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Crystal and Molecular Structure of *cis*-Dichlorobis(N,N-Dimethyl O-Ethylthiocarbamate)platinum(II)

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The structure of cis-*dichlorobis(N,N-dimethyl-O-ethylthiocarbamate)platinum(II) has been determined from three-dimensional X-ray data. The complex crystallizes in the orthorhombic system, space group* Pbca, *with eight molecules in a unit cell of dimensions* a = *14.681(5),* b = *17.136(6),* c = *14.357(5) Å. A full-matrix least-squares refinement has led to a value of the conventional R index (on F) of 0.044 for the 1501 observed reflections with $I \geqslant 3\sigma(I)$. The complex is a typical square-planar Pt(II) species. Structural parameters: Pt–Cl 2.320(4) and 2.321(4); Pt–S 2.285(4) and 2.291(4) Å; Cl(1)–Pt–Cl(10) 90.5(2), S(1)–Pt–S(10) 87.1(2), Cl(1)–Pt–S(1) 91.1(2) and Cl(10)–Pt–S(10) 91.8(2)°.*

Introduction

Pd^{II} and Pt^{II} metals react with N,N-dimethyl O-ethylthiocarbamate (DMTC), to give square-planar complexes, having formula $M(DMTC)_2X_2$ (M = Pd, Pt; X = Cl, Br, I). It has been shown that the DMTC ligand is bonded to the metal through the thiocarbonil sulfur atom [1]. In addition IR and ^1H nmr spectra indicate that all Pd^{II} complexes assume the *trans* configuration, both in solution and in the solid state [1]. In particular the *trans* configuration for $Pd(DMTC)_2X_2$, (X = Cl and Br) has been confirmed also by accurate X-ray structure analyses [2, 3]. As far as the Pt^{II} complexes are concerned both *cis*- and *trans*-isomers have been isolated. The tendency towards forming *cis*-isomers decreases along the series Cl > Br > I and in fact only the *trans*-isomer has been isolated for the iodine analogue [1]. A systematic X-ray structure investigation has been undertaken on these complexes in order to define their configuration and in particular to study the influence of the anionic ligands on their geometry. This paper reports on the crystal and molecular structure of the title compound, *cis*-$Pt(DMTC)_2Cl_2$.

Experimental

Single crystals of *cis*-dichlorobis(N,N-dimethyl O-ethylthiocarbamate)platinum(II), suitable for an X-ray structural analysis, prepared according to the method previously described [1], were obtained from a mixture of benzene and hexane in a ratio of 1:1 by volume.

Precession photographs and single crystal diffractometry showed that the crystals belong to the orthorhombic system, space group *Pbca*, with a = 14.681(5), b = 17.136(6), c = 14.357(5) Å, V = 3612(2) Å^3, D_o = 1.97, D_c = 1.958 g cm^{-3} for Z = 8, $\lambda(\text{MoK}\bar{\alpha})$ = 0.7107 Å, $\mu(\text{MoK}\bar{\alpha})$ = 86.9 cm^{-1}. Intensity data were collected from a crystal of approximate dimensions 0.3 × 0.11 × 0.12 mm on a Philips PW 1100 four-circle diffractometer operating in the $\theta/2\theta$ scan mode (scan width = 1.2°, scan speed = 0.03° s^{-1}) and by using graphite-monochromatized MoK$\bar{\alpha}$ radiation. 3162 independent reflections up to θ = 25° were measured, of which 1501 had $I \geqslant 3\sigma(I)$, $\sigma(I)$ being calculated from counting statistics. During the data collection two standard reflections were measured every 180 min to check the stability of the crystal and electronics. Intensities were corrected for Lorentz and polarization effects and converted to an absolute scale by Wilson's method. An experimental absorption correction was applied [4].

