

RADIAL DISTRIBUTION FUNCTION METHOD APPLIED TO STRUCTURAL STUDIES OF ORGANOMETALLIC CLUSTERS CONTAINING HEAVY METALS IN POWDER SAMPLES

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Summary

The distances between the heavy metal atoms of organometallic clusters can be measured directly in a powder sample (amorphous or polycrystalline). These distances produce the strongest, simply identified peaks in the radial distribution function (RDF), which is obtained by Fourier transformation of the X-ray powder diffraction pattern. The various models of cluster structure can be tested directly by comparing the experimental RDF with the calculated one. Practical possibilities of the method are investigated with the help of some substances of known structure.

Introduction

The development of direct methods for determining the molecular structure of compounds in amorphous and polycrystalline powder samples is an urgent problem. The present paper considers the possibility of its solution by the method of radial distribution functions (RDF) of atoms as applied to organometallic clusters. The RDF $G(r)$ is a spectrum of the interatomic distances of an isotropic sample, in particular, of a powder. Every pair of atoms corresponds to a $G(r)$ peak at a value of r equal to the distance between these atoms. This means that, in principle, the RDF provides the possibility of measuring interatomic distances in a powder.

In the general case, a one-dimensional spectrum, which is the superposition of contributions from all pairs of atoms in the system cannot be readily interpreted because of overlapping peaks. The method is practicable if the distances of interest are manifested in the RDF as peaks with dominant intensities. This is the situation observed for organometallic clusters involving compact groups of heavy metal atoms surrounded by ligands containing much lighter atoms. The peak intensity is approximately proportional to the product of the number of electrons in the pair which has induced the peak. As a result, the distances in the metallic nucleus of a cluster manifest themselves in the RDF as the most intensive peaks, and their

positions give the values of metal-metal distances in a first approximation. The intensity and shape of the RDF peaks can be calculated using the cluster structure model. This allows one to test various geometrical types of arrangements of metal atoms directly.

The RDF method is well known to be a basic method for structural investigations of non-crystalline substances (amorphous solids, liquids, solutions). However, it has never been applied to cluster compounds, which seem to be the most promising objects for its application in chemistry. Therefore, the aim of the present work was to study and demonstrate the possibilities of the RDF method applied to particular clusters. We used polycrystalline powders, whose molecular structures have been determined by X-ray analysis of single crystals.

The next section gives the main relations used for both experimental determination and model calculation of the RDF. Thereafter follows a brief account of the experimental technique and the method of RDF calculations. The last section is devoted to the data obtained from particular clusters of various geometries, containing very heavy metals (Au, Os, Re).

Some relations of the RDF method

The above formulation of the problem, with heavy atoms used as "labelled ones" pertains to the RDF obtained from experimental X-ray diffraction patterns. Such powder diffractograms are well known, particularly for polycrystalline specimens. The RDF $G(r)$ is determined as the Fourier transformation of the structure-sensitive part of the scattering curve $I(q)$, the so-called reduced intensity $qi(q)M(q)$ [1-4]

$$G(r) = \frac{2r}{\pi} \int_0^{q_{\max}} qi(q)M(q) \sin(qr) dq \quad (1)$$

Here, $q = 4\pi \sin \vartheta / \lambda$; ϑ is the half-angle of scattering; λ is the wavelength of the radiation;

$$i(q) = \frac{K}{P(q)A(q)} I(q) - \sum_j n_j f_j^2(q) - I_{\text{incoh}}(q); \quad (2)$$

K is the normalizing constant which reduces $I(q)$ to absolute (electronic) units; P and A are the so-called corrections for polarization and absorption, respectively; I_{incoh} is the incoherent (Compton) scattering intensity; \sum_j is the sum over types of atoms in the stoichiometric unit of a substance to which $I(q)$ is normalized; n_j and $f_j(q)$ are the number of j -type atoms and their atomic scattering amplitude, respectively; and

$$M(q) = \left[\sum_j n_j f_j(0) \right]^2 / \left[\sum_j n_j f_j(q) \right]^2. \quad (3)$$

As mentioned above, $G(r)$ consists of peaks at values of r equal to the interatomic distances. However, since the systems under discussion involve atoms with strongly differing atomic numbers, and the experimental information is limited (finite q_{\max} in eq. 1), $G(r)$ is not merely a weighted sum of the interatomic distance distributions [2,5]. The $G(r)$ peaks are of complicated shape. A full $G(r)$ is

represented as the superposition of the contributions from the distances between the k - and j -type atoms, $G_{kj}(r)$, as follows:

$$G(r) = -4\pi\rho_0 r^2 \left[\sum_j n_j f_j(0) \right]^2 + \sum_{kj} G_{kj}(r), \quad (4)$$

$$G_{kj}(r) = \frac{2r}{\pi} \int_0^{q_{\max}} q i_{kj}(q) M(q) \sin(qr) dq$$

where ρ_0 is the mean density of the stoichiometric units. To compare theoretical RDFs for geometrical models of atomic arrangement with experimental ones, it is necessary to calculate the so-called partial structure functions $i_{kj}(q)$, i.e. the diffraction at every pair of atomic types separately, and then to integrate formula (4) numerically.

