



PHYSICAL CHEMISTRY 2006

Proceedings

*of the 8th International Conference
on Fundamental and Applied Aspects of
Physical Chemistry*

September 26-29,
Belgrade, Serbia

ISBN 86-82139-26-X
Title: Physical Chemistry 2006. (Proceedings)
Editors Prof. dr A. Antić-Jovanović
Published by: The Society of Physical Chemists of Serbia, Studentski trg 12-16, P.O.Box 137, 11001 Belgrade, Serbia
Publisher: Society of Physical Chemists of Serbia
For publisher: Prof. dr S. Anić, president of the Society of Physical Chemists of Serbia
Printed by: "Jovan" Printing and Published Comp;
250 Copies; Number of Pages: x + 442; Format B5;
Printing finished in September 2006.
Text and Layout: Aleksandar Nikolić
250 – copy printing

STACKING INTERACTIONS BETWEEN CHELATE AND PHENYL RINGS IN SQUARE-PLANAR COMPLEXES OF Cu, Ni, Pt AND Pd

D. N. Sredojević², Z. D. Tomić¹ and S. D. Zarić²

¹*'Vinča' Institute of Nuclear Sciences, Laboratory of Theoretical Physics and Condensed Matter Physics, Belgrade, P. O. Box 522, Serbia,*

²*Department of Chemistry, University of Belgrade, Studentski trg 16, Belgrade, Serbia, szaric@chem.bg.ac.yu*

Abstract

Previous analysis of geometrical parameters in the crystal structure of square-planar complexes, with and without chelate rings, of all transition metals from Cambridge Structural Database shows that there are stacking interactions between the phenyl ring and the chelate ring with delocalized π -bonds. To investigate whether the type of metal atom influence this interaction we compare stacking parameters for the complexes with and without chelate rings in the complexes containing Cu(II), Ni(II), Pd(II) and Pt(II) metals. While the overall picture is similar for all four cases, complexes of Pd and Pt without chelate ring show tendency to form shorter contacts towards aromatic carbon. It was found that this behaviour is associated with the presence of cyano or isocyano derivatives as ligands.

Introduction

The noncovalent interactions of π -systems have been studied intensively in recent years. The importance of these interactions have been shown in different molecular systems from supramolecular structures to biomolecules. Recently, a few studies of noncovalent interactions with chelate ring as a π -system were published [1-4]. Chelate ring can be involved in CH/ π interactions with organic moieties [1-2] and in stacking interactions with phenyl rings [3-4].

Our previous results [4] show that there are stacking interactions between chelate and phenyl rings in square-planar transition metal complexes, indicating that chelate rings can behave similar to organic aromatic rings. Here we present results about stacking interactions of chelate and phenyl rings in square-planar complexes of Cu, Ni, Pd, and Pt.

Results And Discussion

By searching Cambridge Structural Database (CSD) many complexes with planar chelate ring with delocalized π -bonds and phenyl group were found. There are only four of metals (Cu, Ni, Pd, Pt) that have enough large number of structures that makes possible to analyze structures of these metals. All these metals have large tendency to make square-planar complexes.

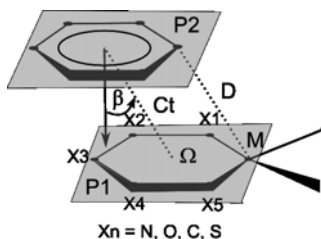


Fig. 1. Geometrical parameters describing interaction of square-planar complex with phenyl ring.

Crystal structures of complexes with and without chelate ring were separately analyzed for any of these four metals. As was shown for Cu [3] and all metals together [4], complexes of Ni, Pt and Pd (Figure 2) with chelate rings also show tendency for shorter metal-carbon distances, below the sum of van der Waals radii ($\Delta > 0$).