The structure was determined by the heavy-atom technique. A Patterson synthesis revealed the position of Pt atom. The positions of the remaining non-hydrogen atoms were derived from subsequent difference Fourier maps. The structure was refined by full-matrix least-squares procedure. The function $\Sigma w[|F_o|-|F_c|]^2$ was minimized and unit weights were applied. The scattering factors were those of the International Tables for X-ray Crystallography [5]. The correction for the real and imaginary parts of the anomalous dispersion was applied to platinum,

TABLE I.

a) Atomic coordinates ($\times 10^4$)

Atom	X/a(σ)	Y/b(σ)	Z/c(σ)
Pt	1211(0)	784(0)	6800(0)
Cl(1)	1184(3)	247(3)	8283(3)
Cl(10)	1787(3)	1943(3)	7393(4)
S(1)	772(3)	−378(3)	6161(4)
S(10)	1097(3)	1303(3)	5334(4)
O(1)	−53(8)	−1470(7)	7135(10)
O(10)	2879(9)	1720(7)	5317(10)
N(1)	−861(9)	−418(8)	6990(10)
N(10)	1903(11)	2654(9)	4975(9)
C(1)	−96(11)	−760(9)	6811(13)
C(2)	794(17)	−1913(14)	7134(22)
C(3)	721(23)	−2523(20)	7834(22)
C(4)	−1097(17)	360(12)	6620(23)
C(5)	−1566(13)	−779(15)	7548(18)
C(10)	2019(14)	1932(12)	5217(13)
C(20)	3104(13)	896(12)	5410(23)
C(30)	4091(15)	815(22)	5409(25)
C(40)	987(17)	3012(14)	4911(21)
C(50)	2691(18)	3166(13)	4768(22)

b) Anisotropic thermal parameters ($\times 10^3$)

Atom	U_{11} (σ)	U_{22} (σ)	U_{33} (σ)	U_{23} (σ)	U_{13} (σ)	U_{12} (σ)
Pt	40(1)	41(1)	60(1)	−2(1)	1(1)	−2(1)
Cl(1)	78(3)	72(3)	63(3)	3(3)	3(3)	−6(3)
Cl(10)	73(3)	60(3)	87(4)	−14(3)	−15(3)	−21(3)
S(1)	72(3)	46(3)	68(3)	−13(3)	13(3)	−11(2)
S(10)	65(3)	65(3)	87(4)	20(3)	−9(3)	−20(3)
O(1)	61(8)	55(8)	151(15)	47(8)	17(9)	12(7)
O(10)	63(8)	64(9)	101(11)	6(8)	−7(8)	−5(7)
N(1)	49(7)	61(9)	53(11)	−1(8)	13(7)	3(7)
N(10)	70(11)	59(10)	54(10)	27(8)	−9(8)	−9(9)
C(1)	71(11)	37(9)	62(11)	2(13)	−6(11)	−1(10)
C(2)	98(16)	75(13)	165(24)	68(15)	36(16)	27(14)
C(3)	81(22)	127(23)	309(34)	39(25)	61(21)	64(22)
C(4)	96(20)	47(13)	125(25)	28(14)	−18(17)	16(15)
C(5)	50(12)	89(19)	144(27)	13(21)	−15(14)	18(13)
C(10)	88(15)	63(13)	49(13)	19(11)	−17(12)	7(12)
C(20)	76(14)	58(14)	151(22)	5(18)	−6(17)	15(12)
C(30)	64(16)	160(28)	150(30)	−23(30)	−1(21)	24(17)
C(40)	108(21)	62(15)	117(21)	50(16)	9(20)	12(14)
C(50)	97(19)	79(17)	107(21)	31(15)	−26(19)	−36(14)

chlorine and sulphur [6]. The refinement was carried out allowing all non-hydrogen atoms to vibrate anisotropically, whilst hydrogens were located in calculated idealized positions (C–H = 0.95 Å), but not varied. The final conventional R value for the 1501 observed reflections with $I \geqslant 3\sigma(I)$ was 0.044.

