Crystal and Molecular Structure of Palladium(II) and Silver(I) Complexes with Oxotetrazolinate Ligands [1-Me-$N_4C(O)$]$^-$

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Dedicated to Professor Erwin Weiss on the occasion of his 85th birthday

The structures of (n-Bu_3P)$_2$Pd[1-Me-$N_4C(O)$]$_2$ (**1**) and of (Ph_3P)$_3$Ag[1-Me-$N_4C(O)$] · 1-Me-4-H-$N_4C(O)$ (**2**) were determined by X-ray crystallography. The oxotetrazolinate ligands are N^4-coordinated in contrast to the corresponding S-coordinated tetrazole-thionates.

Key words: Oxotetrazolinate, Palladium, Silver, Phosphines, X-Ray Crystallography

Introduction

Metal complexes with the anion of 1-R-tetrazole-thiones have been prepared by reactions of chlorido complexes with 1-R-tetrazole-5-thionate [1, 2]. The preparation of metal complexes with these heterocycles by [2+3] cycloaddition of azido complexes with organic isothiocyanates has been intensively studied [3 – 6], recently by Kim [5], Mohr [6] and their coworkers. S-coordination of these heterocyclic ligands instead of N-coordination [3] has been proven by X-ray diffraction [5 – 7]. It seems possible that such complexes with anionic ligands are also formed by reaction of 1-substituted tetrazoline-5-thiones with phosphine Pd(0), Pt(0), Rh(I), Ir(I) complexes (oxidative addition?) [8]. Also a series of metal complexes with neutral 1-R-tetrazoline-thiones has been synthesized [9].

We report here on the structure of complexes with the anion of 1-R-tetrazolinones. The latter are accessible by oxidation of 1-R-tetrazoline-5-thiones [10] or by [2+3] cycloaddition of aluminum triazide [11], trimethyl silylazide or sodium azide with aryl-isocyanates [12, 13]. Tetrazolinones have found interest as insecticides and herbicides [14] and exist in the keto form [12, 13]. Silver(I) [10] and copper(II) "salts" [13] of oxotetrazolinate have been reported.

Table 1. Bond lengths (Å) and angles (deg) of **1** and **2** in comparison.

	1	**2**	Neutral 1-methyl-tetrazolinone
Metal–N	2.019(4)	2.357(3)	
N(metal)–N	1.353(6)	1.323(4)	1.360(4) (NH–N)
N=N	1.294(6)	1.303(4)	1.270(4)
N–N(Me)	1.352(6)	1.347(4)	1.361(4)
N(Me)–C(O)	1.371(7)	1.360(4)	1.365(4)
C=O	1.222(7)	1.258(4)	1.228(4)
C(O)–N(metal)	1.370(6)	1.359(4)	1.356(4) (C(O)–NH)
N–C(Me)	1.450(7)	1.445(5)	1.446(4)
Metal–P	2.321(1)	2.5013(7)	
		2.5229(8)	
		2.5266(7)	
C(O)–N(metal)–N	108.9(4)	107.5(3)	
N(metal)–N=N	110.0(4)	111.4(3)	
N=N–N(Me)	106.8(4)	106.3(3)	
N–N(Me)–C(O)	110.9(4)	109.4(3)	
N(Me)–C(O)–N(metal)	103.3(4)	105.5(3)	

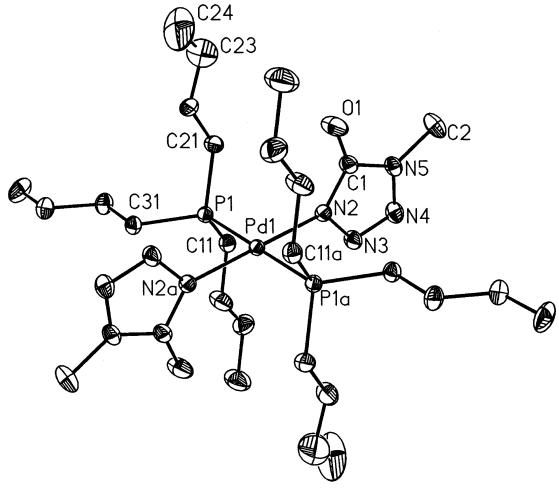


Fig. 1. Molecular structure of **1** in the crystal. Bond lengths (Å) and angles (deg): P1–C11 1.820(6), P1–C21 1.817(5), P1–C31 1.823(5); C21–P1–C11 105.1(3), C21–P1–C31 105.5(2), C21–P1–Pd 111.9(2), C11–P1–Pd 110.6(2), C31–P1–Pd 116.4(2), N2–Pd–P1 88.8(2), N2–Pd–P1 91.2(2), P1–Pd–P1 180.0, N2–Pd–N2 180.0. For other data see Table 1.

