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Crystal structure of tetrakis(trimethyl-μ-S,S,N-thiocyanatoplatinum), $[\{Pt(CH_3)_3SCN\}_4]$

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Abstract

The crystal structure of trimethyl(thiocyanato)platinum(IV), $[\{Pt(CH_3)_3SCN\}_4]$, has been determined by an X-ray diffraction study. The compound is a member of the tetrameric trialkylplatinum family in which platinum ions occupy the tetrahedral corners of a cubane-like framework. It differs from the other members in that the framework is highly elongated because the entire thiocyanato ligand is incorporated into the skeleton. Each thiocyanato ligand is bonded to three platinums: to one Pt through N ($\bar{d}$(Pt–N) 2.08 Å) and to two others through S ($\bar{d}$(Pt–S) 2.55 Å). The framework is further distorted because the PtNC angles are decidedly non-linear, averaging 165°

Results and discussion

The crystal structures of the chloride [1], iodide [2], hydroxide [3–5], azide [6], and thiomethyl [2 (see Table 3), 7] derivatives of trimethylplatinum are known. In all cases, Pt occupies the tetrahedral corners of a cubane-like framework and each of the remaining corners is occupied by a μ_3-bridging atom. Platinum completes its octahedral coordination with three facially oriented methyl groups. The synthesis, and the IR, and ^{1}H NMR spectra of the thiocyanate derivative as well as of its pyridine adducts were first reported in 1970 [8]; a nearly identical report appeared shortly thereafter [9]. This single-crystal X-ray diffraction study confirms the predicted tetrameric nature of the title compound and clarifies the coordination of the ambidentate thiocyanate group.

The thiocyanate derivative was prepared by the procedure described in ref. 8. As is typical for trimethylplatinum derivatives, no melting point could be observed, but thermal decomposition began at 214°C (cf., "mp (decompn), 203–205°" [9]). Two

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pseudotriplets (δ 1.48, $^2J(^{195}\mathrm{Pt}-^1\mathrm{H})$ 73.2 Hz and δ 1.09, $^2J(^{195}\mathrm{Pt}-^1\mathrm{H})$ 74.4 Hz) appeared in the ^{1}H NMR spectrum (JEOL FX-270; in C_6D_6, which was assigned δ 7.27) with a 2/1 intensity ratio. Pale yellow crystals crystallized over a five-week period from a benzene solution. X-ray data were collected from an irregularly shaped fragment (0.17 × 0.28 × 0.30 mm) mounted on the tip of a glass capillary and lightly coated with epoxy. A four-circle, computer-controlled Syntex $P\bar{1}$ diffractometer, with graphite-monochromatized Mo-K_α radiation (λ 0.71069 Å), was used. Accurate cell parameters were obtained by least-squares treatment of 15 independent reflections with 2θ values between 20 and 27°. 3665 unique reflections were collected up to $2\theta < 45°$. A decay correction was not applied as the intensities of three reflections, remeasured after every 97 during data collection, showed no systematic variation. 2182 observed reflections with $I > 3\sigma(I)$ were corrected for Lorentz and polarizations effects. An analytical absorption based upon 17 faces failed to improve the quality of the data set owing to the difficulty of accurately describing the very irregular shape of the crystal, and therefore was omitted.

Crystal data. $C_{16}H_{36}Pt_4S_4N_4$, $M = 1193.11$, monoclinic, space group $P2_1/n$ (C_{2h}^5 No. 14), *a* 10.877(3), *b* 13.182(4), *c* 20.189(5) Å, β 105.29(2)°, *V* 2792(1) Å^3, d_{expt} 2.9, d_{calc} 2.838 g cm^{-3} for $Z = 4$, μ(Mo-K_α) 213 cm^{-1}, $F(000) = 2144$.