The calculations were carried out on the CYBER 76 computer of the C.I.N.E.C.A. with the SHELX-76 program for crystal structure determination [7].

Final positional and thermal parameters of non-hydrogen atoms are given in Table I. Interatomic distances and angles are listed in Table II. Least-squares planes and dihedral angles are shown in Table III. Shorter intramolecular non-bonding distances are reported in Table IV.

Description of the Structure

The stereochemical arrangement of the complex, with the atomic numbering system used in the analysis is shown in Fig. 1.

TABLE II.

a) Bond distances (Å)

Pt–Cl(1)	2.320(4)	O(1)–C(2)	1.457(20)
Pt–Cl(10)	2.321(4)	C(2)–C(3)	1.454(25)
Pt–S(1)	2.285(4)	S(10)–C(10)	1.738(19)
Pt–S(10)	2.291(4)	C(10)–N(10)	1.296(18)
S(1)–C(1)	1.709(16)	N(10)–C(40)	1.480(20)
C(1)–N(1)	1.293(16)	N(10)–C(50)	1.483(20)
N(1)–C(4)	1.475(18)	C(10)–O(10)	1.322(17)
N(1)–C(5)	1.447(19)	O(10)–C(20)	1.457(19)
C(1)–O(1)	1.304(16)	C(20)–C(30)	1.456(23)

b) Bond angles (°)

Cl(1)–Pt–S(1)	91.1(2)	C(1)–O(1)–C(2)	121.8(14)
Cl(1)–Pt–Cl(10)	90.5(2)	O(1)–C(2)–C(3)	108.1(19)
Cl(10)–Pt–S(10)	91.8(2)	Pt–S(10)–C(10)	105.8(6)
S(10)–Pt–S(1)	87.1(2)	S(10)–C(10)–N(10)	121.0(14)
Pt–S(1)–C(1)	109.0(5)	C(10)–N(10)–C(40)	122.1(15)
S(1)–C(1)–N(1)	125.6(12)	C(10)–N(10)–C(50)	121.0(17)
C(1)–N(1)–C(4)	122.8(16)	C(40)–N(10)–C(50)	116.8(15)
C(1)–N(1)–C(5)	122.5(14)	S(10)–C(10)–O(10)	124.3(13)
C(4)–N(1)–C(5)	114.7(16)	C(10)–O(10)–C(20)	119.5(13)
S(1)–C(1)–O(1)	121.1(12)	O(10)–C(20)–C(30)	108.6(22)
N(1)–C(1)–O(1)	113.2(14)	O(10)–C(10)–N(10)	114.6(16)

TABLE III. Equations of Some Planes with Their Dihedral Angles (°) and Distances (Å) of the Atoms to the Plane. The equation of the plane is in the form $AX_0 + BY_0 + CZ_0 = D$, in orthogonal Å space. An asterisk denotes an atom not used in the plane calculation.

Plane A: $0.4063\ X_0 + 0.3639\ Y_0 + 0.8382\ Z_0 = 7.6446$

S(1)	−0.006	Pt*	1.749
O(1)	−0.007	C(2)*	0.221
N(1)	−0.007	C(3)*	0.639
C(1)	0.020	C(4)*	−0.108
		C(5)*	0.018

Plane A′: $-0.0583\ X_0 + 0.2448\ Y_0 + 0.9678\ Z_0 = 7.8693$

S(10)	−0.005	Pt*	1.804
O(10)	−0.006	C(20)*	−0.242
N(10)	−0.006	C(30)*	−0.362
C(10)	0.017	C(40)*	0.133
		C(50)*	−0.146

Plane B: $0.3981\ X_0 + 0.4011\ Y_0 + 0.8250\ Z_0 = 7.4887$
S(1), N(1), C(1)

Plane B′: $-0.0863\ X_0 + 0.2583\ Y_0 + 0.9622\ Z_0 = 7.8063$
S(10), N(10), C(10)

