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The Chloromethylation of Triethylamine in Dichloromethane. Crystal and Molecular Structure of (Chloromethyl)triethylammonium Tetrachloroplatinate(II), $[N(C_2H_5)_3(CH_2Cl)]_2[PtCl_4]$

MERCÈ MAS, JOAN SOLA*

Departament de Química, Divisió Inorgànica, Universitat Autònoma de Barcelona, Bellaterra 08193 (Barcelona), Catalunya, Spain

XAVIER SOLANS

Departament de Cristal.lografia i Mineralogia, Universitat de Barcelona, Gran Via 585, Barcelona 08007, Catalunya, Spain

and MAGDALENA AGUILO

Cristal.lografia, Facultat de Químiques de Tarragona, Universitat de Barcelona, Pl. Imperial Tarraco, s/n, Tarragona 43005, Catalunya, Spain

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Abstract

In a reaction system leading to the preparation of platinum(II) aminothiolate complexes, a side reaction occurs in which the CH_2Cl_2 solvent acts as alkylating agent towards NEt_3. A single-crystal X-ray analysis shows that a quaternary chloroalkylammonium salt, $[N(C_2H_5)_3(CH_2Cl)]_2[PtCl_4]$, is isolated. The enhancement of the alkylating ability of dichloromethane in this system is discussed.

Introduction

As a part of our systematic approach to the coordination chemistry of γ-mercaptoamines [1–9] we are currently working on the complexing ability of these ligands towards platinum ions. In one of the reaction systems studied, an unusual behaviour of dichloromethane, acting as alkylating agent, has been found.

The heterogeneous deprotonation reaction in CH_2Cl_2 of the cationic polymeric compound $[Pt(S–NH)_2]_n[PtCl_4]_n$ with excess of NEt_3 leads to the dimeric chelate complex $[Pt(S–N)Cl]_2$ [10] which is similar to those obtained with palladium ions [5–8] (S–NH and S–N are, respectively, the zwitterionic and anionic forms of the ligand 1-methyl-3-(mercaptomethyl)piperidine) [11]). In addition to that main product, a side reaction occurs in which NEt_3 results alkylated by CH_2Cl_2 yielding a quaternary chloroalkylammonium salt. This has been isolated as $[PtCl_4]^{2-}$ and its crystal structure determined by X-ray diffraction.

Experimental

The starting complex $[Pt(S–NH)_2][PtCl_4]$ was prepared by mixing equimolar aqueous solutions of $K_2[PtCl_4]$ and mercaptoamine [8–11].

Preparation of $[N(C_2H_5)_3(CH_2Cl)]_2[PtCl_4]$

A suspension of 0.5 mol of $[Pt(S–NH)_2][PtCl_4]$ in CH_2Cl_2 containing 10 mmol of NEt_3 was stirred until a homogeneous solution formed (~24 h). Upon slow evaporation of this solution, orange crystals separated. *Anal.* Found: C, 26.60; H, 5.42; N, 4.57; Cl, 33.53; S, 0.40. Calc. for $C_{14}H_{34}Cl_6N_2Pt$: C, 26.35; H, 5.37; N, 4.39; Cl, 33.33%. From the mother liquors the complex $[Pt(S–N)Cl]_2$ can be isolated in a 50% yield [10].

The most intense bands (cm^{-1}) of the IR spectrum, which does not show the typical pattern of the mercaptoalkylpiperidine ligand, are 3020(s, sharp), 2970(s), 1450(vs, br), 1400(m), 1350(m), 1260(s), 1190(m), 1175(m), 1030(s), 990(m), 950(m), 900(m), 815(s), 805(s), 795(m), 310(m). This latter has been associated to ν(Pt–Cl) [12]. The absence of ligand in the isolated compound, being also supported by the analytical composition, was confirmed by X-ray diffraction studies.