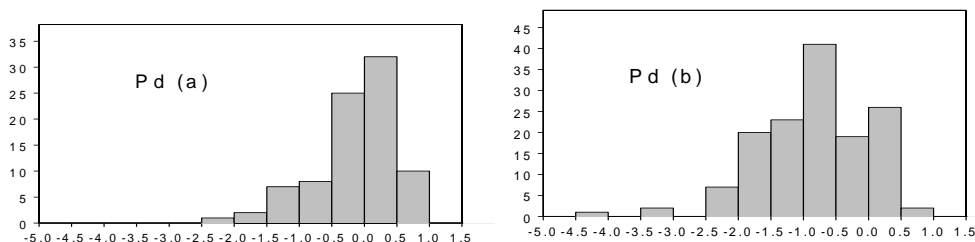


Fig. 2. Histograms showing the distribution of parameter Δ (Å) in crystal structure with (a) and without (b) chelate ring for Pd complexes. The parameter Δ is difference of sum of the van der Waals radii and the distance between the metal and the closest phenyl carbon (D) (Figure 1) ($\Delta = \Sigma vdW - D$).

Distributions of the angle θ in structures of Pd with and without chelate ring are shown in Figure 3. In the structures with chelate ring, phenyl ring has large tendency to be oriented approximately parallel to the mean coordination plane (Figure 3a). Other metals (Cu, Ni, and Pt) show similar tendency.

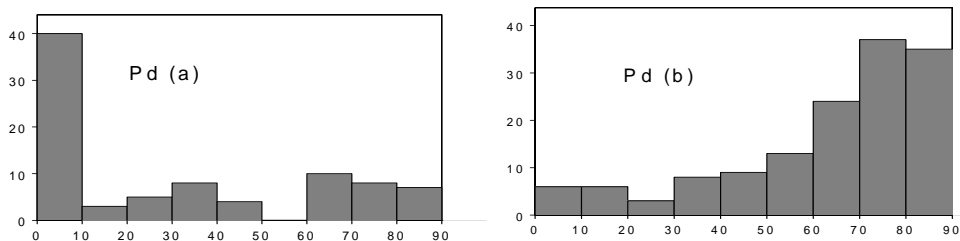


Fig. 3. Histograms showing the distribution of the dihedral angle θ (°) between the mean plane of the phenyl ring (P2) and the mean plane of the metal with coordinated atoms (P1) with (a) and without (b) chelate ring for Pd.

However, there are some differences for structures without chelate rings among metals. While in Ni and Cu complexes there is very small number of structures with $\theta < 20^\circ$ in cases of Pt and Pd there is larger number of structures with $\theta < 20^\circ$. We screened these complexes and found that in most cases when the dihedral angle is small ($\theta < 20^\circ$) there are short metal-carbon distances ($\Delta > 0.0 \text{ \AA}$). Further analyses show that in many cases these complexes possess common constitution of coordination sphere with coordinated cyano or isocyno phenyl derivatives.

Conclusion

Interactions of phenyl and chelate rings in crystal structures of square-planar complexes of every of four metals (Cu, Ni, Pd and Pt) show very similar behaviour. In complexes with chelate ring there are shorter metal-carbon distances and parallel orientation of phenyl ring with respect of chelate ring indicating that there are stacking interactions. However, there are some differences among metals for structures without chelate rings.

References

- [1] G. A. Bogdanović, A. S. Biré, S. D. Zarić, *Eur. J. Inorg. Chem.*, 2002, 1599-1602.
- [2] A. Castineiras, A. G. Sicilia-Zafra, J. M. Gonzáles-Pérez, D. Choquesillo-Lazarte, J. Nicolás-Gutiérrez, *Inorg. Chem.*, 2002, **41**, 6956-6958.
- [3] Z. D. Tomić, S. B. Novaković, S. D. Zarić, *Eur. J. Inorg. Chem.*, 2004, 2215-2218.
- [4] Z. D. Tomić, D. N. Sredojević, S. D. Zarić, *Crystal Growth & Design.*, 2006, **6**(1), 29-31.