Plane C: $0.6654\ X_0 - 0.4791\ Y_0 + 0.5725\ Z_0 = 6.1282$
Pt, S(1), C(1)

Plane C′: $-0.5530\ X_0 + 0.7508\ Y_0 + 0.3612\ Z_0 = 3.5520$
Pt, S(10), C(10)

Plane D: $0.3807\ X_0 + 0.4260\ Y_0 + 0.8207\ Z_0 = 7.4504$
N(1), C(4), C(5)

TABLE III. *(continued)*

Plane D′: $0.0519\ X_0 + 0.2583\ Y_0 + 0.9647\ Z_0 = 8.2100$
N(10), C(40), C(50)

Plane E: $0.3778\ X_0 + 0.3477\ Y_0 + 0.8581\ Z_0 = 7.8852$
N(1), C(1), O(1)

Plane E′: $-0.0330\ X_0 + 0.2660\ Y_0 + 0.9634\ Z_0 = 7.9987$
N(10), C(10), O(10)

Plane F: $0.2198\ X_0 + 0.3583\ Y_0 + 0.9074\ Z_0 = 8.3751$
O(1), C(1), C(2)

Plane F′: $-0.0921\ X_0 + 0.0724\ Y_0 + 0.9931\ Z_0 = 7.4050$
O(10), C(10), C(20)

Plane G: $0.4058\ X_0 + 0.3639\ Y_0 + 0.8384\ Z_0 = 7.6402$
S(1), O(1), N(1) C_1* +0.027

Plane G′: $-0.0579\ X_0 + 0.2451\ Y_0 + 0.9678\ Z_0 = 7.8652$
S(10), O(10), N(10) C_{10}* +0.023

Plane H: $0.3943\ X_0 + 0.4191\ Y_0 + 0.8178\ Z_0 = 7.3990$

N(1)	+0.009	C(4)	−0.003
C(1)	−0.003	C(5)	−0.003

Plane H′: $0.0505\ X_0 + 0.2694\ Y_0 + 0.9617\ Z_0 = 8.2422$

N(10)	−0.006	C(40)	+0.002
C(10)	+0.002	C(50)	+0.002

(continued overleaf)

TABLE III. *(continued)*

Plane K: $0.9455\ X_0 - 0.2884\ Y_0 - 0.1509\ Z_0 = -0.1779$

Pt	−0.002	S(1)	+0.101
Cl(1)	−0.096	S(10)	−0.099
Cl(10)	+0.096		

Dihedral Angles (°)

Plane A–Plane H	3.4	Plane A′–Plane H′	6.4
Plane A–Plane K	81.2	Plane A′–Plane K	74.2
Plane B–Plane C	57.0	Plane B′–Plane C′	53.9
Plane D–Plane E	4.9	Plane D′–Plane E′	4.9
Plane F–Plane E	9.5	Plane F′–Plane E′	11.7
Plane G–Plane H	28.8	Plane G′–Plane H′	6.4
Plane A–Plane A′	3.4		

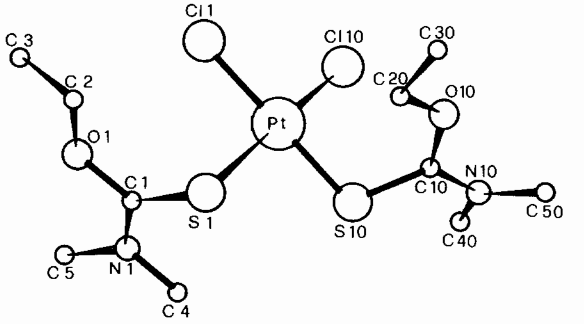

Fig. 1. The molecular structure of *cis*-Pt(DMTC)$_2$Cl$_2$ with the atomic numbering system. Positions of the hydrogen atoms were not determined and are not shown.

