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Crystal and Molecular Structure of Tetrakis(N-ethylthiourea)platinum(II) Iodide

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The crystal structure of tetrakis(N-ethylthiourea)-platinum(II) iodide, $[Pt(CS(NH_2)(NHC_2H_5))_4]I_2$, has been determined from three-dimensional X-ray diffraction data. The triclinic crystals belong to the $P\bar{1}$ space group: $a = 8.096(8)$, $b = 13.165(12)$, $c = 14.248(12)$ Å, $\alpha = 101.7(1)$, $\beta = 108.5(1)$, $\gamma = 102.1(1)$°. The observed and calculated ($Z = 2$) densities are 2.13(1) and 2.127 g cm^{-3} respectively. 5306 independent reflections with $F_o^2 > 3\sigma(Fo^2)$ were collected by counter methods. Least-squares refinement gave a final discrepancy factor of 0.038. The stereochemistry around the platinum is almost square-planar with the sulphur atom of each thiourea group bound to the metal. Pt–S distances range from 2.309(3) to 2.335 (3) Å. The thiourea groups have quite regular geometry and dimensions. The structure is stabilized in the solid state by a network of N–H $\cdots$ I^- hydrogen bonds.

Introduction

Thiourea and N-alkyl substituted thioureas are ligands of interest for the presence in the molecule of two potential donor sites, the sulphur atom of the CS group and the nitrogen atom of NH_2, NHR or NRR′ groups (R, R′ = alkyl groups).

Several studies were made about the coordinating ability of these ligands mainly with the aim of determining the bonding site. Several authors[1–6] reported sulphur as the donor atom in palladium(II) and platinum(II) complexes of thiourea, while some others[7,8] suggested the hypothesis of coordination through the nitrogen atom in Pd(II) and Pt(II) complexes of N-methylthiourea on the basis of spectroscopic evidence.

In order to clarify the mode of coordination of platinum complexes of this kind, an X-ray structural determination of some of them was undertaken starting with the tetrakis(N-ethylthiourea)Pt(II) complex whose iodide salt was chosen as the more suitable for the X-ray analysis.

Experimental

Preparation

Tetrakis(N-ethylthiourea)platinum(II) iodide, $Pt(Etu)_4I_2$, was prepared by dissolving 0.5 mmol of solid PtI_2 in a warm (50–60°C) solution of 2 mmol of N-ethylthiourea (Etu) in 5 ml of ethanol 95%. The clear solution, concentrated under vacuum, gave a crystalline product upon standing at 4–5°C. Analytical data for $Pt(Etu)_4I_2$: % Calcd., Pt 22.53, S 14.81, I 29.32. % Found, Pt 22.49, S 14.69, I 29.04.

Data Collection

Well formed yellow prisms, which were stable in air and under X-rays, were grown from aqueous solution. The symmetry was found to be triclinic and the cell constants, measured on calibrated Weissenberg and Precession photographs, resulted to be as follows: $a = 8.096(8)$, $b = 13.165(12)$, $c = 14.284(12)$ Å, $\alpha = 101.7(1)$, $\beta = 108.5(1)$, $\gamma = 102.1(1)$°.*

The density, measured by flotation in a chloroform–bromoform mixture was 2.13(1) g cm^{-3} in good agreement with the value of 2.127 g cm^{-3} calculated on the basis of two $Pt(ctu)_4I_2$ entities per unit cell. Thus, assuming two molecules per unit cell, the centrosymmetric space group $P\bar{1}$ could be chosen, which was then confirmed during the refinement. A single crystal of dimensions 0.12 × 0.14 × 0.12 mm was mounted, with its a^* axis coincident with the Φ axis of the goniostat, on a Siemens AED automatic single crystal diffractometer equipped with a scintillation counter and pulse-height analyser. The intensities of 6906 independent reflections were recorded by the Θ–2Θscan technique using Zr filtered Mo Kα radiation with a procedure similar to that previously described[9]. A

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* The reduced cell according to the Buerger convention is: $a = 8.096(8)$, $b = 13.165(12)$, $c = 13.977(14)$ Å; $\alpha = 70.8(1)$, $\beta = 75.2(1)$, $\gamma = 77.9(1)$°. The transformation matrix between the cell in the text and the reduced cell is $\bar{1}00/010/\bar{1}0\bar{1}$. The structural analysis refers to the cell reported in the text.

fixed symmetrical scan range of 0.80° from the computed Mo Kα peak was used. At each end of the scan stationary-crystal stationary-counter background counts were taken for a time equal to the scan time. Intensity data were collected for the independent reflections up to Θ(Mo Kα) = 30°. At greater values very few intensities were measured above background counts. The intensities of three standard reflections, measured every 100 reflections to monitor crystal stability and orientation, remained constant throughout the run.