Our main interest in the problem of the distribution of metal atoms in a cluster nucleus will be only certain, mainly the shortest, intramolecular distances and their contributions to the $G(r)$ of the system. In this case, a good approximation to $i_{kj}(q)$ is the Debye formula [1-4]

$$q i_{kj}(q) M(q) = f_k(q) f_j(q) M(q) \sum_m \frac{N_{kj}^m}{r_{kj}^m} \exp\left(-\frac{\sigma_{kj}^m}{2} q^2\right) \sin(\bar{r}_{kj}^m q) \quad (5)$$

where summation is carried out over the various types of distances between the k - and j -type atoms. This partial $i_{kj}(q)$ corresponds to a quasi-gaussian distribution for all types of distances with a radial density of the j -type atoms around the k -type ones, $\rho_{kj}^m(r)$

$$4\pi r \rho_{kj}^m(r) = \frac{N_{kj}^m}{\sqrt{2\pi} \sigma_{kj}^m \bar{r}_{kj}^m} \left\{ \exp\left[-\frac{(r - \bar{r}_{kj}^m)^2}{2\sigma_{kj}^m{}^2}\right] - \exp\left[-\frac{(r + \bar{r}_{kj}^m)^2}{2\sigma_{kj}^m{}^2}\right] \right\} \quad (6)$$

Here, and in eq. 5, the parameters for the m -type distances are \bar{r}_{kj}^m and σ_{kj}^m , which are the mean distance and root-mean-square deviation from it, respectively; and N_{kj}^m , which is the generalized coordination number,

$$N_{kj}^m = (2 - \delta_{kj}) \sum_t n_k^t C_{kj}^{tm} \quad (7)$$

Here $\delta_{kj} = 0$ at $k \neq j$ and $\delta_{kk} = 1$; n_k^t is the number of structurally equivalent k -type atoms, in stoichiometric units, with the t -type atomic surrounding; and C_{kj}^{tm} is the coordination number of the j -type atoms around the k -type ones for the m -type distances in the same t -type surrounding.

Thus, to compare this with an experimental RDF, the spatial molecule (cluster) model is transformed into the corresponding sets of interatomic distances r_{kj}^m and coordination numbers N_{kj}^m . The fit of the model to the experiment is verified by varying r_{kj}^m and σ_{kj}^m . When adjusting r_{kj}^m , one should use values close to the typical bond lengths, whilst in the case of valency-unbonded pairs of atoms, it is necessary to estimate typical r_{kj}^m values taking into account characteristic valence angles and limitations imposed by the model geometry adopted. In contrast to N_{kj}^m and r_{kj}^m , the quantity σ_{kj}^m is not an interesting molecular parameter to a chemist. However, it determines the shape of a model RDF (peak width and shape) substantially. This parameter is an analogue of the thermal parameters in X-ray single-crystal struct-

ural studies. For intramolecular distances, it is a result of amplitudes and correlation of the atomic motions in an oscillating molecule.

Experimental and RDF calculation technique

To measure the X-ray scattering intensity curves, $I(q)$, the powders, which had been ground up in a mortar, were placed into a thin-walled capillary tube (0.5–0.7 mm diameter, 0.01 mm thick walls) at the DRON-2 diffractometer axis. Only a few milligrams of the substance were required, in contrast to the standard reflection scheme of powder diffractometers. Monochromatic Mo- K_α radiation was used, which was provided by a flat graphite monochromator placed in the diffracted beam. This particular geometry of the experiment allowed us to eliminate the fluorescence of the metal atoms. An additional slit was set on the GUR-5 goniometer between the sample and the receiving slit of the monochromator to reduce the volume "visible" by the system to sizes slightly over the capillary tube diameter. As a result, unwanted air scattering (which is rather high at small scattering angles) was essentially reduced. The scattering intensity was measured at discrete angles within $1.5^\circ \leq 2\vartheta \leq 105\text{--}110^\circ$. The steps in the 2ϑ angle, determined by the sharpness of the peak, varied from 0.05 to 0.1° at small and middle angles, up to 0.4° at the $I(q)$ tails. The time taken to accumulate 2×10^4 pulses from the scintillation counter was measured at every angle. The 2ϑ resolution, estimated from the half-widths of quartz powder reflexes, was about 0.4° , which was a fairly rough value from the viewpoint of crystallographic standards. The low resolution made it possible to increase the scattering intensity to be measured. At the same time, such a resolution was sufficient to obtain the RDF in the range of close distances (up to $r \sim 8\text{--}10 \text{ \AA}$) without essential distortions. The overall time of the X-ray experiment with one sample was about 35–40 h.

The scattering curve was corrected for polarization [4] and for absorption in a cylindrical sample [6] (the parameter μR was determined experimentally by measuring the absorption of the sample). The parameters of the analytical approximation formulae were taken from refs. 7, 8 for the atomic form factors $f_j(q)$, from ref. 9 for CH, CH₂, CH₃ and OH groups, and from ref. 10 for the Compton scattering intensity. Anomalous dispersion corrections were taken from ref. 11. $I(q)$ was normalized to electronic units by a somewhat simplified method [12].