The structure described by the cell constants, the symmetry operations of the space group and the atomic parameters consists of the packing of discrete neutral molecules of *cis*-Pt(DMTC)$_2$Cl$_2$ separated by van der Waals contacts. The closest Pt····Pt approach is 6.83 Å and all remaining intramolecular contacts agree with those predicted from radii sum rules.

The *cis*-Pt(DMTC)$_2$Cl$_2$ molecules display, at a first glance, a *cis*-square planar coordination around the platinum atom and almost ideal C_s symmetry. Nevertheless the least-squares plane (Table III) through the five atoms of the coordination sphere indicates that this portion of the molecule deviates significantly from planarity towards a tetrahedral configuration, where the steric pressure between the ligands is certainly smaller. That there is still considerable steric crowding in the vicinity of the platinum atom is verified also by some of the shorter intramolecular non-bonding distances, listed in Table IV.

The thiocarbamic moieties N(1)C(1)S(1)O(1) and N(10)C(10)S(10)O(10) are tilted with respect to the coordination plane by 81.2 and 74.2°, respectively. In addition both ligands are not exactly planar, the C(1) and C(10) atoms being 0.03 and 0.02 Å about the plane of the three bonded atoms S(1), O(1), N(1) and S(10), O(10), N(10) respectively. The disposition of bonds and angles about N(1) and N(10), along with the planarities of these parts of the molecule, indicate that the hybridization of both nitrogens is sp^2. In addition the planes of aminic groups [N(1)C(1)C(4)C(5)] and [N(10)C(10)C(40)-C(50)] are tilted from those of the thiocarbamic ligands [C(1)S(1)O(1)N(1)] and [C(10)S(10)O(10)-N(10)] by 3.4 and 6.4°, respectively. Similar geometrical features have been already found in some palladium(II) complexes of thiocarbamic esters [2, 3, 8].

TABLE IV. Shorter intramolecular Non-bonding Distances (A).

S(1)·······Cl(1)	3.28	S(10)·······Cl(10)	3.31
S(1)·······N(1)	2.68	S(10)·······N(10)	2.65
S(1)·······O(1)	2.63	S(10)·······O(10)	2.71
S(1)·······C(2)	2.98	S(10)·······C(20)	3.03
S(1)·······C(4)	3.09	S(10)·······C(40)	2.99
Cl(1)······Cl(10)	3.29	Cl(10)······C(10)	3.14
O(1)······ C(5)	2.59	O(10)······C(50)	2.61
C(4)······ C(5)	2.46	C(40)······ C(50)	2.52

The Pt–Cl distances of 2.320(4) and 2.321(4) Å, which are equal within the experimental error, are slightly longer than predicted from radii-sum rules (2.30 Å) [9] but fall within the range found recently for Pt–Cl distances in several square-planar *cis*-[PtCl$_2$(PEt$_3$)L] complexes [10].

The Pt–S distances of 2.285(4) and 2.291(4) Å, which are significantly shorter than the sum of covalent radii, 2.35 Å [9], are close to the observed metal–sulphur distances in other Pd^{II} and Pt^{II} complexes of thiocarbamic esters, *e.g.* 2.296(6) Å in dichloro(O-methyl–N-allylthiocarbamato)palladium(II) [11], 2.288(1) and 2.30(1) Å in bis(thiobiureto)-M^{II}, (M = Pd, Pt) [12].

Within both thiocarbamic ligands the C–S, C–O and C–N bonds around the trigonal carbons C(1) and C(10) have a partial double-bond character, which can be estimated to about 20%, 35% and 75% respectively [9, 13, 14]; however these values would give an apparent bonding capacity for the carbon atom greater than 4.0. Nevertheless the observed C–S, C–O and C–N distances agree with those found for other complexes of thiocarbamic esters, where also a high double bond character has been postulated for these bonds [2, 3, 8, 11, 12, 15–18].

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