Raman bands, and no assignments were made for these modes.

There seems to be surprisingly strong coupling of the $(C{\equiv}N)$ stretching coordinates with $[(CH_3)_3Pt(NCS)py]_2$ but very weak coupling with $[(CH_3)_3Pt(NCS)AsPh_3]_2$. In the spectrum of the former compound, two strong infrared $(C{\equiv}N)$ stretching bands are observed with a separation of 49 cm^{-1}. This drops to 11 cm^{-1} in the PPh_3 compound, and only one infrared band was observed with the $AsPh_3$ derivative.

Although the $AsPh_3$ derivative was prepared in the same way as they py and PPh_3 compounds, its properties are somewhat different. The compound was the only one to dissociate appreciably in solution. Pyridine appears to be the best ligand for stabilizing the dimeric thiocyanate-bridged structure.

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REFERENCES AND NOTES

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2. Fulbright Fellow from the Institute of General and Inorganic Chemistry, University of Palermo, Italy.
3. Recently, a review of organoplatinum chemistry has appeared; J. S. Thayer, *Organometal. Chem. Rev., A* **5**, 53 (1970).
4. W. J. Pope and S. J. Peachey, *J. Chem. Soc.* **95**, 571 (1909).
5. R. E. Rundle and J. H. Sturdivant, *J. Am. Chem. Soc.* **69**, 1561 (1947).
6. G. Donnay, L. B. Coleman, N. G. Krieghoff, and D. O. Cowan, *Acta Cryst.* **B24**, 157 (1968).
7. T. G. Spiro, D. H. Templeton, and A. Zalkin, *Inorg. Chem.* **7**, 2165 (1968).
8. D. O. Cowan, N. G. Krieghoff, and G. Donnay, *Acta Cryst.* **B24**, 287 (1968).
9. H. S. Preston, J. C. Mills, and C. H. L. Kennard, *J. Organometal. Chem.* **14**, 447 (1968).
10. W. M. Scovell, G. C. Stocco, and R. S. Tobias, *Inorg. Chem.* **9**, 2682 (1970).
11. G. L. Morgan, R. D. Rennick, and C. C. Soong, *Inorg. Chem.* **5**, 372 (1966).
12. W. M. Scovell and R. S. Tobias, *Inorg. Chem.* **9**, 945 (1970).
13. P. A. Bulliner, V. A. Maroni, and T. G. Sprio, *Inorg. Chem.* **9**, 1887 (1970).
14. D. E. Clegg, *Ph.D. thesis*, University of Queensland, 1970.
15. D. E. Clegg and J. R. Hall, *J. Organometal. Chem.* **22**, 491 (1970).
16. M. N. Hoechstetter, *J. Mol. Spectry.* **13**, 407 (1964).
17. K. Kite, J. A. S. Smith, and E. J. Wilkins, *J. Chem. Soc., A*, 1744 (1966).
18. A general discussion of these effects can be found in R. S. Tobias, *Adv. Chem. Ser.*, **98**, 98 (1970).
19. D. E. Clegg and J. R. Hall, *J. Organometal Chem.* **17**, 175 (1969).
20. A. Turco, C. Panattoni, and E. Frasson, *Nature* **187**, 772 (1962).
21. A. Mawby and G. E. Pringle, *Chem. Commun.* 385 (1970).
22. C. S. Gibson, R. V. G. Ewens, and M. E. Foss, *Nature* **162**, 693 (1948).
23. M. E. Foss and C. S. Gibson, *J. Chem. Soc.* 299 (1951).
24. A. D. Gel'man and E. A. Gorushkina, *Dokl. Akad. Nauk. SSR* **57**, 259 (1947).

Note added in proof. A report describing a somewhat different synthesis $[(CH_3)_3PtNCS]_4$ together with the characterization of the compound and the product of the reaction with pyridine has appeared: J. M. Homan, J. M. Kawamoto and G. L. Morgan, *Inorg. Chem.*, **9**, 2533 (1970).