Table 1

Final atomic coordinates for $[\{Pt(CH_3)_3SCN\}_4]$

Atom	*x*	*y*	*z*
Pt(1)	0.6554(2)	0.4990(1)	0.36569(8)
C(2)	0.831(4)	0.501(4)	0.430(2)
C(3)	0.597(6)	0.392(4)	0.425(3)
C(4)	0.602(5)	0.612(4)	0.420(2)
N(5)	0.472(3)	0.497(3)	0.300(2)
C(6)	0.386(4)	0.495(3)	0.254(2)
S(7)	0.260(1)	0.490(1)	0.1828(6)
Pt(8)	0.3303(2)	0.6256(2)	0.1090(1)
C(9)	0.162(6)	0.609(4)	0.033(3)
C(10)	0.245(6)	0.744(4)	0.140(3)
C(11)	0.389(5)	0.722(4)	0.045(2)
N(12)	0.502(4)	0.648(3)	0.184(2)
C(13)	0.595(4)	0.639(3)	0.226(2)
S(14)	0.734(1)	0.6192(9)	0.2860(6)
Pt(15)	0.8326(2)	0.4861(1)	0.22450(9)
C(16)	0.991(5)	0.491(4)	0.300(2)
C(17)	0.911(4)	0.376(4)	0.177(2)
C(18)	0.913(5)	0.589(4)	0.171(2)
N(19)	0.674(3)	0.478(2)	0.141(2)
C(20)	0.565(3)	0.474(3)	0.106(2)
S(21)	0.415(1)	0.471(1)	0.0602(6)
Pt(22)	0.3277(2)	0.3363(2)	0.12290(9)
C(23)	0.373(4)	0.220(3)	0.068(2)
C(24)	0.244(5)	0.232(4)	0.170(2)
C(25)	0.155(6)	0.337(4)	0.046(3)
N(26)	0.502(4)	0.325(2)	0.198(2)
C(27)	0.595(5)	0.340(3)	0.239(2)
S(28)	0.736(1)	0.3635(8)	0.2954(6)

Table 2

Bond distances (Å) for $[\{\mathrm{Pt(CH_3)_3SCN}\}_4]$

Pt(1)–C(2)	2.01(5)	Pt(8)–C(9)	2.06(6)
Pt(1)–C(3)	2.06(6)	Pt(8)–C(10)	2.01(6)
Pt(1)–C(4)	2.03(6)	Pt(8)–C(11)	2.02(5)
Pt(1)–N(5)	2.07(4)	Pt(8)–N(12)	2.10(4)
Pt(1)–S(14)	2.56(2)	Pt(8)–S(7)	2.56(2)
Pt(1)–S(28)	2.57(2)	Pt(8)–S(21)	2.53(2)
Pt(15)–C(16)	1.99(5)	Pt(22)–C(23)	2.02(5)
Pt(15)–C(17)	2.03(5)	Pt(22)–C(24)	2.02(6)
Pt(15)–C(18)	2.06(6)	Pt(22)–C(25)	2.08(6)
Pt(15)–N(19)	2.06(4)	Pt(22)–N(26)	2.10(4)
Pt(15)–S(14)	2.54(2)	Pt(22)–S(7)	2.57(2)
Pt(15)–S(28)	2.56(2)	Pt(22)–S(21)	2.52(2)
C(6)–N(5)	1.13(5)	C(20)–N(19)	1.21(4)
C(6)–S(7)	1.71(4)	C(20)–S(21)	1.65(4)
C(13)–N(12)	1.14(6)	C(27)–N(26)	1.14(6)
C(13)–S(14)	1.69(5)	C(27)–S(28)	1.67(5)

