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Crystal Structure of Bis(pyrrole-*N*-carbothioate)bis(triphenylphosphine)nickel(II), $C_{46}H_{38}N_2S_2P_2Ni$

JANE WELCH, CRAIG TUCKER, ROBERT BEREMAN and PHIRTU SINGH

Department of Chemistry, North Carolina State University, Raleigh, N.C. 27695-8204, U.S.A.

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Abstract

The crystal structure of $Ni(C_4H_4NCOS)_2[(C_6H_5)_3P]_2$, $Ni(ptc)_2(Ph_3P)_2$, has been determined by single crystal X-ray diffraction methods. This species exists as a square planar complex. The structure is monoclinic, $P2_1/n$, $a = 12.759(4)$, $b = 10.069(2)$, $c = 16.158(6)$ Å, and $\beta = 91.96(3)°$. The unit cell contains 2 formula units with an observed density of 1.31 g cm^{-3} (1.34 calculated). The final R index = 0.047 ($R_w = 0.038$) for 2618 non-zero reflections having $I > 3\sigma(I)$.

Experimental

Prismatic ruby red crystals were synthesized by the procedure of Baird [1] and recrystallized from tetrahydrofuran, from which a representative crystal was ground to spherical shape (0.2 mm diameter). A 1 Å data set (maximum $\sin\theta/\lambda = 0.5$) was collected on a Syntex P$\bar{1}$ diffractometer. The diffractometer was equipped with a graphite monochrometer and molybdenum radiation ($\lambda = 0.71069$ Å). Final unit cell dimensions were obtained by a least squares fit of 14 high angle reflections ($2\theta > 18°$). Systematic absences indicated that the crystal belonged to the monoclinic space group $P2_1/n$ ($h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$). One check reflection collected every 30 reflections revealed no unexpected variation in intensity. Four thousand and forty eight unique reflections in the range of $5° < \theta < 50°$ were recorded. Two thousand six hundred and eighteen of these (having $I > 3\sigma(I)$) were used in the structure analysis. Since the crystal had been ground to spherical shape and had a low absorption coefficient (6.82 cm^{-1}), no absorption corrections were made. No extinction corrections were made and none were indicated. Lorentz and polarization corrections were made. Atomic scattering factors were taken from the International Tables for X-Ray Crystallography [2], except for hydrogen which was taken from Stewart, Davidson, and Simpson [3], and for nickel which was taken from Cromer and Mann [4]. All crystallographic calculations were performed using the program library of Professor Hodgson at the University of North Carolina at Chapel Hill. All diffractometer data were collected at room temperature. Pertinent crystal, data collection, and refinement parameters are summarized in Table I.

Table I. Single Crystal X-ray Crystallographic Analysis

Crystal data	
Formula	$C_{46}H_{38}N_2O_2S_2P_2Ni$
Molecular weight	835.6
Crystallization medium	THF
Crystal size	sphere 0.2 mm
Cell dimensions	a = 12.759(4) Å b = 10.069(2) Å c = 16.158(6) Å β = 91.96(3)
Volume	2075.0(1) (Å^3)
Space group	$P2_1/n$
Molecules/unit cell	2
Density obs. (aqueous KI)	1.31 (g cm^{-3})
Density calc.	1.34 (g cm^{-3})
$F(000)$	868 e$^-$
Data collection	
Diffractometer	Syntex P$\bar{1}$
Radiation	Mo Kα (0.7069 Å)
Monochrometer	graphite crystal
Temperature	ambient
2θ range	5–50°
Scan type	$\theta/2\theta$
Scan speed	4°/min
Octants collected	$-h00$, hkl
Background measurement	1/2 of total scan time at beginning and end of each scan
Standard reflections	1 every 30 reflections
Reflections collected	4048
Reflections observed	2618
Linear absorption coefficient	6.82 cm^{-1}
Refinement	
System used	library of Derek Hodgson
Solution	Multan
Final R index	R = 0.047 R_w = 0.038
Goodness-of-fit	1.52
Largest Δ/σ	0.04
Data-to-parameter ratio	11

