Intermolecular Interactions between Chelate Rings and Phenyl Rings in Square-Planar Copper(II) Complexes

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Keywords: Chelate rings / Delocalized π-bonds / Copper / Aromaticity / Stacking interactions

Analysis of the geometrical parameters in crystal structures of square-planar copper(II) complexes from the CSD shows that the short noncovalent copper(II)–phenyl carbon distances are a consequence of the interaction between the phenyl ring and the chelate ring with delocalized π-bonds. The data show a correlation between the distances between the centers of the chelate and phenyl rings and the copper(II)–carbon distances, as well as a mutual slipped-parallel orientation of the phenyl and chelate rings.

Introduction

The investigation of noncovalent interactions is of continuing interest.[1−8] Noncovalent interactions involving metal atoms has gained particular attention with the recognition that metal atoms can bind to the phenyl ring; and this can be explained in terms of cation−π interactions.[9−14] Cationic metal complexes are involved in similar metal−ligand aromatic cation−π interactions[15−18] that can also be considered as a type of X−H···π hydrogen bond.[19−22] The importance of this interaction in protein structures has been shown previously.[15]

Recently, a few studies of noncovalent interactions of chelate rings with delocalized π-bonds have been published.[23−25] We have reported[24] the structure of the square-planar bis(acetone-1-naphthoylhydrazinato)copper(II) complex. In this structure the closest intermolecular distance between the copper(II) and aromatic carbon atom is 3.185(3) Å, which is below the sum of van der Waals radii (4.05 Å). Similar arrangements have been found previously,[26−28] and on the basis of geometrical characteristics it was proposed that phenyl carbon is part of the copper(II) coordination sphere. Besides providing linkages, these contacts may also serve as a path for exchange interactions. The EPR studies on the single-crystal samples of (L-tryptophanyl-glycinato)copper(II)[29] suggest that magnetic interactions are transmitted through cation−π contacts.

The observed mutual slipped-parallel (offset face to face) orientation of the chelate ring, with delocalized π-bonds, and the phenyl ring,[24] resemble the stacking orientation of two benzene molecules.[30] We assumed that chelate rings with delocalized π-bonds can be involved in noncovalent interactions in ways similar to aromatic organic molecules. A calculation of the partial atomic charges of the chelate and phenyl rings in the bis(acetone-1-naphthoylhydrazinato)copper(II) complex has been performed.[24] The distribution of charges in these two rings is very similar to that observed in complexes with the slipped-parallel interaction between two benzene rings, further supporting the stacking interaction between the phenyl and chelate rings.[24]

The role of the chelate ring in the position of the phenyl ring has also been discussed in the analysis of the crystal structure of aqua(2-benzylmalonato)(1,10-phenanthroline)copper(II) trihydrate.[25]

The assumption that copper(II)−carbon contacts arise as a result of the interactions between the chelate and phenyl rings prompted us to investigate the chelate-ring to phenyl-ring interactions in the crystal structures of copper(II) complexes. We now report on a study based on analyzing the crystal structures in the Cambridge Structural Database (CSD), since by analysing crystal structures from databases it is possible to elucidate the facts about intermolecular and intramolecular interactions.[31−33] To the best of our knowledge this is the first systematic study of chelate-ring to phenyl-ring interactions.

Results and Discussion

For the investigated data set of 487 crystal structures we calculated the closest intermolecular distance between the copper(II) and phenyl carbon (D) atoms (Scheme 1). This distance has a range of 3.06−8.96 Å. In order to establish

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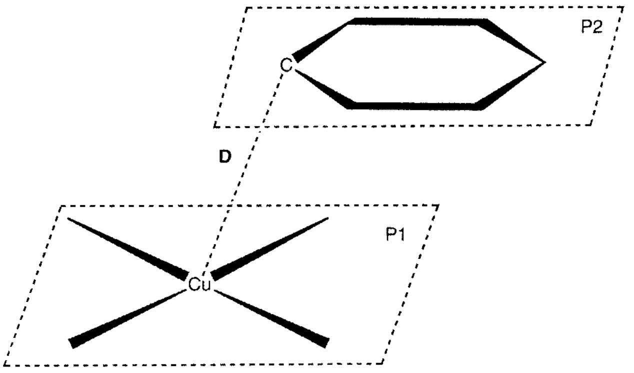
DOI: 10.1002/ejic.200400086

if the presence of the chelate ring has an influence on the copper(II)−carbon distance, the distribution for the copper(II)−carbon distances (D) were compared for complexes with and without a chelate ring (Figure 1).