The data were processed as previously described[9]. 5306 independent reflections with $F_o^2 > 3\sigma(Fo^2)$ were used for the analysis.

The shape anisotropy measured at $\chi = 90°$ showed a maximum of 5% variation in intensities over the Φ range used in the collection of data, therefore no absorption correction [μ(Mo Kα) = 80.82 cm^{-1}] was applied.

Solution and Refinement

The structure was solved using a combination of Patterson and Fourier methods. The isotropic least squares refinement converged at $R = 0.070$. Refinement was then continued allowing all atoms to vibrate anisotropically and convergence was reached at $R = 0.038$ ($R_w = 0.044$).

The refinement was carried out with a two-block approximation of the normal equation matrix, using one block for the positional coordinates and one block for the temperature factors and the scale factor.

The function minimized during the refinement was $2w(|F_c|-|F_o|)^2$ with weights w equal to $4Fo^2/\sigma^2(Fo^2)$. Atomic form factors given by ref. 10 were used. The effects of anomalous dispersion were included in the calculated structure factors[11]; the values of $\Delta f'$ and $\Delta f''$ for Pt, I and S were those computed by Cromer[12].

A table of the observed and calculated structure amplitudes is available upon request. Final positional and thermal parameters are given in Table I.

Discussion

In Figure 1 the structure and the numbering scheme of the cationic complex $[Pt(Etu)_4]^{++}$ are reported. The platinum atom is four coordinated with the four sulphur atoms in a square-planar configuration.

Analogous results were recently found for the complex tetrakis(N,N'-Diethylthiourea)platinum(II)[13].

In Table II interatomic bond lengths and angles are reported. The *cis* S–Pt–S angles are significantly dis-

TABLE I. Final Positional and Thermal Parameters (all × 10^4)[a]. Standard deviations are given in parentheses.

	x	y	z	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Pt	1665(0)	796(0)	1502(0)	99(1)	32(0)	48(0)	32(0)	16(0)	33(0)
I(1)	5619(1)	2680(1)	4504(1)	144(1)	61(1)	65(1)	62(0)	35(1)	45(0)
I(2)	2747(1)	3473(1)	8056(1)	166(1)	19(1)	42(1)	56(0)	46(1)	64(0)
S(1)	821(3)	–351(2)	2414(2)	132(4)	49(4)	83(4)	51(1)	51(2)	56(2)
S(2)	4034(3)	309(2)	1154(2)	142(4)	57(4)	109(4)	43(1)	30(2)	63(2)
S(3)	2091(3)	1904(2)	461(2)	191(5)	71(4)	95(4)	47(1)	36(2)	44(1)
S(4)	–833(3)	1358(2)	1549(2)	145(4)	99(4)	64(4)	69(2)	30(2)	41(1)
N(11)	4280(10)	–323(6)	3402(6)	143(14)	41(14)	63(13)	56(6)	31(8)	43(5)
N(12)	1966(12)	–1775(7)	3276(7)	188(18)	27(16)	57(17)	48(5)	50(9)	62(6)
N(21)	2500(10)	–1782(6)	920(6)	132(13)	33(12)	24(13)	30(4)	6(7)	51(5)
N(22)	5597(12)	–1232(7)	1225(7)	202(19)	138(19)	113(19)	66(7)	50(11)	72(7)
N(31)	3354(13)	3524(7)	2237(6)	244(20)	–4(17)	44(16)	49(6)	36(9)	41(5)
N(32)	3278(14)	4009(7)	760(7)	313(25)	12(19)	91(19)	51(6)	53(9)	49(6)
N(41)	807(10)	2218(7)	3619(6)	136(14)	59(15)	44(13)	66(6)	6(8)	38(5)
N(42)	–2076(11)	2340(9)	2805(7)	128(15)	129(20)	53(16)	113(10)	–13(12)	62(6)
C(11)	2509(12)	–838(7)	3079(7)	163(17)	22(16)	61(15)	44(6)	17(8)	32(5)
C(12)	5690(14)	–782(10)	3877(9)	142(18)	35(20)	23(18)	80(9)	82(14)	63(7)
C(13)	7570(16)	–77(11)	4039(11)	156(21)	45(24)	66(24)	88(10)	50(17)	98(11)
C(21)	4026(12)	–1033(7)	1108(7)	147(16)	73(16)	62(15)	50(6)	26(9)	39(5)
C(22)	2338(18)	–2937(9)	828(10)	273(28)	86(23)	44(25)	45(7)	34(12)	74(9)
C(23)	2175(25)	–3533(11)	–245(12)	498(51)	213(37)	–17(37)	61(9)	–33(16)	84(11)
C(31)	2995(13)	3246(7)	1222(7)	175(18)	17(16)	44(16)	39(5)	35(9)	41(5)
C(32)	3853(19)	4639(9)	2894(9)	325(33)	–34(25)	11(24)	51(7)	11(11)	47(7)
C(33)	2158(26)	5067(12)	2673(11)	505(55)	177(43)	–3(36)	86(12)	–43(17)	64(10)
C(41)	–638(13)	2014(7)	2783(7)	155(17)	32(16)	82(16)	42(6)	15(9)	48(6)
C(42)	964(15)	2732(9)	4686(8)	204(22)	52(22)	77(19)	71(8)	4(11)	46(6)
C(43)	1376(20)	3946(11)	4929(11)	295(33)	7(28)	70(29)	67(9)	–22(15)	76(10)

