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1:3 Platinum(II) Halide Complexes with Thiocarbamic Esters. The Crystal and Molecular Structure of Chloro-tris(N-propyl-O-ethylthiocarbamate)platinum(II) Chloride

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Abstract

The complexes {[PtL$_3$X]X}, where L = N-ethyl O-ethylthiocarbamate (ETC), N-propyl O-ethylthiocarbamate (PTC) and X = Cl, Br, were prepared and characterized by IR spectroscopy. The structure of {[Pt(PTC)$_3$Cl]Cl} was determined from three-dimensional X-ray diffractometer data. The complex crystallized in the triclinic system, space group $P\bar{1}$ with two molecules in a unit cell of dimensions: a = 16.935(4), b = 10.697(3), c = 8.949(3) Å, α = 114.1(1), β = 83.4(1), γ = 98.4(1)°. Full-matrix least-squares refinement converged at R = 0.056 (R_w = 0.061). The structure consists of separated molecules, each containing the [Pt(PTC)$_3$Cl]$^+$ cation which holds the Cl$^-$ anion by hydrogen bonds through the NH groups of the three PTC molecules.

Introduction

The synthesis and characterization of platinum(II) and palladium(II) halide complexes with O-ethylthiocarbamate (TC) [1] and its N-methyl (MTC) [2, 3] and N,N-dimethyl (DMTC) [4] derivatives have been reported previously. Moreover, cytostatic activity tests indicate the platinum-MTC derivatives as being the most promising as a possible antitumor agent [5a]. With both metals the three ligands give adducts of formula ML$_2$X$_2$ (M = Pd, Pt; X = Cl, Br, I), whereas 1:3 and 1:4 complexes have been isolated with MTC and TC only. The 1:4 complexes have an ionic structure in the solid state; they dissolve in various solvents releasing ligand molecules. In particular [Pd(MTC)$_4$]X$_2$ (X = Cl, Br) afford in benzene a dissociative equilibrium to give 1:3 and 1:2 species [2], whereas [Pt(MTC)$_4$]X$_2$ (X = Cl, Br) release only one ligand molecule, forming stable 1:3 species [3]. Accordingly the 1:3 palladium derivatives dissociate in benzene, where the 1:3 platinum analogues are monomers. For this reason the palladium complexes were formulated as ionic species [Pd(MTC)$_3$X]X and the platinum complexes as neutral species Pt(MTC)$_3$X$_2$, for which a square pyramidal configuration with a chlorine atom in an elongated apical position was supposed. The platinum-MTC 1:3 complex crystals were unsuitable for X-ray structure determination, and so the study was extended to the ligands N-ethyl O-ethylthiocarbamate (ETC) and N-propyl O-ethylthiocarbamate (PTC) [5b].

The present paper reports the synthesis and characterization of {[PtL$_3$X]X} (L = ETC, PTC; X = Cl, Br) and the crystal and molecular structure of chlorotris(N-propyl O-ethylthiocarbamate)platinum(II) chloride, {[Pt(PTC)$_3$Cl]Cl}.

Experimental

The starting materials were commercial PtX$_2$ (X = Cl, Br; Alfa Products). ETC and PTC were prepared by reacting C$_2$H$_5$–C(S)–S–CH$_2$–COONa with ethylamine (70% solution in water; Carlo Erba) and n-propylamine (Carlo Erba) in water, as reported for MTC [2].

Preparation of the Complexes

{[Pt(ETC)$_3$X]X} (X = Cl, Br) and {[Pt(PTC)$_3$Cl]Cl} were prepared by stirring PtX$_2$ (1.0 mmol)

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in a benzene solution of the ligand (4.1 mmol in 3.5 ml). In about fifteen minutes yellow solutions were formed. By adding n-hexane (10–12 ml) until turbidity, small amounts of 1:4 species separated. Further addition of n-hexane to the filtrate gave oily products, which gradually solidified giving yellow-green (Cl) or bright-yellow (Br) crystals. The solids were filtered, washed with n-hexane and dried *in vacuo*. {[Pt(PTC)$_3$Cl]Cl} recrystallized from benzene/n-hexane in two forms, either needles or plates.