Scheme 1

In the complexes without a chelate ring the peak of distribution is in the region above the sum of the van der Waals radii (4.05 Å), while in the complexes with a chelate ring the peak of distribution is in the region below the sum of the van der Waals radii. Hence, in the presence of a chelate ring with delocalized π-bonds there is a close contact between the copper(II) atom and the carbon atom of the phenyl ring.

Another important difference between complexes with and without a chelate ring is seen when looking at the distribution of the dihedral angles θ, the angle between the mean plane of the phenyl ring (P2) and the mean coordination plane (P1) (plane consisting of copper and coordinated atoms). The planes are shown in Scheme 1. In the histogram for the structures with chelate rings, the peak of distribution is in the region of the small angle θ, where the phenyl ring is oriented in an approximately parallel manner to the mean coordinating plane (Figure 2). In the histogram for the structures without the chelate rings the peak of distribution is in the region of the large angle θ, where the phenyl ring is almost normal to the coordinating plane; there are no structures with a dihedral angle of less than 10° (Figure 2).

The data in Figure 1 and Figure 2, the short copper(II)−carbon distances, and the tendency for a parallel orientation of the phenyl ring in complexes with chelate rings, indicate possible phenyl-ring to chelate-ring stacking interactions.

In order to verify that the interaction between the chelate ring and the phenyl ring is really responsible for the shorter copper(II)−carbon distances observed in the complexes with chelate rings, the values of the distances between the centers of the chelate and phenyl rings (Ct) are plotted versus the copper(II)−carbon distance (D) (Figure 3). The plot shows that there is a correlation between the distance Ct and the distance D; the copper(II)−carbon distances are shorter when there is a short distance between the centers of the chelate and phenyl rings. This correlation can only exist if the chelate and phenyl rings tend to overlap each other. Hence, the interaction between the phenyl and chelate rings is responsible for the short copper(II)−carbon distances.

The positions of the phenyl rings with respect to the chelate rings, indicates that, in all cases with small θ angles, the two rings are in mutual slipped-parallel orientations (offset face to face). This is in agreement with the previously observed slipped-parallel orientation in the bis(acetone-1-naphthoylhydrazinato)copper(II) complex.[24] Additional support for the idea that the interaction between the chelate ring and the phenyl ring is similar to the interaction between two benzene molecules has been provided by the distribution of the calculated partial atomic charges[24] which are similar to those observed in complexes with stacking interactions between two benzene molecules.[30]

Conclusion

Our analyses of the geometrical parameters in the crystal structures of copper(II) square-planar complexes from the CSD show that in cases where a chelate ring with delocalized π-bonds is present, the peak of the distribution of the copper(II)−phenyl carbon distances is in the region be-

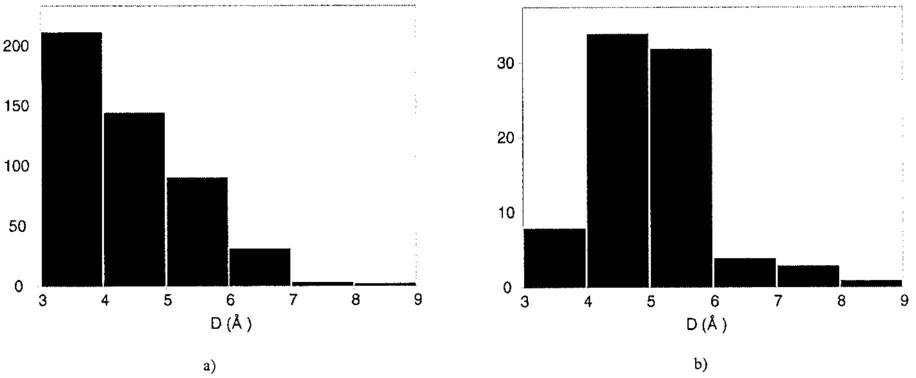
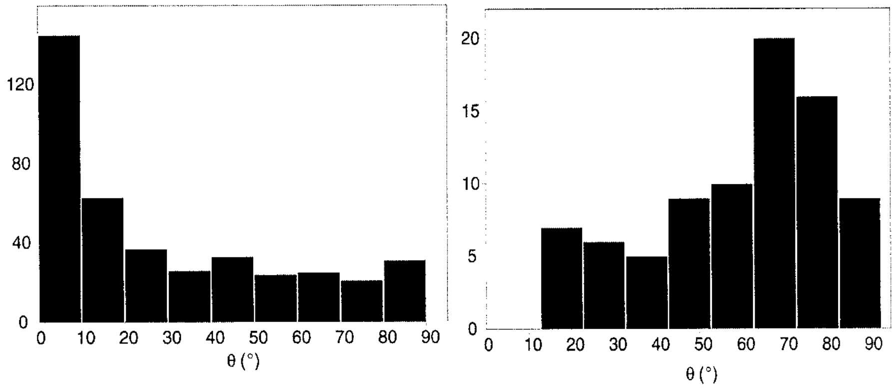


