CONTACT CONFORMERS IN CRYSTALS OF COORDINATION COMPOUNDS

E. É. Lavut, P. M. Zorkii,
and N. Yu. Chernikova

UDC 541.63

In a continuation of the systematic study of contact conformers (coexisting molecules having different structures), a comparison of the structures of symmetrically independent molecules in the crystals of 37 coordination compounds have been compared. Fourteen cases of contact conformers have been detected and systematized. The earlier suggestion that contact conformers are more typical of crystals of coordination compounds than of organic crystals has been confirmed.

In most molecular crystal structures, all the chemically identical molecules (or polyatomic ions) are related by symmetry operations, and therefore have completely identical structures. At the same time, there also exist crystals in which molecules of the same kind occupy several systems of equivalent positions. The symmetrically independent molecules are situated in different environments (that is in different force fields) and may have different geometries. Thus in crystals of this kind, the coexistence in direct contact of molecules having different structures (conformers) is possible. These molecules have been called contact conformers [1].

Contact conformers in organic molecular crystals were examined in detail in [2], where the geometries of the independent molecules were compared for a large number of structures, and the principal types of contact conformers characteristic of crystals of organic compounds were distinguished. In [3], an analogous study of the crystal structures of coordination compounds was begun. In the present study, we have increased considerably (by a factor of 3) the volume of data on the comparison of molecules in crystals of coordination compounds, and this has made it possible to systematize various manifestations of contact conformers in substances of this class.

For a quantitative comparison of the geometries of the independent molecules, we used the procedure and program described in [4]. The integral criterion of similarity in molecules was the quantity $s = \left(\sum_{i=1}^{N} R_i^2/N \right)^{1/2}$, where N is the number of atoms in the molecule, and R_i represents the distances between corresponding atoms for the closest arrangement of the molecules (so-called deviations). The molecules being compared were assumed to be conformers when $s > 0.2$ Å. From the magnitude of the deviations it was possible to distinguish differing fragments of the molecules, and to determine the type of conformers* by comparing the values of the bond lengths and valence and twisting angles in the two independent molecules.

We examined structures of symmetrically independent molecules in the crystal structures of 37 coordination compounds (12 of these were described in [3]). Most of the crystals examined are homomolecular. In the case of heteromolecular structures we were interested only in molecules (or ions) containing a transition metal atom. The geometries of the molecules as a whole (hydrogen atoms were not considered) and the separate coordination polyhedra were compared. In nine structures, the independent molecules were found to be practically equal ($s \leq 0.1$ Å), in 14 they were close ($0.1 < s \leq 0.2$ Å), and contact conformers ($s > 0.2$ Å) were detected in 14 cases.† This result confirms the earlier suggestion [3] that the coexistence of conformers is more typical of crystals of coordination compounds than of organic crystals (~40 and ~20% respectively [1] of the number of structures with symmetrically nonequivalent molecules).

---

*In some cases, where the molecules being compared are fairly large, they may also be conformers for $s \leq 0.2$ Å.

†Molecules having high intrinsic symmetry can be superimposed in several ways, for which the values of the criterion s will differ slightly. In these cases we took the minimum value of the criterion s.

Chemistry Department, M. V. Lomonosov Moscow State University. Translated from Zhurnal Strukturnoi Khimii, Vol. 22, No. 5, pp. 89-93, September-October, 1981. Original article submitted July 8, 1980.