The complexes are soluble in benzene, dichloromethane and acetone, and are slightly soluble in diethyl ether and in water.

Anal. for {[Pt(ETC)$_3$Cl]Cl} Calcd. for $C_{15}H_{33}Cl_2N_3O_3S_3Pt$: C, 27.06; H, 4.99; N, 6.31%. Found: C, 27.10; H, 5.02; N, 6.48%. M.p., 110–11 °C (dec); ν(Pt–Cl) = 320 cm^{-1}.

Anal. for {[Pt(ETC)$_3$Br]Br} Calcd. for $C_{15}H_{33}Br_2N_3O_3S_3Pt$: C, 23.88; H, 4.40; N, 5.57%. Found: C, 23.92; H, 4.38; N, 5.56%. M.p., 99–100 °C (dec); ν(Pt–Br) = 223 cm^{-1}.

Anal. for {[Pt(PTC)$_3$Cl]Cl} Calcd. for $C_{18}H_{39}Cl_2N_3O_3S_3Pt$): C, 30.55; H, 5.55; N, 5.93%. Found: C, 30.58; H, 5.68; N, 5.91%. M.p., 92 °C (dec); ν(Pt–Cl) = 321 cm^{-1}.

The IR spectra were carried out on a Perkin Elmer Mod. 580B Infrared Spectrophotometer in the 4000–200 cm^{-1} region (Nujol mulls between CsI plates).

Collection and Reduction of X-ray Intensity Data

Single crystals of chlorotris(N-propyl O-ethylthiocarbamate)platinum(II) chloride, {[Pt(PTC)$_3$Cl]Cl}, suitable for an X-ray structural analysis, were grown from benzene/n-hexane as yellow plates. Precession photographs and single crystal diffractometry showed that the crystals belong to the triclinic system, space group $P\bar{1}$ (after structure determination) with a = 16.935(4), b = 10.697(3), c = 8.949(3) Å, α = 114.1(1), β = 83.4(1), γ = 98.4(1)°, V = 1460.7 Å^3, D_o = 1.60 (by flotation), D_c = 1.609 g cm^{-3} for Z = 2, λ(MoKα) = 0.7107 Å, μ(MoKα) = 52.6 cm^{-1}.

Intensity data were collected from a crystal of approximate dimensions 0.4 × 0.22 × 0.12 mm on a Philips PW 1100 four-circle diffractometer, operating in the $\theta/2\theta$ scan mode (scan width = 1.50°, scan speed = 0.030° s^{-1}, total background time = 20 s) and by using MoKα radiation, monochromatized by a graphite crystal. 4508 independent reflections (2θ scan limit = 4 ÷ 50°) were measured, of which 3703 had $I \geqslant 3\sigma(I)$. During the data collection two standard reflections (3 $\bar{1}$ 2 and $\bar{3}$ 1 $\bar{2}$) were measured every 180 min to check the stability of the crystal and the electronics. Intensities were corrected for Lorentz and polarization effects and were put on an absolute scale by Wilson's method. An experimental absorption correction was applied [6].

TABLE I. Final Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) with e.s.d.s in Parentheses.