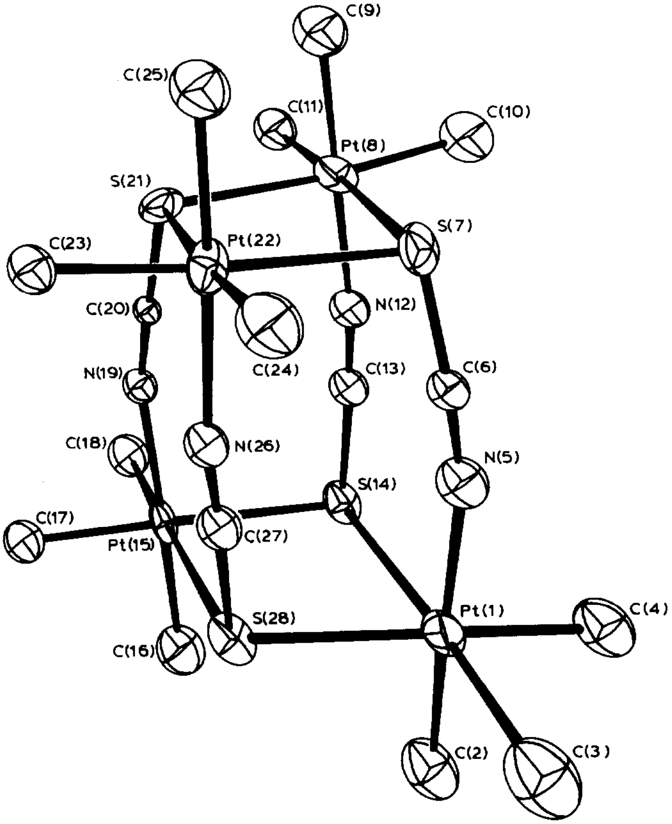

Fig. 1. An ORTEP drawing of $[\{\mathrm{Pt(CH_3)_3SCN}\}_4]$ including the atom numbering scheme.

Structure determination

The atomic coordinates of all 28 non-hydrogen atoms were estimated from a model of the structure proposed in papers by Morgan and by Tobias and their colleagues. These assumed positions were used as input to MULTAN [10] resulting in the location of two sets of eight atoms: the four-membered Pt_2S_2 rings and the methyl C's in the same plane. Least-squares refinement followed by a difference Fourier disclosed the positional parameters of the remaining four methyl C's, and the four C's and four N's of the thiocyanato ligands. No hydrogen atoms were