Results

1-Methyl-1,4-dihydro-5*H*-tetrazol-5-one was obtained from the corresponding thione compound [10], and the complexes **1** and **2** were prepared by reaction of its potassium salt with $(n\text{-}Bu_3P)PdCl_2$ or $(Ph_3P)_2AgCl$, respectively [1]. Complex **2** crystallized from CH_2Cl_2/Et_2O with one molecule of neutral 1-methyl-1,4-dihydro-5*H*-tetrazol-5-one. The X-ray structure determination showed the *trans*-coordination in **1** (Fig. 1, Table 1), as has been proposed from its low dipole moment of 2.1 D [1]. The angles in the coordination sphere of **1** are close to 90° (N2–Pd–P1 = 88.8, 91.2°). In **2** (Fig. 2) a distorted tetrahedral $AgNP_3$ coordination is found (angles N1–Ag–P = 100 – 107° and P–Ag–P = 108 – 115°). The neutral 1-methyltetrazolin-5-one in **2** is attached to the coordinated heterocyclic ligand by a hydrogen bond between the N–H and the carbonyl group (Fig. 2). Metal-N-coordination could be already derived from the intensive keto absorption at 1675 cm^{-1} in the IR spectra [1]. The different N–N bond lengths within the tetrazoline ring of **1** and **2** clearly point to a dominant formula as shown in Scheme 1. Moreover the similarity of the bond lengths of the (formal) anionic and the neutral tetrazolinone

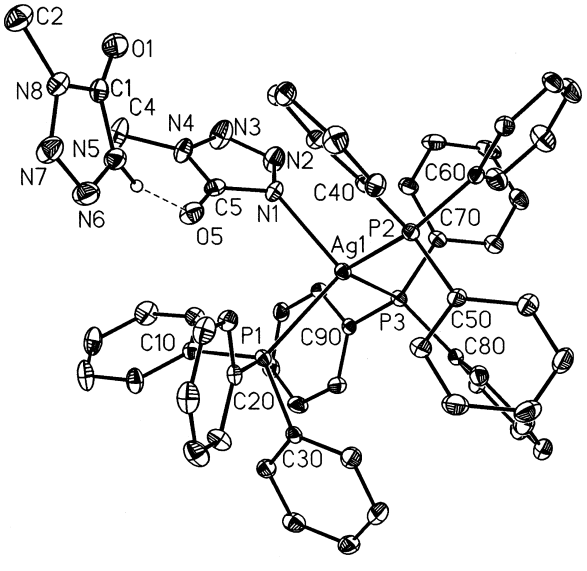
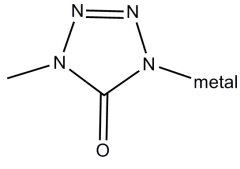


Fig. 2. Molecular structure of **2** in the crystal. Bond lengths (Å) and angles (deg): P1–C10 1.825(3), P1–C20 1.836(3), P1–C30 1.828(3); N1–Ag–P1 100.24(7), N1–Ag–P2 107.91(6), N1–Ag–P3 105.66(7), P1–Ag–P2 115.98(2), P1–Ag–P3 108.68(2), C10–P1–C20 105.03(13), C20–P1–C30 102.4(1), C10–P1–Ag 114.7(9). For other data see Table 1.

Table 2. Crystallographic data and data related to data collection and structure solution for **1** and **2**.

	1	**2**
Formula	$C_{28}H_{60}N_8O_2P_2Pd$	$C_{38}H_{52}AgN_8O_2P_3$
M_r	709.18	1093.86
Crystal size, mm^3	$0.32 \times 0.27 \times 0.2$	$0.25 \times 0.2 \times 0.18$
Crystal color and habit	colorless prisms	
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a, Å	8.6495(7)	12.3373(6)
b, Å	10.7669(9)	25.9072(10)
c, Å	11.0568(9)	16.6568(8)
α, deg	76.041(1)	90
β, deg	69.328(2)	93.965(1)
γ, deg	89.415(1)	90
V, $Å^3$	931.8(2)	5311.2(4)
Z	1	4
D calcd., $g\,cm^{-3}$	1.26	1.37
Absorption coef., mm^{-1}	0.6	0.5
$F(000)$, e	376	2256
Diffractometer	Siemens P4 with area detector	
T, K	193	193
2Θ range, deg	3.92 – 46.68	2.92 – 46.52
Index range	$-7 \le h \le 9$	$-13 \le h \le 13$
	$-11 \le k \le 11$	$-21 \le k \le 22$
	$-12 \le l \le 12$	$-18 \le l \le 18$
Refl. measured / unique	4149 / 2177	21832 / 6623
R_{int}	0.0396	0.0585
Refl. observed (4σ)	2000	5715
No. ref. variables	191	650
$R1$ / $wR2$ [$F \ge 4\sigma(F)$]	0.0446 / 0.1219	0.0355 / 0.0680
$R1$ / $wR2$ (all data)	0.0567 / 0.1320	0.0445 / 0.0723
GoF	1.025	1.123
Larg. diff. peak / hole, $e\,Å^{-3}$	1.299 / −0.524	0.706 / −1.003



Scheme 1.

in **2** reveals that the metal–N bond in these complexes has covalent character.

Oxo-tetrazolinate metal complexes could be formed also by cycloaddition of organic isocyanates R-N=C=O to coordinated azide ligands [3], but such complexes could not be isolated from the reaction of $[(Ph_3P)_2M(N_3)_2]$ (M = Pd, Pt) with H_3C-N=C=O. Instead, the corresponding isocyanato complexes were observed [3].

Experimental

X-Ray structure determinations

Crystals were mounted on a glass fiber with fluoropolyether oil. 1200 frames were measured in Θ (0 – 360°)

with χ = 28° and ω = 2Θ = 25°; 65 frames were measured in ω (15 – 35°) with χ = 280 °, 2Θ = 29° and ψ = 0. The structures were solved and refined using SHELXTL and SHELX-93 [15]. Crystal data and details of the structure solution and refinement are summarized in Table 2.

CCDC 835333 (**1**) and 835334 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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