Atom	x	y	z	U_{eq}*
Pt	6735(1)	9394(1)	6436(1)	64(1)
Cl(1)	7032(2)	11735(4)	7076(5)	89(2)
Cl(2)	8552(2)	8746(4)	4057(5)	86(1)
S(1)	7213(2)	9668(5)	8871(5)	87(2)
S(2)	5984(2)	9290(4)	4392(5)	88(2)
S(3)	6297(2)	7136(4)	5922(5)	84(2)
O(1)	8500(6)	10957(12)	10463(13)	95(5)
O(2)	5890(6)	7800(12)	1253(12)	101(5)
O(3)	6952(7)	4990(11)	5768(19)	126(7)
N(1)	8618(6)	10556(12)	7816(14)	73(5)
N(2)	6991(6)	7662(12)	2211(14)	76(5)
N(3)	7827(8)	6692(15)	5646(20)	107(7)
C(1)	8168(8)	10445(15)	9032(17)	81(6)
C(2)	8023(13)	10959(25)	12013(22)	137(13)
C(3)	8460(21)	11911(26)	13385(24)	169(15)
C(4)	9472(9)	11140(18)	7955(21)	96(8)
C(5)	9586(16)	12708(26)	8524(43)	168(17)
C(6)	9350(22)	13221(42)	7583(63)	289(32)
C(7)	6317(8)	8188(16)	2531(17)	82(6)
C(8)	5108(10)	8410(27)	1418(23)	141(12)
C(9)	4816(14)	7885(38)	−145(29)	206(20)
C(10)	7268(11)	6733(19)	534(20)	102(8)
C(11)	7170(22)	5325(28)	205(36)	186(16)
C(12)	7374(23)	4736(26)	1295(31)	177(17)
C(13)	7091(9)	6264(15)	5818(21)	88(7)
C(14)	6139(15)	4325(25)	6024(42)	171(17)
C(15)	5960(16)	3349(39)	4459(38)	191(20)
C(16)	8500(12)	5856(23)	5367(37)	154(14)
C(17)	9169(19)	6648(42)	6389(48)	235(25)
C(18)	9171(17)	7395(31)	8021(38)	166(16)
HN(1)	8392	10245	6796	73
HN(2)	7319	7905	3138	76
HN(3)	7937	7579	5597	107

Solution and Refinement

The structure was determined by the heavy-atom technique. A Patterson synthesis revealed the position of Pt atoms. The positions of the remaining non-hydrogen atoms were derived from subsequent difference Fourier maps. The structure was refined by a full-matrix least-squares procedure. The function $\Sigma w\Delta^2$ ($\Delta = |F_o| - |F_c|$) was minimized and w was $[\sigma^2(F_o) + 0.00244\ F_o^2]^{-1}$. Weighting-scheme analysis showed no serious dependence of the mean $w\Delta^2$ as a function of either $|F_o|$ and $\lambda^{-1}\sin\theta$. Atomic scattering factors were taken from ref. [7]. Allowance was made for the anomalous scattering of platinum, chlorine and sulphur atoms using values of $\Delta f'$ and $\Delta f''$ from ref. [7]. The refinement was carried out allowing all non-hydrogen atoms to vibrate aniso-

TABLE II. Bond Distances (Å) and Angles (°) with e.s.d.s in Parentheses.