RDF calculation requires preliminary smoothing of the noise on the diffraction curve. For polycrystalline X-ray patterns this was carried out after the data had been transformed into the function

$$F(q) = \frac{I(q)}{\sum_j n_j f_j^2(q) + I_{\text{incoh}}(q)} \quad (8)$$

used in the normalization procedure [12]. The cubic spline smoothes only the $F(q)$ tail for the q range in which the intensities of separate narrow Bragg peaks become of the order of the noise amplitude and therefore indistinguishable from the noisy experimental data. Further RDF calculations employ smoothed data within this range and experimental data for lower values of q . The solid line $qi(q)M(q)$ in Fig. 5 shows vividly the two ranges of smoothed and unsmoothed values (boundary at $q \approx 7.8 \text{ \AA}^{-1}$). The RDF was calculated by numerical integration of eq. 1. For that

purpose the function $qi(q)M(q)$ was approximated by the interpolating cubic spline [13], and the integral (1) was expressed as an analytical formula through the spline coefficients. q_{\max} in eq. 1 was within 13–14 \AA^{-1} . The function $qi(q)M(q)$ approximated to zero at q_{\max} .

Experimental results and discussion

Simple systems with one type of distance between the heavy atoms

Simple clusters, mainly binuclear with respect to heavy metals, are employed to clarify two questions experimentally. First, the extreme sensitivity of the method, that is, how many light atoms can a cluster have per heavy atom for the metal–metal bond to give an RDF peak with a reliably identified intensity? The metal–metal peak gains in intensity solely as a result of the large scattering amplitude $f_j(q)$ of a metal (see eqs. 5,4). However, another intensity factor – the coordination numbers N_{kj}^m – increases with the number of light atoms for metal–ligand and ligand–ligand distances. Therefore, the metal–metal peak may become indistinguishable from the others on the RDF. The second problem is the accuracy of metal–metal distance determination. Two factors are of importance here. The first, more subjective, factor deals with the experimental accuracy and the way the data are processed. The second factor concerns the overlapping metal–metal and metal–ligand peaks of the RDF. The latter group of peaks can shift the maximum observed, even if the main contribution to it has been made by the metal–metal distance.

Table 1 lists the model compounds investigated in the present work and some of their parameters required for discussing the above-mentioned problems. Figure 1 (solid line) shows the RDF of diaurated malonitrile (first line in Table 1). Here and everywhere the so-called difference RDFs are plotted. The function $G(r)$ oscillates about the r -axis and shows deviations of the real interatomic distance distribution of the system from the hypothetical uniform (random) atomic distribution described by the first term of eq. 4 with a positive sign. In these plots the absolute value of any

TABLE 1

SOME OF THE CHARACTERISTICS OF THE COMPOUNDS UNDER STUDY ^a

No.	Compound	Amount of l.a. per heavy atom	r^{RDF} (\AA)	r^{cryst} (\AA)	
1.	(AuPPh ₃) ₂ C(CN) ₂	22.5	2.935	2.912	[14]
2.	(π -C ₅ H ₅)Fe(π -C ₅ H ₄)(AuPPh ₃) ₂ (BF ₄)	25	2.785	2.768	[15]
3.	Re ₂ (CO) ₁₀ ·1.22C ₆ O ₆ H ₁₂	17.3	3.085	3.02	[16]
4.	Os ₃ (CO) ₁₂ ·1.53C ₆ O ₆ H ₁₂	26.4	2.91	2.877	[17]
5.	(AuPPh ₃) ₃ O(BF ₄)	22	3.10	3.032; 3.034; 3.162; 3.215	[18]
6.	(AuPPh ₃) ₄ N(BF ₄)	21.5	2.955	3.012; 3.138; 3.16; 3.321; 3.489; 3.504	[19]

^a l.a. means a light atom of the type O,C,N or OH, CH, CH₂, CH₃ group; a P atom is assumed to equal 2 l.a.; r^{RDF} = position of the peak maximum on the RDF with the main contribution made by the distance between heavy atoms; r^{cryst} = distance between heavy atoms from single-crystal X-ray crystallography.

