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Geometrical Characteristics of Four-Coordinate Complexes of Ni, Pd, and Pt Containing Triphenylphosphine as Ligand

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Abstract. A statistical analysis based on crystal structure results of 4-coordinated complexes of Ni, Pd, and Pt containing triphenylphosphine as ligand has been performed using the Cambridge Structural Data Base. Distorted square-planar coordination appears as the most probable one presented by these metals.

Keywords: Structural data base; Four-coordinate complexes (Ni, Pd, Pt); Triphenylphosphine.

Geometrische Charakteristika von vier-koordinierten Komplexen des Ni, Pd und Pt mit Triphenylphosphin als Ligand

Zusammenfassung. Es wurde unter Verwendung der Cambridge Strukturdatenbank eine statistische Analyse von Resultaten an vier-koordinierten Komplexen des Ni, Pd und Pt mit Triphenylphosphin-Ligand durchgeführt. Dabei ergab sich eine verzerrte quadratisch-planare Koordination als die am meisten wahrscheinliche Geometrie.

Introduction

The present work deals with a study on the coordination geometry of Ni, Pd, and Pt complexes observed in crystal structures as retrieved from the Cambridge Structural Data Base, CSD[1]. Data containing triphenylphosphine (PPh_3) as main ligand were considered, since just only a few examples displaying cyclopentadiene, cycloctadiene and acetylacetonate as bridging ligand were found, too few for a statistical analysis.

Method

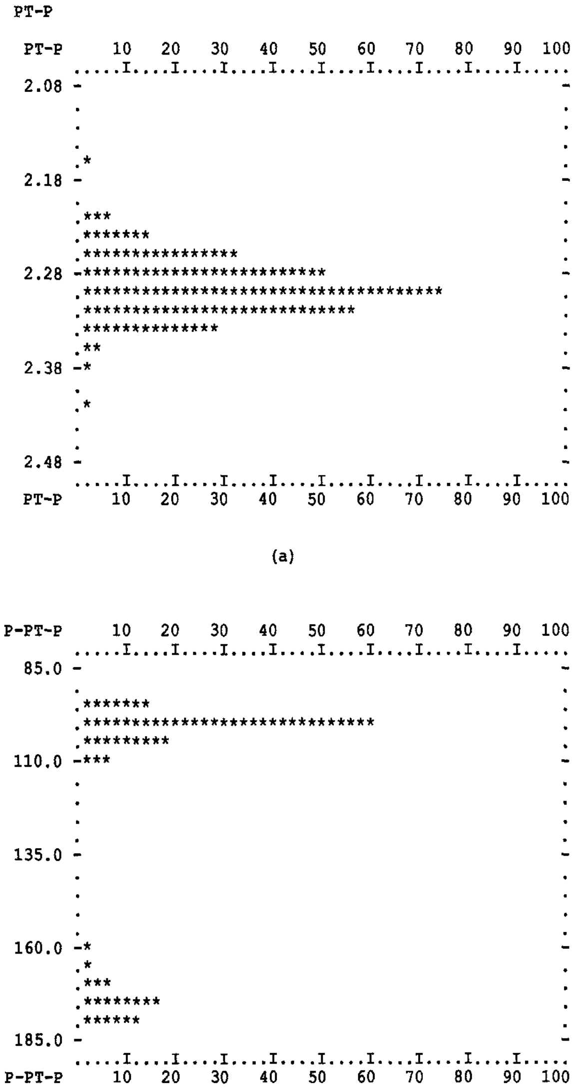
Out of the 78641 entries (CSD, January 1990 version), 1150, 770 and 1456 correspond to these metals after the following acceptance criteria: 1) data free of error at 0.02Å level, 2) structures without disorder, 3) R factor less than 0.100, 4) atomic coordinates present, and 5) no other metals bonded to the target ion. Of those entries 37, 55 and 165 hits presenting at least one PPh_3 as ligand may be put in the following order:

	Ni		Pd		Pt	
P*Ph*$_3$	SP	T	SP	T	SP	T
1	9	4	27	0	42	0
2	14	8	27	0	123	0
3	0	2	0	0	0	0
4	0	0	0	1	0	0

Initially, a classification concerning the type of coordination, either square-planar (SP) or tetrahedral (T), was performed. Both types are presented around the Ni and Pd atoms (see above), while the square-planar is the only one exhibited by the Pt atom.