Pt–Cl(1)	2.318(4)	S(2)–Pt–S(3)	90.2(2)
Pt–S(1)	2.303(5)	S(1)–Pt–S(3)	90.1(2)
Pt–S(2)	2.303(5)	S(1)–Pt–S(2)	166.2(2)
Pt–S(3)	2.289(5)	Cl(1)–Pt–S(3)	173.5(3)
S(1)–C(1)	1.70(1)	Cl(1)–Pt–S(2)	87.6(2)
S(2)–C(7)	1.69(1)	Cl(1)–Pt–S(1)	90.5(2)
S(3)–C(13)	1.72(2)	Pt–S(1)–C(1)	110.3(6)
O(1)–C(1)	1.32(2)	Pt–S(2)–C(7)	111.3(6)
O(1)–C(2)	1.52(2)	Pt–S(3)–C(13)	110.0(6)
N(1)–C(1)	1.29(2)	C(1)–O(1)–C(2)	121(1)
N(1)–C(4)	1.49(2)	C(1)–N(1)–C(4)	123(1)
C(2)–C(3)	1.43(3)	O(1)–C(1)–N(1)	116(1)
C(4)–C(5)	1.53(3)	S(1)–C(1)–N(1)	124(1)
C(5)–C(6)	1.30(7)	S(1)–C(1)–O(1)	120(1)
O(2)–C(7)	1.31(2)	O(1)–C(2)–C(3)	107(2)
O(2)–C(8)	1.53(2)	N(1)–C(4)–C(5)	113(2)
N(2)–C(7)	1.30(2)	C(4)–C(5)–C(6)	117(3)
N(2)–C(10)	1.49(2)	C(7)–O(2)–C(8)	120(1)
C(8)–C(9)	1.40(3)	C(7)–N(2)–C(10)	123(1)
C(10)–C(11)	1.40(4)	O(2)–C(7)–N(2)	114(1)
C(11)–C(12)	1.45(5)	S(2)–C(7)–N(2)	125(1)
O(3)–C(13)	1.33(2)	S(2)–C(7)–O(2)	121(1)
O(3)–C(14)	1.49(3)	O(2)–C(8)–C(9)	107(2)
N(3)–C(13)	1.28(2)	N(2)–C(10)–C(11)	116(2)
N(3)–C(16)	1.49(3)	C(10)–C(11)–C(12)	125(2)
C(14)–C(15)	1.40(4)	C(13)–O(3)–C(14)	124(2)
C(16)–C(17)	1.47(4)	C(13)–N(3)–C(16)	124(2)
C(17)–C(18)	1.35(5)	O(3)–C(13)–N(3)	115(2)
		S(3)–C(13)–N(3)	125(1)
		S(3)–C(13)–O(3)	119(1)
		O(3)–C(14)–C(15)	104(2)
		N(3)–C(16)–C(17)	112(2)
		C(16)–C(17)–C(18)	130(3)

TABLE III. Torsion Angles (°) with e.s.d.s in Parentheses.

S(2)–Pt–S(3)–C(13)	133.4(7)
S(1)–Pt–S(3)–C(13)	−60.4(7)
S(1)–Pt–S(2)–C(7)	−156(1)
Cl(1)–Pt–S(2)–C(7)	121.0(7)
Cl(1)–Pt–S(1)–C(1)	−55.2(6)
S(2)–Pt–S(1)–C(1)	−137(1)
S(3)–Pt–S(1)–C(1)	131.2(6)
S(3)–Pt–S(2)–C(7)	−65.1(7)
Pt–S(1)–C(1)–O(1)	166(1)
Pt–S(1)–C(1)–N(1)	−15(1)
Pt–S(2)–C(7)–O(2)	168(1)
Pt–S(2)–C(7)–N(2)	−12(2)
Pt–S(3)–C(13)–O(3)	170(1)
Pt–S(3)–C(13)–N(3)	−16(2)
C(2)–O(1)–C(1)–S(1)	−4(2)
C(1)–O(1)–C(2)–C(3)	−163(2)
C(2)–O(1)–C(1)–N(1)	177(1)
C(4)–N(1)–C(1)–O(1)	4(2)
C(4)–N(1)–C(1)–S(1)	−175(1)
C(1)–N(1)–C(4)–C(5)	−87(2)
N(1)–C(4)–C(5)–C(6)	−62(4)
C(8)–O(2)–C(7)–S(2)	4(2)
C(7)–O(2)–C(8)–C(9)	176(2)
C(8)–O(2)–C(7)–N(2)	−176(1)
C(10)–N(2)–C(7)–O(2)	2(2)
C(10)–N(2)–C(7)–S(2)	−178(1)
C(7)–N(2)–C(10)–C(11)	−101(2)
N(2)–C(10)–C(11)–C(12)	−46(4)
C(14)–O(3)–C(13)–S(3)	−8(2)
C(13)–O(3)–C(14)–C(15)	107(2)
C(14)–O(3)–C(13)–N(3)	177(2)
C(16)–N(3)–C(13)–O(3)	1(3)
C(16)–N(3)–C(13)–S(3)	−173(2)
C(13)–N(3)–C(16)–C(17)	−135(2)
N(3)–C(16)–C(17)–C(18)	52(5)

TABLE IV. Some Mean Planes with the Distances (Å) and Angles (°) of the Atoms to the Plane.

