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Synthesis and X-ray structure of nickel(II) benzylpiperazine-dithiocarbamate complex [Ni(*bp*dtc)(PPh_3)$_2$]ClO_4·PPh_3

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HIGHLIGHTS

- Synthesis and properties of [Ni(*bp*dtc)(PPh_3)$_2$]ClO_4·PPh_3.
- The X-ray structure of [Ni(*bp*dtc)(PPh_3)$_2$]ClO_4·PPh_3 was determined.
- The C—H···O, C—H···C and C—H···π contacts stabilize the crystal structure.
- Extraordinary large P—Ni—P angle as compared with other complexes of this type.

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ABSTRACT

A mixed-ligand nickel(II) dithiocarbamate complex of the composition [Ni(*bp*dtc)(PPh_3)$_2$]ClO_4·PPh_3 was synthesized, characterized (elemental analysis, UV–Vis, IR and NMR spectroscopy and molar conductivity measurements) and its X-ray structure was determined. The three ligands are arranged in a distorted square-planar geometry (an S_2P_2 donor set), with the bond lengths and angles within the vicinity of the central atom as follows: Ni—P = 2.2150(6) and 2.2529(6) Å, Ni—S = 2.2267(6) and 2.2129(6) Å, P—Ni—P = 105.11(2)°, S—Ni—S = 78.26(2)°. The P—Ni—P angle of the studied complex falls outside the interval of 98.37–102.92° determined for thirteen formerly reported structural analogues involving the [Ni(*n*dtc)(PPh_3)$_2$]$^+$ moiety with a combination of dithiocarbamate (*n*dtc) and triphenylphosphine (PPh_3) ligands. In the crystal, the complex cations, perchlorate anions and PPh_3 molecules of crystallization are linked through intramolecular C—H···O and C—H···π and intermolecular C—H···O, C—H···C and C—H···π contacts to a three-dimensional architecture.

1. Introduction

Dithiocarbamates represent an exciting group of widely used compounds [1], which (in forms of salts or acids) easily form negatively single-charged anions usable as S-donor ligands suitable for the formation of the coordination compounds [2,3]. Some of the dithiocarbamate complexes have also found application as pesticides (e.g. ziram [4]) or engine oil additives (e.g. MoDTC/ZDDP [5]). As for the nickel dithiocarbamate complexes, they are studied for many years and recently their representatives were reported as the substances with diverse properties and interesting application potential, such as visual detection of gaseous NO_2 at low concentrations in live cell [6], higher antibacterial and antifungal activities as compared with commercially available antibiotics [7], acceleration of graphite oxidation [8] and removal of selected anionic dyes from aqueous solutions [9]. Focusing on benzylpiperazine-dithiocarbamate (*bp*dtc) transition metal complexes, i.e. the complexes involving the same type of dithiocarbamate as herein described one, only eight such compounds were reported in the literature to date, concretely: [*M*(*bp*dtc)$_2$]$_2$ [*M* = Mn(II), Co(II), Ni(II), Cu(II), Zn(II)] [10], the nickel(II) complexes [Ni(*bp*dtc)(phen)$_2$]*X* (*X* = ClO_4^-, SCN^-) [11] and the nickel(IV) complexes [Ni(*bp*dtc)$_3$]ClO_4 [12].

In this work we report the preparation, spectral (UV–Vis, IR, NMR) and structural (single-crystal X-ray analysis) properties of a square-planar nickel(II) complex involving the bidentate-coordinated benzylpiperazine-dithiocarbamato ligand and two PPh_3 molecules (an S_2P_2 donor set). As for the nickel(II) dithiocarbamate complexes involving the [Ni(*n*dtc)(PPh_3)$_2$]$^+$ moiety, it should be noted that Cambridge Structural Database (CSD ver. 5.34, May 2013 update) [13] contains thirteen compounds involving a complex species of the mentioned type, where *n*dtc stands for a general dithiocarbamate anion bearing the S_2CN moiety. Moreover, we discuss the unusually large P—Ni—P bond angle. The fact, that herein described complex represents, according to CSD, only the second

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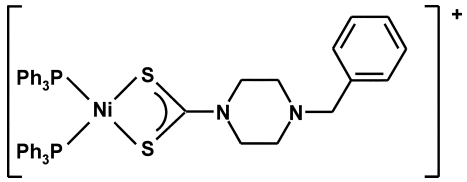
Table 1
Crystal data and structure refinement for [Ni(*bp*dtc)(PPh_3)$_2$]ClO_4·PPh_3.