0020-1693/86/$3.50

A trial structure was obtained from direct methods using Multan [5]. Subsequent difference Fourier maps revealed locations of remaining atoms. This trial structure refined routinely. Hydrogen positions were calculated. The hydrogen parameters were added to the structure factor calculations but were not refined. The final cycles of full matrix least-squares contained the scale factor, coordinates, and anisotropic temperature factors in a single matrix. The shifts in the final cycle were zero. The final R index was 0.047. A final difference Fourier revealed no missing or misplaced electron density. The data fit criteria (based on non-zero reflections) were

$$R = \Sigma||F_o| - |F_c||/\Sigma F_o = 0.049$$

$$R_w = \Sigma w[||F_o| - |F_c||]/\Sigma F_o^2 = 0.038$$

$$GOF^* = \Sigma(w[||F_o| - |F_c||]^2/N_o - N_v)^{0.5} = 1.52$$

The refined structure was plotted using the SHELXTL structure package (Fig. 1). Coordinates, distances and angles are given in Tables II and III. Thermal parameters are available (see 'Supplementary Material').

Results and Discussion

The pyrrole-*N*-carbothioate is bound in a monodentate manner to the Ni(II), with two triphenylphosphine molecules completing the coordination sphere. This structure exhibits square planar geometry because symmetry operations, defined by the space group, generate the remaining half of the molecule surrounding Ni(II). Analysis of IR spectrum data in the CO stretching region shows a band shifted to 1620 cm^{-1} from 1560 cm^{-1} supporting the monodentate bonding we see [1]. This structure contains the largest M–S bond distance (2.909(1) Å), and the largest C–N bond distance (1.425(4) Å), of any monothiocarbamate (monodentate and bidentate) reported to date. The C–S bond distance (1.739(4) Å) is comparable to the 4-coordinate structure of Zn(Pipmtc)·2Pip (1.79 Å) even though the Zn structure is tetrahedral [6].

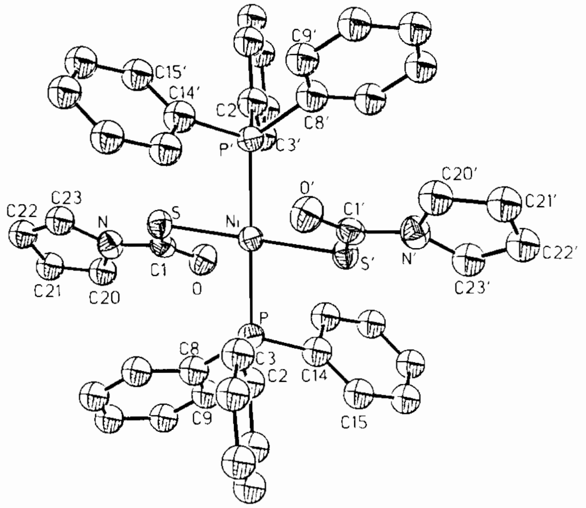

Fig. 1. Bis(pyrrole-*N*-carbothioate)bis(triphenylphosphine)-nickel(II). Rings are numbered sequentially.