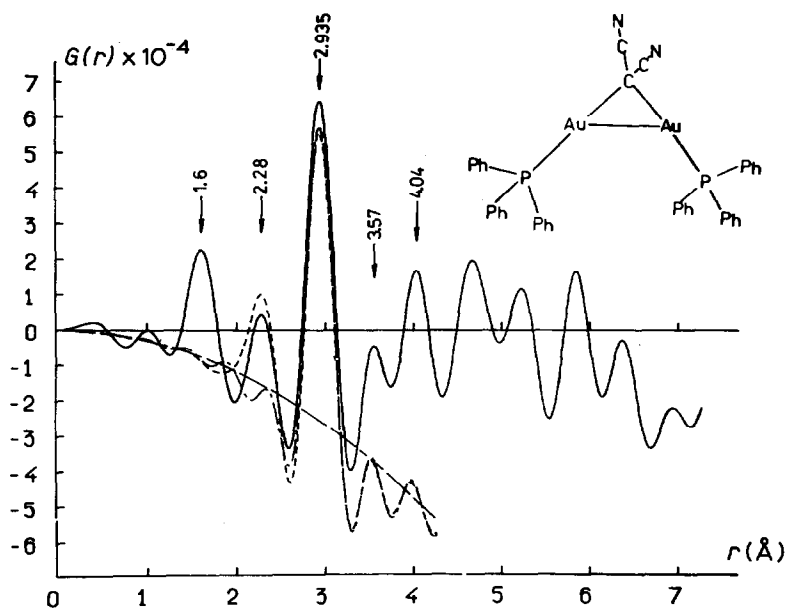


Fig. 1. RDF $G(r)$ for bis(triphenylphosphinegold)malonitrile. Here and in analogous figures: (—) experimental $G(r)$ from eq. 1; Model contributions calculated by eqs. 4–7: (---) contribution from the interatomic distances between the heavy metal atoms (here AuAu); (· · · · ·) total contribution from all the nearest distances including the metal atoms (here AuAu + AuP + AuC); (— · —) term $-4\pi\rho_0 r^2 [\sum_j n_j f_j(0)]^2$ from eq. 4. Parameters of model contributions (in the series AuAu, AuP, AuC); \bar{r}_{kj} 2.935, 2.28, 2.1 Å; σ_{kj} 0.09, 0.09, 0.09 Å; $N_{kj} = 2, 4, 4$; ρ_0 0.00115 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 given in the top right-hand corner.

distance contribution to the RDF, $G_{kj}(r)$ in eq. 4, must be measured from the parabola $-4\pi r^2 \rho_0 [\sum_j n_j f_j(0)]^2$.

The RDF of Fig. 1 shows three peaks in the range of r up to around 3 Å. The first peak, at r 1.6 Å, arises from contributions mainly by the distances in the triphenylphosphine ligands. The second one is determined by the AuP and AuC distances. The third peak at $r \approx 3$ Å is in the region where AuAu distances must be manifested. To confirm this interpretation of the peaks, Fig. 1 also shows model calculations by eqs. 4–7 for contributions from the closest distances involving the Au atoms (AuAu, AuP, and AuC, dashed line). The generalized coordination numbers N_{kj} were calculated from eq. 7 according to the molecule scheme shown in the top right-hand corner of Fig. 1. For example, for the AuAu distance there are two structurally equivalent Au atoms in stoichiometric units ($n_{\text{Au}}^1 = 2$, only one term in the sum over t) with the coordination number $C_{\text{AuAu}}^{11} = 1$ (one Au neighbour for each of these two Au atoms). Hence, $N_{\text{AuAu}} = 2$. The interatomic distances \bar{r}_{kj} for AuP and AuC are taken from ref. 14. Taking into account the position of the RDF maximum, the distance \bar{r}_{AuAu} is somewhat shifted relative to that reported [14]. The vibrational widths of the distance distributions, σ_{kj} , are chosen so that eqs. 4,5 describe the peak shapes adequately. The model curves shown in the following figures were obtained in the same way.

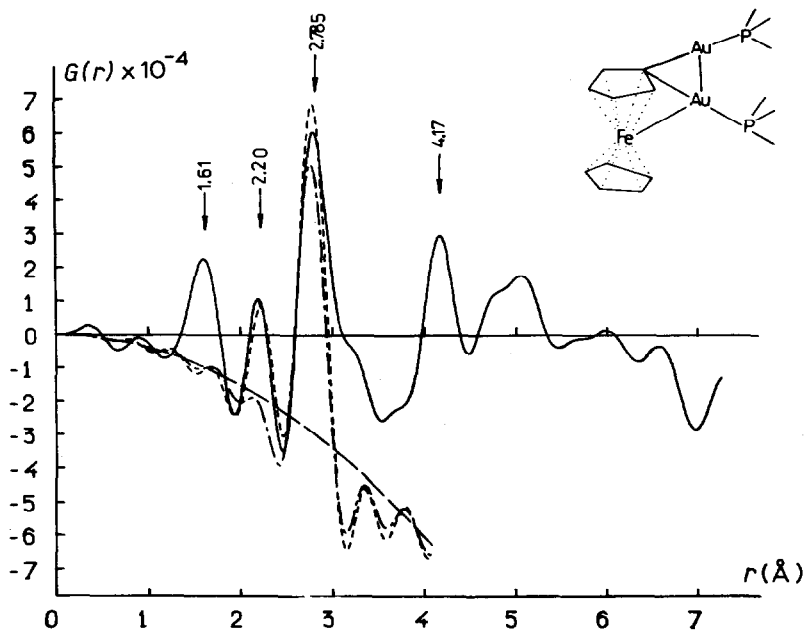


Fig. 2. $G(r)$ for $(\eta\text{-C}_5\text{H}_5)\text{Fe}(\eta\text{-C}_5\text{H}_4)\text{Au}_2(\text{PPh}_3)_2(\text{BF}_4)$. Model parameters (in the series AuAu, AuFe, AuP, AuC): \bar{r}_{kj} 2.768, 2.818, 2.28, 2.2 Å; σ_{kj} 0.11, 0.11, 0.1, 0.1 Å; N_{kj} 2,2,4,4; ρ_0 0.0009405 Å⁻³.