X-ray Data Collection, Structure Determination and Refinement

Crystal Data

$[C_7H_{17}NCl]_2PtCl_4$, $M_r = 638.2$, monoclinic, $a = 11.486(2)$, $b = 11.903(2)$, $c = 8.394(1)$ Å, $\beta = 92.59(2)°$, $V = 1146.4(5)$ Å^3, $P2_1/n$, $D_x = 1.829$ g cm^{-3}, $Z = 2$, $F(000) = 620$, λ(Mo Kα) = 0.71069 Å, μ(Mo Kα) = 70.7 cm^{-1}. Room temperature.

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*Author to whom correspondence should be addressed.

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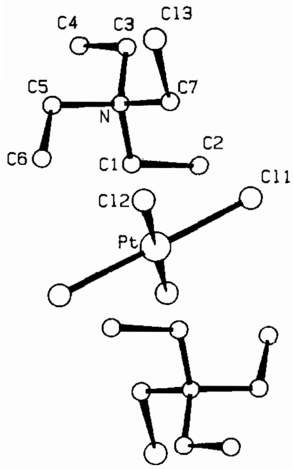

Fig. 1. A view of $[N(C_2H_5)_3(CH_2Cl)]_2[PtCl_4]$ showing the atom numbering scheme.

TABLE I. Bond Lengths (Å) and Bond Angles (°) for $[N(C_2H_5)_3(CH_2Cl)]_2[PtCl_4]$[a]

Cl(1)–Pt	2.310(2)	Cl(2)–Pt–Cl(1)	90.2(1)
Cl(2)–Pt	2.304(3)		
		C(3)–N–C(1)	111.7(7)
C(7)–Cl(3)	1.795(16)	C(5)–N–C(1)	108.2(7)
C(1)–N	1.520(12)	C(5)–N–C(3)	108.0(7)
C(3)–N	1.539(12)	C(7)–N–C(1)	105.7(9)
C(5)–N	1.552(11)	C(7)–N–C(3)	109.7(10)
C(7)–N	1.519(20)	C(7)–N–C(5)	113.8(9)
C(2)–C(1)	1.626(15)	C(2)–C(1)–N	113.3(9)
C(4)–C(3)	1.519(18)	C(4)–C(3)–N	114.1(10)
C(6)–C(5)	1.541(22)	C(6)–C(5)–N	111.7(8)
		N–C(7)–Cl(3)	111.0(9)

[a] e.s.d.s given in parentheses.

An equidimensional crystal (0.07 × 0.07 × 0.07 mm) was selected and mounted on a Philips PW-1100 four-circle diffractometer. The unit-cell parameters were determined from 25 reflections and refined by least-squares. Intensities were collected with graphite monochromatized Mo Kα radiation using the ω-scan technique, scan width 1°, scan speed $0.03° \, s^{-1}$. 1474 independent reflections were measured in the range $2° \leqslant \theta \leqslant 25°$, 1366 of which were assumed as observed applying the condition $I \geqslant 2.5\sigma(I)$. Three reflections were measured every two hours as orientation and intensity control, significant decay was not observed. Lorentz-polarization but no absorption corrections were made. The Pt ion was located from a Patterson synthesis and the remaining non-hydrogen atoms from a weighted Fourier synthesis. The structure was isotropically and anisotropically refined by full-matrix least-squares method using the SHELX76 computer program [13]. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where $w = (\sigma^2(F_o) + 0.0105|F_o|^2)^{-1}$ and f, f' and f'' were taken from the International Tables of X-ray Crystallography. A difference synthesis revealed the position of 9 (of 17) hydrogen atoms which were refined with an overall isotropic temperature factor and anisotropically the remaining atoms. The final R value was 0.032 (R_w = 0.035) for all observed reflections. Atom numbering and the list of bond lengths and bond angles are given, respectively, in Fig. 1 and Table I. A stereoscopic view is provided in Fig. 2.