Empirical formula	$C_{66}H_{60}N_2ClO_4P_3S_2Ni$
Formula weight	1196.35
Temperature (K)	105(2)
Wavelength (Å)	0.71073
Crystal system, space group	Triclinic, *P*-1
Unit cell dimensions	
a (Å)	12.4202(4)
b (Å)	15.5481(5)
c (Å)	16.3981(4)
α (°)	108.220(3)
β (°)	99.674(2)
γ (°)	100.033(3)
V (Å^3)	2876.87(15)
Z, D_{calc} (g cm^{-3})	2, 1.381
Absorption coefficient (mm^{-1})	0.591
Crystal size (mm)	0.40 × 0.30 × 0.10
F (000)	1248
ϑ range for data collection (°)	2.92 ⩽ ϑ ⩽ 25.00
Index ranges (*h*,*k*,*l*)	−12 ⩽ *h* ⩽ 14 −18 ⩽ *k* ⩽ 17 −19 ⩽ *l* ⩽ 19
Reflections collected/unique (R_{int})	21,308/10,121 (0.0308)
Data/restraints/parameters	10,121/0/712
Goodness-of-fit on F^2	1.024
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0335, wR_2 = 0.0755
R indices (all data)	R_1 = 0.0497, wR_2 = 0.0820
Largest peak and hole (eÅ^{-3})	0.679, −0.295



Scheme 1. Structural formula showing the complex cation of [Ni(*bp*dtc)(PPh_3)$_2$]ClO_4·PPh_3.

structurally characterized transition metal *bp*dtc complex (besides [Ni(*bp*dtc)(phen)$_2$]ClO_4·$CHCl_3$ [11]), should be mentioned as well.

Table 2
Selected bond lengths (Å) and angles (°) of [Ni(*bp*dtc)(PPh_3)$_2$]ClO_4·PPh_3.

Bond lengths		Bond angles	
Ni1—S1	2.2267(6)	S1—Ni1—S2	78.26(2)
Ni1—S2	2.2129(6)	S1—Ni1—P1	167.03(2)
Ni1—P1	2.2150(6)	S1—Ni1—P2	87.81(2)
Ni1—P2	2.2529(6)	S2—Ni1—P1	88.78(2)
S1—C1	1.721(2)	S2—Ni1—P2	164.59(2)
S2—C1	1.723(2)	P1—Ni1—P2	105.11(2)
C1—N1	1.304(3)	Ni1—S1—C1	85.73(7)
P1—C20	1.831(2)	Ni1—S2—C1	86.11(7)
P1—C30	1.822(2)	Ni1—P1—C20	114.70(7)
P1—C40	1.816(2)	Ni1—P1—C30	108.78(7)
P2—C50	1.831(2)	Ni1—P1—C40	116.50(7)
P2—C60	1.826(2)	Ni1—P2—C50	125.11(7)
P2—C70	1.832(2)	Ni1—P2—C60	108.06(7)
		Ni1—P2—C70	111.47(7)

2. Experimental

2.1. Materials and methods

Chemicals and solvents used in this work were purchased from Sigma–Aldrich Co., Fluka Co. and Lachema Co. The starting complex [Ni(*bp*dtc)$_2$] was prepared as formerly described in the literature [10].

Elemental analysis (C, H, N) was performed on a Flash 2000 CHNO-S Analyser (Thermo Scientific). The chlorine content was determined using the Schöniger method. The nickel content was determined by the chelatometric titration with murexide as an indicator. The molar conductivity of the 10^{-3} M nitromethane solution was measured by an LF 330/SET conductometer (WTW GmbH) at 25 °C. Electronic absorption spectrum (UV–Vis) was recorded on a Specord M40 device using the Nujol technique. IR spectrum (450–4000 cm^{-1} region; KBr technique) was recorded on a Perkin–Elmer Spectrum one FT-IR spectrometer. The measurement of room temperature magnetic susceptibility was performed using the Faraday method on a laboratory designed instrument equipped with a Sartorius 4434 MP-8 microbalance, and using Co[Hg(NCS)$_4$] as a calibrant. ^{1}H, ^{13}C and ^{31}P NMR spectra of $CDCl_3$ solution was measured at 300 K on a Varian 400 device. ^{1}H and ^{13}C

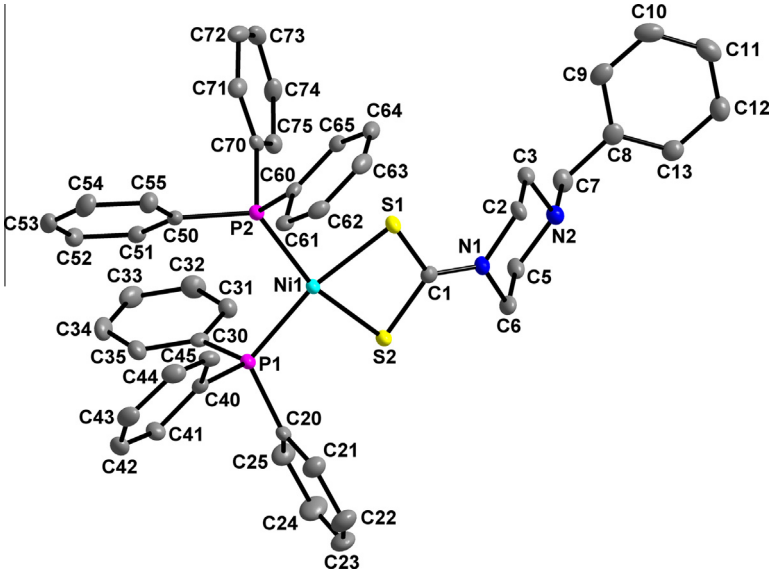


Fig. 1. The molecular structure of [Ni(*bp*dtc)(PPh_3)$_2$]ClO_4·PPh_3 with non-hydrogen atoms drawn as thermal ellipsoids at the 50% probability level, the hydrogen atoms, perchlorate anion and PPh_3 molecule of crystallization were omitted for clarity.