Figure 1. Histograms showing the distribution of the parameter *D*, copper(II)−carbon distance, in structures with (a) and without (b) chelate rings



a) b)

Figure 2. Histograms showing the distribution of the dihedral angle θ between the mean plane of the phenyl ring and the mean plane of copper(II) with coordinated atoms (Scheme 1); a) with chelate rings; b) without chelate rings

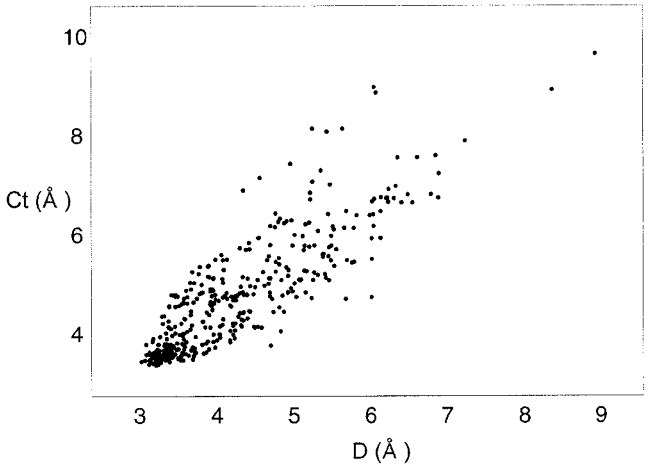


Figure 3. Plot of the distances between the centers of the chelate and phenyl rings (Ct) versus the copper(II)−carbon distance *D*

low the sum of van der Waals radii. The correlation between the copper(II)−carbon distances and the distances between the centers of the chelate and phenyl rings, as well as the mutual slipped-parallel orientation of the two rings, show that stacking interactions between phenyl and chelate rings are similar to the stacking interactions between two benzene rings.

Experimental Section

A Cambridge Structural Database (CSD)[34] search was performed for mononuclear copper(II) complexes having exactly four single bonds to atoms belonging to groups 5A, 6A or 7A. The oxidation state of copper was taken as those given by the authors. To exclude the possible influence of the constraints in the molecule we only looked at the intermolecular contacts between the copper(II) atom and the carbon atom of the phenyl ring. As a convenient choice for this investigation, we concentrated on square-planar copper(II) complexes due to the relative planarity of such molecules, and the absence of steric hindrance for the approach of other molecule into the axial position. To minimize the possible steric influence towards the approach of two molecules, the *trans* angles around the copper atom were constrained to lie between the 150 and 180°. To avoid problems which could possibly arise as a result of "structural inhomogeneity", we used structures that contain the phenyl ring as part of the complex molecule, and only those with one complex species in the asymmetric unit. Polymeric, disordered, and structures with $R > 0.10$ were excluded. This gave 487 entries. Among them 405 structures had five-membered or six-membered chelate rings. The bond lengths in the chelate rings indicate that in all the structures the chelate rings have delocalized π-bonds. When considering the influence of the chelate ring on the position of the phenyl ring, we took the distance between the centroids of the phenyl and chelate rings as a criteria. In cases with more than one chelate ring in the complex, we accepted the closest chelate ring as the one that is involved in the interaction with the phenyl ring.

Acknowledgments

The authors would like to thank Prof. E. W. Knapp and Prof. M. B. Hall for support. This work was supported by the ministry of science of the republic of serbia (grant I01795).

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[1] G. A. Jeffrey, W. Saenger, *Hydrogen Bonding in Biological Structures*, Springer, Berlin, **1991**.
[2] G. R. Desiraju, T. Steiner, *The Weak Hydrogen Bonds in Structural Chemistry and Biology*, Oxford University Press, **1999**.
[3] E. V. Pletneva, A. T. Laederach, D. B. Fulton, N. M. Kostic, *J. Am. Chem. Soc.* **2001**, *123*, 6232.
[4] N. Juranic, M. C. Moncrieffe, V. A. Likic, F. G. Prendergast, S. Macura, *J. Am. Chem. Soc.* **2002**, *124*, 14221.
[5] S. Yanagisawa, K. Sato, M. Kikuchi, T. Kohzuma, C. Dennison, *Biochemistry* **2003**, *42*, 6853.
[6] E. A. Meyer, R. K. Castellano, F. Diederich, *Angew. Chem. Int. Ed.* **2003**, *42*, 1210.
[7] T. Steiner, *Angew. Chem. Int. Ed.* **2002**, *41*, 48.
[8] O. Yamauchi, A. Odani, M. Takani, *J. Chem. Soc., Dalton Trans.* **2002**, 3411.
[9] J. C. Ma, D. A. Dougherty, *Chem. Rev.* **1997**, *97*, 1303.
[10] W. Schmitt, C. E. Anson, J. P. Hill, A. K. Powell, *J. Am. Chem. Soc.* **2003**, *125*, 11142.
[11] R. Amunugama, M. T. Rodgers, *Int. J. Mass Spectrom.* **2003**, *227*, 339.
[12] T. Lovell, F. Himo, W. G. Han, L. Noodleman, *Coord. Chem. Rev.* **2003**, *238*, 211.
[13] W. L. Zhu, X. J. Tan, J. H. Shen, X. M. Luo, F. Cheng, P. C.

