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The molecular structure of some amorphous organogold compounds studied by the radial distribution function method

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Abstract

The method of radial distribution functions (RDF) of atoms obtained from powder X-ray diffraction patterns has been applied to the determination of the molecular structure of a number of polynuclear organogold derivatives in the form of amorphous powders. The distances between Au atoms producing the strongest peaks on RDF have been measured directly. The modes of addition of $(AuPPh_3)^+$ cation to aurated phenylacetylene, acetonitrile and diaurated malonitrile and the presence of binuclear groupings $(AuPPh_3)_2$ with a direct Au–Au bond, connected with cyclopentadienyl rings in tetragold derivatives of ferrocene, have been found.

The systematic study of the reactions of organic monovalent Au derivatives has yielded the new types of polynuclear Au complexes [1]. The structure of most of them has been reliably determined by single-crystal X-ray diffraction studies. However, in a number of cases, for the compounds obtained in the form of powders, the structure of the above complexes is usually assumed on the basis of spectral methods data, the analogies known and the similarity of their chemical behaviour [2–5]. Earlier [6] by using model compounds, it has been demonstrated that the distances between heavy atoms and sometimes the configuration of their relative positions in organometallic clusters can be determined by radial distribution functions (RDF) of powders. In the present work, the RDF techique was used to study the structure of a number of polynuclear organogold derivatives resulting from synthesis in the form of amorphous powder samples.

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Experimental

Here we describe the study of the following organogold complexes: $PhC{\equiv}C(AuPPh_3)_2BF_4$ (**1**) [2], $(\pi\text{-}C_5H_4)_2Fe(AuPPh_3)_4(BF_4)_2$ (**2**) [3], $NCCH_2(AuPPh_3)_2BF_4$ (**3**) [4], $(NC)_2C(AuPPh_3)_3BF_4$ (**4**) [5].

The experimental technique of X-ray scattering and the method of RDF calculation are presented in ref. 6. In the amorphous substances, in contrary to the polycrystalline ones, the noise of experimental data not only on the tail but over the whole scattering curve can be smoothed since the diffraction pattern contains only wide, diffuse peaks. Smoothing for substances **3** and **4** was according to ref. 6, and for **1** and **2** we used a special RDF calculation technique with the smoothing for liquids and amorphous bodies [7]. The formulae for model RDF calculations based on the supposed molecule structure are also given in ref. 6. Model parameters r_{kj} and σ_{kj} used in the text and figure captions are the mean distance between atoms of the k and j type and the mean-square deviation (due to molecule oscillations), respectively; N_{kj} is the total coordination number (formula 7 in ref. 6), the parameter defined by the arrangement of atoms in a molecular model. Parameter ρ_0, the mean density of the stoichiometric units, for amorphous substances had to be estimated by comparison with the density of crystals of molecules with closely analogous structures.

Results and Discussion

Figure 1 shows the RDF of the product of $(AuPPh_3)^+$ addition to $PhC{\equiv}CAuPPh_3$ (**1**). In the range of intramolecular distances (up to $r \approx 3.2$ Å) it is fully analogous to the RDF of binuclear Au derivatives, e.g. the RDF of diaurated malonitrile previously investigated [6]. The first two peaks are formed by the contributions from the C–C and P–C distances inside ligands ($r_{max} = 1.59$ Å) and those of Au–P and Au–C ($r_{max} = 2.29$ Å). The third peak with $r_{max} = 3.08$ Å, being the strongest, indicates directly the presence of closely located Au atoms in close proximity in the molecule. Its intensity, as is evident from the result of the model calculation in Fig. 1, corresponds to one Au–Au distance per stoichiometric unit $PhC{\equiv}C(AuPPh_3)_2BF_4$. Thus, the way of $(AuPPh_3)^+$ addition to diaurated phenylacetylene can be shown by the scheme at the top of Fig. 1, resulting in three-center two-electron bond formation with a bridging carbon atom [1] and a Au–Au bond length of about 3.08 Å. The Au–Au distance is probably somewhat smaller than this, since the peak maximum can be shifted by the contributions of far intramolecular and intermolecular distances. In this case, such contributions are essential, which is seen from the fact that the right-hand slope of the Au–Au model peak passes considerably lower than the experimental RDF.