There are more than twenty light atoms per each Au atom in diaurated malonitrile, but the metal-metal peak dominates in the RDF. Model calculations show its intensity to result almost completely from this distance contribution. The position of the maximum differs only by 0.023 Å from the AuAu distance determined by a single-crystal X-ray study [14], since this molecule has no interatomic distance that can noticeably shift the AuAu peak. An additional contribution from the AuFe distance to the AuAu peak appears in the diaurated derivative of ferrocene (Fig. 2, second line in Table 1) and must be taken into account in the model calculations. This contribution shifts the total peak very little, since the AuAu and AuFe distances are similar (2.768 and 2.818 Å) [15]. As before, the AuAu distance is dominant in the RDF and is determined from the position of the peak maximum with an accuracy of 0.017 Å.

For a great coordination number of light atoms, the distance metal-light ligand atom might cause essential difficulties in precise determination of the metal-metal distance if both types of interaction contribute to the same RDF peak. Figure 3 and the third line in Table 1 give an example. The five oxygen atoms around every Re atom in binuclear rhenium decacarbonyl* result in the combined contribution, ReRe + ReO (dashed line), to the peak near 3 Å, which substantially exceeds the contribution from ReRe alone (dash-dot line). The intensity of this peak in the experimental RDF cannot be interpreted without the ReO contribution. Since

* The powders $\text{Re}_2(\text{CO})_{10}$ and $\text{Os}_3(\text{CO})_{12}$ (Fig. 4) were quantitatively diluted with glucose powder. This reduced the strong absorption of X-rays observed for the pure samples and imitated a typical composition of clusters containing large organic ligands.

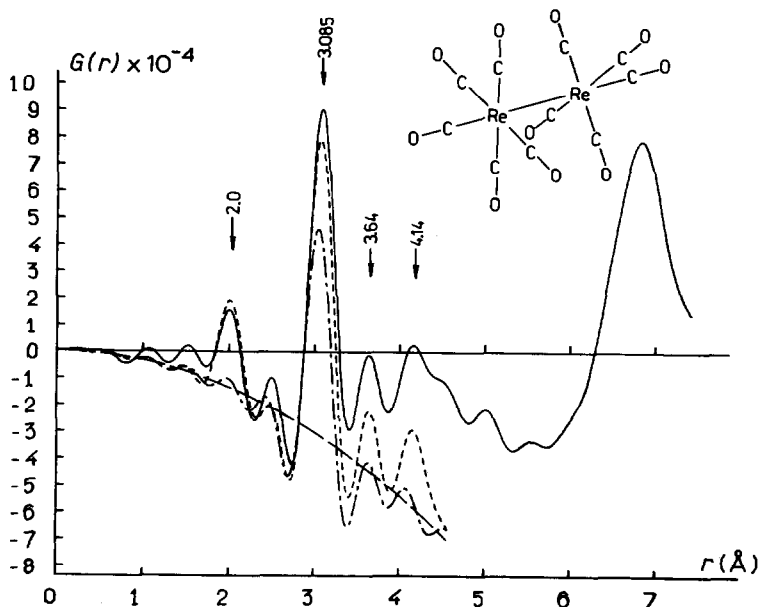


Fig. 3. $G(r)$ for the mixture of mole composition $\text{Re}_2(\text{CO})_{10}:1.22\text{C}_6\text{O}_6\text{H}_{12}$ (D-glucose). Closest distance parameters (ReRe, ReC, ReO): \bar{r}_{kj} 3.04, 2.0, 3.15 Å; σ_{kj} 0.075, 0.115, 0.12 Å; N_{kj} 2, 20, 20; ρ_0 0.001636 Å⁻³. Account is also taken of the ReC and ReO distances, including the C and O atoms bonded to a neighbouring atom Re: \bar{r}_{kj} 3.64, 4.2 Å; σ_{kj} 0.14, 0.15 Å; N_{kj} = 16, 16.

