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Crystal and Molecular Structure of *Trans*-Dithiocyanatobis(N-Methyl O-Ethylthiocarbamate)palladium(II)

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Trans-*dithiocyanatobis(N-methyl O-ethylthiocarbamate)palladium(II) has been prepared and studied by IR and visible spectroscopy. Its molecular structure has been determined from three-dimensional X-ray data. The complex crystallizes in the triclinic system, space group* $P\bar{1}$ *with one molecule in a unit cell of dimensions* a = *9.522(7),* b = *8.352(7),* c = *5.658(6) Å,* α = *93.1(1),* β = *96.5(1),* γ = *88.8(1)°. Full-matrix least squares refinement has led the conventional R index (on F) to 0.029 for the 900 observed reflections having* $I \geq 2.5\ \sigma(I)$*. The complex is a typical square-planar Pd(II) species. Relevant structural parameters are: Pd–S 2.319(1) and 2.331(2) Å, S(1)–Pd–S(2) 82.9(1)°.*

Introduction

Recently we have been interested in the preparation and the study of transition metal complexes with sulphur-donor organic ligands. In a previous work we reported the 1:2 complexes of palladium(II) and platinum(II) with N,N-dimethyl O-ethylthiocarbamate (DMTC) [1]. Furthermore we prepared the analogues with N-methyl O-ethylthiocarbamate (MTC) with the aim of studying the influence of the number of the nitrogen-substituents on the stoichiometry and the properties of the compounds. With this ligand we have been able to isolate complexes of formula $M(MTC)_2X_2$ and $[M(MTC)_4]X_2$, where M = Pd or Pt; X = halide [2]. However, by using palladium(II) thiocyanate, instead of halides, only $Pd(MTC)_2(SCN)_2$ was obtained and every attempt to prepare the corresponding 1:4 adduct failed. As the above complex is sparingly soluble in the common organic solvents the existence of a polymeric structure was suspected. Therefore X-ray single crystal analysis has been undertaken in order to establish the structure of the compound.

Experimental

Preparation of the Complex

To an ethanol solution (5 ml) of the MTC ligand [3] (4 mmol), $K_2Pd(SCN)_4$ (1 mmol) in ethanol (10 ml) was slowly added with stirring. The orange solid was filtered, washed with ethyl ether and dried *in vacuo* over P_2O_5. M.p. 146° (dec). Found: C = 26.1; H = 3.8; N = 12.1. Calcd.: C = 26.0; H = 3.9; N = 12.1.

The IR spectra in the 4000–400 cm^{-1} region were recorded on a Perkin-Elmer Mod. 621 Infrared Spectrophotometer, using Nujol mulls between KBr windows. Far IR spectra were run on a Beckman IR 11 Spectrophotometer in Nujol mulls between polythene disks. The electronic spectra of solid samples were taken at 25 °C by a Beckman DK2A Spectrophotometer using Nujol mulls on paper.

Crystal Data

Single crystals of *trans*-$Pd(MTC)_2(SCN)_2$, suitable for X-ray structural analysis, were grown from ethanol solutions. Precession photographs and single crystal diffractometry showed that the crystals belong to the triclinic system, space group $P\bar{1}$ with $a = 9.522(7)$, $b = 8.352(7)$, $c = 5.658(6)$ Å, $\alpha = 93.1(1)$, $\beta = 96.5(1)$, $\gamma = 88.8(1)°$, $V = 446.29$ Å^3, $D_o = 1.72$, $D_c = 1.717$ g cm^{-3} for $Z = 1$. Intensity data were collected from a crystal of approximate dimensions 0.19 × 0.06 × 0.10 mm on a Philips PW 1100 four-circle diffractometer operating in the $\theta 2/\theta$ scan mode (scan width = 1.2°, scan speed = 0.020° s^{-1}) and by using MoK$\bar{\alpha}$ radiation, monochromatized by a graphite crystal. 1089 independent reflections up to $\theta = 22°$ were measured, of which 900 had $I \geq 2.5\ \sigma(I)$, $\sigma(I)$ 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 polarisation effects and put in

TABLE I. Atomic Coordinates ($\times 10^4$) and Thermal Parameters[a] ($\times 10^4$) with Their e.s.d.s in Parentheses for the Non-hydrogen Atoms.