Figure 2 shows the RDF of tetranuclear ferrocene derivative **2** where bonding of each cyclopentadienyl ring with a binuclear fragment including the Au–Au bond is assumed, as can be seen from the scheme of the molecular structure. Here, again, we have a typical strong peak at $r = 2.83$ Å, confirming the presence of Au–Au bonds of about the same length. The model calculation shows its intensity to be exhausted mainly by the contribution of distances Au–Au and Au–Fe in the structure assumed. Furthermore, up to $r \approx 5.5$–6 Å, the present RDF is similar in form to that of the ferrocene derivative containing the binuclear group $(Ph_3PAu)_2$ which is

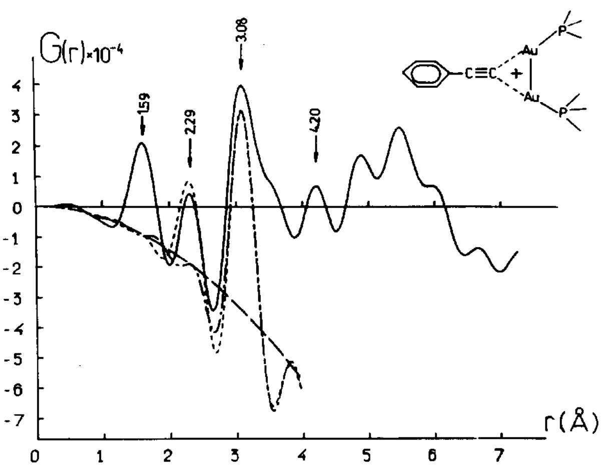


Fig. 1. The RDF of $PhC{\equiv}C(AuPPh_3)_2BF_4$ (1) together with the result of model calculation. Here and in the following figure: ——— Experimental RDF $G(r)$ (see definition in ref. 6); ·–·–· contribution from the distances between Au atoms; - - - - - - total contribution from all the nearest interatomic distances including Au atoms; — — — term $-4\pi\rho_0 r^2[\sum_j n_j f_j(0)]^2$ from eq. 4 in ref. 6. The absolute values of the contributions of different distances to RDF are measured from the latter curve. The parameters of model calculations (in the following order AuAu, AuP, AuC): $r_{kj} = 3.08, 2.29, 2.2$ Å; $\sigma_{kj} = 0.12, 0.1, 0.11$ Å; $N_{kj} = 2, 4, 4$; $\rho_0 = 0.00105$ Å^{-3}. The arrows indicate the positions of the maxima of the $G(r)$ peaks observed (values in Å). A schematic diagram of the important elements of the molecular structure is presented at the top right-hand corner.

analogously bound to only one of the cyclopentadienyl rings [8]. The RDF of this compound of known structure, has been obtained (see ref. 6, Fig. 2). Such a similarity confirms the suggested type of the Au-ferrocene bonding proposed for the sample under discussion. Unfortunately, in this case, the RDF fails to testify