Results and Discussion

Tables 1–3 summarize the results for the tetrahedral and the square planar coordination. Due to the number of data, only the Pt–P and P–Pt–P histograms



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PT-P

 PT-P      10   20   30   40   50   60   70   80   90  100
       .....I....I....I....I....I....I....I....I....I.....
 2.08  -                                                 -
       .                                                 .
       .                                                 .
       .                                                 .
       .*                                                .
 2.18  -                                                 -
       .                                                 .
       .***                                              .
       .*******                                          .
       .****************                                 .
 2.28  -*************************                        -
       .*************************************            .
       .****************************                     .
       .**************                                   .
       .**                                               .
 2.38  -*                                                -
       .                                                 .
       .*                                                .
       .                                                 .
       .                                                 .
 2.48  -                                                 -
       .....I....I....I....I....I....I....I....I....I.....
 PT-P      10   20   30   40   50   60   70   80   90  100
```

(a)

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P-PT-P     10   20   30   40   50   60   70   80   90  100
       .....I....I....I....I....I....I....I....I....I.....
 85.0  -                                                 -
       .                                                 .
       .*******                                          .
       .******************************                   .
       .*********                                        .
110.0  -***                                              -
       .                                                 .
       .                                                 .
       .                                                 .
       .                                                 .
135.0  -                                                 -
       .                                                 .
       .                                                 .
       .                                                 .
       .                                                 .
160.0  -*                                                -
       .*                                                .
       .***                                              .
       .********                                         .
       .******                                           .
185.0  -                                                 -
       .....I....I....I....I....I....I....I....I....I.....
P-PT-P     10   20   30   40   50   60   70   80   90  100
```

(b)

Fig. 1. (a) Pt–P and (b) *P*–Pt–P histograms for the 2 P*Ph*$_3$ set

Table 1. Summary of the geometrical results corresponding to the tetrahedral coordination (Å, °)

a) 1 PPh_3: Ni–P=2.298(47) Å (4 compounds, too few)

b) 2 PPh_3

	Ni–P	Pl1 ^ Pl2	P–Ni–P
Xm	2.294	91.0	113.4
S	0.053	4.1	5.7
Range	2.221–2.423	81.7–94.5	105.3–121.1
N	16	8	8

c) 3 PPh_3: Ni–P=2.301(29) Å (2 compounds, too few)

Xm and *S* stand for the unweighted mean and the standard deviation of the sample, *N* is the number of data entering in averages, the Pl1 and Pl2 coordination planes are defined as: *L*1–*M*–*L*2 and *L*3–*M*–*L*4. The corresponding Pd complex, being just one Pd (PPh_3)$_4$, was left out

Table 2. Summary of the geometrical results corresponding to the square-planar coordination (Å, °)

a) 1 PPh_3

		M–P	Pl1 ^ Pl2
Ni	*Xm*	2.193	5.7
	S	0.044	3.6
	Range	2.136–2.275	2.0–13.8
	N	9	9
Pd	*Xm*	2.267	6.6
	S	0.037	5.2
	Range	2.220–2.362	1.0–19.3
	N	32	32
Pt	*Xm*	2.279	6.6
	S	0.042	6.2
	Range	2.209–2.354	1.3–32.8
	N	52	52

b) 2 PPh_3

		M–P	Pl1 ^ Pl2
Ni	*Xm*	2.188	6.9
	S	0.034	5.4
	Range	2.147–2.249	0.0–27.5
	N	24	12
Pd	*Xm*	2.332	7.8
	S	0.015	6.1
	Range	2.281–2.369	0.0–21.9
	N	56	28
Pt	*Xm*	2.296	6.3
	S	0.032	4.7
	Range	2.151–2.366	0.0–23.9
	N	262	131

Xm, *S*, *N* and Pl1, Pl2 have the same meaning as in Table 1 of the 2 P*Ph*$_3$ set are shown in Fig. 1. It is worth noting that, although given the small amount of samples (9), the average Ni–P distances, (2.193 and 2.188 Å) for the square planar coordination, are significantly shorter at a 99.9% level [2], than those of the tetrahedral case (2.294 Å). Within Table 2 and with the exception of the Ni complexes, (small size sample for 1 P*Ph*$_3$ set), the *M*–P (*M*=Pd, Pt) distances increase with the number of P*Ph*$_3$ involved in the coordination (at 99.9 and 99.0% significant levels, respectively). It can be also noted that the *M*–P distances increase following the sequence Ni, Pd, and Pt for the 1 P*Ph*$_3$ and Ni, Pt, Pd for the 2 P*Ph*$_3$ set respectively (the differences within each sequence being significant at the 99.9, 80.0 and 99.9, 99.9% level, respectively).