TABLE II. Coordinates and their Standard Deviations

	x/a	*y/b*	*z/c*
Ni(II)	0.0000	0.0000	0.0000
P	0.1619(1)	0.0882(1)	0.0089(1)
S	−0.0082(1)	−0.0075(1)	−0.1367(1)
O	0.0100(2)	0.2540(2)	−0.1251(2)
N	0.0117(2)	0.1724(3)	−0.2558(2)
C1	0.0054(2)	0.1565(4)	−0.1685(2)
C2	0.2555(3)	−0.0383(3)	0.0462(2)
C3	0.2226(3)	−0.1695(4)	0.0523(2)
C4	0.2957(3)	−0.2658(4)	0.0769(3)
C5	0.3988(3)	−0.2334(5)	0.0950(3)
C6	0.4307(3)	−0.1031(5)	0.0884(2)
C7	0.3611(3)	−0.0059(4)	0.0628(2)
C8	0.2312(2)	0.1531(4)	−0.0805(2)
C9	0.2609(3)	0.2850(4)	−0.0858(3)
C10	0.3134(3)	0.3298(5)	−0.1552(3)
C11	0.3343(3)	0.2447(6)	−0.2189(3)
C12	0.3049(3)	0.1131(5)	−0.2136(3)
C13	0.2536(3)	0.0672(4)	−0.1446(2)
C14	0.1612(3)	0.2276(3)	0.0817(2)
C15	0.2263(3)	0.2395(4)	0.1514(2)
C16	0.2150(4)	0.3486(5)	0.2034(3)
C17	0.1402(4)	0.4435(5)	0.1870(3)
C18	0.0745(4)	0.4310(4)	0.1186(3)
C19	0.0843(3)	0.3233(4)	0.0665(3)
C20	0.0503(3)	0.2862(4)	−0.2913(3)
C21	0.0539(4)	0.2651(5)	−0.3741(3)
C22	0.0144(4)	0.1372(5)	−0.3900(3)
C23	−0.0101(4)	0.0804(4)	−0.3171(3)
HC3	0.146	−0.194	0.038
HC4	0.272	−0.363	0.082
HC5	0.451	−0.305	0.114
HC6	0.508	−0.078	0.101
HC7	0.385	0.092	0.056
HC9	0.244	0.349	−0.038
HC10	0.337	0.427	−0.158
HC11	0.372	0.279	−0.270
HC12	0.322	0.048	−0.260
HC13	0.231	−0.030	−0.141
HC15	0.282	0.168	0.164
HC16	0.262	0.359	0.255
HC17	0.133	0.523	0.225
HC18	0.018	0.502	0.105
HC19	0.034	0.313	0.015
HC20	0.074	0.371	−0.261
HC21	0.079	0.330	−0.418
HC22	0.006	0.092	−0.447
HC23	−0.040	−0.013	−0.308

**GOF*, goodness of fit.

TABLE III. Bond Distances (Å) and Bond Angles (°)

Bond distances		Bond angles	
Ni–S	2.909(1)	S–Ni–P	95.1(3)
Ni–P	2.249(1)	S–C1–O	127.2(2)
S–C1	1.739(4)	S–C1–N	114.1(2)
O–C1	1.207(1)	Ni–S–C1	105.1(1)
N–C1	1.425(4)	Ni–P–C2	109.4(1)
P–C2	1.833(3)	Ni–P–C8	123.7(1)
P–C8	1.839(4)	Ni–P–C14	108.5(1)
P–C14	1.831(4)	P–C2–C3	119.2(3)
C2–C3	1.390(5)	P–C2–C7	120.7(3)
C3–C4	1.394(5)	P–C8–C9	121.3(4)
C4–C5	1.376(5)	P–C8–C13	118.8(3)
C5–C6	1.379(6)	P–C14–C15	125.0(3)
C6–C7	1.375(5)	P–C14–C19	115.9(3)
C7–C2	1.402(4)	C3–C2–C7	119.8(3)
C8–C9	1.384(5)	C2–C3–C4	118.9(3)
C9–C10	1.400(6)	C3–C4–C5	121.4(4)
C10–C11	1.372(6)	C4–C5–C6	119.4(3)
C11–C12	1.380(6)	C5–C6–C7	120.6(3)
C12–C13	1.391(5)	C6–C7–C2	119.9(3)
C13–C8	1.386(5)	C9–C8–C13	119.8(4)
C14–C15	1.381(5)	C8–C9–C10	119.8(4)
C15–C16	1.393(6)	C9–C10–C11	120.6(4)
C16–C17	1.369(6)	C10–C11–C12	119.6(4)
C17–C18	1.370(6)	C11–C12–C13	120.3(4)
C18–C19	1.380(5)	C12–C13–C8	120.4(3)
C19–C14	1.390(5)	C15–C14–C19	119.0(3)
N–C20	1.379(4)	C14–C15–C16	119.2(4)
C20–C21	1.356(5)	C15–C16–C17	121.3(4)
C21–C22	1.404(6)	C16–C17–C18	119.7(4)
C22–C23	1.354(6)	C17–C18–C19	119.9(4)
C23–N	1.378(5)	C18–C19–C14	121.0(3)
		C1–N–C20	122.6(3)
		C1–N–C23	128.2(3)
		C21–N–C23	109.0(3)
		N–C20–C21	107.8(4)
		C20–C21–C22	107.4(4)
		C21–C22–C23	108.7(4)
		C22–C23–N	107.1(4)

Supplementary Material

Available from the authors on request.

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