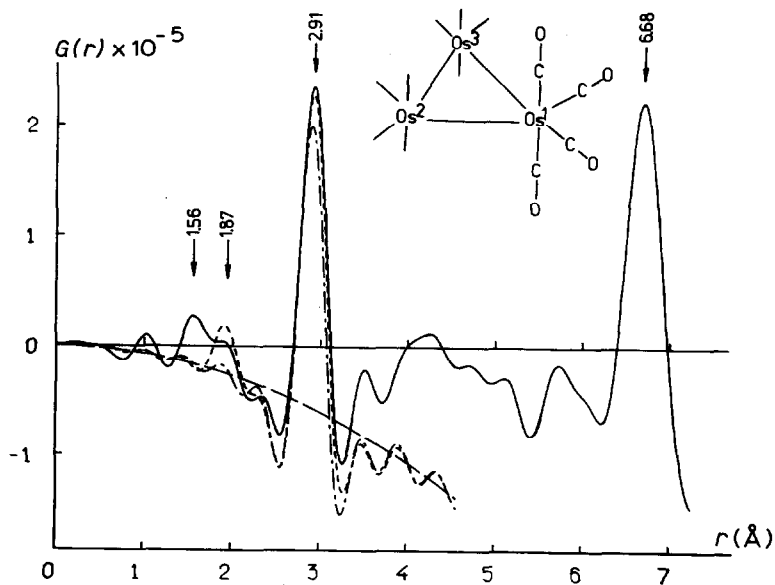


Fig. 4. $G(r)$ for the mixture of mole composition $\text{Os}_3(\text{CO})_{12}:1.53\text{C}_6\text{O}_6\text{H}_{12}$. Parameters of model calculations: (OsOs, OsO, OsC): \bar{r}_{kj} 2.89, 3.06, 1.93 Å; σ_{kj} 0.1, 0.13, 0.13 Å; N_{kj} 6, 24, 24; ρ_0 0.0007649 Å⁻³.

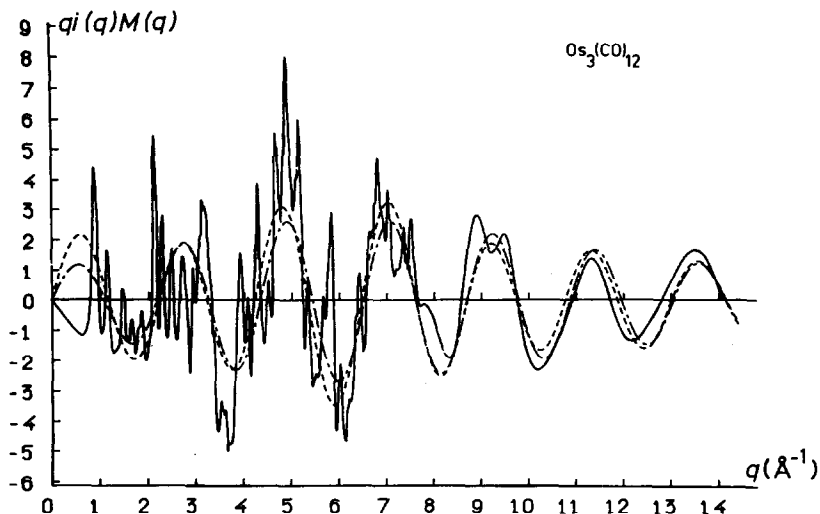


Fig. 5. Reduced scattering intensity for the system $\text{Os}_3(\text{CO})_{12}$ + glucose. The correspondence between the line types and distance contributions is the same as that in the figures with RDFs. For parameters of the contributions from particular terms in eq. 5, see caption to Fig. 4. Up to $q \approx 7.8 \text{ \AA}^{-1}$ the experimental $qi(q)M(q)$ line is an interpolating cubic spline, passing via experimental values, and then via smoothed ones (see the text below eq. 8).

$r_{\text{ReO}} \approx 3.15 \text{ \AA}$, the peak maximum is essentially shifted (by 0.065 \AA) at r 3.085 \AA relative to the published [16] ReRe distance of 3.02 \AA . Nevertheless, even in this unfavourable case, the single ReRe interaction in the dimer makes up the basic intensity of the peak. Taking into account the typical distance $r_{\text{ReO}} 3.15 \text{ \AA}$, model calculations give $r_{\text{ReRe}} 3.04 \text{ \AA}$ (see Fig. 3).

The effect of distances interfering decreases with increasing metal–metal coordination number. For example, upon passing from the dimer $\text{Re}_2(\text{CO})_{10}$ to the triangle of heavy atoms $\text{Os}_3(\text{CO})_{12}$, the contribution from the OsOs distances becomes predominant (Fig. 4). The peak maximum observed at 2.91 \AA is shifted by 0.033 \AA relative to the OsOs length of 2.877 \AA [17]. The modelling of the peak, taking into account $r_{\text{OsO}} 3.06$, gives $r_{\text{OsOs}} 2.89 \text{ \AA}$.

The presence of bonds between heavy metals is often qualitatively manifested directly in the diffraction curve. Figure 5 shows the reduced scattering intensity $qi(q)M(q)$ for the powder mixture of $\text{Os}_3(\text{CO})_{12}$ with glucose, its RDF depicted in Fig. 4. The narrow peaks of the Bragg reflections, usually discussed when interpreting a powder diffraction, are as if they are on a low-frequency support, which continuously turns into smooth oscillations at large q . This support results from the diffraction at intramolecular distances between chemically bonded atoms. The bonds lead to a narrow distribution (6) with small $\sigma_{k_j}^m$, and hence to a slowly damped regular contribution (5), shown by the dashed line in Fig. 5. Its high intensity results from the heavy atoms.