[a] Coefficients b_{ij} are defined by $T = \exp[-10^4(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{12}hk+b_{13}hl+b_{23}kl)]$.

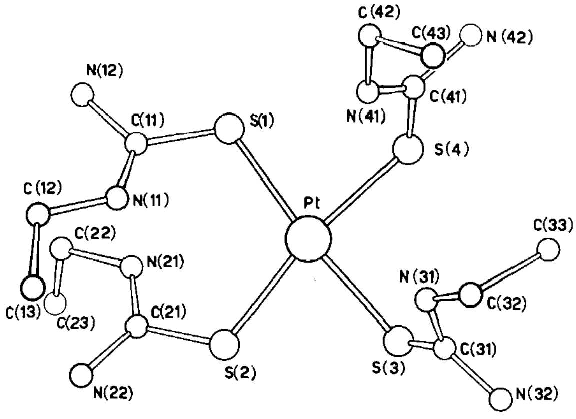

Figure 1. The cationic complex $[Pt(etu)_4]^{++}$ viewed along the normal to the cordination plane.

torted from the ideal value of 90°, with the exception of S(3)–Pt–S(4), and the *trans* S–Pt–S angles are different from 180°.

Relevant least-squares planes are reported in Table III. Of the four independent platinum–sulphur distances three are equal, with an average value of 2.312(3) Å which is sensibly shorter than the sum of the covalent radii (2.35 Å)[14], while the fourth bond, Pt–S(3), is sensibly longer than the other three. A similar feature is observed for the four Pt–S–C angles. In fact three of them are equal with an average value of 114.8(4)° while the fourth, Pt–S(3)–C(31), has a somewhat smaller value. S(1), S(2) and S(4) would seem, therefore, to be more sp^2 hybridized than S(3).

In theory the ethylthiourea molecule, coordinating through the sp^2 hybridized sulphur atom, has two different bonding sites, that is *syn* and *anti* with respect to the ethyl group, which give rise to two different configurations, *Z* and *E*[15]. It is worth noting that in the present complex all the four ligand molecules share the *syn* site with the platinum atom, giving rise to the *Z* configuration. The torsion angles Pt–S–C–N(ethyl), according to the convention of Klyne and Prelog[16], are in sequence 25.3, 22.8, 0.3 and 2.4° for the four ligand groups.

Figure 2 is a schematic representation of the ethylthiourea ligand with reported values for the bond lengths and angles averaged over the four groups of the structure. Each thiourea group has bond lengths and angles which differ in value from the corresponding ones in the other three groups, but these differences are not significant and allow to average the values over the four groups. These averaged values can be considered in good agreement with those reported in the

TABLE II. Bond Lengths (Å) and Bond Angles (degrees). Standard deviations are given in parentheses.

Pt–S(1)	2.318(3)	S(1)–Pt–S(2)	104.7(1)
Pt–S(2)	2.309(3)	S(1)–Pt–S(3)	172.2(1)
Pt–S(3)	2.335(3)	S(1)–Pt–S(4)	84.7(1)
Pt–S(4)	2.309(3)	S(2)–Pt–S(3)	81.0(1)
S(1)–C(11)	1.723(10)	S(2)–Pt–S(4)	168.9(1)
S(2)–C(21)	1.753(10)	S(3)–Pt–S(4)	89.1(1)
S(3)–C(31)	1.736(8)	Pt–S(1)–C(11)	115.4(4)
S(4)–C(41)	1.740(10)	Pt–S(2)–C(21)	115.0(4)
C(11)–N(11)	1.332(12)	Pt–S(3)–C(31)	108.7(4)
C(11)–N(12)	1.337(14)	Pt–S(4)–C(41)	114.0(4)
C(21)–N(21)	1.320(11)	S(1)–C(11)–N(11)	123.2(8)
C(21)–N(22)	1.319(15)	S(1)–C(11)–N(12)	116.7(7)
C(31)–N(31)	1.338(13)	N(11)–C(11)–N(12)	120.0(9)
C(31)–N(32)	1.329(15)	C(11)–N(11)–C(12)	122.9(9)
C(41)–N(41)	1.312(11)	N(11)–C(12)–C(13)	111.1(11)
C(41)–N(42)	1.330(16)	S(2)–C(21)–N(21)	120.5(8)
N(11)–C(12)	1.447(15)	S(2)–C(21)–N(22)	115.5(7)
N(21)–C(22)	1.474(14)	N(21)–C(21)–N(22)	123.9(9)
N(31)–C(32)	1.468(14)	C(21)–N(21)–C(22)	124.6(9)
N(41)–C(42)	1.491(14)	N(21)–C(22)–C(23)	110.4(11)
C(12)–C(13)	1.526(17)	S(3)–C(31)–N(31)	122.1(8)
C(22)–C(23)	1.524(21)	S(3)–C(31)–N(32)	117.8(7)
C(32)–C(33)	1.556(26)	N(31)–C(31)–N(32)	120.1(8)
C(42)–C(43)	1.505(18)	C(31)–N(31)–C(32)	124.8(10)
		N(31)–C(32)–C(33)	110.1(9)
		S(4)–C(41)–N(41)	124.2(9)
		S(4)–C(41)–N(42)	113.7(7)
		N(41)–C(41)–N(42)	122.1(10)
		C(41)–N(41)–C(42)	124.8(10)
		N(41)–C(42)–C(43)	112.1(11)