TABLE 1. Contact Conformers in Crystals of Coordination Compounds

No.	Compound	s, Å	R_{max}, Å	Types of conformational differences	Literature cited
1	$(CuC_5H_{10}N_2O_2)_4$	0,21	0,77	$M(c_1-c_2)$	5
2	$(AgN_5C_{17}H_{27})ClO_4$	0,23	0,54	П, $M(c_0-c_1;\ c_1-c_2)$	6
3	$\overline{MoC(O)(CMe)_4C(CF_3)O}C(O)(C_5H_5)$	0,28	0,78	φ_3, θ	7
4	$TcCl_3(PMe_2Ph)_3$	0,32	0,63	φ_2, φ_3	8
5	$[Co(C_4H_{13}N_3)_2]\ [Co(CN)_6]\cdot 2H_2O$	0,34	0,79	$M(\delta-\lambda)$	9
6	$[Co(C_6H_{16}N_4)\ (C_2H_4NO_2)]_3I_4\cdot H_2O$	0,35	0,82	$M(\delta-\lambda;\ c_0-c_1)$	10
7	$[ReH_2(NO)\ (PPh_3)_3]_2\cdot C_6H_6$	0,36	0,73	$\varphi_2(3)$	11
8	$[Fe(C_5H_5)\ (C_8H_{13}N)]_2[ZnCl_4]\cdot H_2O$	0,46	1,36	φ_1, φ_2	12
9	$Fe(CNCMe_3)_5$	0,51	1,33	$\varphi_3(4)$, 0	13
10	$Cu\{S_2CN(C_4H_9)_2\}_2I_3$	0,64	1,81	$M(c_0-c_1)$, φ_1, $\varphi_3(2)$	14
11	$[Cu(C_8H_7O_3)_2(C_5H_5N)_2]\cdot H_2O$	0,66	1,48	$M(c_0-c_1)$, φ_1	15
12	$[Pd(C_{10}H_8N_2)\ (C_{17}H_{14}O)]_2\cdot C_6H_6$	0,83	1,58	П, φ_2	16
13	$[(MeOOC)HC{=}C(COOMe)]Pd(PEt_3)_2\times$ $\times(C{\equiv}CPh)$	0,88	2,85	$\varphi_1(5)$, φ_2, 0	17
14	$[(MeC_6H_4{-}N{=}CH)\ (MeC_6H_4)N]HgPh$	1,02	1,92	П, $M(c_0-c_1)$, $\varphi_2(3)$	18

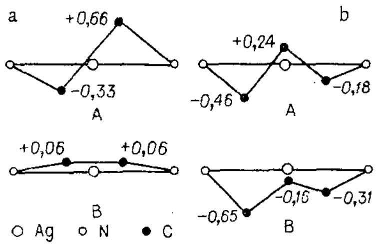

Fig. 1. Conformations of the metal-containing rings in $[AgN_5C_{17}H_{27}]^+$: a) five-membered ring; b) six-membered ring.

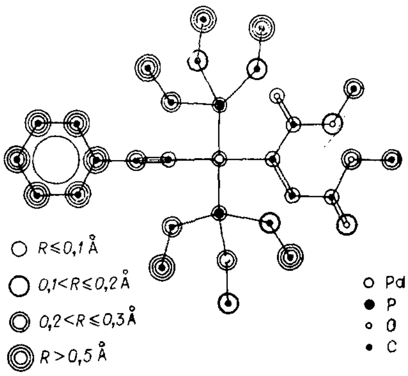

Fig. 2. Structure of the complex $[(MeOOC)\cdot HC=C(COOMe)]\cdot Pd(PEt_3)_2(C\equiv CPh)$.

Table 1 lists compounds in which contact conformers were detected and gives the values of the criterion s and the maximum deviations (R_{max}) for the molecules as a whole (compounds 5-8 and 11 were taken from [3]). The numbering of the substances in Table 1 is subsequently used to identify them. It should be noted that all the observed cases of contact conformers correspond to nonrigid molecules. At the same time, in seven structures with nonrigid molecules, contact conformers were not detected.

It can readily be seen that the manifestations of contact conformers should be much more varied in crystals of coordination compounds than in organic crystals. Thus in contrast to the approach used in [2], we distinguish not "types of contact conformers" but "types of conformational differences." The type of contact conformer in the present work is regarded as a definite combination of conformational differences.

Table 1 shows the types of differences observed in the structures of specific substances. We can explain the symbols used in Table 1. The letter П denotes any differences in the coordination polyhedron (comparison of the polyhedra gives $s > 0.1$ Å). The letter M indicates differences in the conformation of metal-containing rings, not affecting the coordination polyhedron. These differences are described in more detail in brackets. The letter c with a numerical subscript denotes a particular conformation of the metal-containing ring; different subscripts correspond to different conformations, and the subscript 0 indicates that the ring is planar. For example, the notation c_0-c_1 indicates that the metal-containing ring is planar in one molecule, and not in the other. This case is encountered most frequently. The symbol $\delta-\lambda$ shows that the metal-containing rings in independent molecules have different chirality.

These two types of conformational differences are specific for coordination compounds. Moreover, it might be expected that molecules of these compounds (in their organic parts) should show the same types of differences as were found in organic crystals. In fact, two of these were detected: rotation about a single bond and distortion of a valence angle (outside the coordination polyhedron).* These correspond to the symbols φ and θ in Table 1. Rotations about single bonds are separated into several types, depending on which groups of atoms are rotated: φ_1 denotes the rotation of a terminal bond, φ_2 rotation of a phenyl ring, and φ_3 rotation of some other polyatomic group. The numbers in brackets show the number of times a particular form of rotation appears in the structure of the given compound (if the molecule has crystallographic symmetry, the number of independent rotations is noted).