Atom	X/a (σ)	Y/b (σ)	Z/c (σ)	U_{11} (σ)	U_{22} (σ)	U_{33} (σ)	U_{23} (σ)	U_{13} (σ)	U_{12} (σ)
Pd	0	0	0	250(4)	412(5)	328(4)	−107(3)	39(3)	43(3)
S(1)	1403(2)	1625(2)	−1958(3)	526(11)	498(11)	479(11)	−95(9)	167(9)	0(9)
S(2)	−527(2)	2407(2)	1973(3)	287(9)	514(11)	574(11)	−232(9)	64(8)	24(8)
O(1)	−2930(4)	3791(5)	2926(7)	336(23)	440(26)	497(26)	−222(21)	36(20)	66(19)
N(1)	−3165(5)	1992(6)	−104(9)	294(28)	530(33)	379(30)	−136(26)	12(24)	81(25)
N(2)	2711(6)	−151(8)	−5495(10)	636(40)	740(44)	490(37)	−162(33)	214(32)	−75(34)
C(1)	−2307(6)	2711(7)	1556(11)	382(36)	345(35)	428(38)	−49(30)	68(31)	49(29)
C(2)	−4701(6)	2161(9)	−262(14)	404(41)	578(50)	681(54)	−169(42)	−54(38)	105(35)
C(3)	−2082(7)	4545(8)	5011(12)	413(39)	442(40)	560(43)	−135(35)	74(33)	−6(33)
C(4)	−3089(7)	5571(10)	6287(14)	479(45)	656(50)	579(49)	−323(43)	153(38)	−56(40)
C(5)	2151(7)	527(8)	−4043(12)	403(39)	535(43)	456(41)	−78(35)	36(33)	−94(32)

[a] Anisotropic temperature factors are in the form $\exp[-2\pi^2(\Sigma_{ij}U_{ij}a_i^*a_j^*h_ih_j)]$.

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

Pd–S(1)	2.331(2)	O(1)–C(3)	1.470(7)
Pd–S(2)	2.319(1)	N(1)–C(1)	1.302(7)
S(1)–C(5)	1.669(7)	N(1)–C(2)	1.459(7)
S(2)–C(1)	1.700(6)	N(2)–C(5)	1.147(8)
O(1)–C(1)	1.331(6)	C(3)–C(4)	1.494(8)
S(1)–Pd–S(2)	82.9(1)		
S(1)–Pd–S(2)′	97.1(1)	S(2)–C(1)–O(1)	120.6(4)
Pd–S(1)–C(5)	109.7(2)	S(2)–C(1)–N(1)	125.1(4)
Pd–S(2)–C(1)	108.3(2)	O(1)–C(1)–N(1)	114.2(5)
C(1)–O(1)–C(3)	118.5(4)	O(1)–C(3)–C(4)	105.9(5)
C(1)–N(1)–C(2)	123.5(5)	S(1)–C(5)–N(2)	176.0(6)

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

Plane A:

$0.2175X_o + 0.7129Y_o - 0.6667Z_o = 0.6309$

C(1)	−0.012	C(2)*	−0.146
N(1)	0.004	C(3)*	−0.158
O(1)	0.004	C(4)*	−0.218
S(2)	0.004	Pd*	−0.631

Plane B: [N(1)O(1)S(2)]:

$0.2178X_o + 0.7129Y_o - 0.6666Z_o = 0.6346$

C(1)*	−0.016

Plane C: [N(1)C(1)C(2)]:

$0.1167X_o + 0.7813Y_o - 0.6132Z_o = 1.041$

Dihedral angles (°)	
Plane A–Plane C	7.63
Plane B–Plane C	7.64

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 positions of S atoms. 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 palladium and sulphur only [6]. The refinement was carried out allowing all non-hydrogen atoms to vibrate anisotropically, whilst hydrogens were put in calculated idealized positions (C–H = 0.95 Å), but not varied. In particular the staggered conformation was assumed both for methyl and ethyl groups. The final conventional R value for the 900 observed reflections with $I \geqslant 2.5\ \sigma(I)$ was 0.029. 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. Some planes and dihedral angles are shown in Table III. Shorter intramolecular non-bonding distances are reported in Table IV.