Table 3

Bond angles (°) for $[\{Pt(CH_3)_3SCN\}_4]$

S(14)–Pt(1)–S(28)	82.2(6)	Pt(8)–S(7)–Pt(22)	96.4(6)
S(7)–Pt(8)–S(21)	82.2(6)	Pt(1)–S(14)–Pt(15)	97.6(6)
S(14)–Pt(15)–S(28)	82.8(6)	Pt(8)–S(21)–Pt(22)	98.5(6)
S(7)–Pt(22)–S(21)	82.4(6)	Pt(1)–S(28)–Pt(15)	96.9(6)
C(2)–Pt(1)–C(3)	91(2)	C(9)–Pt(8)–C(10)	86(2)
C(2)–Pt(1)–C(4)	89(2)	C(9)–Pt(8)–C(11)	88(2)
C(3)–Pt(1)–C(4)	90(2)	C(10)–Pt(8)–C(11)	88(2)
C(2)–Pt(1)–N(5)	179(2)	C(9)–Pt(8)–N(12)	178(2)
C(3)–Pt(1)–S(14)	175(2)	C(10)–Pt(8)–S(21)	174(2)
C(4)–Pt(1)–S(28)	176(2)	C(11)–Pt(8)–S(7)	175(2)
C(2)–Pt(1)–S(14)	89(2)	C(9)–Pt(8)–S(7)	91(2)
C(2)–Pt(1)–S(28)	88(2)	C(9)–Pt(8)–S(21)	88(2)
C(3)–Pt(1)–N(5)	89(2)	C(10)–Pt(8)–N(12)	93(2)
C(3)–Pt(1)–S(28)	93(2)	C(10)–Pt(8)–S(7)	97(2)
C(4)–Pt(1)–N(5)	90(2)	C(11)–Pt(8)–N(12)	90(2)
C(4)–Pt(1)–S(14)	94(2)	C(11)–Pt(8)–S(21)	93(2)
N(5)–Pt(1)–S(14)	92(1)	N(12)–Pt(8)–S(7)	91(1)
N(5)–Pt(1)–S(28)	93(1)	N(12)–Pt(8)–S(21)	93(1)
C(16)–Pt(15)–C(17)	90(2)	C(23)–Pt(22)–C(24)	87(2)
C(16)–Pt(15)–C(18)	88(2)	C(23)–Pt(22)–C(25)	85(2)
C(17)–Pt(15)–C(18)	86(2)	C(24)–Pt(22)–C(25)	86(2)
C(16)–Pt(15)–N(19)	176(2)	C(23)–Pt(22)–S(7)	175(1)
C(17)–Pt(15)–S(14)	178(1)	C(24)–Pt(22)–S(21)	176(1)
C(18)–Pt(15)–S(28)	177(1)	C(25)–Pt(22)–N(26)	176(2)
C(16)–Pt(15)–S(14)	89(2)	C(25)–Pt(22)–S(7)	92(2)
C(16)–Pt(15)–S(28)	90(2)	C(25)–Pt(22)–S(21)	91(2)
C(17)–Pt(15)–N(19)	87(1)	C(23)–Pt(22)–N(26)	92(2)
C(17)–Pt(15)–S(28)	96(1)	C(23)–Pt(22)–S(21)	95(1)
C(18)–Pt(15)–N(19)	90(2)	C(24)–Pt(22)–N(26)	92(2)
C(18)–Pt(15)–S(14)	95(2)	C(24)–Pt(22)–S(7)	95(2)
N(19)–Pt(15)–S(14)	94(1)	N(26)–Pt(22)–S(7)	92(1)
N(19)–Pt(15)–S(28)	92(1)	N(26)–Pt(22)–S(21)	91(1)
Pt(1)–S(14)–C(13)	99(2)	Pt(1)–S(28)–C(27)	97(2)
Pt(8)–S(7)–C(6)	100(2)	Pt(8)–S(21)–C(20)	100(1)
Pt(15)–S(14)–C(13)	100(2)	Pt(15)–S(28)–C(27)	100(2)
Pt(22)—S(7)–C(6)	100(1)	Pt(22)–S(21)–C(20)	100(1)
Pt(1)–N(5)–C(6)	166(4)	N(5)–C(6)–S(7)	177(4)
Pt(8)–N(12)–C(13)	166(3)	N(12)–C(13)–S(14)	177(4)
Pt(15)–N(19)–C(20)	163(3)	N(19)–C(20)–S(21)	178(4)
Pt(22)–N(26)–C(27)	166(3)	N(26)–C(27)–S(28)	176(5)

included in the refinement. Full-matrix least-squares refinement, with anisotropic thermal parameters for only Pt and S resulted in a final R value of 0.076 and R_w of 0.089; the "goodness of fit" and the overdetermination ratio were 2.32 and 14.3, respectively. The atomic coordinates are listed in Table 1, bond distances in Table 2, and bond angles in Table 3. Lists of thermal parameters and observed and calculated structure factors are available from the author.

The earlier intepretation [8,9] of spectroscopic data as resulting from a tetrameric species with an internal thiocyanato ligand has been confirmed (see Fig. 1). The cubane-like framework found for all previous tetrameric trialkylplatinum derivatives [1–7,11] is elongated to accommodate an entire thiocyanato ligand in each of four pseudo-parallel edges. Platinum atoms occupy four D_{2d} corners and sulfur atoms the alternate set, creating two four-membered $\overline{\mathrm{PtSPtS}}$ rings ($\bar{d}$(Pt–S) 2.55 Å, $<$ Pt–S–Pt 97.3°, $<$ S–Pt–S 82.4°) and four eight-membered $\overline{\mathrm{PtSCNPtSCN}}$ rings ($\bar{d}$(Pt–N) 2.08 Å, $<$ Pt–N–C 165°). Each Pt completes its octahedral coordination sphere with three facially arranged methyl groups ($\bar{d}$(Pt–C) 2.03 Å); there was no significant difference between the length of the Pt–C bond *trans* to N (e.g., Pt(1)–C(2)) and that of the corresponding bond *trans* to S (e.g., Pt(1)–C(4)). The closest intramolecular Pt $\cdots$ Pt approach, the diagonal of the four-membered ring, is 3.83 Å.

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