TABLE III. Equations of Least-squares Planes and Displacements of Atoms from Planes (Å). Planes are defined in terms of crystallographic axes. E.s.d.s. of atom displacements range between 0.05 and 0.10 Å.

	$\Phi(1)$	$\Phi(2)$	$\Phi(3)$	$\Phi(4)$	$\Phi(5)$
Pt	–0.08				
S(1)	0.02	0.00			
S(2)	0.03		0.00		
S(3)	0.02			0.00	
S(4)	0.02				0.00
C(11)		0.00			
N(11)		0.00			
N(12)		0.00			
C(21)			0.02		
N(21)			0.01		
N(22)			0.01		
C(31)				0.01	
N(31)				0.00	
N(32)				0.00	
C(41)					–0.02
N(41)					0.01
N(42)					0.01

$\Phi(1)$	$\Phi(2)$	41.3°
$\Phi(1)$	$\Phi(3)$	41.6
$\Phi(1)$	$\Phi(4)$	72.1
$\Phi(1)$	$\Phi(5)$	64.0

$\Phi(1)$ $1.873x + 5.756y + 7.843z - 1.864 = 0$

$\Phi(2)$ $-3.503x + 4.534y + 12.133z - 2.481 = 0$

$\Phi(3)$ $-1.246x - 0.617y + 13.781z - 1.072 = 0$

$\Phi(4)$ $-7.924x + 4.218y + 1.795z + 0.774 = 0$

$\Phi(5)$ $-2.350x - 11.423y + 6.598z + 0.330 = 0$

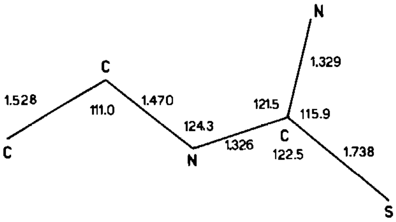

Figure 2. Schematic representation of the ethylthiourea ligand.

TABLE IV. Short Intermolecular Contacts between Nitrogen Atoms and Iodide Ions.[a]

N(11)	I(1)	3.73 Å
N(12)	I(1^{i})	3.72
N(12)	I(2^{ii})	3.64
N(22)	I(2^{i})	3.68
N(31)	I(1)	3.69
N(32)	I(2^{iii})	3.65
N(32)	I(2^{iv})	3.74
N(41)	I(1)	3.57
N(42)	I(1^{v})	3.52

[a] Subscripts refer to atoms at: i) $1-x$ $-y$ $1-z$; ii) $-x$ $-y$ $1-z$; iii) x y $z-1$; iv) $1-x$ $1-y$ $1-z$; v) $x-1$ y z.

literature. The two sulphur bonded carbon–nitrogen bonds are equivalent and show a high double bond character[9]. The C–S bond is sensibly longer than the sum of the double bond radii of S[17] and C[18]. The ethyl carbon–nitrogen and carbon–carbon bonds are regular for a single C–N[19] and C–C[18] bond. The two S–C–N angles are different, the S–C–N (ethyl) being the greater presumably for steric hindrance caused by the bulky residue of the molecule. All the four thiourea ligands are planar with the exception of their terminal methyl groups. The torsion angles C–N–C–C are 172.7, –81.0, 72.9 and –79.9° for the four ligand molecules. Cations and iodide anions are packed with a network of hydrogen bonds between I and N (Table IV). I(1) is 4.29 Å far from Pt and lies in a direction roughly normal to the coordination plane of the complex.

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