TABLE IV. Shorter Intramolecular Non-bonding Distances (Å). Primed atoms are related to unprimed ones by the centre of symmetry at the origin.

S(2)·····O(1)	2.639(7)
O(1)·····C(2)	2.661(9)
S(2)·····N(1)	2.669(8)
S(1)·····N(2)	2.815(8)
S(2)·····C(3)	2.910(8)
S(1)·····S(2)	3.078(5)
S(1′)·····S(2)	3.485(5)

Results and Discussion

Vibrational Spectrum

An usual method for inferring the type of the thiocyanate-to-metal coordination by IR measurements involves observation of the CN, CS and SCN group frequencies. However difficulties in making the assignments arise from the fact that the frequency ranges expected for the thiocyanate may overlap with those of the thiocarbamate. In the spectrum of the complex assignments of the most significative bands have been made as follows: i) ν(CN) = 2110 cm^{-1}; ν(CS) = 706 cm^{-1}; δ(SCN) = 432 cm^{-1} (thiocyanate); ii) ν(CN) = 1578 cm^{-1} (thiocarbamate).

The frequencies observed for the thiocyanato group and the thiocarbamate are consistent with sulphur-coordination of both ligands [1, 8]. The band at 290 cm^{-1} is assigned to the palladium–sulphur (thiocyanate) bond stretching mode in a *trans* square-planar environment. Furthermore the very low value of the ν(N–H) frequency (3190, 3115 cm^{-1}) is indicative of strong hydrogen-bond interactions.

Electronic Spectrum

The electronic spectrum of the complex is typical of a square-planar arrangement of the ligands around the palladium atom. The position in energy of the d–d band ($\bar{\nu}$ = 20,000 cm^{-1}) agrees with the value expected for S-bonded thiocyanato complexes [9].

Description of the Structure

The stereochemical arrangement of the complex, with the atomic numbering scheme used in the analysis is shown in Fig. 1. 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 Pd(MTC)$_2$(SCN)$_2$ linked together in one-dimensional chains parallel to z-axis by a hydrogen-bonding system N(2)····H–N(1′) and N(2′)····H–N(1), the N····N distance being 2.92 Å. (Primed atoms are related to unprimed ones through the operation $-x, -y, 1-z$). The closest Pd····Pd approach is 5.66 Å and all remaining intermolecular contacts agree with those predicted from van der Waals radii.

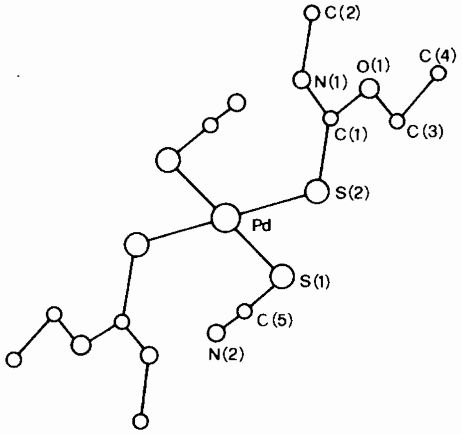

Fig. 1. The molecular structure of *trans*-Pd(MTC)$_2$(SCN)$_2$ with the atomic numbering scheme. Positions of the hydrogen atoms were not determined and are not shown.

The palladium is coordinated to four sulphur atoms (two from the MTC ligands and two from the thiocyanato groups). The donor atoms and the metal are strictly coplanar as the molecular centrosymmetry is also crystallographic. Therefore the only departure from the ideal square-planar geometry is represented by the inequality of the two S–Pd–S angles, [82.9(1)° and 97.1(1)°, respectively], which could be justified by the non-bonding ligand-to-ligand interactions. The S–Pd–S angles can differ as the thiocarbamate ligand has quite different contacts with the two adjacent SCN groups.

The thiocarbamic group is not exactly planar, the C(1) atom being about –0.02 Å out of the plane of the three bonded atoms S(2), O(1) and N(1). The N–C bond length and the C–N–C angle indicate that the N(1) hybridization is sp^2. In addition the plane of the aminic group, [C(1)–N(1)–C(2)], is tilted from that of the thiocarbamic group, [C(1)–S(2)–O(1)–N(1)], by 7.6°.