We can examine the types of conformational differences listed for specific examples. In the structure of the palladium complex 12, the independent molecules differ even within the coordination polyhedron (for the comparison of the polyhedra, s = 0.14 Å). The polyhedron in the molecule A can be described as a very extensively flattened tetragonal pyramid with the Pd atom at the apex, and that in the molecule B can be described as a tetrahedron (also flattened) with the metal atom at the center.

In the silver complex 2, two of the five metal-containing rings have different conformations in independent molecules. The five-membered ring $\overline{\text{Ag—N—C—C—N}}$ is planar in molecule B, and not in molecule A. The six-membered ring $\overline{\text{Ag—N—C—C—C—N}}$ has two different nonplanar conformations. The deviations of the C atoms in these rings from the N–Ag–N planes are shown in Fig. 1.

The independent molecules of the palladium complex 13 differ in the rotations about single bonds and the magnitude of one valence angle. Figure 2 gives the values of the deviations for the superposition of the coordination polyhedra; they show that differences appear only in the triethylphosphine and phenylethynyl ligands. In fact, five of the six ethyl groups are oriented in different ways in the independent molecules; the differences in the angles of rotation ($\Delta\varphi$) lie in the range from 12 to 68°. The phenyl rings are also rotated in different ways ($\Delta\varphi = 27°$). In addition, the nonequivalent molecules of the complex differ in the value of the angle $Pd-C\equiv C$ (178.2 and 171.2° in molecules A and B respectively). Generally speaking, a difference of 7° is not very large, but it is extremely significant for the angle at the triple bond $C\equiv C$. In a study [17] of the structure of the palladium complex 13, it was pointed out that one of the triethylphosphine ligands in molecule B is rotated through 120°C, compared with the position in molecule A. Our analysis does not confirm this description, however.

In the molybdenum complex 3, the independent molecules differ in the orientation of the CF_3 group. Somewhat unexpected features are the appreciable deviations ($\Delta\theta$) in the values of the valence angles of the type $F-C-F$ and $C-C-F$ ($\Delta\theta_{max} = 13.3°$), and also the difference of 0.12 Å for one of the interatomic $C-F$ distances. A similar picture is observed for the iron complex 9. Four of the five t-butyl groups in the nonequivalent molecules are rotated in different ways. Moreover, the differences in the valence angles $H_3C-C-CH_3$ reaches 12.4°, and the lengths of one of the terminal $C-C$ bonds differ by 0.14 Å. This marked deviation for one of several identical bonds, and also the scatter in the valence angles in the symmetric groups CF_3 and CMe_3, apparently indicate that the x-ray structural analysis of these compounds has a low accuracy.

To supplement Table 1, mention may be made of various specific conformational differences which appear in individual compounds. In the silver complex 2, the C atom of one of the two methyl groups is positioned in different ways in the independent molecules: in molecule B it lies in the average plane of a part of the polydentate ligand, and in molecule A it is displaced from it by 0.33 Å. The nonequivalent molecules of the palladium complex 12 differ in the conformation of the bipyridyl ligand: It is planar in one molecule, but in the other the six-membered rings are rotated slightly relative to one another. In the rhenium complex 7, the P atoms of the triphenylphosphine ligands in some cases are displaced from the planes of the phenyl groups joined to them, and in the two independent molecules they deviate to different extents and from different rings.

In conclusion it may be noted that in papers devoted to the x-ray structural study of crystals with symmetrically nonequivalent molecules, the question of the relationship between the geometries of the independent molecules is dealt with to different extents. In some studies [8, 16, 18], considerable attention is paid to this question. In [6, 7, 13, 14], the structures of the symmetrically nonequivalent molecules were not compared, and in [17] the comparison was inaccurate.

LITERATURE CITED

1. P. M. Zorkii and A. E. Razumaeva, Zh. Strukt. Khim., 20, 463 (1979).
2. A. E. Razumaeva and P. M. Zorkii, Zh. Strukt. Khim., 21, No. 2, 77 (1980).

---

*We have in mind differences in the valence angles not associated with differences in the conformations of the rings.