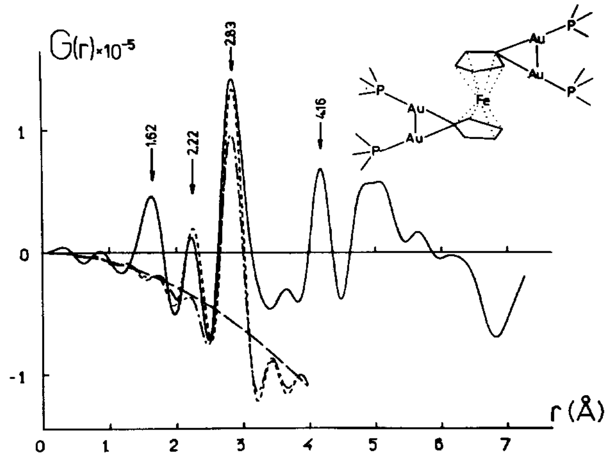


Fig. 2. The RDF of $(\pi\text{-}C_5H_4)_2Fe(AuPPh_3)_4BF_4$ (2). The parameters of model calculation (Au–Au, Au–Fe, Au–P, Au–C): $r_{kj} = 2.82, 2.87, 2.28, 2.2$ Å; $\sigma_{kj} = 0.11, 0.11, 0.1, 0.1$ Å; $N_{kj} = 4, 4, 8, 8$; $\rho_0 = 0.000523$ Å^{-3}.

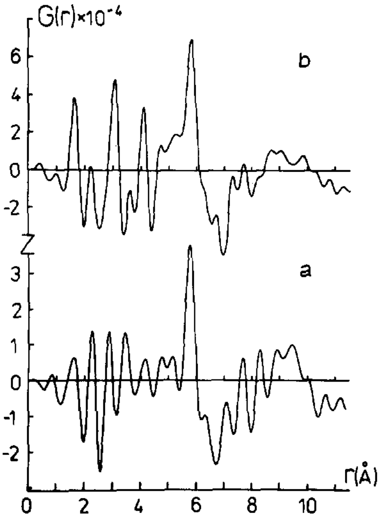
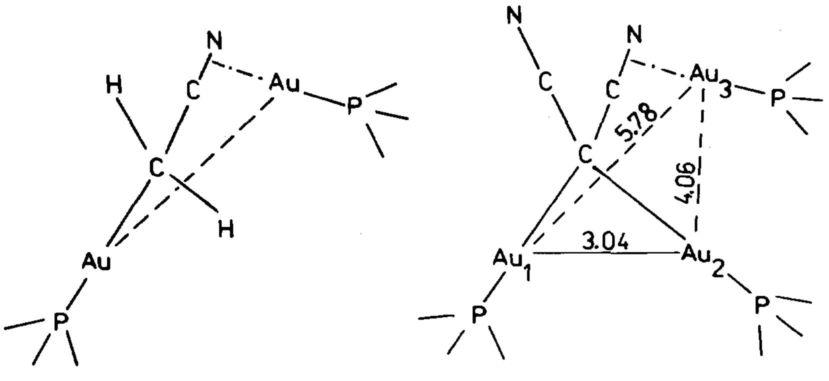


Fig. 3. (a) The RDF of $CH_2CN(AuPPh_3)_2BF_4$ (**3**); (b) $(CN)_2C(AuPPh_3)_3BF_4$ (**4**).

directly to the bonding of both fragments containing gold atoms to just one molecule of ferrocene, since the prominent peaks of the far intramolecular distances Au–Au are absent. In the amorphous substance, in contrast to a crystal, the molecules with a continuous and fairly wide set of angles of turn of one cyclopentadienyl ring relative to the other are likely to occur. This results in a considerable broadening of the distance distribution between Au atoms bonded to different rings. In such a case, the corresponding RDF peaks will not stand out against the background of intermolecular distances.