(A) Distances (Å)

Plane 1 :	$0.8270x + 0.0001y - 0.5622z = 5.6644$			
	Pt	0.147(5)	S(2)	−0.128(6)
	Cl(1)	0.021(6)	S(3)	0.018(6)
	S(1)	−0.128(6)	Cl(2)[a]	3.664(6)
Plane 2 :	$0.4512x - 0.8676y - 0.2089z = -2.4180$			
	S(1)	0.000(7)	C(2)[a]	−0.08(3)
	C(1)	−0.009(17)	C(3)[a]	−0.43(3)
	N(1)	0.002(14)	C(4)[a]	0.10(2)
	O(1)	0.002(13)	C(5)[a]	−1.26(3)
	Pt[a]	−0.541(4)	C(6)[a]	−2.12(5)
Plane 3 :	$0.3060x + 0.9311y - 0.1983z = 9.7851$			
	S(2)	0.000(6)	C(8)	0.09(3)
	C(7)	−0.003(18)	C(9)	0.17(4)
	N(2)	0.001(14)	C(10)	0.04(2)

(continued overleaf)

TABLE IV. *(continued)*

	O(2)	0.001(14)	C(11)	−1.17(3)
	Pt[a]	−0.455(4)	C(12)	−2.12(3)
Plane 4 :	$-0.0810x + 0.0002y - 0.9967z = -5.6331$			
	S(3)	0.001(4)	C(14)[a]	−0.10(3)
	C(13)	−0.034(17)	C(15)[a]	1.20(3)
	N(3)	0.012(16)	C(16)[a]	0.14(3)
	O(3)	0.009(16)	C(17)[a]	−0.78(4)
	Pt[a]	−0.452(2)	C(18)[a]	−2.11(3)
(B) Dihedral angles (°)				
Plane 1–Plane 2	60.6(3)			
Plane 1–Plane 3	68.6(4)			
Plane 1–Plane 4	60.4(4)			

[a] An atom not used in the plane calculation.

tropically. H-atoms bonded to N-atoms were located from Fourier difference maps but were not refined. The final conventional *R* value for the 3703 observed reflections [$I \geqslant 3\sigma(I)$] was 0.056 (R_w = 0.061).

The calculations were carried out on the IBM 370/158 computer of the University of Padua with the SHELX-76 program for crystal structure determination [8].

Final positional and thermal parameters of non-hydrogen atoms are in Table I, and a selection of functions derived from them are presented in Tables II–IV.

Results and Discussion

The IR spectra of the isolated complexes are indicative of coordination through the sulfur atom. In fact the band of the ligands in the 1540–1520 cm^{-1} region, assigned mainly as ν(C–N) with a small δ(N–H) contribution, shifts in all the complexes to higher frequency. This band, present in the pure ligands at 1530 cm^{-1} (ETC) and 1525 cm^{-1} (PTC), is observed in the complexes {[PtL$_3$-X]X} in the 1585–1595 cm^{-1} interval. The broad bands of the ligands in the ν(N–H) region (3400–3260 cm^{-1}) shift towards lower frequencies in the complexes, in the 3050–3100 cm^{-1} range, with a shoulder around 3160 cm^{-1} suggesting hydrogen bonds. A similar trend was observed for the corresponding MTC compounds and for the 1:4 MTC and TC derivatives.