The thiocyanate moiety, which is approximately linear with the S–C–N angle of 176.0(6)°, does not lie in the coordination plane. In fact the S-bonded thiocyanate ion is bent out of the plane by about 2.9°.

A comparison of pertinent bond distances and angles in *trans*-Pd(MTC)$_2$(SCN)$_2$ and other S-bonded thiocyanato complexes is given in Table V [10–19]. The present M–S–C angle, 109.7(2)°, is among the highest values found (97–110°) for the related compounds. With the exception of the C–N distances for [Cu(en)$_2$]Hg(SCN)$_4$, NH$_4$Ag(SCN)$_2$ and α-[Pt$_2$(SCN)$_2$Cl$_2$(Pr$^i_3$P)$_2$] the S–C and C–N lengths in M–SCN moieties are similar for all the molecules reported in Table V.

The observed bond distance for Pd–S(1) of 2.331(2) Å is slightly shorter than the sum of the covalent radii, 2.35 Å [20], for a σ-bonded sulphur atom and for a square-planar palladium atom, but falls

TABLE V. Comparison of Bond Distances (Å) and Angles (°) in *trans*-$Pd(SCN)_2(MTC)_2$ and in Other S-bonded Thiocyanate Complexes.

Compound	Pd–S	S–C	C–N	M–S–C
trans-$Pd(SCN)_2(MTC)_2$[a]	2.331(2)	1.669(7)	1.147(8)	109.7(2)
trans-$Pd(SCN)_2[P(OPh)_3]_2$[b]	2.352(2)	1.672(8)	1.16 (1)	99.2(1)
trans-$Pd(SCN)_2(Ph_2P{\cdot}C{\vdots}C{\cdot}Bu^t)_2$[c]	2.336(3)	1.635(14)	1.170(19)	98.0(4)
cis-$Pd(NCS)(SCN)(Ph_2P[CH_2]_3NMe_2)$[d]	2.295(2)	1.658(8)	1.146(11)	107.3(3)
$K_2Pd(SCN)_4$[e]	2.312(10)	1.64 (4)	1.24 (5)	109 (1)
	2.392(9)	1.68 (5)	1.15 (6)	101 (2)
$Hg(SCN)_2$[f]		1.62 (2)	1.18 (3)	97.6(5)
$[Cu(en)_2]Hg(SCN)_4$[g]		1.57	1.34	102.5
$Se(SCN)_2$[h]		1.69	1.13	104
$Cd(etu)_2(SCN)_2$[i]		1.55 (5)	1.19 (10)	109 (4)
α-$[Pt_2(SCN)_2Cl_2(Pr^i_3P)_2]$[l]		1.66	1.31	108
$NH_4Ag(SCN)_2$[m]		1.707	1.095	110

[a] This work. [b] Ref. 10. [c] Ref. 11. [e] Ref. 13. [f] Ref. 14. [g] Ref. 15. [h] Ref. 16. [i] Ref. 17. [l] Ref. 18. [m] Ref. 19.

within the range of the Pd–S distances in S-bonded thiocyanato complexes of palladium(II) [10–13]. Considering now the Pd–S distances in *trans*-$Pd(MTC)_2(SCN)_2$ and related *trans*-dithiocyanates [10, 11, 13] a mean of 2.345 Å is obtained. It is also worth noting the significant increase of Pd–S distance from 2.331(2) Å in the present complex to 2.352(2) Å in *trans*-$Pd(SCN)_2[P(OPh)_3]_2$ [10].

As for the palladium–MTC ligand interaction the Pd–S(2) distance of 2.319(1) Å, which is close to the observed value in the related compound *trans*-$Pd(DMTC)_2Br_2$ [21], falls within the range of distances in other Pd(II) complexes of thiocarbamic esters [22–24].

Within the thiocarbamic ligand the C–S, C–O and C–N bonds around the trigonal carbon C(1) have a partial double bond character, which can be estimated to about 30%, 25% and 75% respectively [20, 25, 26]; however these values would give an apparent bonding capacity for the carbon atom of more than 4.0. Nevertheless the observed C–S, C–O an C–N distances agree with those found for the related compound *trans*-$Pd(DMTC)_2Br_2$ [21] and other palladium(II) complexes of thiocarbamic esters, where also a high double-bond character has been postulated for these bonds [22–24].

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