Figure 3 shows the RDFs of the product of the addition of cation $(AuPPh_3)^+$ to aurated acetonitrile **3** and to diaurated malonitrile **4**. The simultaneous consideration of these bi- and trinuclear cation complexes of gold substantially assists the structural interpretation of RDF. On the RDF of **3** only one strong peak is observed at $r = 5.74$ Å. Unfortunately, the contribution of intermolecular distances to the region of such r is so large that quantitative modelling of RDF is impossible here [6]. However, the random relative position and orientation of complexes in an amorphous substance means that the intermolecular distances have diffuse distributions and give rise to the broad peaks which form some of the background on the RDF. Thus a sharp prominent peak, visible against this background, can be assigned with certainty to the intramolecular distance Au–Au. The shape of the RDF at smaller r, for example, in the region of 3 Å, is not typical of compounds with an Au–Au bond, investigated previously [6] and described here. There is no peak of notable intensity, and the model calculation under the assumption, for instance, of the Au–Au bond length of 2.86 Å and typical $\sigma_{AuAu} = 0.1$ Å gives rise to a peak with a height beyond the scope of the figure. Thus, complex **3** has Au atoms which are widely spaced at 5.74 Å. This conclusion confirms the assumption of the coordination of the cation $(AuPPh_3)^+$ by the CN-group of aurated acetonitrile proposed previously [4]. The latter is also consistent with the fact that binuclear alkyl cation complexes of gold, where the structural fragment of carbometallocycle



(3) (4)

Fig. 4. The schemes of the structures of complexes 3 and 4, whose RDFs are shown in Fig. 3.

with a sp^3 hybridized bridging carbon atom should be realized, have so far not been obtained [1].

By transition to trinuclear complex 4 the prominent peak, which probably refers to the same distance as in 3, remains on its RDF at $r = 5.78$ Å. The shape of the RDF in the region of the nearest distances becomes typical for the substances with the Au–Au bond: the model calculation shows a peak at $r = 3.04$ Å to correspond by intensity to one Au–Au distance per stoichiometric unit (trinuclear gold complex). It was assumed that the Au–Au bond of the diaurated malonitrile fragment manifests itself here. The intensive narrow peak at $r = 4.06$ Å also results from the Au–Au distance in a complex. Thus, Au atoms in adduct 4 form a triangle with sides of about 3.04, 4.06 and 5.78 Å.

The analysis of the possible schemes of addition of the third group $(AuPPh_3)^+$ to diaurated malonitrile with respect to the distances found, have led to the model of complex 4, presented in Fig. 4. Atom Au(3) interacts with π-system of bond C≡N. The estimate with the help of atom coordinates and distances in diaurated malonitrile [5] demonstrates: if the angle between the planes Au(1)–Au(2)–C and Au(1)–Au(2)–Au(3) lies between 20° and 40°, the distance from Au(3) to the center of the C≡N bond is in the vicinity of 3 Å and with regard to model uncertainties it can be a bit less. At such a distance, the coordination interaction, resulting in the formation of an adduct, is quite possible.

The cation $(AuPPh_3)^+$ seems to be analogously bound to aurated acetonitrile in complex 3, whose structure is shown in Fig. 4. Complex 3 can be considered as some structural analogue of complex 4 where one of the CN-groups and the group $AuPPh_3$ are substituted by hydrogen. Here, it should be noted, that by considering the model of complex 3 independently, it would be possible to explain the only experimentally observed long distance Au–Au in terms of the bonding of $(AuPPh_3)^+$ to the lone electron pair of the nitrogen atom. As a result, one would have an approximately linear fragment C≡N → Au, assuming a Au ← N distance of about 2.1–2.2 Å. In this case, we have an interesting example, where the interpretation of a more informative RDF (three Au–Au distances) of a more complicated substance assists in providing a reasonable explanation of the RDF of a simpler compound, which give less detailed information.

Conclusion

By studying the molecular structure of noncrystallized compounds, one usually employs spectral methods which permit the detection of various characteristic atomic groupings. For clusters and polynuclear compounds the RDF method can be considered as one more method for which a group of heavy atoms (two or more) at sufficiently small distances from each other is the characteristic structural fragment. However, it can only be effective in the determination of the structure in conjuction with other methods. As can be seen from the discussion of the results, here we had to use previously obtained evidence for the organic part of the molecule. Still, for the class of compounds under consideration, direct data on the arrangement of heavy atoms are the key to elucidating their structure. Thus, the RDF method can prove to be rather useful.

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