The prepared complexes below 400 cm^{-1} present only one absorption assignable as ν(Pt–Hal); the corresponding band of medium intensity is at 320 cm^{-1} in the chloro derivatives and at 223 cm^{-1} in {[Pt(ETC)$_3$Br]Br}. For the analogous MTC complexes this absorption was at 319 cm^{-1} (X = Cl) and 226 cm^{-1} (X = Br). Preliminary ^{1}H NMR data in d$_6$-benzene indicate that these complexes, as the MTC analogues, do not release ligand molecules, having the stoichiometry most stable in such a solvent.

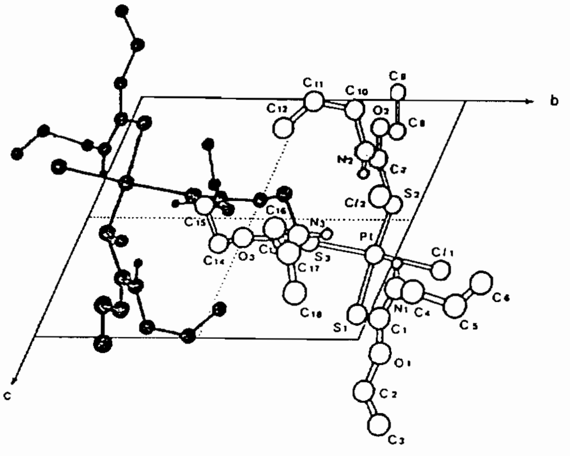

Fig. 1. The crystal packing, as viewed down *a*.

The crystal structure (Fig. 1) described by the cell constants, the symmetry operation of the space group and the atomic parameters consist of [Pt(PTC)$_3$Cl]$^+$ cations and Cl$^-$ anions linked together by strong hydrogen bonds and by van der Waals forces to form the crystallographic asymmetric unit.

The [Pt(PTC)$_3$Cl]$^+$ cations display, at a first glance, a square-planar coordination around the platinum atom. Nevertheless, the least-squares plane (Table IVa) through the five atoms of the coordination sphere indicates that this portion of the molecule deviates significantly from planarity toward a tetrahedral configuration, where the steric pres-

TABLE V. Some Intramolecular Non-bonding Distances (A) with e.s.d.s in Parentheses.

Cl(1)–S(2)	3.20(1)	C(1)–C(4)	2.44(2)
S(1)–O(1)	2.63(1)	C(4)–C(6)	2.42(6)
S(1)–N(1)	2.65(1)	O(2)–C(10)	2.64(2)
S(1)–C(2)	2.97(2)	N(2)–C(11)	2.45(3)
S(2)–O(2)	2.61(1)	N(2)–C(12)	3.04(3)
S(2)–N(2)	2.66(1)	C(7)–C(8)	2.46(3)
S(2)–C(8)	2.93(2)	C(7)–C(10)	2.45(2)
S(3)–O(3)	2.64(1)	C(10)–C(12)	2.53(4)
S(3)–N(3)	2.67(1)	O(3)–C(16)	2.68(2)
S(3)–C(14)	3.02(3)	N(3)–C(17)	2.45(4)
O(1)–C(4)	2.68(2)	N(3)–C(18)	3.09(4)
N(1)–C(5)	2.51(3)	C(13)–C(14)	2.49(3)
N(1)–C(6)	3.02(5)	C(13)–C(16)	2.45(3)
C(1)–C(2)	2.48(2)	C(16)–C(18)	2.55(4)

sure between the ligands is certainly smaller. That there is still some steric crowding in the vicinity of the platinum atom is also verified by some of the shorter intramolecular non-bonding distances, listed in Table V.

The thiocarbamic moieties N(1)C(1)S(1)O(1), N(2)C(7)S(2)O(2) and N(3)C(13)S(3)O(3), which are planar within experimental error, are tilted with respect to the coordination plane by 60.6(3), 68.6(4) and 60.4(4)° respectively, their hydrogen NH atoms pointing to the ionic chlorine atom (Fig. 2).