Moreover, some additional differences could be observed if the situation of the 2 P*Ph*$_3$ ligands (*cis* versus *trans*) is taken into account (Table 3). Smaller *M*–P

Table 3. Geometrical results corresponding to the square-planar coordination for the 2 P*Ph*$_3$ set (Å, °), depending on the relative position of P*Ph*$_3$

a) *Cis* position

		Ni	Pd	Pt
M–P	*Xm*	2.175	2.329	2.292
	S	0.023	0.023	0.035
	Range	2.147–2.249	2.281–2.369	2.151–2.366
	N	20	20	196
Pl1^Pl2	*Xm*	9.6	8.6	6.8
	S	6.5	6.3	4.4
	Range	5.5–27.5	0.9–21.9	0.2–22.2
	N	10	10	98
P–*M*–P	*Xm*	108.9	102.6	100.8
	S	3.9	4.1	3.8
	Range	99.6–113.0	98.1–109.3	93.1–111.6
	N	10	10	98

b) *Trans* position

		Ni	Pd	Pt
M–P	*Xm*	2.241	2.333	2.311
	S	0.011	0.009	0.017
	Range	2.225–2.249	2.319–2.351	2.267–2.343
	N	4*	36	66
Pl1^Pl2	*Xm*	0*	7.4	5.3
	S	0	6.0	5.5
	Range	–	0.0–18.2	0.0–23.9
	N	2	18	33
P–*M*–P	*Xm*	180.0*	174.3	176.3
	S	0.0	5.5	3.0
	Range	180.0–180.0	161.3–180.0	169.5–180.0
	N	2	18	33

* The complex is placed at a symmetry center, so only one half of the complex has been considered

lengths for *cis* than for *trans*, and P–*M*–P angles decreasing along the series Ni, Pd, Pt, for the *cis* set; however, no significant differences from linearity have been observed for the *trans* set.

If all P–*M* lengths are averaged for each metal (considering neither the number of P*Ph*$_3$ involved nor the type of coordination), the values agree quite well with those reported by Orpen et al. [3] (CSD September 1985 version, 49854 entries); the main differences concern the long Ni–P bond, 2. 321 Å (12) (6 data in that paper), versus 2.296(47) Å (15 compounds and 24 distances) displayed by the tetrahedral coordination in the present study; however, the differences may not be significant due to the scarce number of data.

The deformation of the square planar coordination tested by computing the least-squares plane through the four ligands (those mid point of the double bond,

Table 4. Summary of the double and triple bonds involved in the coordination (Å); no compounds were found for Pd

a) Double bond C=C	Ni	Pt
Xm	1.432	1.490
S	0.016	0.058
Range	1.412–1.452	1.416–1.621
N	4	12
b) Triple bond C≡C		
Xm	1.240	1.262
S	0.016	0.036
Range	1.227–1.255	1.204–1.296
N	3	5

Table 5. *Trans* effect: influence of the Cl and P*Ph*$_3$ ligand on the *M* – Cl bond

a) Cl atom *trans* to Cl		Ni	Pd	Pt
M–Cl	*Xm*	2.154	2.292	2.301
	S	–	0.014	0.003
	Range	–	2.279–2.307	2.298–2.305
	N	1	3	4
b) P*Ph*$_3$ *trans* to Cl		Ni	Pd	Pt
M–Cl	*Xm*	–	2.378	2.347
	S	–	0.026	0.019
	Range	–	2.360–2.416	2.311–2.396
	N	0	4	11

when this is involved in the coordination) present larger deviations than the corresponding expected χ^2 values, thus the angles between planes, defined as $L1{-}M{-}L2$ and $L3{-}M{-}L4$, are considered ($L1{=}L2{=}\mathrm{P}Ph_3$ when 2 PPh_3 *cis*-set is used) as a measure of the distortion in the coordination. Inspection of Tables 1–3 shows a broad variety of distortion from the square planar coordination, which is indicated by the wide range of the estimator.

The lengthening of double or triple bonds involved in the coordination versus the unaffected ones[4], 1.317(15) and 1.181(14) Å, has been considered and the results are presented in Table 4. The influence of ligands on *trans* metal-ligand distances (*trans* effect ligands such as Cl and PPh_3 considered as modest and strong σ-donor and modest π-acceptors [5]) is reflected in Table 5, which shows greater M–Cl (M=Pd, Pt) lengths when the phosphine (and not Cl) is acting as *trans*-ligand. Unfortunately, quite a few examples of both cases have been found within the analyzed data.

A list of refcode may be obtained from the authors on request.

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