3. N. Yu. Chernikova, E. É. Lavut, and P. M. Zorkii, Koord. Khim., 5, 1265 (1979).
4. A. E. Razumaeva and P. M. Zorkii, Vestn. Mosk. Gos. Univ., Ser. Khim., 21, 27 (1980).
5. R. Mergehenn and W. Haase, Acta Crystallogr., B33, 1877 (1977).
6. M. S. Nelson, S. G. McFall, M. G. B. Drew, A. H. Othman, and N. B. Mason, J. Chem. Soc. Chem. Commun., 167 (1977).
7. J. L. Davidson, M. Green, J. Z. Nyathi, et al., J. Chem. Soc. Chem. Commun., 714 (1976).
8. G. Bandoli, D. A. Clementi, and U. Mazzi, J. Chem. Soc. Dalton Trans., 125 (1976).
9. M. Konno, F. Marumo, and Y. Saito, Acta Crystallogr., B29, 739 (1973).
10. D. A. Buckingham, P. J. Cresswell, R. J. Dellaca, et al., J. Am. Chem. Soc., 96, 1713 (1974).
11. G. Giani, D. Guisto, M. Manassero, and A. Albinati, J. Chem. Soc. Dalton Trans., 1943 (1976).
12. C. S. Gibbons and J. Trotter, J. Chem. Soc., A, 2659 (1971).
13. J. M. Bassett, M. Green, J. A. K. Howard, and F. G. A. Stone, J. Chem. Soc. Chem. Commun., 853 (1977).
14. J. G. Wijnhoven, T. E. M. van den Hark, and P. T. Beurskens, J. Cryst. Mol. Struct., 2, 189 (1972).
15. R. J. Hobson, M. F. C. Ladd, and D. C. Povey, J. Cryst. Mol. Struct., 3, 377 (1973).
16. C. G. Pierpont, R. M. Buchanan, and H. H. Downs, J. Organomet. Chem., 124, 103 (1977).
17. T. Yasuda, Y. Kai, N. Yasuoka, and N. Kasai, Bull. Chem. Soc. Jpn., 50, 2888 (1977).
18. L. G. Kuz'mina, N. G. Bokii, Yu. T. Struchkov, et al., Zh. Strukt. Khim., 18, 122 (1977).

AN X-RAY STRUCTURAL STUDY OF NONVALENCE INTERACTIONS AND COORDINATION IN ORGANOMETALLIC COMPOUNDS.

XX.* THE CRYSTAL STRUCTURE OF PHENYLMERCURY 2-DIMETHYLAMINOTHIOPHENOLATE

L. G. Kuz'mina, Yu. T. Struchkov,
E. M. Rokhlina, A. S. Peregudov,
and D. N. Kravtsov

UDC 548.737

The structure of phenylmercury 2-dimethylaminothiophenolate has been determined by x-ray diffraction (R = 0.0277 from 3227 reflections). The mercury atom has the typical linear configuration of the valence bonds, which have their usual lengths, Hg–C 2.076(6) and Hg–S 2.365(2) Å. At the same time, for the observed conformation of the molecule, the Hg atom approaches the N atom of the dimethylamino-group to a distance of 2.657(6) Å, corresponding to a secondary bond. The nitrogen atom has a pyramidal bond configuration, and its unshared electron pair is oriented towards the mercury atom. The presence of the secondary bond Hg...N does not lead to significant bending of the S–Hg–N unit (the angle at the Hg atom is 178.0(2)°).

INTRODUCTION

The ^{19}F NMR spectra of the PhHg-, Ph_3Sn-, and Ph_3Pb-derivatives of 2,6-dibromo-4-fluorothiophenol [2] and the ^{35}Cl NQR spectra of the corresponding derivatives of 2,6-dichlorothiophenol [3] indicate the existence of intramolecular coordination interactions in the PhHg-derivatives of o-halogeno-substituted thiophenols, both in solution and in the crystal.

On the other hand, according to the results of a study of exchange equilibria involving the PhHg-, Ph_2Sb-, Ph_3Sn-, and Ph_3Pb-derivatives of substituted thiophenols [4, 5], the five- and six-membered chelate rings in o-substituted phenylmercury thiophenolates in all cases are more stable than the chelate rings in the other organometallic derivatives of o-substituted thiophenols. At the same time, the study of organometallic derivatives of o-substituted thiophenols by x-ray structural analysis has shown, in particular, that there is no intra-

---

* For Part XIX, see [1].

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR. Translated from Zhurnal Strukturnoi Khimii, Vol. 22, No. 5, pp. 94-99, September-October, 1981. Original article submitted June 17, 1980.