Discussion

The crystal structure of the title compound consists of discrete $[PtCl_4]^{2-}$ anions and pairs of centrosymmetry-related chloroalkylammonium cations linked by ionic forces. The crystallographically imposed inversion center located at the platinum atom ensures the planarity of the anion which is practically a perfect square. The Pt–Cl bond lengths (Table I) are nearly the same as in $K_2[PtCl_4]$ [14, 15]. No additional Pt–Cl contacts are present (Pt–Cl(3) distance is 4.70 Å).

The local symmetry around the nitrogen atom in the cation departs slightly from a regular tetrahedron. The C–Cl distance (1.795 Å) is similar to the values found in CH_2Cl_2 (1.77 Å) [15] and in the complex $[Co(\eta\text{-}C_5Me_5)(CH_2Cl)(CO)Cl]$ (1.803 Å) [16]. All these values are slightly larger than the sum of covalent radii (1.765 Å) [15].

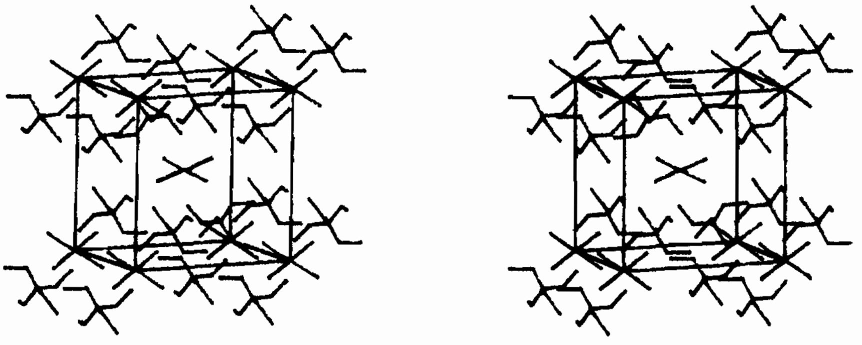

Fig. 2. A stereoscopic view of the unit-cell of the title compound.

The tridimensional lattice may be described as formed by parallel linear arrangements of $[PtCl_4]^{2-}$ and chloroalkylammonium ions related, respectively, by two-fold screw axes. The bigger size of the alkylammonium cations compared to that of the K^+ ions keeps the metal centers much more separated (the shortest Pt–Pt distance, 8.394 Å, is found along *c*) than in $K_2[PtCl_4]$ (4.13 Å) [14]. $PtCl_4$ planes are not stacked as in this potassium salt but tilted with respect to the direction of the alignment, the normal vector of those planes forming an angle of 54.3° with the *c* direction (Fig. 2).

Reactions concerning dichloromethane as alkylating agent are scarce in the literature. Some examples include the alkylation by CH_2Cl_2 or $CHCl_3$ of $[PtS(PPh_3)_2]_2$ leading to $[Pt_2(\eta\text{-}S)(\eta\text{-}SR)(PPh_3)_4]^+$ R = CH_2Cl, $CHCl_2$ [17] or the preparation of the *gem*-dithiolato compound $[(PR_3)_2Pt(S_2CH_2)]$ from $[(PR_3)_2PtCl_2]$ and NaSH in CH_2Cl_2 as solvent [18]. The latter has also been used in the photochemical preparation of the compound $[Co(\eta\text{-}C_5Me_5)(CH_2Cl)(CO)Cl]$ from $[Co(\eta\text{-}C_5Me_5)(CO)_2]$, recently claimed as the first complex isolated from a CH_2Cl_2 oxidative–addition reaction [16]. All these systems involve d^8 metal ions and have in common the presence of strong nucleophilic centers. In the reaction system leading to $[N(C_2H_5)_3(CH_2Cl)][PtCl_4]$ the weak nucleophilicity of triethylamine may have been enhanced by the presence of platinum either as mercaptocomplexes or as $[PtCl_4]^{2-}$. In this connection the alkylation of amines by primary alcohols in the presence of platinum chlorocomplexes has been reported [19].

Supplementary Material

Final atomic coordinates, temperature factors and observed *versus* calculated structure factors have been deposited with the Editor-in-Chief.

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