Mok, R. Y. Ji, K. X. Chen, H. L. Jiang, *J. Phys. Chem. A* **2003**, *107*, 2296.
[14] D. Kim, S. Hu, P. Tarakeshwar, K. S. Kim, J. M. Lisy, *J. Phys. Chem. A* **2003**, *107*, 1228.
[15] S. D. Zaric, D. Popovic, E. W. Knapp, *Chem. Eur. J.* **2000**, *6*, 3935.
[16] S. D. Zaric, Chem. Phys. Lett. **1999**, *311*, 77; M. Milcic, S. D. Zaric, *Eur. J. Inorg. Chem.* **2001**, 2143.
[17] J. Sponer, J. E. Sponer, J. Leszczynski, *J. Biomol. Struct. Dyn.* **2000**, *17*, 1087.
[18] E. C. Magnuson, J. Koehler, G. Lamm, G. R. Pack, *Int. J. Quantum Chem.* **2002**, *88*, 236.
[19] S. D. Zaric, *Eur. J. Inorg. Chem.* **2003**, 2197.
[20] H. Suezawa, T. Yoshida, Y. Umezawa, S. Tsuboyama, M. Nishio, *Eur. J. Inorg. Chem.* **2002**, 3148.
[21] H. Kumita, T. Kato, K. Jitsukawa, H. Einaga, H. Masuda, *Inorg. Chem.* **2001**, *40*, 3936.
[22] D. U. Miodragovic, S. M. Milosavljevic, M. J. Malinar, M. B. Celap, N. Todorovic, N. Juranic, *Enantiomer* **2002**, *7*, 375.
[23] G. A. Bogdanovic, A. S. Bire, S. D. Zaric, *Eur. J. Inorg. Chem.* **2002**, 1599.
[24] Z. D. Tomic, V. M. Leovac, S. V. Pokorni, D. Zobel, S. D. Zaric, *Eur. J. Inorg. Chem.* **2003**, 1222.
[25] A. Castiñeiras, A. G. Sicilia-Zafra, J. M. González-Pérez, D. Choquesillo-Lazarte, J. Niclós-Gutiérrez, *Inorg. Chem.* **2002**, *41*, 6956.
[26] R. Fazlic, V. Divjakovic, V. M. Leovac, S. Y. Chundak, *Acta Crystallogr., Sect. C* **1991**, *47*, 714.
[27] H. Masuda, A. Odani, O. Yamauchi, *Inorg. Chem.* **1989**, *28*, 624.
[28] O. R. Nascimento, A. J. Costa-Filho, D. I. De Morais, J. Ellena, L. F. Delboni, *Inorg. Chim. Acta* **2001**, *312*, 133.
[29] A. J. Costa-Filho, O. R. Nascimento, L. Ghivelder, R. Calvo, *J. Phys. Chem. B* **2001**, *105*, 5039.
[30] S. Tsuzuki, K. Honda, T. Uchimaru, M. Mikami, K. Tanabe, *J. Am. Chem. Soc.* **2002**, *124*, 104.
[31] C. Janiak, *J. Chem. Soc., Dalton Trans.* **2000**, 3885.
[32] S. D. Zaric, D. Popovic, E. W. Knapp, *Biochemistry.* **2001**, *40*, 7914.
[33] T. Dudev, Y. I. Lin, M. Dudev, C. Lim, *J. Am. Chem. Soc.* **2003**, *125*, 3168.
[34] F. H. Allen, S. Bellard, M. D. Brice, B. A. Cartwright, A. Doubleday, H. Higgs, T. Hummelink, B. G. Hummelink-Peters, O. Kennard, W. D. S. Motherwell, J. R. Rodgers, D. G. Watson, *Acta Crystallogr., Sect. B* **1979**, *35*, 2331.

Received February 2, 2004