From the foregoing, the above questions can be answered as follows. One metal–metal bond per cluster molecule (binuclear cluster) can be detected reliably by the RDF, providing the sample contains not more than 25–30 light atoms per heavy one. If the metal–metal coordination number exceeds $N_{k_j} = 2$ in a dimer, the

extreme number of light atoms per heavy one in a cluster may be increased. The accuracy of the bond length determination is 0.02–0.03 Å (deviation from crystallographic data). For strong side contributions to the RDF peak, this accuracy may require model calculations taking into account typical lengths of the interfered distances.

Clusters involving complex groups of several heavy atoms

The possibilities and problems of the RDF method for complex clusters are demonstrated below by two examples. Figure 6 shows the RDF for the oxonium salt of triphenylphosphinegold whose molecular structure has been investigated in a single crystal [18]. The two oxonium cations, each containing three Au atoms, are combined into a centrosymmetric dimer shown at the top of Fig. 6. The Au atoms form a six-membered ring in a chair conformation. There are two types of closest AuAu distances in this structure [18]: short distances of about 3.03 Å shown by dashes, and long ones of 3.16 and 3.21 Å shown by dots. The RDF shows a pronounced peak, with its maximum at 3.10 Å, which points directly to the existence of a cluster. Owing to the finite resolution of the method and also to the natural (vibrational) width of the distance distributions (eq. 6), the contributions from all the AuAu distances are not resolved in this peak. The position of the peak can be used to estimate directly a certain mean AuAu distance in the cluster.

Model calculations may give more detailed information on the structure of a cluster nucleus. Figure 6 shows the peak (dashes) reconstructed on the basis of the

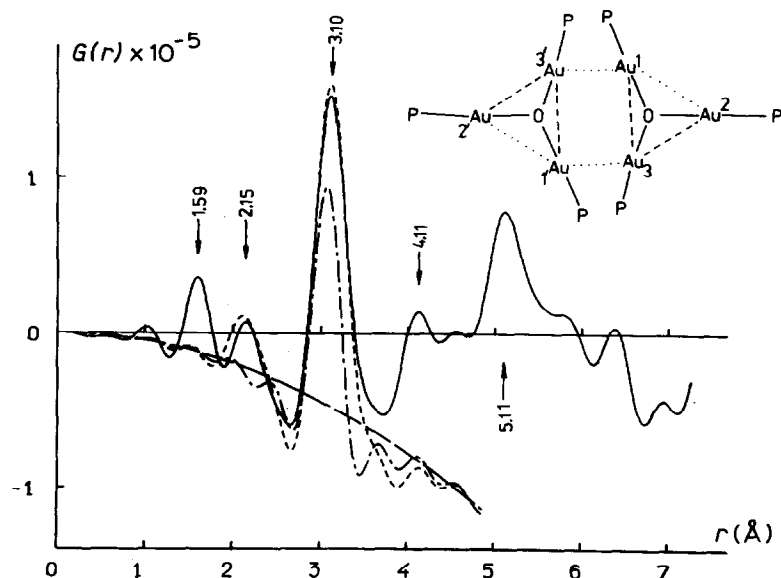


Fig. 6. $G(r)$ for tris(triphenylphosphinegold)oxonium tetrafluoroborate. The scattering intensity and RDF are normalized to the trimer Au_3 (see Table 1). RDF reconstruction parameters (short AuAu, (long AuAu), AuP, AuO, AuC): \bar{r}_{kj} 3.06, (3.16, 3.21); 2.2, 2.05, 3.35 Å (to a C atom bonded with a P one); σ_{kj} 0.12, (0.22, 0.22), 0.12, 0.12, 0.15 Å; N_{kj} = 4, (2, 2), 6, 6, 18; ρ_0 0.0007983 Å⁻³. The dash-dotted line shows the contribution from short AuAu distances with \bar{r}_{AuAu} 3.06 Å.

structure described above. The fit to the experiment is very good. It was attained under important assumptions on the σ_{AuAu} values. The small value of σ_{AuAu} 0.12 Å, corresponding approximately to the vibrational distance dispersion observed in dimers was ascribed to short \bar{r}_{AuAu} , i.e. the presence of AuAu bonds was assumed. The value of σ_{AuAu} 0.22 Å was attributed to long \bar{r}_{AuAu} , which most probably meant the absence of direct bonding between the Au atoms.

The success of the above reconstruction, however, does not guarantee a unique adequate model in the case of an unknown structure. There might also be some other models with close coordination numbers N_{AuAu} , so that by varying σ_{AuAu} one can attain a satisfactory fit to the experiment. However, physically imposed limitations on σ_{kj} , external chemical and structural information, and the experience gained all make it possible to choose a sufficiently small set of plausible structures. Quantitative RDF modelling in the range of long distances would facilitate a more adequate choice of the model. However, at $r > 3-3.2$ Å, the contribution from intermolecular distances increases rapidly and cannot be taken into account quantitatively in complex systems. Therefore, only in favourable cases can one extract some qualitative information on the distances giving the most pronounced peaks in this range of r .