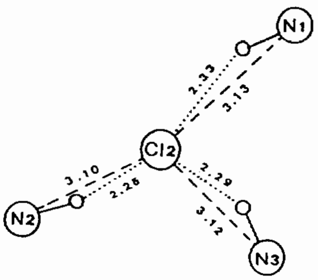

Fig. 2. Coordination of the Cl(2) anion. Selected distances and angles are: Cl(2)···N(1), 3.13(1); Cl(2)···N(2), 3.10(1); Cl(2)···N(3), 3.12(2) A. Cl(2)H(1)N(1), 142(2); Cl(2)H(2)-N(2), 144(2); Cl(2)H(3)N(3), 144(2)°.

The Pt–Cl(1) distance of 2.318(4) Å in the present complex, only slightly longer than that predicted from available covalent radii, 2.30 Å, [9], is very close to the analogous distance in *cis*-Pt-(DMTC)$_2$Cl$_2$ [10].

The Pt–S distances of 2.289(5) and 2.303(5) Å are significantly shorter than the sum of covalent radii, 2.35 Å, [9], for a σ-bonded sulfur atom and for a square-planar platinum atom, but are close to the metal–sulfur distances observed in other Pd^{II} and Pt^{II} complexes of thiocarbamic esters [10, 11].

Within the thiocarbamic ligands the C–S, C–O and C–N bonds around the trigonal carbon atom have a partial double-bond character. Nevertheless the observed C–S, C–O and C–N distances agree with those found for other complexes of thiocarbamic esters.

The most striking feature in the structural data is the difference in the two Pt–Cl bond lengths Pt–Cl(1), 2.318(4) and Pt–Cl(2), 3.521(5) Å. The long Pt–Cl(2) bond length does not raise the question of whether this is a four- or five coordinate complex, since the sum of the ionic radii of Pt and Cl is only 2.45 Å [12]. On the other hand, as shown in Fig. 2, the Cl(2) anion is coordinated through a Cl···H–N interaction to nitrogen atoms of three thiocarbamic groups of the complex cation [Pt-(PTC)$_3$Cl]$^+$. The values of the relevant distances and angles fall within the observed ranges for Cl···H–N hydrogen bonds [13]. Therefore we can assume that the [Pt(PTC)$_3$Cl]$^+$ cation is a four coordinated species whose stereochemical arrangement, with the atomic numbering scheme used in the analysis, is shown in Fig. 3. On the whole each {[Pt(PTC)$_3$-Cl] Cl} unit forms a single molecule; no intermolecular contact was in fact observed. The 1:3 platinum halide complexes with MTC, ETC and PTC, which seem to have the stablest stoichiometry in benzene and chlorinated hydrocarbons, possibly behave in these solvents as non-ionized monomeric molecules. The strong hydrogen bonds are probably broken in water, where the complexes are slightly soluble.

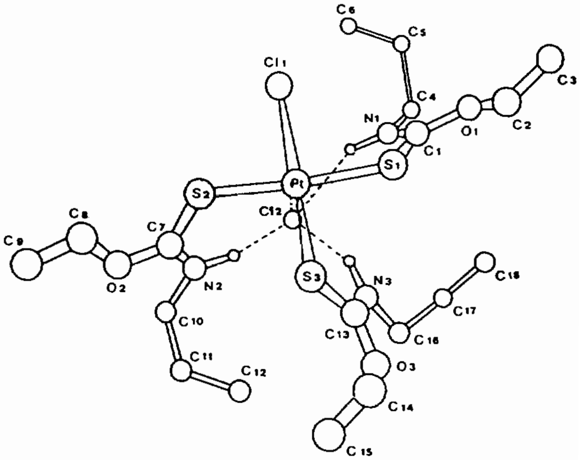

Fig. 3. The structure of Chlorotris(N-propyl O-ethylthiocarbamate) platinum(II) Chloride with the atomic numbering scheme. Positions of the hydrogen atoms are not shown.

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