Figure 7 shows the RDF for the ammonium salt of triphenylphosphinegold. According to recent crystallographic data [19], the four Au atoms, bonded to the central nitrogen atom, form a very distorted tetrahedron. The AuAu distances are listed in Table 1 (line 6). In contrast to the previous case, the AuAu peak on the RDF cannot be reconstructed well on the basis of these distances, since the peak maximum at r 2.955 Å is shifted substantially to the left of the shortest distance in

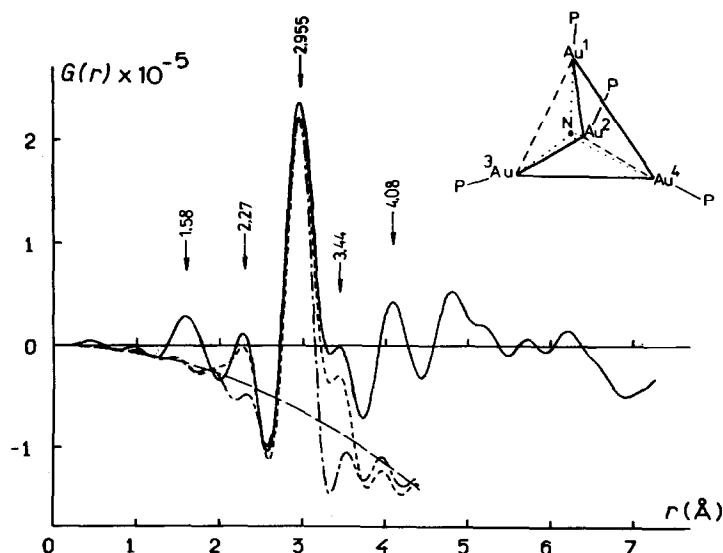


Fig. 7. $G(r)$ for tetrakis(triphenylphosphinegold)ammonium tetrafluoroborate. The intensity and RDF are normalized to the tetramer Au_4 (see Table 1). RDF reconstruction parameters (short AuAu, long AuAu, AuP, AuN, AuC): \bar{r}_{kj} 2.94, 3.3, 2.27, 2.1, 3.34 Å; σ_{kj} 0.12, 0.22, 0.12, 0.15, 0.15 Å; $N_{kj} = 8, 4, 8, 8, 24$; ρ_0 0.0007 Å⁻³. The dash-dotted line shows the contribution from short AuAu distances.

Table 1 *. The intensity of the narrow part of the peak in fact coincides with the contribution of only four AuAu distances, \bar{r}_{AuAu} 2.94 Å and dispersion σ_{AuAu} 0.12 Å corresponding to directly bonded Au atoms (dash-dotted line, Fig. 7). Preserving the approximately tetrahedral coordination of the nitrogen atom, the cluster structure can be presented in the so-called "butterfly" shape (top of Fig. 7). The long distance of 3.3 Å and σ_{AuAu} 0.22 Å must be ascribed to the Au¹Au³ and Au²Au⁴ distances, whose contributions are above the experimental peak at r 2.955 Å. The broader peak of these distances without a direct AuAu bond slightly raises the right-hand side wing of the summary model RDF peak (Fig. 7, dashed line).

Comparison of Figs. 6 and 7 with Figs. 1 and 2 for dimer RDFs shows that a complex cluster in a powder can be detected more easily than a simple dimer. The larger coordination number N_{AuAu} makes the peak of closest distances in a metallic nucleus more prominent, particularly compared to the peaks of other intramolecular distances, the overall ratio of light to heavy atoms being the same as that in dimers. Therefore, the RDF method might be useful as a way of analysing new compounds prior to the time-consuming procedure of growing single crystals for thorough X-ray studies of the structure. On the other hand, the model RDF reconstructions should not be expected to give precise interatomic distances or unambiguous conclusions on the structure in each particular case. Model calculations should be treated as the most direct of all possible ways of determining the basic elements of a heavy atom's surrounding, which gives a better ground for judging a cluster structure, as compared to indirect spectral investigations.

Conclusion

The RDF, as a method for studying substances, holds a position between a classical structural analysis and other, more or less structure-sensitive, methods. As in X-ray crystallography, an experimentally determined quantity depends here directly on the structure of the substance. On the other hand, the nature of an RDF determines the proximity of its interpretation methods with spectral methods. To refer RDF peaks qualitatively to one or another interatomic distance, e.g. as lines of vibrational spectra to definite atomic groups, one needs empirical knowledge of their typical positions and intensities. Detailed interpretation of complex RDF peaks, as well as of complex spectra, requires quantitative reconstruction of line profiles, etc. This determines, first, the importance of crystallographic information on typical distances and configurations of various atomic groupings. Second, it is necessary to accumulate experience of RDF reconstructions in model substances, in particular, in order to determine typical values of vibrational broadening of distance distributions, σ_{kj} . The present paper is just the first step of cluster investigations on sufficiently simple structures available to the author.

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* Besides a trivial cause, the deviation from the crystallographic data might result from temperature variations in the structure, as the RDF was obtained at room temperature, while the crystallographic data correspond to -120°C .

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